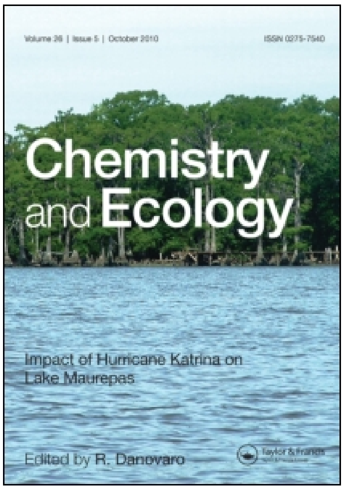

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Nitro polycyclic aromatic hydrocarbons in atmospheric particulate matter of Athens, Greece

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Nitro polycyclic aromatic hydrocarbons in atmospheric particulate matter of Athens, Greece

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Polycyclic aromatic hydrocarbons (PAHs) and nitro polycyclic aromatic hydrocarbons (N-PAHs) are chemical species of proven mutant and carcinogenic activity. In this study, the concentrations of seven different N-PAHs [2-nitronaphthalene (2N-NAP), 2-nitroflourene (2N-FLU), 2-nitroflouranthene (2N-FLA), 3-nitroflouranthene (3N-FLA), 1-nitropyrene (1N-PYR) and 2-nitropyrene (2N-PYR)] were determined in two fractions of atmospheric particulate matter from the atmosphere of Athens: coarse ($2.4\,\mu\text{m} \ll 10\,\mu\text{m}$) and fine ($< 2.4\,\mu\text{m}$). 3N-FLA was not detected, whereas 1N-PYR, mostly originating from emissions from burning fuel, showed the maximum observed concentrations for both fractions and for the whole experimental period (especially during winter). In addition, 2N-FLA, a secondary nitro-PAH produced by photochemical reactions, showed relatively high values. Analysis of statistical data for N-PAH concentrations, using clustering technique, showed that: (1) 1N-NAP, 2N-FLU and 1N-PYR are mainly produced by direct burning; and (2) photochemical reactions are the dominant sources of 2N-NAP, 2N-PYR and 2N-FLA.

Keywords: seasonal variation; correlation studies; burning emissions; photochemical reactions; N-PAHs

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been studied as atmospheric pollutants in urban and industrial environments in recent decades. Many studies have already been published concerning their physical and chemical properties, their environmental fate and their effects on living organisms, incluing mammals and humans. PAHs have been recognised as primary pollutants, significantly influence public health and are considered to be responsible for a number of respiratory diseases such as pharynx cancer. These symptoms are strongly related to their mutant activity, because PAHs are examples of indirect or direct – in some cases – active mutant substances [1–4].

Nitro polycyclic aromatic hydrocarbons (N-PAHs), daughter products of PAHs, are recognised as having greater health effects than their parent PAHs. The Ames bio-test has shown that N-PAHs are responsible for 8–25% of the total mutant activity of particulate matter. However, N-PAHs show mutagenic potencies up to 100,000 times greater, and carcinogenic potencies up to 10 times greater, than PAHs [5–8].

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Particle-size distributions for toxic compounds are a key point with which to assess the impact of pollutants on human health, because particle size controls the deposition behaviour of particulate matter in respiratory organs. Coarse particles deposit mainly in the anterior nasal region and the main extrathoracic region. By contrast, fine particles easily reach the pulmonary alveoli. This distribution is of great concern, due to the ability of fine particles to enter the lungs and reach the cardiovascular system. Importantly, mutagenic compounds such as PAHs and N-PAHs are mainly associated with fine particles [1,7].

N-PAHs in the atmosphere come from primary sources and from reactions involving their parent PAHs. The most abundant N-PAH in diesel or petrol exhaust fumes is 1-nitropyrene (1N-PYR) and it is not known to result from any known gas-phase reactions. Other N-PAHs detected in particles directly released by the combustion chamber of diesel engines are 3-nitroflouranthene (3N-FLA), 9-nitroanthracene (9N-ANTHR) and 2-nitroflourene (2N-FLU). The most abundant N-PAHs in ambient air as a result of gas-phase reactions are 2-nitroflouranthene (2N-FLA) and 2-nitropyrene (2N-PYR). 2N-FLA can be produced from gas-phase reactions between fluoranthene and either OH or NO_3 radicals. 2N-PYR can only be produced by gas-phase reactions of pyrene initiated by the OH radical. Because 2N-FLA and 2N-PYR are produced solely from gas-phase reactions and 1N-PYR is strictly from direct emissions, these compounds can be used as tracers for direct emissions and for the atmospheric photochemical reactions that form N-PAHs [9]. 1-Nitronaphthalene and 2-nitronaphthalene (1N-NAP or 2N-NAP) are reported to be present at low levels in extracts of diesel particulate matter [10–15]. Electrophilic nitration of naphthalene is expected to produce 1N- and 2N-NAP at yields of 95 and 5%, respectively [16]. Gas-phase reactions of naphthalene with the OH radical and NO_2 in reaction chambers that simulate environmental (daily) conditions were found to produce 1N- and 2N-NAP in almost equal abundance [17], whereas gas-phase reactions of naphthalene with N_2O_5 in the dark were found to produce 1N- and 2N-NAP in an abundance of 3:1 [18]. However, it should be noted that there is lack of information in the literature regarding gas-phase emissions of 1N- and 2N-NAP from vehicular exhausts.

The purpose of this study was to determine the distribution of the seven abovementioned N-PAHs, in both coarse and fine particulate atmospheric matter, for 20 samples collected in Athens [3,19]. The analysis and loading of N-PAHs will provide information on the exposure suffered by the inhabitants of Athens. This is the first time that data for N-PAHs (particularly the size distribution) in the atmosphere of Athens have been presented. Athens experiences a typical Mediterranean climate with extensive periods of sunlight and relatively mild autumns. Atmospheric pollution, originating mostly from the traffic emissions that characterise urban areas and where there is potential for *in situ* transformation of primarily emitted PAHs to N-PAHs, was expected to be high. Previous studies [20] in the area have shown a relationship between sunlight and high temperatures and increased mutagenicity (as determined by Ames test) for atmospheric particulates. In addition, determination of N-PAH concentrations in particulate fractions and the statistical analysis of N-PAH concentration data were used to verify our understanding of the origin of N-PAHs in areas with different characteristics and different PAH sources.

2. Materials and methods

2.1. *Sampling of atmospheric particulate matter*

The sampling system used was a General Metal Works Corp. high-volume sampler and a high-resolution head that uses glass fibre filters (GFFs) (Whatman Corp. GFF20.3 × 25.4 cm^2) for the

Figure 1. Sampling site in Patission Street, Athens.

collection and distribution of five different sized (diameter = 10.2, 4.2, 2.1, 1.4, 0.73 μm) particles, and a final filter to collect the finest particles [2]. Sampling flow was $\sim 0.4\,m^3 \cdot min^{-1}$ and the sampling duration was 24 h (all samplings started at 09:00). The volume of air sampled was $\sim 600\,m^3 \cdot d^{-1}$. The sampler was placed on the roof of the Ministry of the Environment building on Patission Street in the centre of Athens (Figure 1). Patission Street is one of the most populated streets in Athens, with daily traffic levels exceeding 60,000 vehicles (diesel and petrol). In addition, because the greater Patission area is overpopulated, indoor heating contributes to exhaust emissions, especially during winter (in Athens buildings are usually heated between December and mid-March). Indoor heating in the Athens area is mostly fueled by diesel.

For this study, two experimental campaigns were conducted during two different periods November 2003 and January and February 2004, with 10 samples collected in each period. Each sample consisted of six filters, which were separated for analysis (see Section 2.3), in two categories: three for coarse particles (dia. = 10.2, 4.2, 2.1 μm) and three for fine particles (dia. = 1.4, 0.73 μm and the finest particles).

2.2. *Quality assurance of analytical method*

Before studying the samples, quality assurance of the data obtained through the analytical procedure was established [19,21]. For this purpose, three blank filters were processed under the abovementioned conditions. The limit-of-detection (LOD) was calculated as equal to three times the standard deviation of the blanks. Chromatograms were studied within the N-PAH time windows, and the peaks detected were converted into concentrations, as shown in Table 1. Method recoveries were also evaluated. Chromatograms were studied in the area where N-PAH peaks theoretically appear. The measured peaks were converted to concentrations and are shown in Table 1.

Table 1. Limits-of-detection (ng·m^{-3}) for six N-PAHs ($n = 3$) determined in atmospheric particulate matter collected on filters per 600 m^3 of air.

N-PAH	N-PAH mass on GFF (ng)	Detection limit per filter (ng)	Detection limit in the atmosphere (pg · m^{-3})
1N-NAP	111 ± 10.4	36.1	60
2N-NAP	31.0 ± 1.69	0.93	1.55
2N-FLU	14.9 ± 0.31	19.2	32
3N-FLA	6.51 ± 6.41	9.13	15
1N-PYR	56.4 ± 7.82	23.5	39
2N-PYR	2.93 ± 2.22	6.67	11

Note: 2N-FLA was not detected either on blank or on experimental filters.

The recovery method was examined for 2N-NAP by comparing the results for blank filters spiked with standard solutions of 2N-NAP and internal standard with those obtained for a standard solution containing the same amount of 2N-NAP and internal standard that had undergone the derivatisation procedure. Recovery of 2 N-NAP found to be 81 ± 7% for $n = 3$.

To calibrate the method, commercially available N-PAH standards (Acros purity 99%) were used. Because a reference material with certified data for N-PAHs in atmospheric particulate matter was not available it was not possible to obtain data on the accuracy and traceability of the method used in our laboratory.

2.3. *Determination of N-PAHs in atmospheric particulate matter*

The methodology used to determine N-PAHs in atmospheric particulate matter was based on previous research [9,22–24]. Filters were separated into two categories, as explained above (20 analyses were carried out for each group of three filters for each of the two categories). Before extraction, filters with suspended particulate matter were spiked with 4-nitro-*p*-terphenyl (internal standard). After adding the internal standard, filters were extracted using Soxhlet apparatus, in the absence of light, with 150 mL of dichloromethane for 20 h at approximately one cycle every 15 min. The extract was then concentrated by rotary evaporation. The sample work-up procedure was as follows. A silica solid-phase extraction tube (200 mg·3 mL^{-1}) was first conditioned by eluting with 6 mL of *n*-hexane. Extract dissolved in a minimum volume (~0.5 mL) of dichloromethane was applied to the top of the clean cartridge, which was then eluted dropwise. The elution was carried out in two aliquots, each using 3 mL of *n*-hexane. The two eluates were combined and evaporated to near dryness and redissolved in 1 mL of methanol. To this was added 0.3 mL of a 0.05% aqueous solution of copper (II) chloride and 50 mg of $NaBH_4$. The resulting mixture was shaken and allowed to stand at room temperature in the dark for 1 h. Water (5 mL) was added and the N-PAHs were extracted with three 5 mL portions of benzene. The organic layers were combined and the solvent was reduced to ~3 mL by rotary evaporation. Hepta-fluorobutyric anhydride (HFBA; 5 μL) was added to the mixture, the flask was sealed and heated in a water bath at 50 °C for 15 min. The reaction mixture was cooled to room temperature, then 2 mL of a 5% aqueous ammonia solution was added to destroy the excess HFBA and terminate the reaction. The mixture was shaken for 5 min. Finally, the organic and aqueous phases were allowed to separate and the former was recovered for subsequent analysis by the GC-ECD technique. Effluents were reduced to 1 mL and then analysed using a Perkin–Elmer gas chromatograph equipped with an electron capture detector and connected. An HP-5-MS column was used (30 m × 0.25 mm i.d., film thickness 0.25 nm). Injections were performed in split mode, with a split ratio of 3.8:1. The temperature programme was: initial temperature, 120 °C, 5 °C·min^{-1} to 180 °C; 4 °C·min^{-1} to 190 °C; 7 °C·min^{-1} to 240 °C; hold time 5 min [25].

2.4. *Cluster analysis – Spearman's factor*

Cluster analysis is a statistical method used to investigate possible relationships between different parameters. One of the most common cluster analysis methods is the hierarchical tree diagram. Pearson's correlation coefficient was chosen to associate each sample with a specific cluster, in order to detect similarities between values (samples) after normalisation has been performed [26].

Spearman's factor is a parametric statistical procedure that examines the extent to which two or more characteristics change over time. It is estimated by taking into account the number of observations (samples) and not the observations themselves. In this study, Spearman's correlation coefficient was estimated to examine the relationship between N-PAHs and common pollutants such as NOx, SO_2 and CO [26].

3. Results and discussion

3.1. *Determination of N-PAHs in two fractions of atmospheric particulate matter*

Arithmetic mean N-PAH concentrations for coarse and fine particles are presented in Figure 2. As shown, 1N-PYR and 2N-FLA show the highest concentrations in both coarse and fine particles. Lower values are found for 2N-FLU, whereas the concentration of 1N-PYR in fine particles is three times higher than in coarse particles [22]. N-PAHs with two aromatic rings, such as 1N-NAP and 2N-NAP, exist mainly in the gas phase, as shown by Araki et al. [27]. Their presence in the particulate phase is expected for two reasons: (1) the establishment of an equilibrium between the gas and particle phases, as found for volatile PAHs in the atmosphere of Athens [19]; and (2) the non-exchangeable fraction effect [28], because N-PAHs are formed and trapped inside the particles.

The high abundance of 1N-PYR may be because this N-PAH is produced directly by cars and central heating. The high abundance of 2N-FLA can be attributed to secondary formation because this N-PAH is the most significant product of chemical reactions that occur in the air phase.

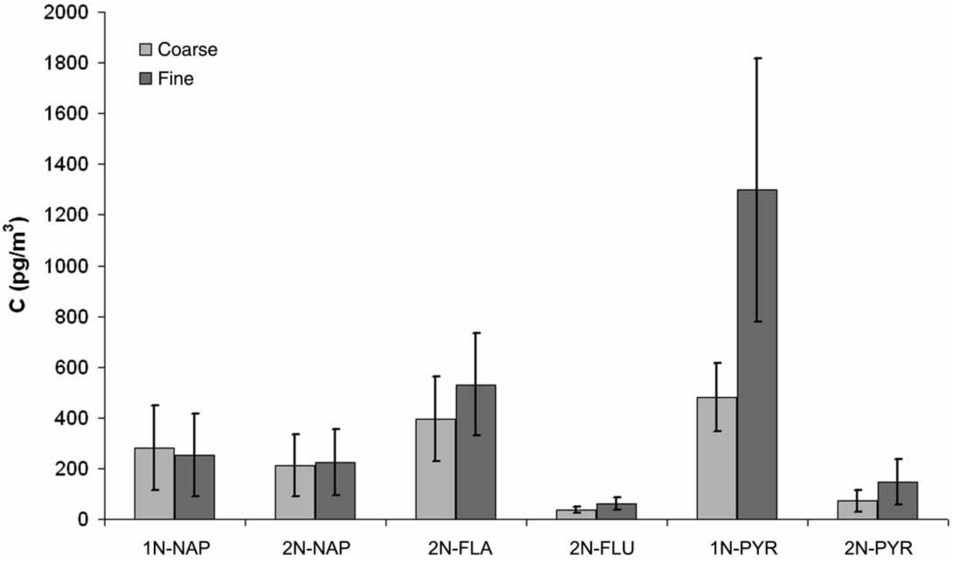

Figure 2. Concentrations, in fine and coarse particles (pg·m^{-3}, mean value $n = 20$), of N-PAHs in the atmosphere for the period November 2003 and January–February 2004 from an urban site in Athens.

Table 2. Comparison of gas-phase and particle-associated N-PAH concentrations (pg·m^{-3}) in the atmosphere for Athens and other locations.

	N-PAH				
City	1N-NAP	2N-NAP	9N-ANTH	2N-FLA	1N-PYR
Birmingham, UK[a]	90, g	70, g	190, t	220, p	90, p
Leeds, UK[b]	nm	nm	nm	nm	50–100, p
Paris, France[c]	80	230	nm	220	230
Vienna, Austria[d]	200	200	300	300	90
Rome, Italy[e]	nm	nm	nm	470, p	70, p
Milan, Italy[f]	nm	nm	nm	1140, p	220, p
Naples, Italy[g]	nm	nm	nm	100, p	100, p
Madrid, Spain[h]	nm	nm	nm	70, p	10, p
Zabrze, Poland[i]	nm	nm	nm	350	nm
Claremont, USA[j]	nm	nm	nm	410, p	20, p
Torrence, CA, USA[k]					
Night	2250, g	1100, g	100	320, p	30, p
Day	2950, g	2850, g	50, p	280, p	40, p
Columbus, OH, USA[l]	nm	nm	50	60	20
Deer Park, TX, USA[m]					
Autumn	750	160	30	70	10
Winter	110	20	6	20	10
Athens[n]					
Autumn	397, p	511, p	nm	1058, p	797, p
Winter	666, p	338, p	nm	751, p	2103, p

Notes: 9N-ANTH, 9-nitroantracene; nm, not measured; g, gas phase; p, particulate phase; t, total gas and particulate phase. [a] Urban site, 25 samples, November 1995 to February 1996 [10]; [b] [29]; [c] one winter sample [30]; [d] four samples [31]; [e] seven samples, September 1991 [32]; [f] 12 samples, March 1991 [32]; [g] three samples, December 1993 [32]; [h] suburban site, ten samples, October 1990 [32]; [i] [33]; [j] suburban site, six samples, September 1985 [34]; [k] suburban site, six samples, January 1986 [35]; [l] suburban site [36]; [m] four samples, September 1990, five samples December 1990 to February 1991; [n] means of ten autumn samples (November 2003) and ten winter samples (January–February 2004), this study.

The Athens atmosphere, as well as the special conditions of the sampling area (intense vehicular traffic, overpopulation), enhance the creation of these two N-PAHs. 2N-FLU is found at lower concentrations because of its volatility, whereas the concentration of 1N-PYR is approximately three times higher in fine particles than in coarse particles because fine particles are mainly produced by burning fuel (central heating and vehicles emissions) [2,22]. The presence of N-PAHs in coarse particles (dia. $> 2.1\,\mu$m) was probably associated with sorption from the gas phase [2]. Table 2 shows the concentrations determined for five N-PAHs in the atmosphere of 14 cities from around the world. It is obvious that the concentrations of 2N-FLA and 1N-PYR determined in this study are quiet high (especially 2N-FLA in autumn and 1N-PYR in winter). This enhances the need for periodic determination of N-PAH concentrations in the Athens atmosphere, due to their mutant activity and the special conditions in Athens (increasing vehicular traffic, overpopulation, high temperatures).

3.2. *Seasonal variation in N-PAH concentrations*

Sampling was conducted during autumn and winter and seasonal variations in N-PAH concentrations were determined for coarse and fine particles and for both periods. As shown in Figures 3 and 4, 2N-NAP is found at higher concentrations during the autumn, in both fine and coarse particles. This may be related to the intense photochemical activity caused by the sun and high temperatures [9]. By contrast, no seasonal variation was shown for the proven photochemical 2N-PAH, N-FLA, indicating that mild winter conditions in Athens may keep photochemical activity high, as needed to provide adequate quantities of N-FLA. The different seasonal patterns for photochemically produced PAHs in coarse particles may be due to a combination of several factors that affect

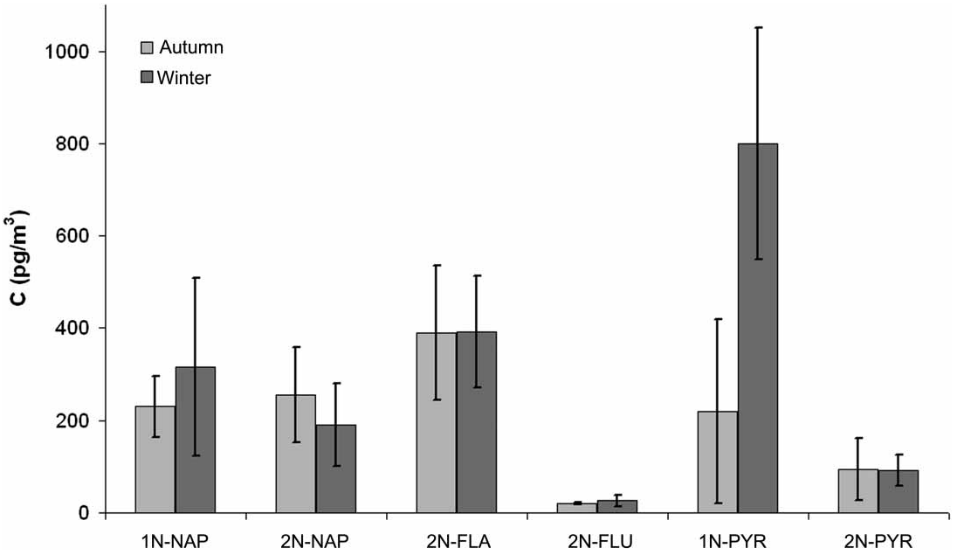

Figure 3. Seasonal (autumn–winter) variation in N-PAH particulate concentrations for fine particles (pg·m^{-3}, mean value $n = 10$) in the atmosphere from an urban site in Athens.

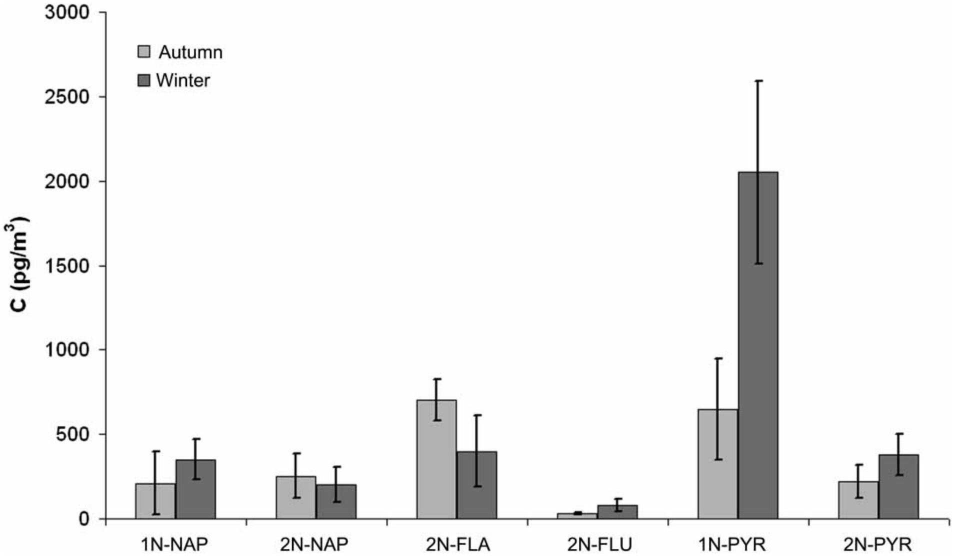

Figure 4. Seasonal (autumn–winter) variation in N-PAH particulate concentrations for coarse particles (pg·m^{-3}, mean value $n = 10$) in the atmosphere from an urban site in Athens.

seasonal variations in the abundance and reactivity of parent PAHs. More data and observations are needed to provide an explanation for this difference.

By contrast, 1N-PYR, which is produced by burning diesel and emissions from diesel vehicles [9,38], reached higher levels during the winter, because of the obvious contribution of central heating.

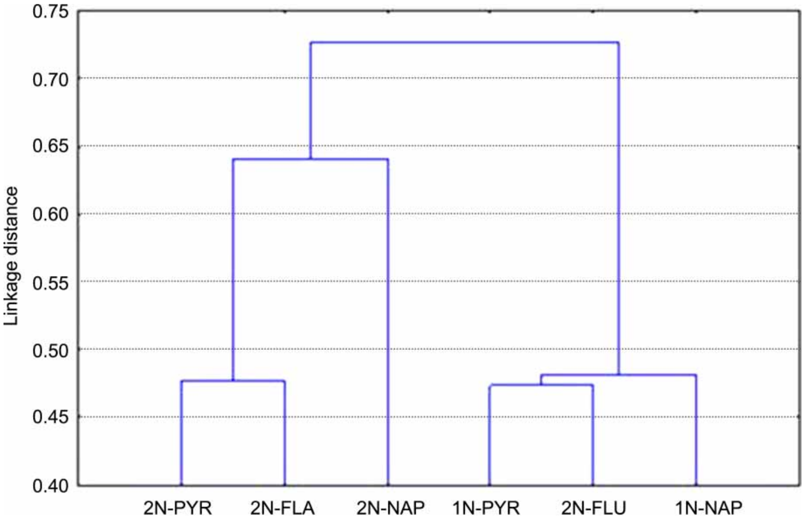

Figure 5. Cluster analysis of particulate atmospheric concentrations of N-PAHs in fine particles for an urban site in Athens.

3.3. *Cluster analysis of N-PAHs concentrations*

Figure 5 shows the cluster analysis of the concentrations of N-PAHs in fine particles for Patission Street.

From Figure 5 the following can be concluded: 2N-FLA, 2N-PYR and 2N-NAP are found in the same cluster as a result of similar variation. This provides evidence for common sources and behaviour. It is known that 2N-FLA is produced in the atmosphere secondary to the reaction of fluoranthene with NO_2, initiated after OH radical attack [9]. 2N-PYR and 2N-NAP are derived from the same source, supporting this insight. In the same way, 2N-FLU and 1N-NAP can be found along with 1N-PYR, providing evidence of primary emissions from diesel engines [5,9,23]. The conclusions derived from cluster analysis of N-PAH concentrations in fine particles further support the relationship between the concentrations and the way that N-PAHs are formed, and provide evidence for the primary emission of 2N-FLY and 1N-NAP and the secondary *in situ* formation of 2N-NAP in the Athens atmosphere.

3.4. *Correlation with common pollutants*

Table 3 presents the estimated Spearman's correlation factors. Data for common pollutants NO, CO, SO_2 are average concentrations for the period of each sampling, kindly provided by the Ministry of Environment. The monitoring station is in the same building as the sampling site, $\sim$5 m below it. From Table 3, several conclusions can be drawn. There is no correlation between N-PAHs and CO, providing evidence that N-PAHs are not related to emisssions from petrol engines. SO_2 is correlated with 2N-FLU, indicating a strong contribution from diesel vehicle and central heating emissions. It should be noted that in the Athens area, the majority of central heating installations use diesel, exactly the same as used for diesel vehicles. A negative correlation between SO_2 and NO, as primary emitted pollutants, and N-PAHs produced by photochemical reactions (2N-FLA, 2N-PYR and 2N-NAP) was detected for the fine particle data. The secondary formation of N-PAHs is probably enhanced by low primary pollutant concentrations in combination with higher temperatures and sunlight. The same negative correlation does not exist for the coarse particle data.

Table 3. Spearman's correlation coefficient of N-PAH concentrations and common pollutant concentrations for 20 samples.

	CO	NO	NO_2	NOx	SO_2
Fine particles					
1N-NAP	0.21	**0.45**	0.42	**0.46**	0.41
2N-NAP	0.06	**−0.47**	**−0.49**	**−0.57**	−0.35
2N-FLU	0.22	**0.57**	**0.69**	**0.58**	**0.58**
2N-FLA	0.33	**−0.46**	−0.34	−0.23	**−0.62**
1-PYR	0.19	0.32	0.32	0.34	0.32
2N-PYR	−0.16	**−0.44**	−0.29	−0.28	**−0.67**
Coarse particles					
1N-NAP	0.00	**0.40**	**0.41**	**0.52**	**0.50**
2N-NAP	−0.38	−0.26	−0.27	−0.38	−0.08
2N-FLU	−0.21	0.39	0.35	0.21	**0.58**
2N-FLA	0.06	−0.21	−0.30	−0.17	−0.34
1-PYR	−0.33	−0.02	−0.19	−0.27	0.01
2N-PYR	0.31	0.02	0.11	0.21	−0.18
Total					
1N-NAP	0.16	0.35	0.37	**0.41**	0.34
2N-NAP	−0.05	−0.32	−0.30	**−0.40**	−0.23
2N-FLU	0.24	**0.75**	**0.80**	**0.75**	**0.70**
2N-FLA	0.02	−0.52	−0.42	−0.38	**−0.59**
1-PYR	0.07	0.33	0.28	0.23	0.33
2N-PYR	0.01	−0.08	−0.05	0.01	−0.42

Note: Statistically significant factors are given in bold ($p < 0.05$).

4. Conclusions

From the data analysis, the following conclusions can be drawn: 1N-PYR and 2N-FLA are found at higher concentrations in both particulate fractions (fine and coarse) and seem to be the most abundant N-PAHs in the Athens atmospheric particulate phase. Cluster analysis provided additional evidence that 2N-FLA, 2N-PYR and 2N-NAP result mainly from photochemical activity, whereas 2N-FLU, 1N-NAP and 1N-PYR are mainly produced by burning diesel in vehicle engines and central heating [5,9,22,39]. Central heating, rather than diesel traffic, may be responsible for the maximum concentration of 1N-PYR found during the winter. Fine particles contain higher levels of 1-NPYR. The concentration of 2N-FLA was found to be negatively correlated with primary conventional pollutants related to emissions from burning fuel, but no seasonal variation was found from autumn to winter, indicating constant photochemical formation under the climatic and atmospheric conditions of Athens.

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