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One-year study of polycyclic aromatic compounds at an urban site in Grenoble (France): seasonal variations, gas/particle partitioning and cancer risk estimation

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Abstract

21 PAHs, 27 oxy-PAHs and 32 nitro-PAHs were measured every third day over a year in both gaseous (G) and particulate PM₁₀ (P) phases in ambient air of Grenoble (France). Mean total concentrations (G+P) of PAHs and oxy-PAHs were in the same range and about 10 ng m⁻³. Nitro-PAHs were 50 to 100 times less concentrated averaging 100 pg m⁻³. Polycyclic aromatic compound (PAC) concentrations were 5 to 7 times higher in “cold” period (October to March) than in “warm” period (April to September). Seasonal variations may be explained by higher primary emissions from residential heating, especially biomass burning in “cold” season. Meteorological conditions and influence of the geomorphology around Grenoble, with the formation of thermal inversion layers leading to the stagnation of pollutants, were additional key parameters. Maximum individual PAC concentrations were observed during two PM₁₀ pollution events in December and February-March. Chemical processes and secondary formation of oxy- and nitro-PAH were probably enhanced by the accumulation of the pollutants during these events. PAC gas/particle partitioning depended on compound molecular weight and vapour pressure. Gas/particle partitioning of oxy- and nitro-PAHs were evaluated using a multi-phase poly-parameter linear free energy relationship model. The PAC cancer risk was assessed using toxic equivalency factors available in the literature (19 PAHs, 10 nitro-PAHs and 1 oxy-PAH). Overall, particle-bound PACs contributed about 76% of the cancer risk. While PAHs accounted for most of the total PAC cancer risk, oxy- and nitro-PAHs could account for up to 24%. The risk quantification across substance classes is limited by toxicological data availability.

Keywords: PAH; OPAH; NPAH; Gas/particle partitioning model; Aerosol; Air quality

1. Introduction

Air pollution is known to strongly impact human health. Recently, the World Health Organization (WHO) estimated that exposure to indoor and outdoor air pollution led to 7 million premature deaths in the world in 2012, with 3.7 million deaths caused by outdoor air pollution (WHO, 2015). According to WHO estimation, exposure to particulate matter (PM) could reduce the life expectancy of Europeans by 9 months (WHO, 2013). Impacts of fine PM on health are related to its size and structure but also to its chemical composition and, notably, to toxic compounds such as heavy metals or polycyclic aromatic hydrocarbons (PAHs) (Delfino et al., 2010; Fuzzi et al., 2015).

PAHs are a group of chemicals composed of at least two fused benzene rings and recognized as carcinogenic, mutagenic and teratogenic substances (IARC, 2010; Kim et al., 2013). Their ubiquitous presence in the atmosphere is of major concern and, therefore, they are regulated, for instance, in Europe and the USA (European Official Journal, 2004; US EPA, 2011). These compounds are mostly emitted by incomplete combustion processes such as residential heating, vehicle exhaust, coal and wood burning in both the gaseous and particulate phases (Ravindra et al., 2008). Once emitted, into the atmosphere, PAHs may undergo chemical oxidation following both homogeneous and heterogeneous reactions to form oxygenated and nitrated PAH derivatives (oxy-PAHs and nitro-PAHs) (Atkinson and Arey, 2007; Keyte et al., 2013). Although oxy- and nitro-PAHs can be secondary compounds, they can also be emitted together with PAHs following the same combustion processes (Chen et al., 2015; Huang et al., 2013; Rogge et al., 1993a, 1993b; Zielinska et al., 2004). Oxy- and nitro-PAHs are probably more mutagenic than their parent PAHs because they act as direct mutagens (Durant et al., 1996; Jariyasopit et al., 2014a, 2014b; Pedersen et al., 2005; Rosenkranz and Mermelstein, 1985). Furthermore, some of these compounds are suspected to be carcinogenic and have been recently classified in the 2A (probably carcinogenic to human) and 2B (possibly carcinogenic to human) groups by IARC (IARC 2012, 2013).

PAHs, nitro- and oxy-PAHs (polycyclic aromatic compounds, PACs) are semi-volatile compounds partitioning between gaseous and particulate phases (Albinet et al., 2008a; Odabasi et al., 1999; Wei et al., 2015a), and are mainly associated with the fine PM fraction (Albinet et al.,

2008b; Allen et al., 1997; Di Filippo et al., 2010, 2015; Ringuet et al., 2012a) following both adsorption and absorption processes (Mader and Pankow, 2002). For regional and global atmospheric chemistry models, it is important to have a reliable estimate of the fraction of PACs that partitions to PM, as this parameter affects the overall performance of these models. This becomes more crucial for semi-volatile PACs that show a large variation of gas/particle partitioning as a response to changes in ambient temperature, relative humidity, and PM chemical composition. Gas/particle partitioning is controlling the long-range atmospheric transport potential of PACs, as well as their reactivity (and, hence, lifetime/persistence) (Lammel et al., 2009; Keyte et al., 2013) and bioavailability (Pankow, 2001; Volckens and Leith, 2003). Therefore, it is important to advance understanding of PAC gas/particle partitioning. Gas/particle partitioning models have been previously tested for semi-volatile PAHs, but hardly for semi-volatile nitro- and oxy-PAHs, except by Huang et al. (2014) and Li et al. (2016), where models showed low performance.

The main purpose of this work was to study a large number of PAHs, nitro- and oxy-PAHs, (≈ 80 compounds), in both the gaseous and particulate phases over the period of one year (2013) at an urban site in a European city. To our knowledge, this is so far the most comprehensive study of these toxic compounds in ambient air. Objectives were to evaluate their occurrence in the atmosphere and their seasonal variations of concentrations and substance patterns. Gas/particle partitioning of semi-volatile nitro- and oxy-PAHs were compared with model predictions. Finally, an assessment of the cancer risk induced by these compounds over the year has been performed including the impact of both gaseous and particulate phases.

2. Experimental

2.1 Sampling site

Measurements were carried out in Grenoble (France) at the urban station of "Les Frênes" (air quality network station of Air Rhône-Alpes, 45° 09' 41" N 5° 44' 07" E), which is considered as representative of air pollution in the city. Grenoble is a half million inhabitant Alpine valley city surrounded by mountains and strongly impacted by PM₁₀ pollution event during winter (Fig. A1 in Appendix A). High PM₁₀ concentration levels are mainly due to the residential heating emissions

and the specific orography of the immediate vicinity of the city. The formation of thermal inversion layers often observed in the cold season leads to the stagnation of pollutants in the valley. In France, the main source of PAHs in ambient air is linked to residential emissions (CITEPA, 2014). Previous studies in Grenoble showed that biomass burning for residential heating is one of the main emission sources of PM in winter (Favez et al., 2010, 2012; Piot et al., 2011; Pissot et al., 2009).

2.2 Sample collection

Both, particulate PM₁₀ (Tissuquartz Pallflex, Ø=150 mm) and gaseous (polyurethane foams, PUF, Tisch Environmental, L=75 mm) phases were collected using a high volume sampler DA-80 (Digitel) every three days from January 2013 to January 2014 (n=123). Sampling duration was 24 h (started at midnight, 30 m³ h⁻¹). PAC samplings were performed according to the EN 15549 and TS 16645 standard procedures (European Committee for Standardization (CEN), 2008, 2014a). Prior to sampling, quartz fiber filters were pre-heated at 500 °C for 12 h while PUFs were pre-cleaned using pressurized solvent extraction (ASE 350, Thermo; one hexane cycle followed by two acetone cycles: 80 °C, 100 bars, 5 min heat time, 15 min static time) (Zielinska, 2008). After collection, samples were wrapped in aluminum foils, sealed in polyethylene bags, sent to the laboratory by express post using cool boxes and then stored at <-10°C until analysis. PM₁₀ were measured using TEOM-FDMS (TEOM 1405F, Thermo) (CEN, 2013).

2.3 Sample extraction and purification

Details about the chemicals used, purity and suppliers are described in the Supplementary Material (Table A1).

For PAH analysis, a known amount of 6-methylchrysene was added to the samples prior to extraction (10 µL on filters and 20 µL on PUF of a solution at 1 ng µL⁻¹) and used as surrogate standard to check the extraction efficiency. For nitro- and oxy-PAHs, a known amount of a mixture containing 2 deuterated oxy-PAHs and 7 deuterated nitro-PAHs were added to the samples prior

to extraction (PUF: 100 μL of a solution at 1 $\text{ng } \mu\text{L}^{-1}$ for nitro-PAH and 5 $\text{ng } \mu\text{L}^{-1}$ for oxy-PAH; filters: 5 μL of a solution of 1 $\text{ng } \mu\text{L}^{-1}$ for nitro- and oxy-PAH) and were used as surrogate standards for oxy- and nitro-PAHs quantification in the samples (Tables A3, A4).

PAH extractions were performed according to the EN 15549 and TS 16645 standard procedures for particle-bound PAH analysis (CEN, 2008, 2014).

PUF samples were extracted with acetone using pressurized liquid extraction (ASE 350, Thermo; two cycles: 80 $^{\circ}\text{C}$, 100 bars, 5 min heat time, 15 min static time). As for PUF pre-cleaning, acetone was preferably used for the ASE extraction instead of dichloromethane (DCM) to avoid any PUF degradation (Desert Research Institute SOP, 2008). Extracts were reduced under a gentle nitrogen stream to a volume of about 200 μL (Zymark, Turbovap II) and adjusted to 2 mL with acetonitrile (ACN). Extracts were then divided in two parts for PAH analysis and nitro- and oxy-PAH analysis, respectively. A clean up step was then applied for PUF extracts dedicated to the analysis of nitro- and oxy-PAHs. The clean-up was performed on silica SPE cartridge (SiOH chromabond, Macherey Nagel, 3 mL, 500 mg) with a first elution with pentane (1 mL discarded) followed by the collection of eluted extract with 9 mL of pentane/DCM, 65:35 (v/v). Purified extracts were then reduced to near dryness under a gentle stream of nitrogen and reconstituted with 100 to 400 μL of ACN (depending on the potential concentration of targeted compounds in the extracts).

Filter samples were cut into punches of 47 mm diameter for PAH and nitro- and oxy-PAH analyses. A punch was used for PAH analysis and extracted using ASE 200 (Thermo; 3 DCM cycles: 120 $^{\circ}\text{C}$, 140 bars, 6 min heat time, 6 min static time). Extracts were reduced under nitrogen steam to near dryness, dissolved in acetonitrile (1 mL) and analyzed by UPLC/UV-Fluorescence. The second punch filter was dedicated to nitro- and oxy-PAH analyses. Filters were extracted using QuEChERS-like procedure developed previously for the analysis of particulate-bound PAH and PAH derivatives (Albinet et al., 2013, 2014). Briefly, punches were placed in centrifuge glass tubes and extracted with acetonitrile (ACN, 7 mL) using a Multi-tube Vortexer (DVX-2500, VWR) for 1.5 min. After extraction, samples were centrifuged for 5 min at 4500 rpm (Sigma 3-16 PK centrifuge). Supernatant extracts were collected and reduced to near dryness under a gentle nitrogen stream. Reduced extracts were then dissolved into DCM (100-200 μL). The same clean up step, described above, was used on filter extracts dedicated to the analysis of nitro- and oxy-PAHs.

Before analysis, 9-fluorenone-d₈ and 1-nitropyrene-d₉ were added to the extracts (5 µL of a solution at 1 ng µL⁻¹ for particulate phase measurements and 15 to 30 µL of a solution at 1 ng µL⁻¹ for gas phase measurements) as internal standard to evaluate the surrogate recoveries in samples.

Additional aerosol chemical characterization was performed to fulfil the requirements for PAC gas/particle partitioning model. This included elemental carbon (EC), organic carbon (OC), anions (Cl⁻, SO₄²⁻)/cation (NH₄⁺), humic like substances (HuLiS) and water soluble organic carbon (WSOC). These species were analyzed on dedicated filter punches following the methodologies described previously (Baduel et al., 2009, 2010; Cavalli et al., 2010; Jaffrezo et al., 2005).

2.4 Sample analysis

2.4.1. PAH analysis

PAH analysis was performed according to the EN 15549 and TS 16645 standard procedures (European Committee for Standardization (CEN), 2008, 2014a). 21 PAHs were analyzed and quantified by UPLC/UV-Fluorescence (Thermo Scientific, Dionex Ultimate 3000) using a C18 UPLC column (Zorbax Eclipse PAH, 2.1 mm x 150 mm x 1.8 µm) with the following elution program: 40/60 (v/v) ACN/H₂O for 0 to 0.9 min, followed by a gradient until 100% ACN at 21.0 min and hold for 8.5 min. Details on UV-Fluorescence detection wavelengths are presented in Table A2. PAHs were quantified using nine-point external calibration curves.

2.4.2. Nitro-PAH and oxy-PAH analysis

32 nitro-PAHs and 31 oxy-PAHs were analyzed by GC/NICI/MS (Agilent 7890A GC coupled to 5975C MS) (Albinet et al., 2006, 2014). 1 µL of the extract was injected in the pulsed splitless mode (MMI, 30 psi). Compounds were separated on an Optima-5MS Accent column (30m x 250 µm x 0.25 µm) using the following temperature program: held at 70 °C for 5.1 min, then ramped to 190 °C at 45 °C min⁻¹, followed by a ramp to 320 °C at 5°C min⁻¹, and subsequently held for 5 min. The carrier gas (He) flow was set to 1.5 mL min⁻¹ throughout the analysis and transfer line heated at 320 °C. Methane was used as the reactant gas (2.5 mL min⁻¹) for chemical ionization with source

and quadrupole temperatures at 150 °C. Analyses were performed in selected ion monitoring mode (SIM). Oxy- and nitro-PAHs were quantified using eight-point internal standard calibration curves with labelled compounds as surrogates (Tables A3 and A4).

2.5 Quality assurance

An evaluation of the calibration response factor drift for nitro- and oxy-PAHs was performed. Compounds showing calibration drifts larger than 30% were not included in the final results. According to this criteria, benzophenone, 2,3-naphthalene dicarboxylic anhydride, and anthrone in gaseous phase and 1,2-naphthoquinone, 2,3-naphthalene dicarboxylic anhydride, anthrone, biphenyl-4,4'-dicarboxaldehyde, and 1,4-chrysenequinone in particulate phase were excluded.

In order to evaluate the background contamination related to sample collection and analysis, PUF and filter field blanks (n=9) and laboratory blanks (n=21) were performed. Analytical blanks were prepared for each extraction batch. Overall, very low blank contamination levels were observed for most of the PACs. Compounds showing field blank values higher than 30% of the annual mean concentrations were excluded from the final results. These included phthalic anhydride, 1,2-naphthalic anhydride, 1,5-dinitronaphthalene, biphenyl-4,4'-dicarboxaldehyde and benzanthrone for the gaseous phase and benzophenone, 2-nitrobiphenyl, 3-nitrobiphenyl, biphenyl-2,2'-dicarboxaldehyde and 2-nitrofluorene for the particulate phase. For other compounds, concentrations were corrected for the field blank. Samples showing PAC concentrations below limit of quantification (LQ) were replaced by LQ/2 for calculations with LQ defined as the lowest concentration of the compound that can be determined for a signal to noise ratio S/N=10.

INERIS participates, every two years, in national and European PAH analytical inter-comparison exercises. The last exercise showed results in good agreement with reference values (Verlhac and Albinet, 2015). PAH extraction efficiencies were checked according to the standard procedures EN 15549 and TS 16645 (CEN, 2008, 2014). Oxy- and nitro-PAH extraction efficiencies were also checked using NIST standard reference material (SRM 1649b, urban dust). Results obtained were in good agreement with NIST reference and indicative concentration values and with the ones

previously reported in the literature, and notably using QuEChERS extraction procedure (Albinet et al., 2014 and references therein).

Uncertainty of measurements were evaluated using the GUM methodology (guide to the expression of uncertainty in measurement) (Albinet et al., 2013, 2014; Macé et al., 2010; Ringuet et al., 2012b). For PAHs, uncertainties ranged between 42% for anthracene and indeno[1,2,3-cd]pyrene and 141% for acenaphthene. For oxy-PAHs, they ranged between 51% for 9,10-anthraquinone and 247% for benzanthrone. For nitro-PAHs they ranged between 31% for 2-nitrofluoranthene and 135% for 6-nitrochrysene. Note that certified concentration values in SRM do not exist for most of oxy- and nitro-PAHs. By neglecting this parameter, uncertainties of measurements were 2 to 6 times lower (Table A8).

Finally, 21 PAHs, 27 oxy-PAHs and 32 nitro-PAHs were quantified and included in the results and discussion (Table A5).

2.6 Gas/particle partitioning model

Partitioning of PACs in air can be described using Equation 1 (Yamasaki et al., 1982),

$$K_P = \frac{c_{ip}/c_{PM}}{c_{ig}} \quad (1)$$

where K_P ($m^3_{air} g^{-1}_{PM}$) is temperature-dependent partitioning coefficient, c_{PM} ($g m^{-3}$) is the concentration of particulate matter in air, c_{ip} is analyte (i) air concentration ($ng m^{-3}$) in particulate phase, and c_{ig} is that in gas phase. K_P can be predicted using models based on single- and poly-parameter linear free energy relationships (sp- and ppLFER). spLFER models have been widely used to predict the partitioning of neutral organic compounds in various environmental compartments, but this approach is limited by the availability of partitioning constants and solute-specific enthalpies of phase transfer required for some compounds. A good example of spLFERs is the K_{OA} model (Finizio et al., 1997) which relates the partitioning of a semi-volatile organic compound in PM to its corresponding octanol-air partitioning coefficient (K_{OA}) (see Section A1.1 in Appendix). In contrast, ppLFER combines solute descriptors and so-called system parameters which can be used independently (Endo and Goss, 2014). Moreover, the solute-specific enthalpies of phase transfer can be calculated for a large number of systems, which is needed for correcting

the partitioning constants for the effect of changes in ambient temperature. In principle, ppLFER should be universal, as it accounts for all types of molecular interactions between solute and matrix (Goss and Schwarzenbach, 2001). In the present study, we first tested the model of Finizio et al., 1997 (Section A.1.1). The model was slightly modified, as we determined the K_{OA} and enthalpies of liquid-gas phase transfer using Abraham solute descriptors and ppLFER equations suggested by Abraham et al. (2010) and Mintz et al. (2007). We then evaluated a multi-phase ppLFER to predict K_P and compared the results with the observed values calculated with Equation 1 (see Section A.1.2 in Appendix).

ppLFER is based on the linear solvation energy relationship developed by Abraham (1993) for condensed phase-air systems (Equation 2). This was later modified by Goss (2005) (Equation 3),

$$\log K_P = eE + sS + aA + bB + lL + c \quad (2)$$

$$\log K_P = sS + aA + bB + vV + lL + c \quad (3)$$

where capital letters E , S , A , B , L , and V are solute-specific Abraham solvation parameters for excess molar refraction (describes interactions between solute's π - and solvent's n -electron pairs), polarizability/dipolarity, solute H-bond acidity, solute H-bond basicity, logarithm of solute hexadecane-air partitioning coefficient (unitless), and McGowan molar volume ($\text{cm}^3 \text{mol}^{-1}$)/100, respectively (Endo and Goss, 2014). The corresponding small letters are known as system parameters, which reflect matrix-specific solute-independent contribution to the K_P . The solute-specific descriptors for semi-volatile PACs in the present study were taken from Absolv database/prediction module (ACD/Labs, 2015). This program contains experimentally determined descriptors for nearly 5000 solutes and, in addition, can estimate these values for solutes not included in the database based on a group contribution method developed by Michael H. Abraham and co-workers. Out of eight substances considered in the present study, only the descriptors for 9,10-anthraquinone were experimentally determined and included in Absolv database. In addition, we obtained the experimental descriptors for 9-nitroanthracene from Stenzel et al. (2013). ppLFER equations were developed for aerosols from urban and non-urban areas in Europe (Arp et al., 2008). We tested these models for the current dataset but found that they largely underestimated

the observed K_P for PACs. The same performance was observed by Arp et al. (2008) for PAHs. Götz et al. (2007) applied a multi-phase ppLFFER approach to predict gas/particle partitioning of semi-volatile organic compounds but the study did not include PACs in the model predictions. In addition, that study considered OM to be a homogeneously mixed phase.

Although the existence of various fractions of OM has been documented since decades - e.g. organic soluble (OS) and water soluble (WS) OM (Saxena and Hildemann, 1996; Winkler, 1974), and organic polymers (OP) (Kalberer et al., 2004; Puxbaum and Tenze-Kunit, 2003), this concept has not been given enough attention when studying the PAC gas/particle partitioning. In the present study, the PAC gas/particle partitioning predictions were made following the method suggested by Shahpoury et al. (2016) using a multi-phase ppLFFER. We considered partitioning to be the product of two processes, adsorption onto soot, $(\text{NH}_4)_2\text{SO}_4$, and NH_4Cl , and absorption into particulate organic matter (OM). We also assumed the diffusion in OM was absorptive even when becoming very slow as a consequence of OM phase state (i.e. semi-solid and solid OM). Furthermore, we assumed OM was constituted of two separate phases, (A) low to high molecular mass both OS and WSOM, and (B) high molecular mass OP. Also, low to high molecular mass substances which tend to be water insoluble (WI), such as aliphatic and polycyclic aromatic hydrocarbons, do contribute to OM. However, an estimate from a previously published study showed that this fraction could form $\leq 2\%$ of OM in urban aerosols (Rogge et al., 1993). Moreover, this fraction is likely mixed in liquid or semi-solid bulk OM, as there is no evidence for physical phase separation between WS- and WI- OM. We acknowledge that the phases considered in the present study may not be fully available for PAC partitioning due to internal mixing and kinetic limitations (slow diffusion in semi-solid and solid phases), and that under high relative humidity, $(\text{NH}_4)_2\text{SO}_4$, and NH_4Cl may be present in dissolved aqueous phase, and subject to liquid-liquid phase separation with OM (You et al., 2014). In addition, we recognize that PACs could show various degrees of enrichment in different PM size-fractions (e.g. higher enrichment in fine and ultra-fine particles than in PM_{10}).

For model calculations, an appropriate ppLFFER equation was applied to each phase – i.e. soot-air (Roth et al., 2005), $(\text{NH}_4)_2\text{SO}_4$ -air, and NH_4Cl -air (at 60% relative humidity) (Goss et al., 2003) for adsorption, and dimethyl sulfoxide-air (water solubility: 1×10^6 mg L^{-1} at 25°C) (Abraham et al.,

2010) and polyurethane ether-air (Kamprad and Goss, 2007) for absorption into phase (A) and (B), respectively. The partitioning constants were corrected for the effect of temperature at the sampling site using the solute-specific enthalpies of phase transfer, which were determined for the corresponding ppLFFER systems. Overall K_P was calculated by summing the individual partitioning constants after normalizing the units and taking into account the mass mixing ratios of the corresponding inorganic and organic components related to the sorption processes. The mass mixing ratios available for adsorption were determined from the measured concentrations of elemental carbon, as well as SO_4^{2-} and Cl^- (assuming to be completely given by $(NH_4)_2SO_4$ and NH_4Cl , respectively), and PM_{10} . The implicit representation of all inorganic salts in PM by these two salts is justified as the ppLFFER system parameters are expectedly similar. For absorption, the corresponding mixing ratios were estimated using the data reported by Rogge et al. (1993) for Rubidoux, ≈ 75 km downwind of Los Angeles. Accordingly, 60% was assigned to phase (A), corresponding to elutable organics, and 40% to phase (B), non-extractable/non-elutable organics. The mixing ratio allocated to phase (A) is fairly close to the measured values of WSOM/OM for samples in the present study (mean \pm standard deviation: 0.46 ± 0.08 , median: 0.47, $n = 120$).

2.7 Carcinogenic risk assessment calculations

Carcinogenic risk assessment induced by the inhalation of the mixture of PACs in the city of Grenoble was performed. This evaluation was done using toxic equivalent factors (TEFs) with benzo[a]pyrene (B[a]P) as the reference compound with conventional value of 1 (OEHHA, 2011). Equivalent atmospheric toxic concentrations (C_{EQ}), expressed in B[a]P equivalent concentrations ($ng\ m^{-3}$), were calculated using Equation 4:

$$C_{EQ} = [\sum_i [PAH](i) \times TEF(i) + \sum_j [OPAH](j) \times TEF(j) + \sum_k [NPAH](k) \times TEF(k)] \quad (4)$$

Excess of individual risk due to the inhalation of the mixture of PACs was calculated using Equation 5:

$$IER = C_{EQ} \times IUR(B[a]P) \times \frac{T_{expo}}{T_m} \quad (5)$$

with IER= Individual excess of risk by inhalation

IUR= Inhalation unit risk with B[a]P as the reference = 1.1×10^{-6} (ng m⁻³)⁻¹ (OEHHA, 2011).

$\frac{T_{expo}}{T_m}$ = ratio between exposition time and life expectancy (= 1, upper bound simplification).

TEF values for PAHs are relatively widely available in the literature (19 TEF used) while few information exists for nitro-PAHs (10 TEF) and oxy-PAHs (only 1 TEF available). TEF values used in this study are shown in Table A7.

3. Results and discussion

3.1 Annual concentrations and seasonal variations

Individual PAH, oxy- and nitro-PAH annual mean concentrations are presented in Table A5 and concentration distributions are shown in Figs. A2, A3 and A4.

The annual mean total (= gaseous + particulate) concentrations of Σ_{21} PAHs were about 23.1 ng m⁻³ and of the same order of magnitude as Σ_{27} oxy-PAHs with a mean annual concentrations of 10.3 ng m⁻³. Annual mean concentrations of Σ_{32} nitro-PAHs were 50 to 100 lower and about 224 pg m⁻³. PAHs accounted for the main fraction ($72 \pm 11\%$) of total PAC (G+P) concentrations while oxy-PAHs and nitro-PAHs accounted for $27 \pm 10\%$ and $1 \pm 0.2\%$, respectively.

The annual trends of PM₁₀, Σ_{21} PAH, Σ_{32} nitro-PAH, Σ_{27} oxy-PAH concentrations together with temperature are presented in Fig. 1. A strong seasonality was observed for all the pollutants with higher concentrations in winter and autumn (from October to March, “cold” period, n=65) and lower concentrations in spring and summer (from April to September, “warm” period, n=58). On average, the PAC concentrations in “cold” period were about 5-7 times higher than those in “warm” period. This typical trend was already reported in previous studies [e.g. Albinet et al., 2008a (France); Bamford and Baker, 2003 (USA); Bandowe et al., 2014 (China); Barrado et al., 2013a (Spain); Chung et al., 2006 (USA); Lin et al., 2015 (China); Marino et al., 2000 (Greece); Ringuet et al.,

2012b; Schnelle-Kreis et al., 2005 (Germany)]. Higher PAC winter concentrations are dominated by additional emission sources in this season, namely residential heating. Atmospheric concentrations may also be enhanced by the meteorological conditions with a more frequent formation of a thermal inversion layer, notably related to the local orography. During the “warm” period, lower primary emissions, and higher photochemical conditions explained the lower PAC concentrations observed.

Interestingly, in the “cold” period PM_{10} concentrations and PAC concentrations were well correlated (Pearson coefficient $r=0.50$, 0.65 , 0.72 for PAHs, oxy-PAHs and nitro-PAHs, respectively) while in the “warm” season, such correlations were not observed ($r=0.01-0.25$). In this period, PAC concentrations decreased dramatically whereas PM_{10} concentrations remained similar ($\approx 24 \mu\text{g m}^{-3}$).

It is worth mentioning that during the winter PM_{10} pollution event (daily PM_{10} concentration $>50 \mu\text{g m}^{-3}$ for at least 3 consecutive days) observed in December (12/09-12/19), the total oxy-PAH concentrations were higher than total PAH concentrations. This indicates that, although the primary PAC emissions were very important (notably from wood burning, Favez et al., 2010), pollutant accumulation during this event possibly enhanced the chemical processes and the secondary formation of oxy-PAHs (Fig. 1). The highest individual PAH and oxy-PAH concentrations were observed during this event (Fig. A2 and A3).

Similarly, the highest nitro-PAH concentrations were observed during the PM_{10} pollution event in February-March, suggesting a combination of both primary emissions and favorable photochemical conditions for the secondary formation of these toxic compounds. The highest individual nitro-PAH concentrations corresponded to both PM_{10} pollution events (Fig. A4).

PAC concentration levels observed in this study were in good agreement for similar sampling site typologies and seasons (Table 1). The measured concentrations in the present study were significantly lower than those obtained in China. Individual PAC concentrations (Table A5) were also in agreement with other studies for almost all the compounds except 1-pyrenecarboxaldehyde (0.05 ng m^{-3}) with significant lower concentrations measured in Grenoble compared to Santiago (Chile) (3.4 ng m^{-3}) (Del Rosario Sienna, 2006) and methyl-nitronaphthalenes (about $2-9 \text{ ng m}^{-3}$)

with concentration levels significantly higher than those in the urban area of Redland (USA) (0.1-0.2 ng m⁻³) (Reisen and Arey, 2005).

3.2 PAC chemical profiles

Phenanthrene, 2-methylnaphthalene, pyrene and fluoranthene accounted for about 74±10% of total PAHs measured in Grenoble on yearly average and were the predominant substances in all seasons (Fig. 2.A). These results are in agreement with those reported previously in the literature (Morville et al., 2011; Possanzini et al., 2004; Reisen and Arey, 2005; Tsapakis and Stephanou, 2004). Interestingly, as observed by Wei et al. (2015a), the contributions of methylnaphthalenes were quite important and accounted for to 30% of the total PAH concentrations. Between “cold” and “warm” periods, an increase of pyrene, phenanthrene, fluoranthene and fluorene contributions and a decrease of 2-methylnaphthalene contribution were observed. Changes in chemical distribution profiles were mainly governed by the differences in sources, gas/particle partitioning (temperature) and PAH photo-reactivity. Considering only the particulate phase, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, chrysene and benzo[e]pyrene were the main PAHs in all seasons and accounted for about 52±10% of the particle-bound PAHs. Profiles were quite similar between both periods and only higher contributions of low molecular mass PAHs (phenanthrene, 2-methylnaphthalene) were noticed.

9-Fluorenone, 1-naphthaldehyde, phthalic anhydride, 1,8-naphthalic anhydride and 1-acenaphthenone were the predominant substances and accounted for about 63±11% of the total oxy-PAHs (Fig.2.B). These compounds were also highlighted in previous studies for their high contribution to oxy-PAH concentrations (Albinet et al., 2007, 2008a; Allen et al., 1997; Bandowe et al., 2014; Ringuet et al., 2012b; Walgraeve et al., 2015, Wei et al., 2015a, b). Main changes from “cold” to “warm” periods were due to the decreasing contributions of 1-naphthaldehyde, 1-acenaphthenone and benzanthrone while the contributions of 1,2-naphthoquinone, 9-fluorenone, phthalialdehyde, 6H-dibenzo[b,d]pyran-6-one, 1,8-naphthalic anhydride, and biphenyl-2'2'-

dicarboxaldehyde increased. Higher contributions of the last substances in the “warm” period may indicate their secondary formation from PAH photochemical reactions (Bunce et al., 1997; Lee and Lane, 2010; Reisen and Arey, 2002; Zhou and Wenger, 2013). For particulate phase only, the main substances were 1,8-naphthalic anhydride, phthalic anhydride, benzanthrone and 1,2-naphthalic anhydride, and accounted for about $71\pm 13\%$ of total particle-bound oxy-PAHs. The higher contribution of phthalic anhydride (secondarily formed, Bunce et al., 1997; Wang et al., 2006) and the lower contribution of benzanthrone (primarily emitted, Fine et al., 2004; Karavalakis et al., 2010, 2011) observed in “warm” period were indicative of the differences of sources and chemical processes.

9-Nitroanthracene, (2+3)-nitrofluoranthene and 1-nitronaphthalene accounted for about $52\pm 10\%$ of total nitro-PAHs on yearly average (Fig. 2.C). This result was in agreement with previous studies (Albinet et al., 2007, 2008a; Bamford and Baker, 2003; Barrado et al., 2013b; Feilberg et al., 2001; Reisen and Arey, 2005; Ringuet et al., 2012b; Wang et al., 2011; Wilson et al., 1995; Zimmermann et al., 2012). The contributions of methyl-nitronaphthalenes and 5-nitroacenaphthene increased from “cold” to “warm” period while those for 9-nitroanthracene and 7-nitrobenz[a]anthracene decreased. Their contribution in the particulate phase also increased during the same period. In particulate phase, (2+3)-nitrofluoranthene, 9-nitroanthracene and 7-nitrobenz[a]anthracene were the dominant substances accounting for about $74\pm 11\%$ of Σ_{32} nitro-PAH_(P). The increase of (2+3)-nitrofluoranthene contribution in the “warm” period was characteristic for higher secondary photochemical processes (Arey et al., 1986).

3.3. Gas/particle phase partitioning

3.3.1 Field observations

Fig. 3. shows the yearly box plot of PAHs, oxy- and nitro-PAHs gas/particle partitioning and the seasonal trends (sigmoid fit) for “cold” and “warm” periods. As previously reported, PAC gas/particle partitioning is dependent on the molecular weight (MW) and vapour pressure (Alam et al., 2014; Albinet et al., 2008a; Delgado-Saborit et al., 2013; Huang et al., 2014; Walgraeve et al., 2015). PAHs with $MW \leq 202 \text{ g mol}^{-1}$ were mainly in the gaseous phase ($>80\%$) while heavier PAHs

($MW \geq 252 \text{ g mol}^{-1}$) were associated with the particulate phase (>95%). Intermediate PAHs with $MW = 216$ to 234 g mol^{-1} were partitioned between both phases. For Oxy-PAHs, lighter compounds with $MW \leq 180 \text{ g mol}^{-1}$ were mainly gaseous (>90%) and heavier ones with $MW \geq 222 \text{ g mol}^{-1}$ were mainly in particulate phase (>80%). The gas/particle distributions of compounds between these both thresholds were more disturbed. For instance, large variabilities were observed for compounds like acenaphthenequinone, 6H-dibenzo[b,d]pyrene-6-one, 1,8-naphthalic anhydride, 9-phenanthrenecarboxaldehyde. Some compounds with the same MW and similar vapour pressure showed very different gas/particle partitioning (e.g. $MW = 208 \text{ g mol}^{-1}$; 9,10-anthraquinone, 1,4-anthraquinone, 9,10-phenanthrenequinone) showing the importance of other parameters like the molecular structure. For nitro-PAHs, lighter substances with $MW \leq 211 \text{ g mol}^{-1}$ were in the gaseous phase ($\approx 90\%$, with the exception of 5-nitroacenaphthene $\approx 50\%$) and heavier nitro-PAHs ($MW \geq 225 \text{ g mol}^{-1}$) were mainly associated with the particulate phase (>80%). Compounds with $MW = 223 \text{ g mol}^{-1}$ were partitioned between both phases with large variabilities. The differences of gas/particle distributions between the “cold” and “warm” period were more pronounced for oxy- and nitro-PAHs than for PAHs and impacted only the compounds with intermediate MWs.

3.3.2 Gas-particle partitioning model evaluation

Gas/particle partitioning prediction is more sensitive for semi-volatile PACs because volatile and non-volatile congeners remain mainly in the gas and particulate phase, respectively. In the present study, acenaphthenequinone, 6H-dibenzo[b,d]pyran-6-one, 9,10-anthraquinone, 9-phenanthrenecarboxaldehyde, 5-nitroacenaphthene, 9-nitroanthracene, 9-nitrophenanthrene, and 3-nitrophenanthrene showed considerable variations of gas/particle partitioning (Fig. 3) and, therefore, were selected for evaluating the model predictions. Figs. 4a and b show the percentage of predictions made with the spLFFER (K_{OA}) and multi-phase ppLFFER model, respectively. As can be seen, the spLFFER model predicted 3 to 63% and 3 to 79% of the observed K_P values for oxy- and nitro-PAHs within one order of magnitude accuracy, respectively. Evidently, percentage of predictions were higher for 9,10-anthraquinone, 9-phenanthrenecarboxaldehyde, 9-nitroanthracene, 9-nitrophenanthrene, and 3-nitrophenanthrene than the rest of the target

compounds. Despite these findings, this model showed a pronounced overall tendency for underestimating K_P (see Fig. A5).

Nitro- and oxy-aromatic compounds may undergo various types of non-specific and specific molecular interactions with OM – i.e. in addition to van der Waals interaction, they may participate in H-bonding as electron donor (Abraham et al., 1990), and due to their polarizable nature they may form π - π or even n - π electron donor/acceptor interactions with the sorbing phase (Zhu and Pignatello, 2005). Octanol (used as a surrogate for OM in the model of Finizio) could simulate various types of interactions with nitro- and oxy-PAHs; however, its polarizability is considerably lower compared to some other organic solvents such as dimethylformamide and dimethyl sulfoxide (see 's' parameter in Table A6). Therefore, it may not be an ideal surrogate for OM, including HuLiS. In this data set, this fraction represents $\approx 50\%$ of the OM, $\approx 2\%$ consisted of HuLiS. WSOM is believed to contain a diverse set of highly oxygenated compounds including carboxylic acids, aldehydes, aromatic acids, and phenols (Paula et al., 2016). For ppLFER model calculations, we selected dimethyl sulfoxide as a surrogate for OSWSOM (organic soluble and water soluble organic matter) (i.e. phase A), because of its relatively high polarizability (s : 2.90, Table A6) and water solubility (1×10^6 mg L⁻¹ at 25°C). Fig. 4a-b and 5a-d show the predictions made with ppLFER model.

As can be seen from Fig. 4, the multi-phase approach noticeably improved the predictions for the target substances. This was less pronounced for 9-nitrophenanthrene and 3-nitrophenanthrene. Accordingly, between 73 to 98% of the data points were predicted within one order of magnitude accuracy for acenaphthenequinone, 9,10-anthraquinone, 9-phenanthrenecarboxaldehyde, 9-nitroanthracene, 9-nitrophenanthrene, and 3-nitrophenanthrene. 50 and 63% of the values were predicted with such accuracy for 6H-dibenzo[b,d]pyran-6-one and 5-nitroacenaphthene, respectively (Fig. 4). No clear distinction was seen in model performance between cold and warm periods, which may suggest that dimethyl sulfoxide could be a good surrogate for OSWSOM even if the chemical composition of this phase and OM in general is changing across seasons as driven by the seasonality of major primary (residential heating, biomass burning, even road transport) and secondary (photochemistry) sources.

K_P for 3-nitrophenanthrene was overestimated for 27% of all data points (Fig. 5c-d), more notably in the “cold” period, which may suggest that the PM surface or bulk OM was not entirely available for partitioning. One should also note that there might be some degree of uncertainty associated with estimating Abraham solute descriptors using ACD/Absolv program, which may lead to under- or overestimation of partitioning constants as well as solute-specific enthalpies of phase transfer. For instance, when estimated solute descriptors for 9-nitroanthracene were used, K_P showed overestimation for most data points by nearly one order of magnitude (not shown here), while using the experimental values (Stenzel et al., 2013), 98% of the data points were predicted within one order of magnitude accuracy (Fig. 4b and 5c-d) (88% within a half-order of magnitude). This highlights the need to determine the experimental Abraham solute descriptors for a larger number of nitro- and oxy-PAHs.

Fig. 6a and b show the mean values for sorption capacities related to adsorption and absorption processes considered in this study. Evidently, absorption was the main partitioning process dominated by the contribution of OSWSOM. This phase, containing mainly polar (Saxena and Hildemann, 1996) and possibly polarizable organic compounds and HuLiS accounted for 93-98% of the K_P for the target analytes on average (Fig. 6). HuLiS has been associated with weak and partly aromatic polyacids with molecular mass in the range of 200 - 500 Da (Kiss et al., 2003; Krivácsy et al., 2000). We assigned a substantial mass fraction to OP but that contributed only 2-5% to the K_P values. The latter may consist of polymers originating from natural sources such as plant cellulose (Puxbaum and Tenze-Kunit, 2003) or from condensation and polymerization of gaseous organics in the atmosphere (Kalberer et al., 2004). Partitioning onto soot dominated the adsorption process (up to 99%) among the phases considered in this study. The results suggest that adsorption onto soluble salts (<0.1% of the total K_P) may be neglected when studying the gas/particle partitioning of nitro- and oxy-PAHs.

3.4. Carcinogenic risk assessment

Fig. 7. shows the annual trend of calculated equivalent toxic concentrations for Σ_{19} PAH, Σ_{10} oxy-PAH and Σ_{10} nitro-PAH. The mean equivalent toxic concentration was 8 times higher in the “cold”

period (1.4 ng m⁻³) than in the “warm” period (0.16 ng m⁻³). The highest equivalent concentration value reached 6 ng m⁻³ during December. The annual mean equivalent concentration was ≈0.8 ng m⁻³. This induces an excess of risk, considering an entire life exposure to the observed concentrations in 2013, ≈8.4×10⁻⁷ equivalent to 10% of the maximum acceptable threshold (=10⁻⁵). These results are consistent with previous studies performed in the French alpine valleys (Albinet et al., 2008a), but are far lower than observations made in China (2013) (10-17 ng m⁻³) (Bandowe et al., 2014; Huang et al., 2013).

The PAHs (19 compounds) accounted for the main part of the cancer risk due to PACs in Grenoble. The number of compounds addressed was not the same, but 19, 10 and 1 for PAHs, nitro- and oxy-PAHs, respectively and concentration level across substance classes was very uneven, with nitro-PAHs 50-100 times lower. Still, oxy- and nitro-PAHs represented only 4% of the cancer risk, on yearly average, and could up to 24% in July. Interestingly, cancer risk induced by PAHs was mainly due to particle-bound compounds and quite constant over the year (87±10%) while, for nitro- and oxy-PAHs, if particulate phase induced the main part of the risk (65±26% on yearly average), gaseous phase was largely more important than for PAHs and could account for 90% of the total risk in spring and summer.

4. Conclusions

A total of 80 PACs were measured in both gaseous and particulate phases, every three days, over a year (2013) in Grenoble (France). To date, this is probably the most comprehensive study of these toxic compounds in ambient air. Yearly mean total concentration of PAHs and oxy-PAHs were in the same order of magnitude while NPAHs were 50 to 100 times less abundant. A strong seasonal variation was observed with higher PAC concentrations in the “cold” period (October to March) than in “warm” period (April to September). This seasonality may be explained by higher emissions from residential heating (and notably wood burning) during the “cold” period and by the formation of thermal inversion layers inducing pollutant accumulation in the Grenoble valley. The highest concentrations measured for PACs were observed during two PM₁₀ pollution events

occurred in 2013. Results obtained show that pollutant stagnation probably favored the formation of oxy- and nitro-PAHs through secondary reactions during these events. PAC partitioning between gaseous and particulate phases showed a strong dependence on compound molecular weight and vapour pressure. ppLFER model using a multi-phase description of the organic and inorganic matter made reasonably good predictions without showing a seasonality effect. This suggests that dimethyl sulfoxide can be a good surrogate for the aerosol OSWSOM regardless of the possible changes in chemical composition of this phase across different seasons. The results indicated that OSWSOM and soot could make substantial contributions to nitro- and oxy-PAH gas/particle partitioning by dominating the absorption and adsorption processes. A better predictability of oxy- and nitro-PAH gas/particle partitioning is limited by experimental data availability (solute descriptors in the ppLFER model). Cancer risk assessment induced by PAC was mainly caused by PAHs. Oxy- and nitro-PAHs contribution to the cancer risk accounted for 24% while nitro-PAH concentrations largely lower and the available toxic equivalent factors for PAH derivatives is very limited. Interestingly, the particulate phase accounted for the main part of total PAC cancer risk (76%).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://www.journals.elsevier.com/science-of-the-total-environment>.

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Table 1

Comparison of mean concentrations (ng m^{-3}) of PAHs, oxy-PAHs and nitro-PAHs measured in Grenoble in 2013 ($n=123$) with those previously reported in the literature. G=gaseous.

Region	Period	Sampling Phase	Type of site	Number of measured compounds	Mean concentration (ng m^{-3})	References
PAHs						
Marseille (France)	Summer	G+PM ₁₀	Urban	15	21.4	Albinet et al., 2007
			Suburban		4.4	
			Rural		16.0	
Birmingham (UK)	Winter	G+PM ₁₀	Traffic roadside	17	87.6	Delgado-Saborit et al., 2013
Barcelona (Spain)	All year	PM ₁₀	Urban	13	13.8	Barrado et al., 2013a
Beijing (China)	All year	PM _{2.5}	Urban	23	143	Lin et al., 2015
Grenoble (France)	Summer	G+PM ₁₀	Urban	21	6.3	This work
	Winter				41.7	
	All year				24.5	
Oxy-PAHs						
Marseille (France)	Summer	G+PM ₁₀	Urban	8	6.3	Albinet et al., 2007
			Suburban		4.2	
			Rural		1.3	
Alpine valleys (France)	Winter	G+PM ₁₀	Suburban	8	17.3	Albinet et al., 2008a
	Summer	G+PM ₁₀			4.6	
Birmingham (UK)	Winter	G+PM ₁₀	Traffic roadside	16	29.1	Delgado-Saborit et al., 2013
Athens (Greece)	Winter	PM _{2.5}	Urban	14	0.55	Andreou and Rapsomanikis, 2009
Boston (USA)	Summer	PM ₁₀	Urban/Roadside	19	10.7	Allen et al., 1997
Augsburg (Germany)	Summer	PM _{2.5}	Urban	6	0.41	Schnelle-Kreis et al., 2007
	Winter				7.4	
Douai (France)	Summer	PM ₁₀	Urban	9	0.38	Mirivel et al., 2010
	Winter				4.5	
Beijing (China)	All year	PM _{2.5}	Urban	5	55.9	Lin et al., 2015
Palaiseau (France)	Summer	PM ₁₀	Suburban	9	0.2	Ringuet et al., 2012b
	Summer				2.8	
	Winter				17.8	
Grenoble (France)	All year	G+PM ₁₀	Urban	27	10.3	This work
Nitro-PAHs						
Marseille (France)	Summer	G+PM ₁₀	Urban	16	0.71	Albinet et al., 2007
			Sub-urban		0.35	
			Rural		0.03	
Baltimore (USA)	Winter	G+PM ₁₀	Urban	26	0.31	Bamford and Baker, 2003
	Summer				0.25	
Fort Meade (USA)	Winter	G+PM ₁₀	Urban	26	0.19	Albinet et al., 2008a
	Summer				0.06	
Alpine valleys (France)	Winter	G+PM ₁₀	Suburban	16	0.52	Albinet et al., 2008a
	Summer				0.12	
Barcelona (Spain)	A year	PM ₁₀	Urban	5	0.12	Barrado et al., 2013a
Mexico City (Mexico)	A year	PM _{2.5}	Urban	9	0.12	Amador-Munóz et al., 2011
Sao Paulo (Brazil)	Summer	PM ₁₀	Urban	16	0.28	De Castro Vasconcellos et al., 2008
Palaiseau (France)	Summer	PM ₁₀	Suburban	19	0.03	Ringuet et al., 2012b
Grenoble (France)	Summer	G+PM ₁₀	Urban	32	0.07	This work
	Winter				0.38	
	All year				0.22	

Figures

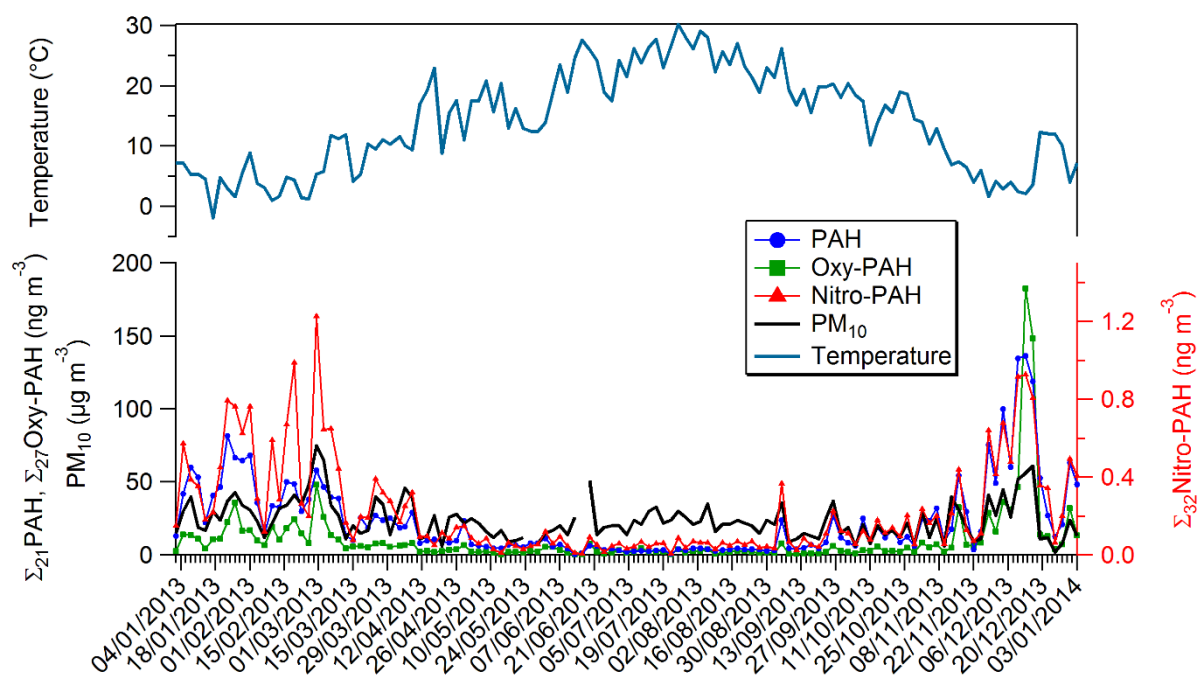


Fig. 1. Annual trends (2013) of PM_{10} , total (= gaseous + particulate) $\Sigma_{21} \text{PAH}$, $\Sigma_{32} \text{nitro-PAH}$, and $\Sigma_{27} \text{oxy-PAH}$ concentrations and temperature at the urban background station of Grenoble-Les Frênes.

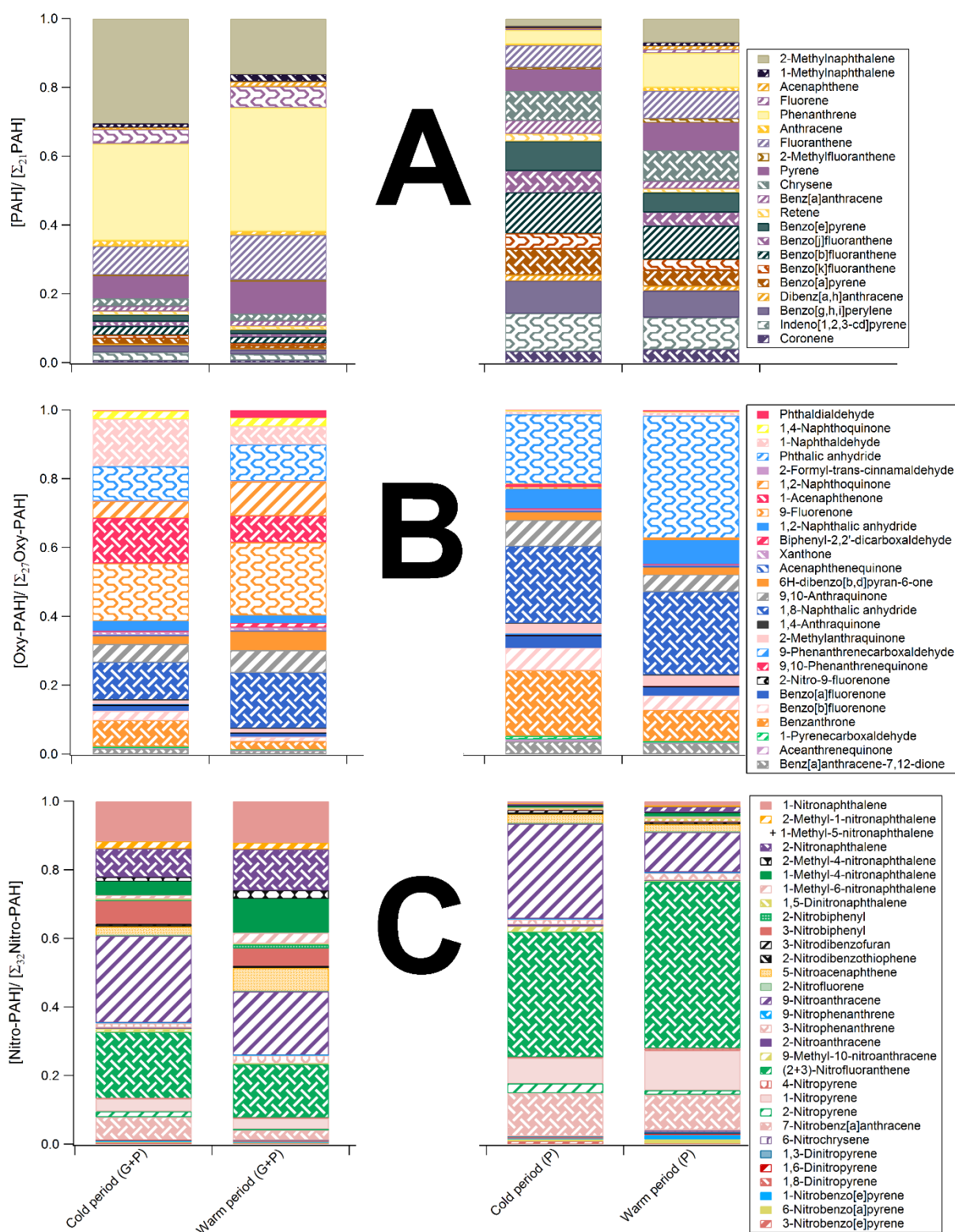


Fig. 2. PAH (A), oxy-PAH (B) and nitro-PAH (C) average chemical profiles during the “cold” (n=65) and “warm” (n=58) periods for both the gaseous and particulate phases (G+P), as well as particulate phase only (P).

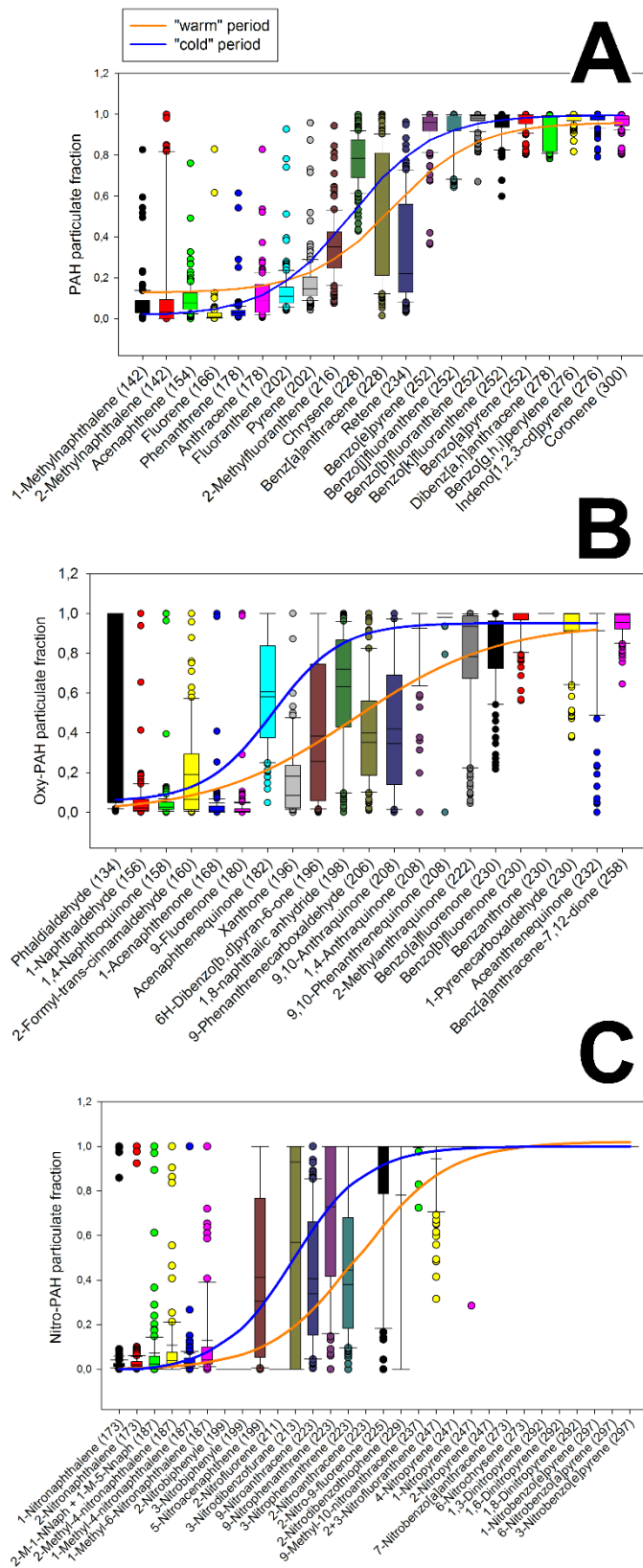


Fig. 3. Gas/particle phase partitioning of PAHs (A), oxy-PAHs (B) and nitro-PAHs (C) classified according to their molecular weight and trends observed for “cold” (n=65) and “warm” (n=58) periods.

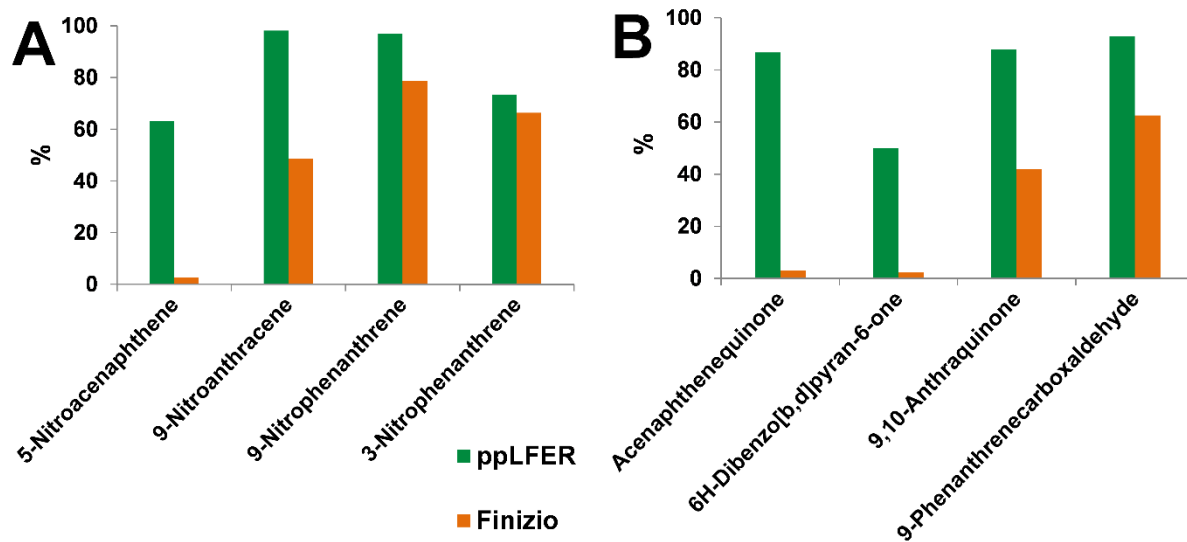


Fig. 4. Percentage of K_P predicted within one order of magnitude accuracy using Finizio and multi-phase ppLFER models.

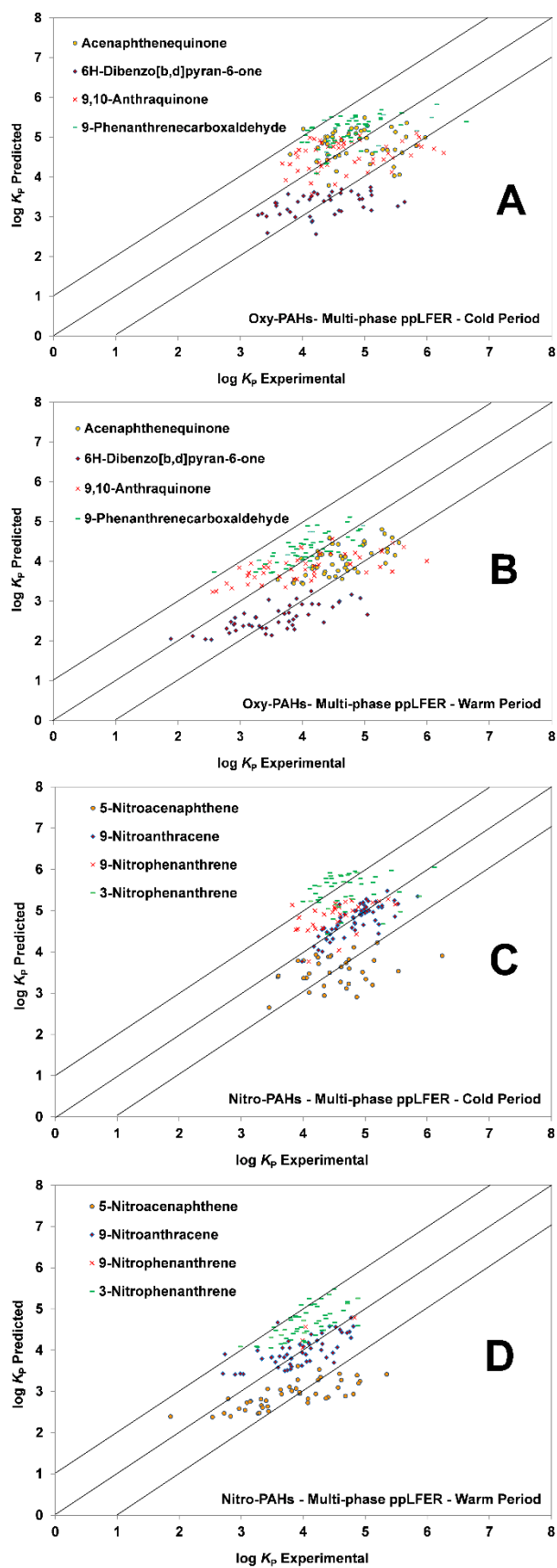


Fig. 5. Predicted versus experimental log K_p ($m^3_{air} g^{-1}PM$) with multi-phase ppLFER for oxy- (A, B) and nitro-PAHs (C, D) during the “cold” (A, C) and “warm” (B, D) periods.

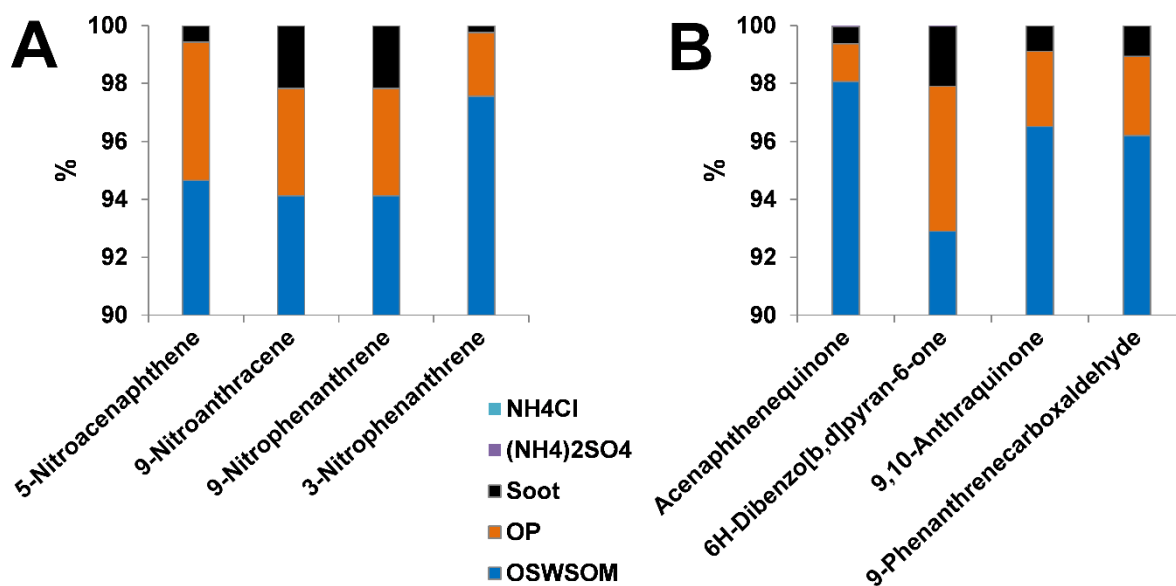


Fig. 6. Contributions of individual phases to K_P determined using multi-phase ppLFER. OSWSOM: both organic soluble and water soluble organic matter; OP: organic polymers. The contributions from $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl were $<0.1\%$ and not visible in the graph.

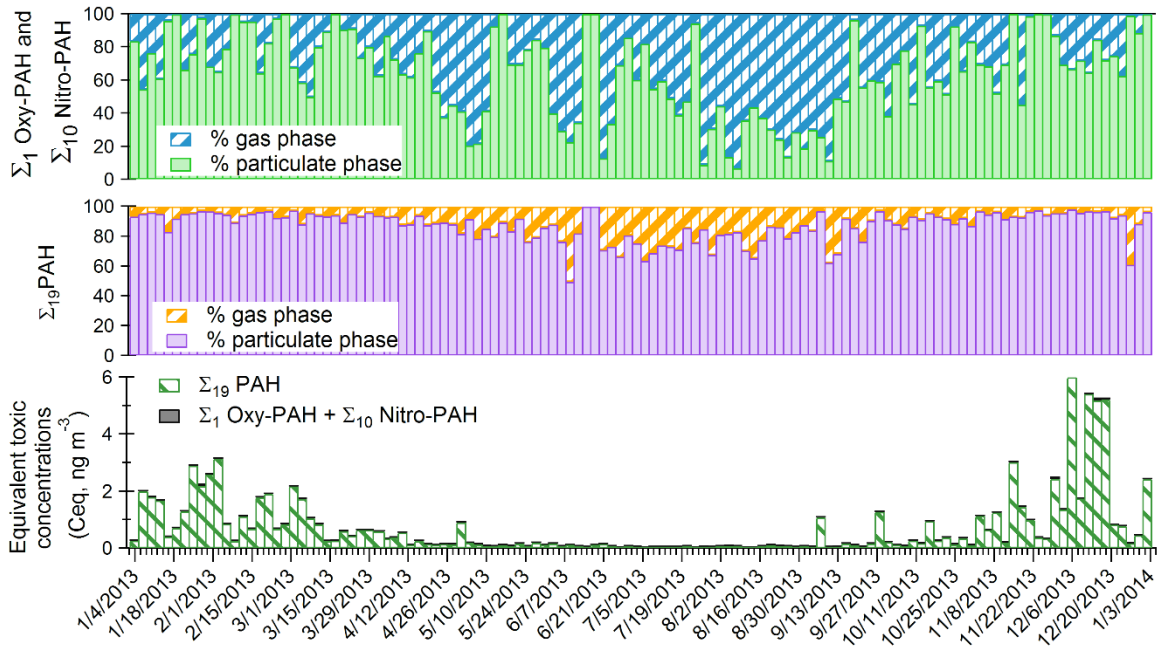


Fig. 7. Annual trend of equivalent toxic concentrations (Ceq) and gas/particle contribution to the cancer risk for Σ_{19} PAHs, Σ_{10} oxy-PAH and Σ_{10} nitro-PAHs.