



Polycyclic aromatic hydrocarbons and their oxygenated derivatives in the urban atmosphere of Athens

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ABSTRACT

Ambient samples of coarse and fine organic particulate matter collected from two urban sites in the city of Athens over one warm and one cold period have been solvent-extracted and quantitatively characterized by gas chromatography–mass spectrometry for their content of polycyclic aromatic hydrocarbons (PAHs) and oxidized PAHs (oxyPAHs). Variable concentrations were observed for the two distinct monthly periods representing a cold, dry period and a summer period, relating to strong local primary emissions and to lower emissions with more stable meteorological conditions, respectively. Additionally, gaseous concentrations of selected PAHs were calculated, revealing that the relative proportions between gaseous and particle phase of individual compounds may differ significantly between summer and late winter, reflecting changes in PAH emission sources and climate conditions. In fact almost all of Σ PAHs were attributed to combustion sources (82–92%), while more than half are considered as comprising of probable human carcinogens (47–62%). Traffic was confirmed as the major contributor of PAHs when appropriate diagnostic ratios and traffic marker compounds were used. This approach also led to the estimation of diesel versus petrol contribution to the atmospheric PAH burden, using the methylphenanthrene to phenanthrene ratio. The fourteen oxygenated polycyclic compounds that were quantified had greater concentrations in the colder period. Among these compounds 9,10-phenanthrenequinone, 1-pyrenecarboxaldehyde and 9H-fluoren-9-one had the highest concentrations.

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1. Introduction

PAHs and oxygenated PAHs (oxyPAHs) are emitted as by-products of almost every type of combustion technology in urban environments including diesel- and petrol-powered motor vehicles, residential heating, fossil fuel combustion in energy and industrial processes, municipal and medical incinerators [1–6]. OxyPAHs, originate also from reactions between PAHs and hydroxyl radicals, nitrate radicals, other organic and inorganic radicals and ozone [7–9] or from photo-oxidation of PAHs by singlet molecular oxygen [10]. Selected PAHs have demonstrated carcinogenic potential [11] and may act as major contributors to the mutagenic activity of ambient aerosols [12]. In fact, oxygen-containing PAH derivatives have been reported as the most mutagenic compounds regarding human-cell mutagens in respirable airborne particles in the north-eastern United States [12]. European Directive number 107 of 2004 [13] uses benzo[a]pyrene as a marker for the carcinogenic risk of PAHs and sets a newly established annual

average target value of 1.0 ng m^{-3} for benzo[a]pyrene found in PM_{10} .

Organic particulate matter pollution in the Greater Athens Area has been the subject of a small number of studies carried out during the last 15 years. These studies have mainly concerned PAHs bound to total suspended particles [14] or PM_{10} [15] or gas to particle partitioning of PAHs [16]. However, neither of the aforementioned studies fulfilled the necessity of monitoring the distribution of particle concentration of PAHs in the fine – respirable ($\text{PM}_{2.5}$) and coarse – inhalable (PM_{10}) size range. Moreover, it is the first time this type of work concerning the organic fraction of particles took place at the “breathing zone” (sampler at ground level) [17], where thousands of people live and work in the centre of Athens. Thus a systematic sampling campaign was necessary, in order to draw trustworthy conclusions about the chemical composition of the organic fraction of aerosol in Athens. The objectives of the present study are the identification and quantification of the PAHs and the oxyPAHs present in the organic extracts, the investigation of seasonal variations and their relationship with other atmospheric pollutants. Moreover, since experimentally determined K_p (gas to particle partition coefficient) values are generally in the same range with the ones obtained from the models [18], we calculated the gaseous concentrations of selected PAHs, in order to obtain

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Table 1
Meteorological parameters and major atmospheric pollutants during the sampling periods.

	T^a (°C)	RH ^b (%)	WS ^c (km h ⁻¹)	CO (mg m ⁻³)	O ₃ (μg m ⁻³)	NO ₂ (μg m ⁻³)	SO ₂ (μg m ⁻³)
August							
Mean	31.07	39.81	2.75	1.41	34.80	27.69	92.78
Min	28.10	31.42	1.59	0.80	7.82	7.17	46.09
Max	33.81	52.58	4.65	2.29	51.67	67.70	161.70
March							
Mean	16.91	49.00	1.80	2.10	13.50	72.59	32.94
Min	10.80	23.19	1.06	0.83	4.50	10.00	20.21
Max	17.90	77.00	5.20	3.50	30.80	67.70	48.25

^a T : temperature

^b RH: relative humidity

^c WS: wind speed.

the sum of PAHs concentrations (gaseous + particle-bound). Finally, we applied statistical diagnostic criteria so as to characterize the emission sources and to distinguish between diesel and petrol emissions.

2. Material and methods

2.1. Area description, sample collection, meteorological parameters and atmospheric pollutants

Two sampling campaigns were carried out between 10 and 27 of August 2003 and 8 and 28 of March 2004 at two sampling sites in Athens (38°02'N, 23°44'E). The first sampling site was located at Athinas Street (ground level) next to the City Hall of Athens (hereafter referred to as Athinas St.) and the second sampling site was on the roof (20 m above ground) of AEDA, a municipality's building (hereafter referred to as AEDA). Athinas St. could be described as the city's commercial and business centre near the central market, while the region surrounded AEDA's building is a typical residential neighborhood of the city-centre, with the blocks of 4–7 storey buildings.

High volume air samplers, equipped with PM₁₀ size selective inlet, PM_{2.5} one stage impactor and backup filter (TE 230 High Volume Impactor, Tisch Environmental Inc., OH, U.S.A.) were used for 24 h sampling at each sampling site. In total 2 samplers were used for 2 sampling sites, one for each site. The flow rate, in order to achieve a 10 and 2.5 μm aerosol diameter cut-off size, was 1.13 m³ min⁻¹, controlled by a Sierra 620 Mass Flow Meter (Sierra Instruments Inc., CA, U.S.A) equipped with a totalizer. The samplers trapped the particulate matter on quartz fibre filters. Field blank samples were used to provide the *a-posteriori* capability to check for transport and storage artefacts [19]. The loaded filters were wrapped in aluminium foil and stored in a freezer (−18 °C) until extraction and analysis.

Meteorological parameters and major atmospheric pollutants were measured at a monitoring station in the centre of Athens by the Ministry for Environment, Physical Planning and Public Works. Table 1 presents the minimum, maximum and average daily values of the meteorological parameters and major atmospheric pollutants measured during the sampling periods.

2.2. Analytical

Solvents of Suprasolv grade (Merck KGaA, Darmstadt, Germany) and silica gel of 230–400 mesh (Merck KGaA, Darmstadt, Germany) were used. Soxhlet thimbles and quartz fibre filters were obtained from Whatman (Whatman International Ltd., Middlesex, U.K.). The PAHs standard mixture consisted of 16 Priority PAH was obtained from Chiron (Chiron AS, Trondheim, Norway). Two authentic standards 4H-cyclopenta[d,e,f]phenanthren-4-one (BCR 338) and 6H-benzo[c,d]pyren-6-one (BCR 339) have been used as

calibration standards for the oxidized PAHs. Hexamethylbenzene and 1-chlorohexadecane (Aldrich) were used as internal standards, added just prior to the GC/MS analysis [20,21]. Silica gel and cotton wool were soxhlet-extracted with methanol–acetone and twice with dichloromethane for 24 h before use. All glasswares were intensively cleaned and baked at 500 °C for 6 h. Prior to their use, quartz filters were baked at 500 °C for 6 h to eliminate potentially existent organics. Following that, they were stored in aluminium foil packages until sampling.

Samples were soxhlet-extracted with dichloromethane for 24 h and, after volume reduction to dryness, were kept in a freezer until silica gel clean up. Each extract was fractionated into compound classes (aliphatic hydrocarbons, PAHs, carbonyl compounds, *n*-alkanols, fatty acids) using flash chromatography [22]. A 30 cm × 1 cm column containing 1.5 g of activated silica gel (150 °C for 3 h) and 5 solvents of increasing polarity (*n*-hexane, toluene, dichloromethane, ethyl acetate, methanol, formic acid) were used to provide 5 fractions of the extract. This study focused on the 2nd and 3rd fractions, characteristic of PAHs and oxyPAHs.

Analysis of all samples was carried out on a HP5890II Gas Chromatograph (GC) interfaced to a VG Trio 1000 Mass Spectrometer. Helium was used as the carrier gas with a head pressure of 12 psi. A DB 5MS fused silica capillary column (30 m, internal diameter 0.25 mm, film thickness 0.25 μm, J&W Scientific, Agilent Technologies, Delaware, U.S.A.) was coupled to the ion source. The GC program included: (a) an isothermal hold for 5 min at 40 °C; (b) a temperature ramp of 12 °C min⁻¹ up to 290 °C; (c) isothermal hold for 6 min at 290 °C; (d) a temperature ramp of 20 °C min⁻¹ up to 325 °C; (e) a final isothermal hold of 10 min. The electron impact ionisation mode conditions were: ion energy 70 eV; ion source temperature 270 °C; mass scan range 15–650 amu. The identification was facilitated by the mass spectral library from NIST (National Institute of Standards and Technology). Relative response factors were calculated for each individual compound. Due to lack of standard mixtures of substituted PAHs, they were quantified using the relative response factor of their parent compounds (e.g. the relative response factor of the pyrene was used for methylpyrene).

Detection and quantitation limits were calculated as the mean plus three and ten times the standard deviation of the blank, respectively. The data below the limit of quantitation were rejected. Individual PAHs quantitation limits ranged between 0.001 and 0.007 ng m⁻³ and the quantitation limit for oxyPAHs was 0.008 ng m⁻³. Blank samples were analysed to quantify sample contamination from materials and from equipment used in collecting and analysing the samples. For every set of samples, we performed one blank test. Recoveries were calculated using a solution containing the 16 PAHs and 2 oxyPAHs standards determined by adding a known standard amount in a blank filter and carrying out the same experimental procedure used for the samples. Recoveries of PAHs and oxyPAHs ranged from 60% to 95%.

Table 2
Mean value (standard deviation) of PM_{2.5} and PM_{10–2.5} mass concentrations (ng m⁻³).

Compound (ng m ⁻³)		August Athinas St.		March Athinas St.		March AEDA	
		PM _{2.5}	PM _{10–2.5}	PM _{2.5}	PM _{10–2.5}	PM _{2.5}	PM _{10–2.5}
Fluorene	Fl	0.01 (0.02)	nd	0.01 (0.02)	0.01 (0.01)	0.03 (0.04)	0.00 (0.01)
Phenanthrene	Phe	0.09 (0.19)	0.00 (0.00)	0.31 (0.32)	0.10 (0.10)	1.00 (0.88)	0.07 (0.06)
Anthracene	Anth	0.02 (0.04)	nd	0.04 (0.06)	0.02 (0.02)	0.18 (0.22)	0.01 (0.02)
Fluoranthene	Fluo	0.14 (0.22)	0.01 (0.01)	1.16 (1.31)	0.15 (0.16)	2.75 (2.57)	0.11 (0.09)
Pyrene	Py	0.09 (0.17)	nd	0.82 (1.09)	0.04 (0.08)	2.28 (2.78)	0.06 (0.07)
Cyclopenta[c,d]pyrene	C[c,d]py	0.01 (0.01)	nd	0.41 (0.55)	0.01 (0.02)	0.68 (0.87)	0.02 (0.02)
Benz[a]anthracene	B[a]anth	0.02 (0.04)	0.00 (0.00)	0.38 (0.75)	0.02 (0.03)	0.46 (0.67)	0.01 (0.01)
Chrysene	Chr	0.05 (0.13)	0.00 (0.00)	0.95 (1.30)	0.01 (0.02)	0.97 (0.99)	0.02 (0.02)
Retene	Ret	nd	nd	0.44 (1.44)	0.02 (0.02)	0.41 (0.64)	0.01 (0.02)
Benzo[b]fluoranthene	B[b]fluo	0.13 (0.16)	nd	9.49 (12.41)	0.06 (0.10)	8.98 (9.58)	0.02 (0.03)
Benzo[k]fluoranthene	B[k]fluo	0.14 (0.35)	nd	2.87 (3.61)	0.03 (0.07)	1.72 (2.24)	0.01 (0.01)
Benzo[a]pyrene	B[a]py	0.10 (0.18)	nd	2.05 (3.44)	0.00 (0.01)	1.54 (2.47)	0.01 (0.01)
Indeno[1,2,3-c,d]pyrene	I[1,2,3-c,d]py	0.10 (0.17)	nd	2.10 (2.38)	0.00 (0.01)	1.83 (1.88)	nd
Benzo[g,h,i]perylene	B[g,h,i]pe	0.21 (0.35)	nd	6.88 (7.25)	0.00 (0.01)	6.05 (5.12)	nd
Dibenzo[a,h]anthracene	D[a,h]anth	0.01 (0.03)	nd	0.14 (0.33)	nd	0.95 (2.10)	nd
Methylphenanthrenes	Mphes	0.04 (0.08)	nd	0.26 (0.33)	0.06 (0.07)	1.02 (1.44)	0.06 (0.10)
Dimethylphenanthrenes	Dmphes	0.01 (0.04)	nd	0.39 (0.56)	0.05 (0.06)	1.40 (2.24)	0.05 (0.06)
Methylpyrenes	Mpys	0.00 (0.01)	nd	0.20 (0.33)	0.01 (0.03)	0.37 (0.39)	0.00 (0.01)
ΣPAH ₁₅		1.12 (1.42)	0.01(0.01)	28.06 (28.91)	0.47 (0.43)	29.82 (26.67)	0.36(0.22)
ΣPAHs		1.17 (1.49)	0.01(0.01)	28.91 (32.61)	0.59 (0.65)	32.61 (29.47)	0.47(0.33)

ΣPAH₁₅: the mean sum 15 un-substituted PAHs, ΣPAHs: the mean sum of all PAHs.

3. Results and discussion

3.1. PAH concentration levels and particle size distribution

Fifteen PAHs (i.e. fluorene, phenanthrene, anthracene, fluoranthene, pyrene, cyclopenta[c,d]pyrene, benz[a]anthracene, chrysene, retene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, benzo[g,h,i]perylene and dibenzo[a,h]anthracene listed in Table 2) and a number of their substituted (methyl-dimethyl) homologues have been identified and quantified in 58 dual (fine and coarse) samples collected during August 2003 and March 2004. Table 2 presents PAH concentrations obtained in the present study. The sum of methylphenanthrenes consisted of 4 isomers, the sum of dimethylphenanthrenes of 8 isomers, and the sum of methylpyrenes of 5 isomers. ΣPAHs concentration ranged from 0.01 to 119.90 ng m⁻³ for PM_{2.5} and to 1.34 ng m⁻³ for PM_{10–2.5}. Results of Table 2 show great differences in PAHs concentrations between fine and coarse particles. The concentrations of ΣPAHs were higher in the fine than in the coarse fraction (*t* test, critical of $|t|$ for confidence interval of $P < 0.0001$). Moreover the concentrations of ΣPAHs in fine particles are significantly higher in March (*t* test, critical of $|t|$ for confidence interval of $P < 0.0001$). In August the concentration of ΣPAHs in the fine fraction (PM_{2.5}) is one order of magnitude greater than the concentration of PM_{10–2.5}. During March (late winter weather conditions) the difference between the ΣPAHs concentrations of fine and coarse particles rose to two orders of magnitude. This is explained by the increased number of combustion processes in the winter months. In our study 98% of the identified and quantified compounds were found in PM_{2.5}. Field studies [23] carried out at traffic tunnels, estimated that 95% of total PAH is associated with a fraction less than 1 μm in diameter.

All compound concentrations were higher in March (cold period) than those in August (warm period) for both fine and coarse airborne particles. The ratio cold to warm ΣPAHs concentration were 25.37 for PM_{2.5} and 7.41 for PM_{10–2.5}, much higher than the ratios found in former studies in Athens [15]. Other studies carried out in Europe and in the U.S.A. found that concentrations of PAHs in winter were generally higher by a factor of 1.5–10 than those in summer in agreement with our results [24–26]. Many factors influence the changes in PAH concentrations and profiles in

the colder period. The main influence arises from changes in the main sources. During the late winter conditions the concentrations of PAHs are generally higher than the summertime, probably due to the increased “fuel–oil” usage for central heating [27,28]. Additionally, higher PAH emissions from traffic due to extended cold start conditions increased the atmospheric PAHs concentrations [29]. In wintertime, more intense ground based temperature inversions also increase the pollutant’s concentrations because of lower atmospheric mixing heights [30]. In contrast to wintertime, the summer holiday season during August leads to much lower vehicular emissions in the centre of Athens in comparison to the cold sampling period. Furthermore, the atmospheric decomposition of PAH due to photodegradation [31] and reaction with ozone [32] or other atmospheric oxidants such as NO₃ and OH [33,34] in the atmosphere and on the filters [35] is higher during the summertime, leading to lower PAHs concentrations.

In fact our results show that a good negative Pearson correlation ($R = 0.74$) exists between fine particulate ΣPAH and O₃ concentrations, pointing out that ozone formation in the urban atmosphere causes degradation of PAH compounds during summertime. This is corroborated by the estimated lifetimes of PAHs, ranging between 10 min and 24 h, for a polluted urban environment as far as their reaction with O₃ is concerned [36]. Concentrations of ΣPAHs and NO₂ (Pearson correlation coefficient: $R = 0.48$) and SO₂ (Pearson correlation coefficient: $R = 0.59$) are positively correlated, suggesting that all concentrations are influenced by the emissions from combustion-related activities. Pearson correlation coefficients between ΣPAHs, meteorological parameters and other atmospheric pollutants are given in Table 3. The statistically significant values ($P > 0.5$) have been marked in Table 3.

3.2. Gas to particle partitioning

A significant component of PAHs budget is miscounted, because direct determination of gas to particle partitioning distributions in ambient air is experimentally a challenging problem [37]. It is increasingly accepted that partitioning of semivolatile organics to aerosols is controlled by an absorptive rather than, or in addition to an adsorptive mechanism [38]. Hence, theoretical and experimental gas/particle partitioning coefficients, $K_{p,i}$ were equated in order to calculate the gaseous concentration of PAHs (Eq. (1), (2)

Table 3
Pearson correlation coefficients between ΣPAHs, meteorological parameters and other atmospheric pollutants.

	T^a	RH ^b	WS ^c	CO	O ₃	NO ₂	SO ₂
August, Athinas St.	-0.33	0.44*	-0.49*	0.38	-0.74*	0.36	0.39
March, Athinas St.	0.13	-0.34	-0.36	0.35	-0.18	0.45*	0.34
March, AEDA	0.06	-0.28	-0.44*	0.18	-0.40	0.48*	0.59*

^a T: mean ambient temperature.

^b RH: mean relative humidity.

^c WS: mean wind speed.

* Values are statistically significant ($P > 0.5$).

and (3)), when gas/particle partitioning is dominated by absorptive partitioning [39].

$$K_{p,i}(\text{experimental}) = K_{p,i}(\text{theoretical}) \quad (1)$$

$$K_{p,i}(\text{experimental}) = \frac{C_{p,i}}{\text{TSP}C_{g,i}} \quad (2)$$

$$K_{p,i}(\text{theoretical}) = \frac{760RTf_{om}}{MW_{om}10^6\zeta_i p_{L,i}} \quad (3)$$

The aforementioned abbreviations stand for: $K_{p,i}$: partitioning coefficient; $C_{g,i}$: gaseous concentration (ng m^{-3}); $C_{p,i}$: particle concentration (ng m^{-3}); TSP: mass concentration of total suspended particles ($\mu\text{g m}^{-3}$); R : the ideal gas constant ($8.206 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$); T : the temperature (K); f_{om} : the mass fraction of the TSP that is the absorbing organic material (om) phase; MW_{om} : the average molecular weight of the absorbing om phase; $p_{L,i}$: the vapour pressure (Torr) of the absorbing compound i as a liquid; ζ_i : the activity coefficient of compound i in the om phase.

The experimental partitioning coefficient $K_{p,i}$ was calculated assuming that $C_{g,i}$ and $C_{p,i}$ are the relative concentrations in the gas and particle phase. Due to the absence of the mass concentration of total suspended particles (TSP), a conversion factor was used to obtain TSP ($\text{PM}_{10}/\text{TSP} = 0.8$ for urban road traffic) [40]. PM_{10} is the average mass concentration of particles with aerodynamic diameter $\leq 10 \mu\text{m}$ ($\mu\text{g m}^{-3}$) measured by our on-site Particle Analyser using Beta-Attenuation (FH62I-R, ESM-Thermo Andersen). The size distribution of PAHs had been the subject of recent articles [41–44]. Particulate matter in fraction $>7.5 \mu\text{m}$ contributed approximately 5.2% to total PAHs concentration at an urban roadside site in Thessaloniki in wintertime [44], whereas the contribution of PM in fraction $>7 \mu\text{m}$ ranged from 4.7% (winter) to 11.9% (summer) at an urban site in Beijing [41]. Moreover, it has been found that PAHs with 3–4 rings that are mainly found in the gas phase are distributed over $10 \mu\text{m}$ and those PAHs with 5–6 rings are found in the accumulation mode [43].

MW_{om} is the average molecular weight of the absorbing organic material phase (om) (g mol^{-1}). For urban particulate material, since secondary aerosol is derived from the oxidation of fairly low molecular weight species [45], a reasonable range for MW_{om} might be around 100–300 [39]. In our estimation, like in octanol–air partition coefficient absorption models [46,47], the assumption that organic compounds present on urban aerosols have, on average, the molecular formula of octanol (74% carbon) has been used, $M_{om} = M_{\text{octanol}} = 130$ [38,48].

Atmospheric f_{om} [49] was taken from various organic carbon measurements in the United States [50], namely 40%, 25%, and 19% for urban, rural, and background areas, respectively. A range of 0.1–0.3 is probably reasonable for f_{om} [39]. For ζ_i , a range of 1–5 seems reasonable for dissolution of a non-polar semivolatle organic compound into the at least somewhat polar organic matter in urban particulate material [39]. Liquid vapour pressure ($p_{L,i}$)

values used in this study were estimated for a number of PAHs at 25°C [51,52].

Mean concentrations in particulate form (PM_{10}) and in gaseous form, total concentrations and % homologue fraction in particulate (PM_{10}) form are listed in Table 4. Concentrations of gaseous PAHs in the summer were generally higher than those in the winter, as expected due to higher ambient temperatures. It is clear from Table 4 that three-ring and most four-ring PAHs such as fluorene, phenanthrene, anthracene, fluoranthene and pyrene were found predominantly in the gas phase, with only a small fraction associated with particulates. Higher condensed molecules with five and more rings are particle-bound, whereas smaller PAHs mainly remain in the gas phase [53].

For all compounds the wintertime concentrations in the particulate form were substantially higher than those in the summertime, although the percentage increase from August to March was different for each compound. The % homologue fraction in particulate form listed in Table 4 was also determined for Rome [54], Marseilles [55], Chicago [56] and Birmingham [57]. Our findings regarding B[b+k]fluo, B[a]py, I[1,2,3-c,d]py, B[g,h,i]pe and D[a,h]anth are in good agreement with those obtained experimentally in the other studies. Chrysene appeared to be more equally divided between the two phases by in March with 34% in particulate phase than in August with only 7.9% in particulate phase. As far as three- and most four-ring PAHs, found predominantly in the gas phase, are concerned, our results appear to underestimate their concentrations in comparison to the measured ones in the other studies. Even under these conditions, the collection of particulate phase alone appears to be adequate to quantify the mean concentration of five-ring carcinogenic PAHs and, in particular, of B[a]py which is used as marker compound by legislation.

The differences between gaseous and particle phase concentrations of selected PAHs are statistically significant in summer and in winter (t test, critical of $|t|$ for confidence interval of $P < 0.0001$). In order to reveal the atmospheric processes responsible for the seasonal variation and distribution between gaseous and particulate phase of PAHs, it is mandatory to analyse the local and the regional meteorology. Particulate PAH levels show a negative correlation with temperature in August. These features can be explained on the basis of mixing height, which reduces with the fall in temperature and restricts the mixing of pollutants in the atmosphere. Aerosol phase PAHs concentrations show a negative correlation with wind speed. Higher wind speed can lead to advection of pollutants. A possible reason for the high concentration of particulate PAHs during late winter season appears to be related with the low temperature during that period, which made favourable conditions for the condensation and/or adsorption of these species on particles present in air. Although some of the meteorological parameters play an important role in controlling the concentrations of PAHs at each site, the site-specific emission sources may also influence their levels in the ambient air. It has been also indicated [58] that PAHs concentrations in the winter season can be attributed to (a) an increase in the consumption of combustible fossil fuels; (b) increased condensation of the PAHs in the gaseous phase at low temperature [59]; (c) lower photochemical degradation under winter solar radiation [60]. Thus, the relative proportions of individual compounds in either gaseous or particulate form may differ significantly between summer and late winter, possibly reflecting changes in PAH emission sources and climate conditions.

3.3. Marker compounds and diagnostic ratios

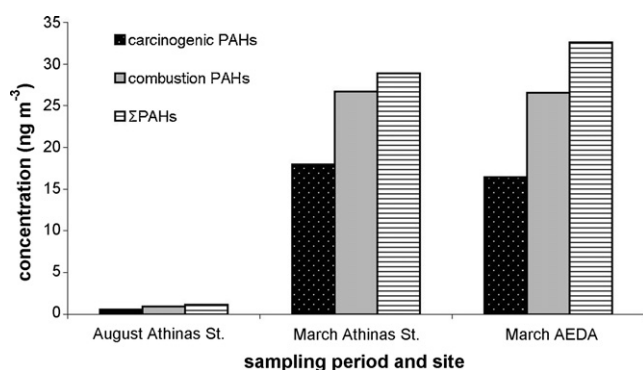
A characteristic group of PAHs, which has been used to reconcile their presence with potential emission sources (combustion sources) is the sum of concentrations of nine major non-alkylated compounds (fluoranthene, pyrene, benz[a]anthracene, chrysene,

Table 4
Mean concentrations (ng m^{-3}) in particulate form (PM_{10}), gaseous form, total and % in particulate (PM_{10}) form.

Summertime	Measured particulate form (PM_{10}) ^a	Estimated gaseous form	Total	% In particulate form (Athens)	% In particulate form (Rome ^b)	% In particulate form (Marseilles ^c)	% In particulate form (Chicago ^d)	% In particulate form (Birmingham ^e)
Flu	0.01	12.20	12.21	0.1		1		3
Phe	0.10	15.94	16.03	0.6		2		6.51
Anth	0.02	3.05	3.07	0.7				26.23
Mphe	0.01	0.53	0.55	2.2				
Fluo	0.15	1.82	1.97	7.5	4	7	15	16.59
Py	0.09	2.66	2.75	3.19			17	16.52
B[a]anth	0.03	0.03	0.05	49.87			65	38.24
Chr	0.06	0.72	0.78	7.9	47		56	34.43
B[b]fluo	0.13	0.00	0.13	98.7	84		88	89.47
B[k]fluo	0.14	0.00	0.14	98.7	84		90	87.5
B[a]py	0.01	0.00	0.01	92.3	99		95	92
I[1,2,3-c,d]py	0.10	0.00	0.10	99.97			98	100
B[g,h,i]pe	0.21	0.00	0.21	99.72			98	100
D[a,h]anth	0.01	0.00	0.01	99.99				100
wintertime								
Flu	0.01	7.28	7.29	0.17				7.74
Phe	0.40	43.10	43.50	0.91				4.48
Anth	0.05	5.29	5.34	0.99				8.69
Mphe	0.09	2.04	2.12	4.16				
Fluo	1.29	9.86	11.15	11.58	10			9.43
Py	0.86	16.78	17.63	4.86				6.21
B[a]anth	0.40	0.25	0.65	61.82				26.48
Chr	0.96	1.90	2.86	33.52	37			34.05
B[b]fluo	9.54	13.20	22.74	41.95	97			86.98
B[k]fluo	2.89	3.91	6.81	42.52	97			93.33
B[a]py	2.05	0.01	2.06	99.37	99			90.12
I[1,2,3-c,d]py	2.11	0.00	2.11	99.97				99.48
B[g,h,i]pe	6.88	0.01	6.90	99.80				96.95
D[a,h]anth	0.14	0.00	0.14	99.81				93.98

^a $\text{PM}_{10} = \text{PM}_{2.5} + \text{PM}_{10-2.5}$.^b [54].^c [55].^d [56].^e [57].

benzofluoranthenes, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene) expressed as CPAHs (combustion PAHs). When the ratio CPAHs to total PAHs is close to unity it has been suggested that PAHs are produced by combustion activities [61]. Moreover, the U. S. Environmental Protection Agency has classified seven PAH compounds as probable and possible human carcinogens: benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene. The average concentration of ΣPAHs in the fine fraction together with the sum of carcinogenic and combustion PAHs is presented in Fig. 1 for both sites. Results given in Fig. 1 show almost all of ΣPAHs concentration is attributed to combustion sources (83–95%) while more than half are considered as

**Fig. 1.** Average concentration of fine particle–phase ΣPAHs , carcinogenic and combustion PAHs.

probable and possible human carcinogens (49–66%). The sampling site at Athinas St., with the sampler placed on the ground, a few meters from the main road is mainly characterized by vehicular emissions having greater carcinogenic PAH concentrations than AEDA site. All compounds that have been named as carcinogenic PAHs are abundant in the exhaust emissions from petrol and diesel vehicles. In general, diesel fuels contained higher amounts of lower molecular weight (2–4 ring) PAH than petrol, whereas petrol vehicles that burn lubrication oil show high PAH emission rates (including heavy PAH, such as dibenzo[a,h]anthracene and indeno[1,2,3-c,d]pyrene) [62].

Fig. 2 shows the mean PAHs profile (percent contribution of each compound to ΣPAH) in fine PM. Compounds with molecular mass ≥ 252 (PAHs with 5 or 6 rings: benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, indeno[1,2,3-c,d]pyrene) are summed and characterized as heavy PAHs. The total PAHs mass was dominated by heavy PAHs in the fine fraction with 58.8% in August, 81.4% and 64.7% in March at Athinas St. and AEDA, respectively. Particulate phase PAHs in the atmosphere are found in the fine particle size range [23,29], while internal combustion engines in motor vehicles generate particles in their exhaust with diameters $< 2.5 \mu\text{m}$ [63]. Heavy PAHs have been used as tracers for vehicular emissions. In particular benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene are strongly related to exhaust emissions from all motor vehicles. Due to their low vapour pressures, PAHs with five or more aromatic rings rapidly condense onto particles once emitted into the atmosphere resulting in a higher proportion of these PAHs in smaller, respirable size particles [23]. Heavy PAHs are less abundant in the total mass of PAHs on coarse particles, with

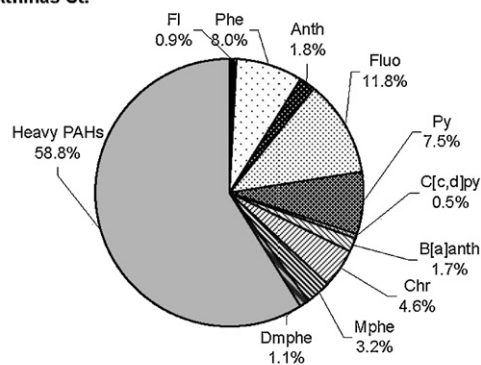
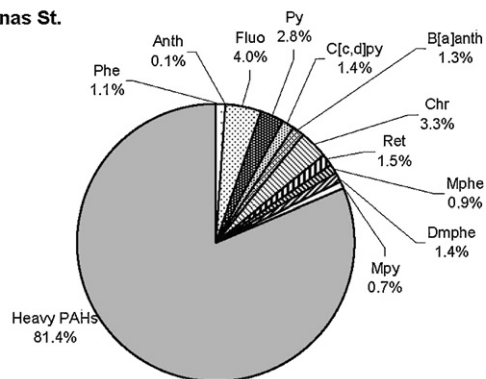
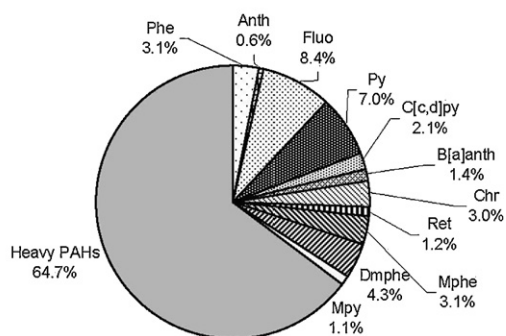
August PM_{2.5} Athinas St.March PM_{2.5} Athinas St.March PM_{2.5} AEDA

Fig. 2. Average mass percent distributions of PAHs in PM_{2.5} (heavy PAHs: PAHs with molecular mass ≥ 252).

a contribution of 16% at Athinas St. and 9% at AEDA only during the cold sampling period. Phenanthrene, fluoranthene and pyrene predominate in the total mass of PAHs on the coarse fraction and are characteristic of coal combustion [64]. Retene with a smaller contribution in both fractions is derived from wood combustion [65].

The presence of some congeners has been used for deriving information about the relative impact of sources of aerosols. Exhaust emissions from petrol vehicles have high abundances of indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene, due to the composition of the lubricating oil used and not the petrol fuel itself [5]. Emissions from diesel vehicles have shown an abundance of benz[a]anthracene and chrysene [62]. The temporal evolution of the sum of the concentrations of the un-substituted identified PAHs (Σ PAHs) in the fine fraction is presented in Fig. 3 for each distinct period of sampling at Athinas St. In March, benzo[g,h,i]perylene in PM_{2.5} at both sites, was positively and significantly correlated to indeno[1,2,3-c,d]pyrene (Pearson correlation coefficient: $R=0.87$, Athinas St., $R=0.85$, AEDA) and to total PAHs concentrations (Pearson correlation coefficient: $R=0.92$ Athinas St., $R=0.86$ AEDA).

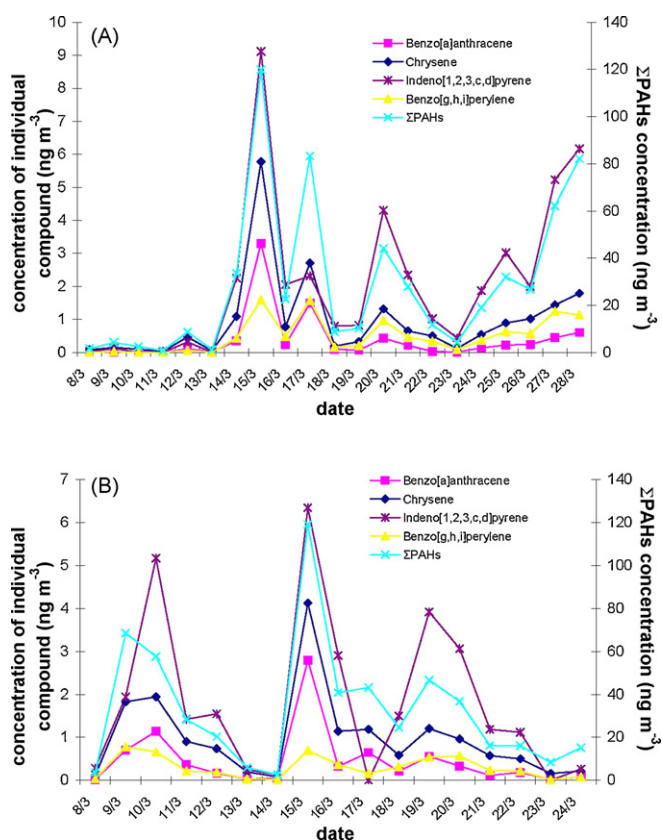


Fig. 3. Time-series of the concentration of selected compounds and Σ PAHs in PM_{2.5} at Athinas Str. (A) and AEDA (B) in March.

Benz[a]anthracene at both sites, was also significantly correlated to chrysene (Pearson correlation coefficient: $R=0.98$, Athinas St., $R=0.98$, AEDA) and to Σ PAHs (Pearson correlation coefficient: $R=0.92$, Athinas St., $R=0.86$, AEDA). The aforementioned good correlations indicate a relative similar significance of petrol and diesel vehicle emissions in Athens. The significant correlation between the petrol markers was also evident for the summer samples (Pearson correlation coefficient: $R=0.98$) and between benzo[g,h,i]perylene and Σ PAHs (Pearson correlation coefficient: $R=0.90$). In antithesis, for the summer data no correlation was found between the diesel markers (Pearson correlation coefficient: $R=0.33$). Also, chrysene was moderate correlated (Pearson correlation coefficient: $R=0.53$) to Σ PAHs. This may be attributed to reduced emissions of heavy and light duty trucks in the centre of Athens, because of the holiday season, or to lower concentrations due to higher ambient temperature.

In general, wintertime PAH levels tend to maximize because of the prevailing atmospheric conditions during this season that do not favour dispersion and decomposition, in addition to the presence of emissions from seasonal sources, such as residential heating facilities. Fuels used for residential heating are primarily oil and secondarily wood. Most residences use low sulphur diesel for heating. For oil burning facilities the low ratio of B[g,h,i]pe/B[a]py has been used as an indication of heating emissions. The B[g,h,i]pe/B[a]py ratios calculated from heating facilities emissions were 0.4 in Thessaloniki [66] and 0.5 in Chicago [67]. In March the calculated ratios were 3.36 in Athinas St. and 3.92 in AEDA, respectively, showing that traffic is the major source contributing to PAHs emissions.

Several diagnostic ratios have been calculated for PM_{2.5} concentrations, providing an indication about the impact of different sources to atmospheric concentrations PAHs. Most of the diagnostic ratios are used to evaluate the contribution of vehicular

emissions (e.g. $I[1,2,3\text{-}c,d]py/(I[1,2,3\text{-}c,d]py + B[g,h,i]pe)$ [26,68], $B[a]anth/(B[a]anth + Chr)$ [26,66,68], $Fluo/(Fluo + Py)$ [22,26], $Phe/(Phe + Anth)$ [68,69]) or contribution of diesel versus petrol (Mphes/Phe[70]). Subsequently, the aforementioned ratios were calculated for the emission rates from diesel trucks, non-catalyst autos and catalyst equipped autos. Moreover, re-suspended road dust coated with “old” PAHs was another potential source for the observed concentrations. The fine aerosol emissions rates from 13 different automobiles and the mass concentration from paved road dust were obtained from Rogge et al. [29,71]. This vehicle fleet consisted of 6 non-catalytic autos, 7 catalytic autos and 2 diesel trucks that were in use in the Los Angeles area. The calculated ratios in our study are plotted in Fig. 4, revealing similarities among fine particles and emission sources.

The concentrations of some marker compounds and their ratios can give some indication about the impact of different sources of airborne compounds. Although this matter has been debated, these marker compounds are often used to indicate the prevalence of gasoline or diesel engines as well as the relative contribution of traffic, and other sources. For this purpose, some molecular diagnostic ratios of the concentrations of PAHs and ratios of emission rates from emissions sources are used and compared. Up to now each ratio was only compared to ratios from other studies or ratios from emission sources, but in Fig. 4 the whole “image” of different ratios for different sources along with ratios from atmospheric concentrations was captured. In Fig. 4 the y axis represents the values of the ratios of emissions sources and the second y axis the values of the ratios of the PAHs concentrations in Athens. Ratios obtained from road dust emissions, diesel trucks emissions and concentrations in August at Athinas St. have the same peaks (ratio *b* and *i*). Moreover ratios obtained from non-catalyst and catalyst vehicles have the same trend (the slope for ratios *a*, *b*, *c* and *j*, peak for ratio *h*) as the ones calculated for PAH concentrations in March at Athinas St. and AEDA. As it can be seen the ratios *c*, *d*, *e* and *f* do not give much insight into the contribution of one source or the other.

3.4. Estimation of diesel contribution using the Mphe/Phe ratio

Diesel contains a relative high amount of alkylated PAHs compared to the non-alkylated compound. The dimethyl phenanthrenes and dimethyl athracenes contribute maxima to the sum concentration of PAHs in diesel fuel and the ratio of these substituted compounds to their non-alkylated compounds is 33.5 [72]. However, when it comes to tailpipe emissions the ratio decreases

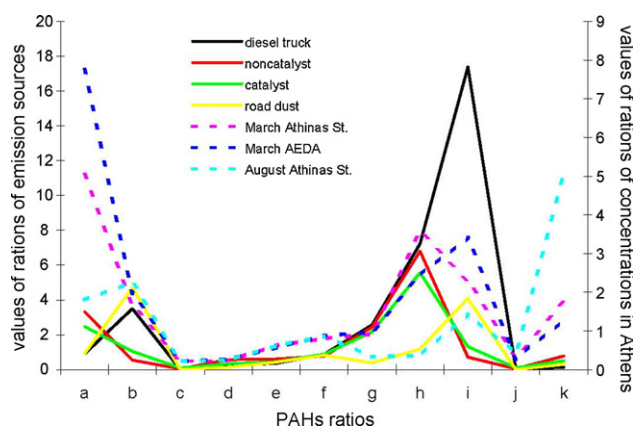


Fig. 4. Diagnostic ratios applied to $PM_{2.5}$, emissions rates for diesel, non-catalyst and catalyst equipped autos and road dust. (a) $B[g,h,i]pe/B[a]py$ [26,66], (b) $B[b+k]fluo/B[g,h,i]pe$ [66], (c) $I[1,2,3\text{-}cd]py/I[1,2,3\text{-}cd]py + B[g,h,i]pe$ [26,68], (d) $B[a]a/B[a]a + Chr$ [26,66], (e) $Fluo/Fluo + Py$ [22,26], (f) $Phe/Phe + An$ [68,69], (g) $Mphes/Phe$ [70,72], (h) $Mphes + Dmpes/Phe$ [70], (i) $Py/B[a]py$ [26], (j) $I[1,2,3\text{-}cd]py/B[g,h,i]pe$ [73], and (k) $B[a]py/Chry$ [69].

significantly. The Mphe/Phe ratio for diesel emission has been estimated 1.4–5.5 [5,72–74]. Fuel aromaticity, engine load, PAH accumulation in lubricant oil, lubricant oil combustion, and cold start behaviour influence the emission rates for PAHs [29], leading to a high Mphe/Phe ratio at low combustion and exhaust temperature, while it decreases with increase in combustion and exhaust temperature [70]. Regarding petrol vehicles an increased dealkylation of the particle phase PAHs in catalyst equipped petrol powered vehicles [75] is observed. Ratios ranging from 0.2 [76] up to 1.0 [5] have been reported for petrol-powered vehicles.

The Mphe/Phe has been used in the past as an indicator of the relative contribution of diesel to petrol vehicle emissions [70,77]. Described in detail by Nielsen [70], the goal of the method was to estimate the proportion of a stable compound (e.g. benzo[a]pyrene or benzo[e]pyrene) that is coming from diesel exhaust and thus to give an estimation of the diesel B[a]py proportion of the city traffic B[a]py contribution. The equation (Eq. (4)) used, is:

$$B[a]py_{diesel} = B[a]py_{site} \times \left[\frac{(Mphe)/Phe_{site} - (Mphe)/Phe_{gasoline}}{(Mphe)/Phe_{diesel} - (Mphe)/Phe_{gasoline}} \right] \quad (4)$$

We assumed that 5.5 is the diesel Mphe/Phe ratio and 0.7 is the non-diesel Mphe/Phe ratio [73] so as to have a benchmark with the previous studies. Specifically, the MePh/Ph diesel traffic value of 5.5 used above was an average of emissions from five types of diesel engine ranging from 1500 to 10,400 cm^3 [73] and Swedish bus simulating typical driving conditions in a European city [74]. The value of 0.7 was from a spark-ignition engine (1600 cm^3). All vehicles run at zero engine loads with a constant speed of 3000 rpm [73]. Eq. (4) was used for the fine particle concentrations of methylphenanthrenes and phenanthrene for both sites in March. The difference $\Delta B[a]py_{diesel} = B[a]py_{diesel,Athinas} - B[a]py_{diesel,AEDA}$ was correlated (Pearson correlation coefficient: $R = 0.9$) with the difference of the B[a]py concentration ($\Delta B[a]py = B[a]py_{Athinas} - B[a]py_{AEDA}$). The correlation is significant in comparison to the ones calculated in the previous studies (Pearson correlation coefficients: $R = 0.69$ in Copenhagen [70], $R = 0.66$ in Birmingham [77]). With the y intercept forced to zero, the gradient gives the fractional contribution of diesel emissions to total traffic emissions of B[a]py and thus a reasonable estimate of emissions of $\Sigma 4-7$ ring PAHs [77]. In our study, diesel contributes $59 \pm 7.5\%$ to overall traffic emissions, a contribution at the same level as the ones estimated in Copenhagen (54%) and in Birmingham (60%).

3.5. Oxygenated polycyclic compounds

Atmospheric concentrations of oxyPAHs have been highly correlated to reactive oxygen species formation [78]. Especially diesel exhaust particles and PAH quinones are assumed to be involved in the formation of oxidative stress and responsible for several health effects as seen in cardiovascular disease [79]. Carboxyaldehydes, polycyclic aromatic ketones and quinones are found on diesel particles, wood smoke particles as well as on particles from gasoline vehicles [28,29]. Oxygenated polycyclic aromatic compounds are also produced through photo-oxidation reactions of PAHs with atmospheric oxidants, including ozone and nitrogen oxides [7,9,80]. Light-induced radical chain reactions initiated by oxyPAHs are most likely to be the degradation pathway for particle-associated PAHs [81] and nitro-PAHs [82]. The only oxyPAHs that were detected above the quantitation limit in the $PM_{10-2.5}$ samples are benzophenone (August $0.05 \pm 0.06 \text{ ng m}^{-3}$, March $0.06 \pm 0.1 \text{ ng m}^{-3}$) and fluorenone (August $0.01 \pm 0.05 \text{ ng m}^{-3}$, March $0.87 \pm 1.75 \text{ ng m}^{-3}$). No compounds were detected in the $PM_{10-2.5}$ samples at AEDA. Fourteen oxygenated polycyclic compounds were identified and quantified in the fine fraction (Table 5).

Table 5
Mean value (standard deviation) of oxyPAHs mass concentrations (ng m^{-3}) during August and March.

	August Athinas St.	March Athinas St.	March AEDA
Benzophenone	0.26 (0.21)	0.15 (0.37)	nd
9H-Fluoren-9-one	0.58 (0.44)	0.65 (1.49)	0.04 (0.12)
Athracene -9,10-dione	0.07 (0.08)	0.09 (0.25)	0.00 (0.02)
Fluorencarboxyaldehyde	0.05 (0.11)	0.09 (0.22)	0.07 (0.27)
Xanthone	0.27 (0.31)	0.36 (1.02)	nd
9,10-phenanthrenequinone	0.63 (0.43)	1.72 (2.67)	0.29 (0.52)
4HCyclopenta[def]phenanthrene	0.09 (0.10)	0.40 (0.78)	0.07 (0.20)
Methyl-Athracene9,10dione	0.29 (0.24)	0.66 (1.15)	0.03 (0.11)
Methyl-phenanthrenecarboxy-aldehyde	0.10 (0.14)	0.48 (1.16)	0.01 (0.03)
7H-Benz[de]athracene-7-one	0.33 (0.39)	0.92 (1.79)	0.01 (0.06)
1-Pyrenecarboxyaldehyde	0.49 (0.60)	0.96 (2.56)	0.01 (0.03)
C2phenanthrene-9-carboxyaldehyde	0.02 (0.05)	0.16 (0.47)	0.02 (0.08)
Benza[a]anthracenone-7,12-dione	0.19 (0.19)	0.24 (0.56)	nd
Benza[a]anthracenone-9,10-dione	0.11 (0.16)	0.03 (0.07)	nd
Σ oxyPAHs	3.48 (2.64)	6.91 (11.30)	0.55 (1.06)

Among these oxyPAHs, 9,10-phenanthrenequinone was found in the greatest amount in both sampling sites, during summer and late winter conditions [0.63 ng m^{-3} (August, Athinas St.), 1.72 ng m^{-3} (March, Athinas St.), 0.29 ng m^{-3} (March AEDA)]. The reported concentrations of 9,10 phenanthrenequinone on urban airborne particulates range up to 2 ng m^{-3} [79,83–85]. Although 9,10-phenanthrenequinone has been quantified in ambient air and its potential toxicity is known, detailed knowledge on its sources remains to be elucidated. A number of oxygenated products, including 9,10-phenanthrenequinone, were identified from the gas phase reaction of phenanthrene with OH radicals in the presence of NO_x [9]. Cho et al. [86] found elevated concentrations of this quinone at receptor sites in the Los Angeles air basin, but Chung et al. [79] did not find the positive correlation they expected between quinone mass loadings and ozone concentrations in Fresno, CA. None correlation was found between ozone and 9,10-phenanthrenequinone's mass concentration in the present study.

Other oxyPAHs that were found in the greatest amount were 1-pyrenecarboxyaldehyde, 9H-fluoren-9-one and 7H-benz[d,e]athracene-7-one. 9H-Fluoren-9-one dominates oxy-polyaromatic hydrocarbon concentrations in the gasoline-powered vehicles, followed by anthraquinone and xanthone [5]. Fig. 5 shows the % percentage concentrations of 6 ketones, 4 quinones and 4 aldehydes in the urban air samples collected at the sampling site at Athinas St. during August 2003 and March 2004. The concentrations between August and March are statistically different (*t* test, critical of $|t|$ for confidence interval of $P < 0.0001$), with a number of significant changes made in the contribution

pattern. The contribution of 9,10-phenanthrenequinone was larger in March, accounting for 26% of the total mass loading, whereas 9H-fluoren-9-one contributed more in the summer. The information is not sufficient yet, to distinguish between direct emission and formation by atmospheric oxidation of PAH.

The average concentrations of total oxyPAHs in August and March were 3.48 ng m^{-3} (sd 2.64) and 6.91 ng m^{-3} (sd 11.30), respectively. However, the reduced photochemical activity and lower ozone concentrations during late winter conditions should have resulted in lower atmospheric formation of oxyPAHs [87]. Hence, increased traffic and domestic heating are the main reasons for the increased atmospheric concentrations in the colder period. Their concentrations at AEDA were significantly lower than at Athinas St. (average 0.55 ng m^{-3}), probably because sampling took place at 20 m above ground, not close to the emission sources that were responsible for the direct emission of oxyPAHs during late winter and that different mechanisms (atmospheric processes) are involved in the generation of the observed distribution. Average summed mass concentrations of oxyPAHs during various campaigns worldwide are listed in Table 6. Our results are in the range of the reported concentrations of oxyPAHs for other urban locations. Table 6 shows that the summer concentrations are lower than the ones measured in Boston. The lowest values are reported for Augsburg, but with the highest cold/warm ratio (12). In the Athens the cold/warm ratio is 2.66 close to one of Santiago de Chile (2.05). The seasonal variation is evident at all sampling sites. This might be due to increase in airborne particulates that contain oxyPAHs in the vicinity of ground surface under the more stable

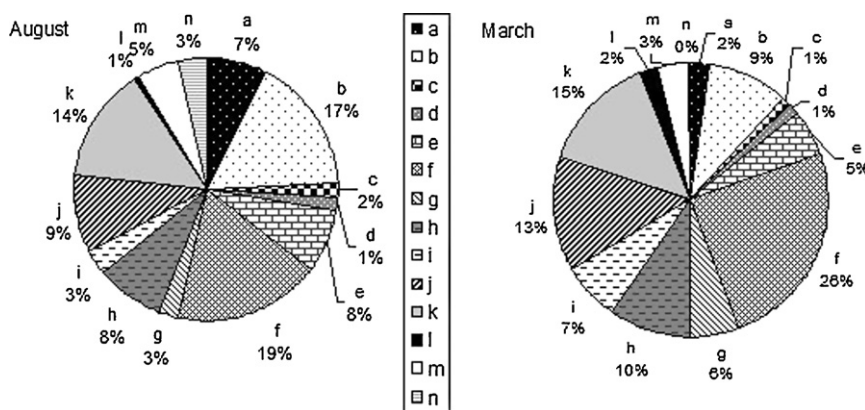


Fig. 5. % Contribution of mean concentrations of oxyPAHs (ng m^{-3}) during August and March. [(a) Benzophenone, (b) 9HFluoren9one, (c) Athracenone, (d) Fluorencarboxyaldehyde, (e) Xanthone, (f) 9,10-phenanthrenequinone, (g) 4HCyclopenta[def]phenanthrene, (h) MethylAthracene9,10dione, (i) Methylphenanthrenecarboxyaldehyde, (j) 7HBenz[de]athracene7one, (k) Pyrenecarboxyaldehyde, (l) C2phenanthrene9carboxyaldehyde, (m) Benza[a]anthracenone7,12dione, (n) Benza[a]anthracenone9,10dione].

Table 6
Mean mass concentrations (ng m^{-3}) of Σ oxyPAHs.

Country, city characterization of sampling site	Sampling period–particles	Mass concentration (ng m^{-3})	Reference
Greece, Athens, Athens St. Urban, roadside (ground level)	August–PM ₁₀ ^a March–PM ₁₀ ^a	3.54 9.43	Present study
Greece, Athens, AEDA Urban (20 m above ground level)	March–PM ₁₀ ^a	0.55	Present study
Germany, Augsburg Urban, roadside (4 m above ground level)	Summer–PM ₁₀ Winter–PM ₁₀	0.1 1.2	[78]
Germany, Munich Urban, roadside (4 m above ground level)	PM ₁₀	10.33	[87]
Chile, Santiago de Chile Urban, roadside	Spring–PM ₁₀ Winter–PM ₁₀	6.0 12.3	[26]
U.S.A., Boston Urban, roadside (4 m above ground level)	Summer–PM ₁₀	10.73	[84]

^a PM₁₀ = PM_{10-2.5} + PM_{2.5}.

atmospheric conditions in winter, or photochemical decomposition of the parent PAHs and oxyPAHs under strong sunlight during summer periods leading to lower mass concentration. An important factor governing the overall aerosol chemistry is the presence of reactive compounds such as certain oxyPAHs, which can trigger radical chain reactions and ultimately change the chemical composition. Hence, the detailed study of the oxygenated PAHs along with their parent compounds is of great need.

4. Conclusions

PM_{2.5} and PM_{10-2.5} particle-associated polycyclic aromatic hydrocarbons (PAHs) and oxidized PAHs (oxyPAHs) were determined in the city of Athens, Greece. All compound concentrations were higher in March (cold period) than those in August (warm period) for both fine and coarse airborne particles. In our study 98% of the identified and quantified compounds were found in PM_{2.5}. Gas phase concentrations were also calculated with three-ring and most four-ring PAHs found predominantly in the gas phase and only a small fraction associated with particulates. Moreover, several diagnostic ratios have been calculated for PAH concentrations in the PM_{2.5} fraction, providing an indication about the impact of different sources to atmospheric concentrations of PAHs, with the emphasis on traffic. Thus diesel versus petrol contribution was estimated using the Mphe/Phe ratio, resulting in a major contribution of diesel to PAHs concentrations, despite the restricted usage of diesel fuel only to heavy and light duty trucks and taxis in Greece. 6 ketones, 4 quinones and 4 aldehydes were collected in the urban air samples at the sampling site at Athinas St. during August and March, with 9,10-phenanthrenequinone found in the greatest amount in both sampling sites, during summer and late winter conditions. Increased traffic and domestic heating are main emission sources of the increased atmospheric concentrations of oxyPAHs in the colder period at Athinas St.

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