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Polycyclic Aromatic Hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): concentrations and sources

Alexandre Albinet ^{*,1}, Eva Leoz-Garziandia ^{*,1}, H el ene Budzinski ², Eric Villenave ³

¹ *Institut National de l'Environnement industriel et des RISques (INERIS), Parc technologique Alata BP2, 60550
Verneuil en Halatte, France*

² *Laboratoire de Physico-& Toxicologie Chimie des syst emes naturels (LPTC), UMR 5472 CNRS, Universit e Bordeaux 1,
33405 Talence, France*

³ *Laboratoire de Physico-Chimie Mol culaire (LPCM), UMR 5803 CNRS, Universit e Bordeaux 1, 33405 Talence,
France*

* Corresponding authors. Tel: +33 3 44 55 64 59, Fax: +33 3 44 55 63 02

E-mail addresses: alexandre.albinet@gmail.com (Alexandre Albinet), eva.leoz@ineris.fr (Eva Leoz-Garziandia)

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Abstract

Ambient measurements (gas + particle phases) of 16 polycyclic aromatic hydrocarbons (PAHs), 17 nitrated PAHs (NPAHs) and 9 oxygenated PAHs (OPAHs) were carried out during July 2004 on three different sites (urban, sub-urban and rural) in the region of Marseilles (South of France). Atmospheric concentrations of these classes of polyaromatics are great of interest because of their high potential mutagenicity and carcinogenicity. OPAH concentrations were of the same order of magnitude as those of PAHs while NPAH concentrations were one to two orders lower. 9-Fluorenone and 9,10-anthraquinone were the most abundant OPAHs, accounting for about 60% and 20% of the total OPAH concentration. Respectively 1- and 2-nitronaphthalene were the most abundant NPAHs and were accounting for about 30-50% and 15-30% of the total NPAH concentration. NPAHs and OPAHs concentration levels were consistent with the characteristics of the sampling sites. Study of source specific ratios (2-nitrofluoranthene/1-nitropyrene) clearly showed those primary NPAH sources influence the urban and sub-urban sites whereas production of secondary NPAHs by gas phase reactions was prevalent at the rural site. The study of NPAH and OPAH sources suggested that gasoline engines were an important source of such compounds whereas the dominant source of 1-nitropyrene, 2-nitrofluorene, 6-nitrochrysene and benz[a]anthracene-7,12-dione seems to be diesel vehicles. Finally, 9,10-anthraquinone presents a double origin: primary diesel emission and photochemical processes. Formation of 9,10-anthraquinone from anthracene ozonation was shown at the rural site. Further investigations will be necessary in order to discriminate when (before or during the sampling) the OPAHs are formed.

Keywords: Polycyclic aromatic hydrocarbons; Nitrated polycyclic aromatic hydrocarbons; Oxygenated polycyclic aromatic hydrocarbons; Atmospheric pollution

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous environmental contaminants. In the atmosphere, they are released as by-products from the incomplete combustion or pyrolysis of organic matter and fossil fuel. They have been intensively these last 30 years studied because of their potential carcinogenic and/or mutagenic properties (IARC, 1987).

PAH derivatives containing nitro or oxygen groups [i.e. nitrated PAHs (NPAHs) and oxygenated PAHs (OPAHs), respectively] have been recognized as direct acting mutagens and carcinogens (Durant et al., 1996; Durant et al., 1998; Hannigan et al., 1998; Lewtas et al., 1990; Pedersen et al., 2004; Pedersen et al., 2005; Schuetzle, 1983). As PAHs they are also formed during combustion processes or, in the atmosphere, by both gas and heterogeneous reactions of PAHs induced by atmospheric oxidants (OH, NO₃, O₃) (Arey et al., 1986; Atkinson et al., 1989; Atkinson et al., 1990; Atkinson and Arey, 1994; Barbas et al., 1996; Environmental Health Criteria (EHC) 229., 2003; Helmig and Harger, 1994; Perraudin et al., 2007; Sasaki et al., 1997).

However, atmospheric sources (primary or secondary) and concentrations of these PAHs derivatives are not yet well documented.

Several monitoring campaigns in various regions, such as Roma, Milano, Napoli (Italy), São Paulo (Brazil) (Ciccioli et al., 1995; Ciccioli et al., 1996), Birmingham (England) (Dimashki et al., 2000), København (Denmark) (Feilberg et al., 2001; Feilberg and Nielsen, 2001), Athína (Greece) (Marino et al., 2000), Barcelona (Spain) (Bayona et al., 1994), Kanazawa (Japan) (Hayakawa et al., 2002), Baltimore (Bamford and Baker, 2003), Los Angeles (Reisen and Arey, 2005), Houston (Wilson et al., 1995) (USA) have already demonstrated the existence of NPAHs in the atmosphere and have proposed different mechanisms explaining their formation. Furthermore, most of the studies concerning NPAHs focus on a limited number of compounds (generally nitrofluoranthene and nitropyrene isomers) and solely in the particulate phase. To the best of our knowledge, only Bamford and Baker (2003) have performed an extensive study on NPAH gas/particle partitioning considering a large variety of compounds (molecular weights between 173 and 292 g mol⁻¹).

The number of studies concerning OPAHs is much more limited. Several OPAHs have been identified in ambient air samples but they still have not been quantified (Alastair et al., 1995; Bodzek et al., 1993; König et al., 1983; Oda et al., 1998; Ramdhal, 1983). The only quantified and identified OPAHs are all very different, from ketones to dione (Allen et al., 1997; Chung et al., 2006; Feilberg et al., 2001; Fraser et al., 1998; Kishikawa et al., 2006; Leoz-Garziandia et al., 2000; Ligocki and Pankow, 1989; Liu et al., 2006; Maria del Rosario Sienna, 2006; Niederer, 1998; Nielsen et al., 1999; Schnelle-Kreis et al., 2001; Tsapakis et al., 2002; Yassaa et al., 2001). OPAHs source studies in real atmosphere are quasi non existent in the literature (Chung et al., 2006; Feilberg et al., 2001; Kishikawa et al., 2006; Liu et al., 2006; Nielsen et al., 1999; Schnelle-Kreis et al., 2001). On the other hand, their formation pathways have already been studied in laboratory (Barbas et al., 1996; Bunce et al., 1997; Esteve et al., 2003; Perraudin et al., 2007; Wang et al., 2007).

The main objectives of this study were to characterize the NPAHs and OPAHs in both the gas and particulate phases in three different sites in the Marseilles area, and to identify the main primary and/or secondary sources of these contaminants. Marseilles (South of France) is an important city (around 1 million inhabitants) of the Mediterranean area characterised by an important solar irradiation, a heavy traffic and several industrial activities. Sampling locations were chosen according to their potentially important O₃ and NO_x concentrations, in order to make possible secondary formation of such compounds. Others atmospheric constituents, such as O₃, NO, NO₂, PM₁₀ and PM_{2.5} were recorded (not at all sampling sites) in order to investigate their correlations with PAHs, NPAHs and OPAHs concentrations.

2. Methods

2.1. Sampling sites and meteorological conditions

Measurements were carried out in the Marseilles area from Thursday 07/22/2004 to Thursday 07/29/2004. These 7 days were characterised by high temperatures (averaging 26 to 32°C) and

intermediate O₃ concentrations (from 66 to 130 µg m⁻³). No precipitation occurred during the entire duration of the campaign. Three different types of sites (urban, sub-urban and rural) were instrumented for the sampling of PAHs and their derivatives (Fig. 1). The urban sampling site (43°18'20"N, 5°23'40"E, 64 m.a.s.l.) was installed downtown in a park named "Cinq Avenues", away from direct emissions of PAHs. Samplers were located on the roof of the Observatory of Marseilles. The downwind sub-urban site (43°17'17"N, 5°30'42"E, 72 m.a.s.l.) was located in the city of "La Penne sur Huveaune" (6 000 inhabitants), distant from direct vehicular sources but close (<1 km) to a Rilsan®'s factory (polyamide from castor oil, Atofina). Samplers were installed on the roof of the municipal stadium. The rural site (43°19'45"N, 5°43'4"E, 701 m.a.s.l.) was located in the massif of "La Sainte-Beaume" in the village of "Plan d'Aups" Sainte-Baume (800 inhabitants), about 30 km from the urban areas of Marseilles, Aix en Provence and Toulon. The sampling site was located in the upper part of the village, far from local sources. The surroundings of the station are covered by typical Mediterranean vegetation.

2.2. *Sample collection*

Both ambient air particulate (on quartz filter, Schleicher & Schuell, Ø=150 mm) and gas (on PUF polyurethane foams, Tisch Environmental, 79 mm long) phases were sampled using modified high volume samplers equipped with PM₁₀ head (Megatec Digitel DA-80, 30 m³ h⁻¹) in order to determine parent PAHs and PAH derivatives concentrations. Prior to sampling, quartz fiber filters were calcined at 500°C during 12 h to remove any organic compounds that may be present on the filters. PUF were pre-washed with dichloromethane using pressurised liquid extraction (PLE; Dionex trade name ASE for accelerated solvent extraction) with a Dionex ASE 300 system (90°C, 100 bars, heat time at 5 min, static time at 5 min, 3 cycles). Samplings were performed every 12 h (starting at 08:00 local time). After collection, filters were stored at -18°C in individual pre-washed glass Petri dishes. PUF were also stored with their glass holder at -18°C. All samples were wrapped in aluminium foil and placed in opaque reclosable poly bags.

Overall, 40 total filters together with 40 PUFs were collected during this sampling campaign. Field blanks (ie, exposed PUFs and filters without any air filtration) were collected bi-weekly for each sampling site.

NO_x (NO and NO₂), O₃, PM₁₀ and PM_{2.5} measurements were performed by AIRMARAIX, the local air quality network, with a 15 min time resolution (Environnement S.A. AC31M; Environnement S.A. 0341M; R&P TEOM 1400A, PM₁₀ and PM_{2.5} head; respectively). All measurements were performed at the urban site. PM₁₀ and PM_{2.5} were not available at the sub-urban site and only O₃ was measured at the rural site.

2.3. Sample extraction and analysis

The complete PAH, NPAH and OPAH analytical procedures are presented in detail elsewhere (Albinet et al., 2006). Briefly, filters and PUF were extracted with dichloromethane using Dionex ASE 200 and ASE 300 systems, respectively. Extracts were divided into two fractions. The first one, being used for the determination of PAH concentrations and the second one for the NPAH and OPAH quantification. Both fractions were evaporated under a nitrogen stream (Zymark Turbovap II) down to a volume of 500 µl and adjusted to 1 ml with acetonitrile (PAHs) or dichloromethane (NPAHs and OPAHs). 15 PAHs (see Table1) were quantified using HPLC with fluorescence/UV detection with a ternary elution gradient (methanol, water, acetonitrile). Two analytical systems were used for the determination of PAH concentrations. The first one was used for high concentration levels (Varian 9012 LC pump, Varian 9075 fluorescence detector, Varian 310 UV detector) and the second one, for very low concentration levels (Dionex P580 pump, Dionex RF200 fluorescence detector, Dionex UVD1705 UV detector). Two reversed-phase columns (Supelco Supercosil LC-PAH C18, 250 mm × 4.6 mm × 5 µm and Alltech Alltima C8, 250 mm × 4.6 mm × 5 µm) connected in series were used in order to have a better separation of PAHs. NPAH and OPAH concentrations were determined simultaneously using gas chromatography-mass spectrometry with negative ion chemical ionisation (GC/NICI-MS) and selective ion monitoring mode (SIM). Analyses were

performed using a Perkin-Elmer Clarus 500 gas chromatograph coupled to a Perkin-Elmer Turbomass Gold mass spectrometer. The column used was a 5% phenyl-substituted methylpolysiloxane (DB-5MS, 30 m × 0.25 mm I.D., 0.25 µm film thickness, J&W Scientific, USA). The method included a liquid chromatography purification procedure on solid phase extraction (SPE) cartridges (alumina and silica). A total of 17 NPAHs and 9 OPAHs were quantified (see Table1).

2.4. Quality assurance

PAH analytical procedure was validated during a (french) national inter-comparison campaign (Leoz-Garziandia, 2004). Three kinds of samples were analysed in order to identify the critical steps of the analytical protocols (low and high concentrations of prepared standard solutions, extracts of natural ambient air samples and diesel Standard Reference Material 2975). For each sample, four replicate analyses were carried out by each laboratory and mean values were calculated.

Application of the OPAH and NPAH analytical procedure has been performed on standard reference material (SRM 1649a: urban dust), giving repeatable results with a mean coefficient of variation (standard deviation/mean) about 0.2 and in good agreement with the few data available in the literature (Albinet et al., 2006).

Analytical limits of detection defined as the lowest concentration of the compound than can be detected ($S/N=3$) were used to calculate the methodology limits of detection for each individual compound. Individual NPAH detection limits in a typical air sample of 360 m³ ranged between 0.01 and 0.07 pg m⁻³. OPAH detection limits for an air sample of 360 m³ ranged between 0.01 and 2.6 pg m⁻³. PAH detection limits ranged between 16.7 and 111.1 pg m⁻³ for HPLC Varian system and between 0.08 and 1.11 pg m⁻³ for HPLC Dionex system.

The formation of NPAHs during sampling by heterogeneous reaction with nitrogen oxides was investigated in previous studies (Arey et al., 1988; Bamford et al., 2003; Dimashki et al., 2000).

During a winter high-NO_x episode, the maximum percentage of artefact formation of the observed NPAHs was less than 2-3% (Arey et al., 1988). Results from a study conducted in a tunnel showed that the formation artefact represented less than 0.1% of the studied NPAHs (Dimashki et al., 2000). Authors concluded that filter artefacts were not significant and were not problematic for NPAH ambient air samplings.

Concerning OPAHs, the study of Liu et al. (2006), carried out with ozone scrubbers dealing with the identification of secondary compounds, does not allow to conclude about the formation of OPAHs during sampling.

3. Results and discussion

3.1. OPAH and NPAH concentrations

Table 1 presents all the OPAH and NPAH (filter + PUF) concentrations measured at the three instrumented sites. This table also presents, when available, the average temperature, and the NO, NO_x, O₃, PM₁₀, PM_{2.5} and each individual PAH concentrations. The arithmetic average of the concentrations of the field blanks was taken into account for the calculation of atmospheric concentrations.

As it can be noted, NPAH and OPAH concentrations are consistent with the characteristics of the sampling sites (urban, sub-urban and rural) with the highest concentrations measured for the sampling stations close to car engine emissions. Concentrations of individual compounds show large daily basis variations related to their sources and sinks.

OPAH concentration levels are of the same order of magnitude as PAHs while NPAH concentrations are one to two orders of magnitude lower. Among all the 17 NPAHs and 9 OPAHs measured, only 1,4-anthraquinone was not detected in all samples either in gas or in the particulate phases. 9-Fluorenone and 9,10-anthraquinone were the most abundant OPAHs quantitatively measured at the three sites and accounting respectively for about 60% and 20% of the total OPAH

concentration. The lightest NPAHs, namely 1- and 2-nitronaphthalene, were the most abundant NPAHs. They account respectively for about 30-50% and 15-30% of the total studied NPAH concentration.

The OPAH concentrations measured at the urban and the sub-urban sites were similar to those already reported in previous studies for comparable sampling seasons (summer or spring) and site characteristics (urban) (Allen et al., 1997; Chung et al., 2006; Fraser et al., 1998; Leoz-Garziandia et al., 2000; Maria del Rosario Sienra, 2006; Tsapakis et al., 2002; Wilson et al., 1995; Yassaa et al., 2001). However, OPAH concentrations determined by Allen et al. (Allen et al., 1997) at Boston in particulate phase, are 10 times higher than those reported here (benzanthrone, benzo[a]fluorenone and benzo[b]fluorenone). In all previous studies with samplings realised in summer season, 9-fluorenone and 9,10-anthraquinone are also the major measured OPAHs.

Atmospheric concentrations of NPAHs such as, 1-, 2-nitronaphthalene, 2+3-nitrofluoranthene, 1- and 2-nitropyrene for the urban and sub-urban sites were similar to those reported in Roma (Ciccioli et al., 1995; Ciccioli et al., 1996), Athína (Marino et al., 2000), Barcelona (Bayona et al., 1994) and Los Angeles (Reisen and Arey, 2005) at similar sampling seasons. Nevertheless, except for 9-nitroanthracene and 2+3-nitrofluoranthene, individual total NPAH concentrations are 2 to 30 times higher (for 3-nitrophenanthrene and 1-nitronaphthalene, respectively) than those reported by Bamford and Baker (Bamford and Baker, 2003) for comparable sampling conditions in Baltimore (Summer; urban and sub-urban sites).

3.2. NPAH and OPAH gas/particle partitioning

In general, the fraction of OPAHs and NPAHs associated with the particulate phase is strongly depending on the molecular weight (Table 1). As in previous reported studies (Atkinson and Arey, 1994; Bamford and Baker, 2003; Fraser et al., 1998; Leoz-Garziandia et al., 2000; Liu et al., 2006; Reisen and Arey, 2005; Wilson et al., 1995), the lightest compounds (1-naphthaldehyde to 9-phenanthrenecarboxaldehyde for OPAHs; 1- and 2-nitronaphthalene for NPAHs) were detected

mainly in the gas phase (>50%). More than 90% of the compounds with a number of aromatics cycles ≥ 4 were detected in the particulate phase in all samples. Despite similar ambient temperatures (26 to 32 °C), the partitioning of the nitrophenanthrene isomers (3 aromatics cycles) measured in the particulate phase presents strong variations between the sampling sites. The variability of the different sources associated with each individual NPAHs could explain these partitioning variations. The same hypothesis may explain the partitioning dissimilarities of benzo[a]fluorenone according to the sampling locations. Finally, it is important to note that a light compound as 2-nitrofluorene (MW=211 g mol⁻¹) was essentially associated to the particulate phase (>80%) at any sampling site.

At the rural site, only 9-phenanthrenecarboxaldehyde presented a significant variation of gas/particle partitioning from day to night-time samples with higher parts on the filters systematically observed during the night. Same changes were observed at the sub-urban site for this OPAH and for three NPAHs namely, 9-nitroanthracene, 3- and 9-nitrophenanthrene. During the day, these gaseous OPAHs and NPAHs are fastly degraded by photolysis. Lower photolysis during night-time period allows a longer life time for these compounds emitted and/or formed in gaseous phase. Such a longer lifetime allows a larger adsorption to ambient particles.

3.3. NPAHs: gas phase formation vs. direct sources

Some source specific ratios of NPAHs were investigated in order to assess the relative importance of primary sources versus secondary sources arising from PAH atmospheric degradation for the three sampling sites. The ratio of 2-nitrofluoranthene on 1-nitropyrene (2-NF/1-NP) concentrations is generally used to evaluate the relative contribution of both types of sources (Bamford and Baker, 2003; Ciccioli et al., 1989; Ciccioli et al., 1996; Feilberg and Nielsen, 2001; Marino et al., 2000; Zielinska et al., 1989a). 2-NF is only produced from the gas phase reaction between fluoranthene and NO₂ initiated by OH during the day and initiated by NO₃ during the night (Arey et al., 1986; Atkinson et al., 1987). 1-NP is strictly arising from direct emissions (it has never been observed to result from any know gas phase reaction) (Arey, 1998; Nielson, 1984; Paputa-Peck

et al., 1983). Assuming reasonably for 2-NF and 1-NP the same removal rates and the same photolysis rates (Fan et al., 1996b; Feilberg and Nielsen, 2000; Kamens et al., 1994), a value for the 2NF/1NP ratio less than five shows the relative extent of primary emission sources whereas a ratio value larger than five will highlight the importance of the secondary formation of NPAHs (Ciccioli et al., 1996). Fig. 2 presents the observed 2+3-NF/1-NP ratios at the three instrumented sites. It should be noted that the separation of both isomers of nitrofluoranthene (2- and 3-nitrofluoranthene) could not be achieved on the 5% phenyl-substituted methylpolysiloxane phase (DB5-MS) used in this study. Considering the relative low proportion of 3-nitrofluoranthene reported in other previous studies [$< 1\%$ in (Bamford and Baker, 2003; Zielinska et al., 1989b) and $< 50\%$ in (Feilberg et al., 2001)], it was finally decided to us to use the 2+3-NF/1-NP ratio with care by fixing here the upper limit at 10 instead of 5. Indeed, the urban and sub-urban sites are clearly influenced by the primary NPAH sources (ratio < 10) whereas “Plan d’Aups” (the rural site) shows an evidence for the production of secondary NPAHs by gas phase reactions (ratio > 10).

The 2-NF/2-NP concentration ratio (2-nitrofluoranthene/2-nitropyrene) is usually used to evaluate the occurrence and the importance of the gas phase production of NPAHs from OH and/or NO_3 initiated oxidation pathways (Arey et al., 1989; Atkinson and Arey, 1994; Zielinska et al., 1989a). 2-NF is the major NPAH product of the gas phase reaction of fluoranthene with OH (Arey et al., 1986) and the only nitrofluoranthene formed from the NO_3 initiated reaction (Zielinska et al., 1986). 2-nitropyrene is the only nitropyrene formed from the reaction with OH but is not formed from the gas phase reaction of pyrene with NO_3 (Arey et al., 1986; Atkinson et al., 1990; Zielinska et al., 1986). Ratios close to 10 indicate day-time OH reactions, and ratios > 100 rather suggest night-time NO_3 formation pathways. At “Plan d’Aups”, the 2-NF/2-NP ratio value [average ratio ($\pm 1\sigma$) = 3.7 (± 4.4)] is consistent with the day-time OH reaction as the dominant gas phase formation pathway compared to the NO_3 initiated reaction.

Focusing on the study of the 2+3-NF and 1-NP concentrations at the same site, an important co-evolution of these compounds during the sampling week ($r=0.83$, $P<0.05$) can be observed. The same phenomenon, but lightly shifted is observed between the variations of the 2+3-NF/1-NP ratio

and the 1-NP concentrations (Fig. 3). These observations suggest an external contribution secondary NPAHs at this site (higher values of the 2+3-NF/1-NP ratio and lower 1-NP concentrations) with the simultaneous existence of local NPAH sources ([2+3-NF] and [1-NP] correlation). A thorough study of the highest 2+3-NF/1-NP ratio values (>10) compared with the wind directions observed during the campaign period, shows that the external contribution of the secondary NPAHs would come from the urban areas of Marseilles (SW) and Aix en Provence (NW) (Fig. 1 and 3). This result is consistent with the observations already made by Marinoni et al. at the same place during ESCOMPTE research program (Marinoni et al., 2005). By contrast, at the urban and sub-urban sites, the 2+3-NF/1-NP ratio is fairly constant and below 5, and the 1-NP and 2+3-NF concentration evolutions are well correlated ($r=0.93$ and 0.76 , $P<0.05$), confirming the primary origin of the measured NPAHs by the proximity of the emissions sources.

3.4. Source apportionment of NPAHs

To assess NPAH source distribution, relationships between ambient NPAH concentrations and NO, NO_x, O₃, PM₁₀ and PM_{2.5} were investigated. The correlation between some NPAHs and more specially those considered as source tracers such as 1-NP (direct emission), 2-NP and 2+3-NF (secondary compounds), were also studied.

At the urban site of “5 avenues”, except for a few compounds such as 1- and 2-nitronaphthalene (1-NN and 2-NN), 9-nitroanthracene (9-NA), 7-nitrobenz[a]anthracene (7-NB[a]A) and 3-nitrophenanthrene (3-NPh), no significant correlation was observed between individual NPAH and NO, NO_x, O₃, PM₁₀ and PM_{2.5} concentrations (Table 2). The lack of significant positive correlations between direct emission tracers (1-NP, predominantly diesel engines) and NO and NO_x may be due to the large contribution of gasoline emissions to the NO and NO_x levels measured at this site compared to diesel sources. Indeed, the gasoline influence is confirmed by the strong correlation between NO ($r=0.72$), NO_x ($r=0.79$) and the ratio $\{(B[ghi]P+Cor)/\Sigma PAHp\}^1$ representative of gasoline emissions and previously used by Marchand et al. (Marchand et al., 2004) for its capacity to

discriminate gasoline to diesel influences.

Therefore, the variations of the NPAH concentrations seem to be linked to changes in the gasoline source contribution ($r=0.80$, $P<0.05$), with a constant contribution from diesel sources represented by a fairly constant $(B[b]F+B[k]F)/\Sigma \text{ PAHp}$ ratio.

¹ $\Sigma \text{ PAHp}$: sum of filter concentrations of 10 PAHs mainly present in the particulate phase: from B[a]A to Cor

Previous studies have already shown the primary diesel sources of 1-NN, 2-NN, 9-NA, 7-NB[a]A (Bezabeh et al., 2003; Chiu and Miles, 1996; Feilberg et al., 2001; Paputa-Peck et al., 1983) whereas such compounds seem to be also emitted by gasoline engines (Table 2). The strong correlation between 3-NPh and NO and the $B[g,h,i]P+Cor)/\Sigma \text{ PAHp}$ ratio lets suppose a gasoline origin of this compound at this site.

At the sub-urban site of “Penne sur Huveaune”, except for 2-nitrofluorene (2-NFluo) and 6-nitrochrysene (6-NChr), all NPAHs (and OPAHs) were significantly correlated with NO and NO_x and interrelated. NPAHs and OPAHs were also correlated with PAHs. On the other hand, no correlation was observed with PAH ratios used to discriminate source influences {i.e. $(B[ghi]P+Cor)/\Sigma \text{ PAHp}$ for gasoline and $(B[b]F+B[k]F)/\Sigma \text{ PAHp}$ for diesel} (Marchand et al., 2004). This could be explained by the very close presence of emission sources to the sampling point, emissions, which are not necessarily traffic oriented. The proximity with the Atofina plant may disturb the PAH, NPAH and OPAH chemical signatures and influence the gas phase distribution, making very difficult the interpretation of the data with respect to the sources.

Despite of an evident production of secondary NPAHs at the rural site of “Plan d’Aups”, no correlation was observed between any NPAH and secondary NPAH tracers (2-NP and 2+3-NF).

At the urban site of “5 avenues” 1-NP, 2-nitrofluorene (2-NFluo) and 6-nitrochrysene (6-NChr) are strongly correlated ($r=0.99$ and 1.00 , respectively). This strong correlation is also observed at the rural site of “Plan d’Aups” (0.98 and 0.97 , respectively). Usually, 1NP is the predominant component in diesel particulate matter. However, it is not always the dominating substance.

Especially in heavy-duty diesel, 2-NFluo concentration may exceed that of 1-NP by a factor of 1.8–15. When 1-NP is the dominant substance, a 2-NFluo concentration equal to 15% of that of 1-NP is commonly observed (Environmental Health Criteria (EHC) 229., 2003). Strong correlations observed in our study and the previous literature data demonstrated that 1-NP, 2-NFluo and 6-NChr are primarily emitted by diesel vehicles.

At the three investigated sites, NPAHs mostly present negative correlation coefficients with O₃ (very noticeable at the sub-urban site of “la Penne sur Huveaune”). Such negative correlations have been already observed in previous works (Bamford and Baker, 2003; Feilberg et al., 2001). Studies of reactions of NPAHs with O₃ carried out in a smog chamber concluded that such degradation may take place. While photolysis remains the main degradation pathway for NPAHs, the reaction with O₃ could be an important night-time sink (Fan et al., 1996a; Fan et al., 1996b).

3.5. Source apportionment of OPAHs

A principal component analysis (PCA) was performed as a first approach. OPAH concentrations, some NPAH tracer concentrations and (B[ghi]P+Cor)/Σ PAHp ratio were compared for all samples (Fig. 4 and Table 3). Prior to the PCA, each compound concentration was normalized to the total OPAH or NPAH concentration. Due to the poor quantification of the 1-naphthaldehyde (low recovery factor), it was not taken into account in the PCA.

The first and the second principal components described 41% and 24% of the variability, respectively (Fig. 4). Four OPAH clusters are observed. The cluster formation as well as its position on the graph is closely related to its homogeneity with respect to potential sources or physicochemical properties.

The 9-fluorenone and to 2-nitronaphthalene cluster (cluster 1) can be explained by their largest presence in the gas phase. In addition, no significant correlations are observed with NPAH tracers and PAH source ratios, nor between 9-fluorenone concentration evolution and PM, NO and NO_x concentrations. Finally, no information could be drawn about the primary and/or secondary origin of

this compound.

A second OPAH cluster was constituted by 9-phenanthrenecarboxaldehyde, benzo[a]fluorenone, benzo[b]fluorenone and benzanthrone. Strong correlations between their concentrations and that of NO suggest a primary origin of these compounds (Table 4). Moreover, the absence of any correlation with the 1-NP and a significant correlation between the 9-phenanthrenecarboxaldehyde and the PAH gasoline ratio (Tables 3 and 4) let suppose a probable gasoline vehicle origin of these OPAHs. In a previous study, Fielberg et al. (Feilberg et al., 2001) showed that the dominant source of benzanthrone in København center, was diesel vehicles; however it has not been clearly established in our case. The results presented in Tables 3 and 4 show a possible contribution of the gasoline vehicles to its emissions.

The proximity between the benz[a]anthracene-7,12-dione (cluster 3) and the second OPAH cluster (see Fig. 4) demonstrates a good correlation between all these compounds suggesting a primary origin. The correlation with 1-NP as well as the absence of any correlation with the PAH gasoline ratio, indicates a potential diesel origin of this compound. This hypothesis is confirmed by the strong correlation observed with 1-NP, 2-Fluo and 6-NChr ($r=0.79, 0.75$ and $0.77, P<0.05$) at the urban site.

The 9,10-anthraquinone is part of the fourth cluster (Fig. 4) and seems to have a double-origin. It is correlated with a primary diesel compound like 1-NP and with secondary compounds such as 2+3-NF and 2-NP (Table 3). Diesel origin is confirmed by the strong correlation observed with the 1-NP, 2-NFluo and 6-NChr at the urban site of “5 avenues “ ($r= 0.62, 0.67$ and $0.66, P<0.05$). The 9,10-anthraquinone is the only OPAH positively correlated with O₃ at the urban site (even though the relation is not statistically significant) (Table 4). This observation suggests the gas phase formation of 9,10-anthraquinone by the ozonation of parent PAHs. The study of Perraudin et al. (Perraudin et al., 2007) in a simulated atmosphere showed that 9,10-anthraquinone and anthrone were the two major primary ozonation products of particle-bound anthracene. The formation of 9,10-anthraquinone by the ozonation of anthracene was studied at the rural site of “Plan d’Aups”. Fig. 5 shows a good correlation between the 9,10-anthraquinone and the O₃ concentrations from 07/23

night to 07/26 night. During the others days of the sampling week, low 9,10-anthraquinone levels are in agreement with high levels of Σ PAH_{g+p}². The absence or the low concentration levels of anthracene in ambient air can explain the low levels of 9,10-anthraquinone whereas high levels of O₃ and of Σ PAH_{g+p} are observed (07/23, 27 and 28 days).

² Σ PAH_{g+p}: sum of total concentration (filter + PUF) of 5 PAHs mainly in the gas phase or partitioned between the gas and the particulate phases, from fluorene to pyrene.

The formation of 9,10-anthraquinone from the anthracene ozonation was observed at this site. However, the next step will be the identification of when, before or during the sampling, this reaction takes place. Only one study has been carried out with ozone scrubbers dealing with the identification of secondary compounds (Liu et al., 2006); it does not allow to conclude about the origin of the reaction. Further investigations on NPAH and OPAH formations in ambient atmosphere will be clearly necessary because of their potential toxicity and the lack of data available.

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Table 1

Total (filter + PUF) PAH, OPAH, NPAH concentrations ($\mu\text{g m}^{-3}$) and associated particulate fraction (%), T ($^{\circ}\text{C}$), NO, NO_x, PM₁₀, PM_{2.5} and O₃ concentrations ($\mu\text{g m}^{-3}$) for the three instrumented sites

	"5 avenues" (urban) (n=12)		"Penne" (sub-urban) (n=14)		"Plan d'Aups" (rural) (n=14)	
	Mean (min-max)	% Filter (min-max)	Mean (min-max)	% Filter (min-max)	Mean (min-max)	% Filter (min-max)
T ($^{\circ}\text{C}$)	32 (25-40)	-	29 (21-37)	-	26 (17-36)	-
NO ($\mu\text{g m}^{-3}$)	3 (0-11)	-	8 (3-15)	-	-	-
NO _x ($\mu\text{g m}^{-3}$)	22 (8-44)	-	20 (3-35)	-	-	-
PM ₁₀ ($\mu\text{g m}^{-3}$)	42 (24-67)	-	-	-	-	-
PM _{2.5} ($\mu\text{g m}^{-3}$)	24 (13-35)	-	-	-	-	-
O ₃ ($\mu\text{g m}^{-3}$)	66 (13-106)	-	81 (14-152)	-	130 (96-168)	-
PAHs ($\mu\text{g m}^{-3}$)						
Fluorene	1 098 (272-2 707)	1 (0-2)	206 (0-1 662)	0 (0-3)	459 (0-5 167)	0 (0-0)
Phenanthrene	8 470 (3 482-15 287)	2 (1-4)	2 033 (0-8 619)	35 (0-100)	570 (7-1,695)	4 (0-15)
Anthracene	767 (3-4 343)	0 (0-1)	2 (0-13)	100 (100-100)	998 (0-6 595)	0 (0-0)
Fluoranthene	3 488 (2 104-4 826)	7 (2-18)	891 (360-2 429)	10 (0-16)	1 001 (402-3 907)	3 (0-14)
Pyrene	5 832 (379-18 169)	14 (1-49)	604 (267-1 484)	16 (5-30)	12 777 (687-27 414)	1 (0-14)
B[a]A	77 (18-157)	- ^a	44 (0-166)	- ^a	9 (2-40)	- ^a
Chrysene	186 (77-336)	- ^a	91 (32-214)	- ^a	23 (7-69)	- ^a
B[e]P	402 (227-553)	- ^a	37 (0-113)	- ^a	33 (5-149)	- ^a
B[b]F	262 (151-366)	- ^a	115 (35-351)	- ^a	32 (9-94)	- ^a
B[k]F	83 (37-127)	- ^a	40 (13-112)	- ^a	12 (3-43)	- ^a
B[a]P	100 (41-165)	- ^a	58 (18-152)	- ^a	18 (4-89)	- ^a
D[a,h]A	21 (10-41)	- ^a	10 (0-29)	- ^a	5 (0-31)	- ^a
B[g,h,i]P	232 (69-461)	- ^a	133 (48-380)	- ^a	25 (9-92)	- ^a
In[1,2,3,c,d]P	193 (73-274)	- ^a	87 (19-223)	- ^a	30 (9-126)	- ^a
Coronene	149 (39-288)	- ^a	69 (25-183)	- ^a	13 (5-41)	- ^a
OPAHs ($\mu\text{g m}^{-3}$)						
1-Naphthaldehyde	484 (0-1 470)	1 (0-3)	814 (109-2 134)	26 (7-73)	184 (0-434)	9 (0-47)
9-Fluorenone	3 577 (1 419-6 908)	4 (1-8)	2 157 (190-5 275)	7 (2-22)	888 (386-1 249)	1 (0-4)
9-Phen ^b	89 (49-183)	47 (26-75)	50 (10-111)	39 (7-67)	7 (2-21)	63 (10-100)
9,10-Anthraquinone	1 398 (378-2 570)	71 (21-100)	774 (73-2 790)	56 (12-100)	176 (42-452)	72 (17-100)
Benzo[a]fluorenone	247 (134-429)	74 (46-97)	113 (32-254)	82 (37-100)	31 (12-112)	45 (11-87)
Benzo[b]fluorenone	152 (80-272)	95 (84-100)	82 (17-191)	93 (71-100)	15 (7-40)	71 (29-100)
Benzanthrone	219 (107-543)	100 (100-100)	144 (24-486)	92 (27-100)	18 (4-62)	94 (48-100)
B[a]A-7,12-dione ^c	120 (58-232)	100 (99-100)	60 (11-195)	95 (75-100)	11 (5-27)	97 (58-100)
NPAHs ($\mu\text{g m}^{-3}$)						
1-Nitronaphthalene	208.4 (3.2-493.6)	3 (0-12)	176.0 (1.6-600.5)	5 (0-15)	9.7 (0.0-38.7)	2 (0-12)
2-Nitronaphthalene	119.7 (0.9-245.8)	1 (0-1)	82.6 (3.4-334.0)	4 (1-20)	8.9 (0.8-25.0)	1 (0-8)
2-Nitrofluorene	21.4 (0.1-92.9)	100 (100-100)	5.3 (0.0-24.4)	79 (0-100)	1.4 (0.0-8.4)	100 (100-100)
9-Nitroanthracene	106.7 (56.6-227.7)	48 (23-80)	28.1 (6.7-91.4)	46 (14-75)	1.6 (0.2-9.8)	77 (0-100)
9-Nitrophenanthrene	8.7 (0.7-47.6)	26 (1-55)	2.6 (0.2-12.0)	59 (25-95)	0.2 (0.0-0.7)	58 (4-100)
3-Nitrophenanthrene	13.7 (6.7-27.6)	22 (8-33)	4.9 (0.7-14.0)	34 (12-66)	0.3 (0.1-1.4)	78 (18-100)
2+3-Nitrofluoranthene	89.9 (37.6-229.3)	99 (93-100)	23.8 (3.4-79.7)	98 (63-100)	2.8 (1.2-8.1)	100 (100-100)
4-Nitropyrene	1.4 (0.7-2.6)	100 (100-100)	0.6 (0.1-1.2)	88 (15-100)	0.0 (0.0-0.1)	100 (100-100)
1-Nitropyrene	60.7 (14.9-222.1)	100 (100-100)	7.9 (1.1-16.4)	93 (53-100)	0.6 (0.0-3.1)	100 (100-100)
2-Nitropyrene	33.6 (12.5-69.8)	100 (100-100)	10.4 (0.6-35.1)	100 (96-100)	1.6 (0.2-4.5)	91 (27-100)
7-Nitrobenz[a]anthracene	3.8 (0.2-9.9)	100 (100-100)	2.0 (0.0-13.0)	100 (100-100)	0.0 (0.0-0.2)	100 (100-100)
6-Nitrochrysene	33.1 (0.1-147.5)	100 (100-100)	0.7 (0.0-4.4)	100 (100-100)	0.3 (0.0-2.5)	100 (100-100)
1,3-Dinitropyrene	0.3 (0.0-0.7)	100 (100-100)	0.2 (0.0-0.6)	100 (100-100)	0.0 (0.0-0.2)	100 (100-100)
1,6-Dinitropyrene	nd	-	nd	-	0.0 (0.0-0.0)	100 (100-100)
1,8-Dinitropyrene	2.5 (0.5-8.7)	100 (100-100)	1.1 (0.2-2.9)	100 (100-100)	0.2 (0.0-0.9)	100 (100-100)
6-Nitrobenzo[a]pyrene	5.9 (0.2-35.6)	100 (100-100)	0.9 (0.0-3.4)	100 (100-100)	0.0 (0.0-0.3)	100 (100-100)

^a cannot be determined (interferences due to PUF deterioration)

^b 9-phenanthrenecarboxaldehyde

^c Benz[a]anthracene-7,12-dione

^d not detected

Table 2

Pearson correlations coefficients (n=12) of total (filter + PUF) concentrations of individual NPAHs with PM₁₀, PM_{2.5}, NO, NO_x, O₃ concentrations and with (B[ghi]P+Cor)/Σ PAHp* and (B[b]F+B[k]F)/Σ PAHp ratios at the urban site of “5 avenues”

	PM _{2.5}	PM ₁₀	NO	NO _x	O ₃	(B[ghi]P+Cor)/Σ PAHp	(B[b]F+B[k]F)/Σ PAHp
1-Nitronaphthalene	0.34	-0.04	0.50	0.79	-0.78	0.81	-0.41
2-Nitronaphthalene	0.33	-0.06	0.36	0.71	-0.73	0.72	-0.34
2-Nitrofluorene	0.10	0.00	-0.16	-0.25	0.35	0.12	0.07
9-Nitroanthracene	0.44	0.22	0.66	0.53	-0.67	0.71	-0.17
9-Nitrophenanthrene	0.13	-0.23	0.03	0.45	0.07	0.11	-0.25
3-Nitrophenanthrene	<u>0.70</u>	<u>0.62</u>	0.81	0.53	-0.48	0.50	-0.32
2+3-Nitrofluoranthene	0.30	0.10	-0.15	-0.05	0.16	0.23	-0.05
4-Nitropyrene	0.25	0.35	0.56	0.13	-0.53	0.45	0.12
1-Nitropyrene	0.17	0.07	-0.11	-0.19	0.31	0.15	0.01
2-Nitropyrene	0.03	0.12	0.58	0.10	-0.59	0.21	0.31
7-Nitrobenz[a]anthracene	0.20	-0.10	0.42	0.68	-0.83	0.65	-0.23
6-Nitrochrysene	0.11	0.03	-0.15	-0.27	0.36	0.09	0.08
6-Nitrobenzo[a]pyrene	0.39	0.19	0.07	0.26	-0.55	-0.36	0.53
(B[ghi]P+Cor)/Σ PAHp	0.48	0.10	0.72	0.79	-0.60		
(B[b]F+B[k]F)/Σ PAHp	-0.27	-0.42	-0.47	-0.63	-0.27		

In bold, correlation significant at the P<0.05 level (2 tailed)

In bold, underlined: no correlation was taken into account because the compound is essentially present in the gas phase

(see Table 1)

*Σ PAHp: sum of filter concentrations of 10 PAHs mainly present in the particulate phase: from B[a]A to Cor

Table 3

Pearson correlation coefficients (n=40) related to the Fig. 4

	2-NN	2+3-NF	1-NP	2-NP	(B[ghi]P+Cor)/ Σ PAH _p
9-Fluorenone	0.47	-0.58	-0.64	-0.24	-0.13
9-phenanthrenecarboxaldehyde	-0.35	0.00	0.32	-0.26	0.46
9,10-Anthraquinone	-0.36	0.62	0.59	0.33	0.00
Benzo[a]fluorenone	-0.26	0.02	0.17	-0.10	0.12
Benzo[b]fluorenone	-0.44	0.10	0.32	-0.07	0.29
Benanthrone	-0.37	-0.04	0.13	-0.09	0.47
Benz[a]anthracene-7,12-dione	-0.48	0.33	0.54	-0.14	0.18

In bold, correlation significant at the P<0.05 level (2 tailed)

Table 4

Pearson correlation coefficients (n=12) of total concentrations (filter + PUF) of OPAHs with PM₁₀, PM_{2.5}, NO, NO_x and O₃ concentrations and with (B[ghi]P+Cor)/Σ PAHp and (B[b]F+B[k]F)/Σ PAHp ratios at the urban site of “5 avenues”

	PM _{2.5}	PM ₁₀	NO	NO _x	O ₃	(B[ghi]P+Cor)/ Σ PAHp	(B[b]F+B[k]F)/ Σ PAHp
9-Fluorenone	0.40	0.10	0.34	0.20	-0.67	0.49	0.28
9-phenanthrenecarboxaldehyde	0.51	0.32	0.86	0.64	-0.50	0.79	-0.41
9,10-Anthraquinone	-0.45	0.01	-0.28	-0.54	0.42	-0.22	0.10
Benzo[a]fluorenone	0.43	0.53	0.82	0.37	-0.48	0.38	-0.18
Benzo[b]fluorenone	0.48	0.50	0.76	0.32	-0.59	0.40	-0.05
Benanthrone	0.48	0.43	0.87	0.57	-0.81	0.58	-0.18
Benz[a]anthracene-7,12-dione	0.32	0.16	0.18	0.05	-0.21	0.29	0.11
(B[ghi]P+Cor)/Σ PAHp	0.48	0.10	0.72	0.79	-0.60	-	-
(B[b]F+B[k]F)/Σ PAHp	-0.27	-0.42	-0.47	-0.63	0.08	-	-

In bold, correlation significant at the P<0.05 level (2 tailed)

Figure Captions

Fig. 1. Sampling sites location.

Fig. 2. 2+3-Nitrofluoranthene/1-nitropyrene concentration ratios (2+3-NF/1-NP) for air samples collected in Marseilles area at the “5 avenues”, “Penne sur Huveaune” and “Plan d’Aups” sites. Black triangles represent the average ratios.

Fig. 3. A: Weekly variations of 1-NP and 2+3-NF concentrations and the 2+3-nitrofluoranthene/1-nitropyrene concentration ratio (2+3-NF/1-NP), at the rural site of “Plan d’Aups”. B: Directions of the prevalent winds are presented for comparison and discussion.

Fig. 4. Correlation circle of normalized single OPAH concentrations (filter + PUF) with normalized 2-NN, 2+3-NF, 1-NP, 2-NP concentrations (filter + PUF) and with (B[ghi]P+Cor)/ Σ PAHp ratio (all sampling sites, n=40).

Fig. 5. Weekly evolution of 9,10-anthraquinone (pg m^{-3}), O_3 ($\mu\text{g m}^{-3}$), Σ PAHg+p* and anthracene (ng m^{-3}) at the rural site of “Plan d’Aups”.

* Σ PAHg+p: sum of total concentration (filter + PUF) of 5 PAHs mainly in the gas phase or partitioned between the gas and the particulate phases, from fluorene to pyrene.



AIX-EN-PROVENCE

Plan d'Aups

5 avenues

MARSEILLE

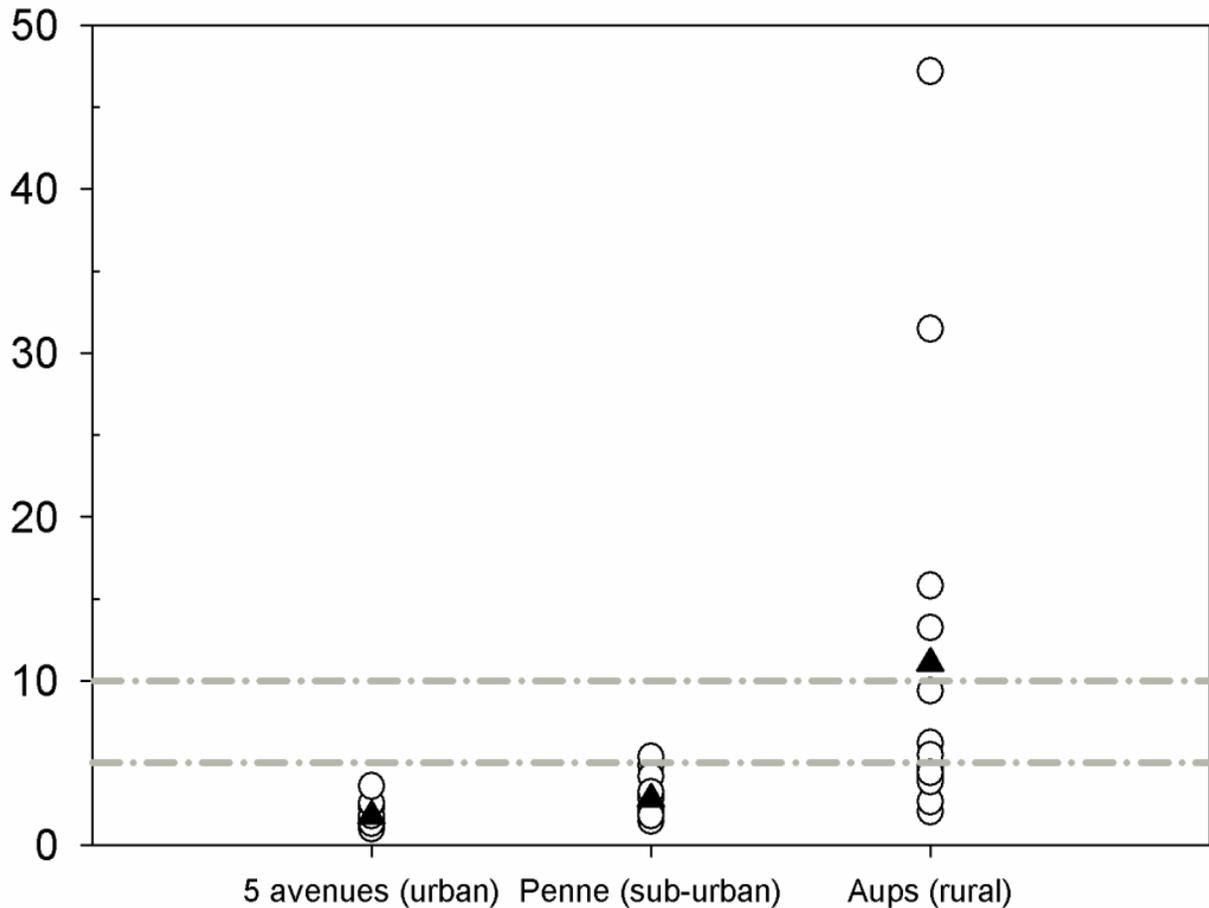
Penne/Huveaune

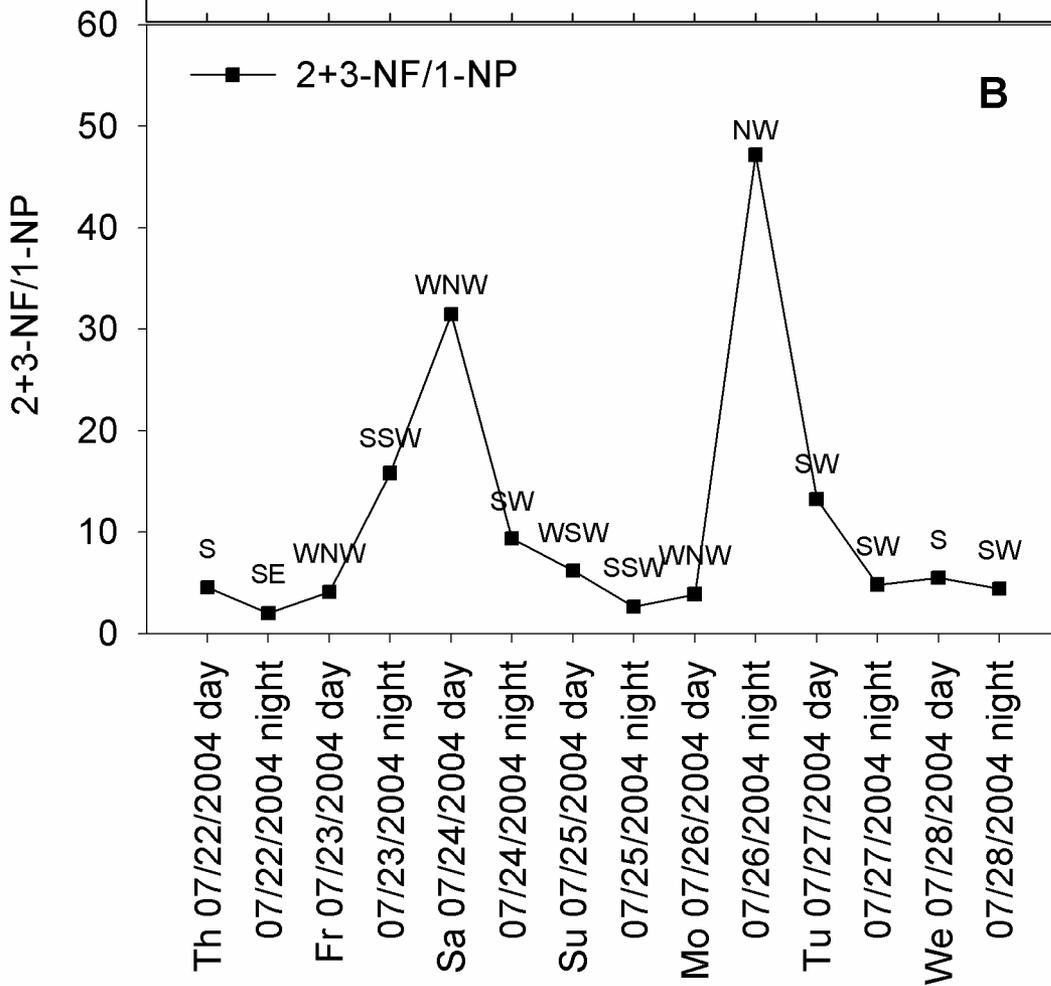
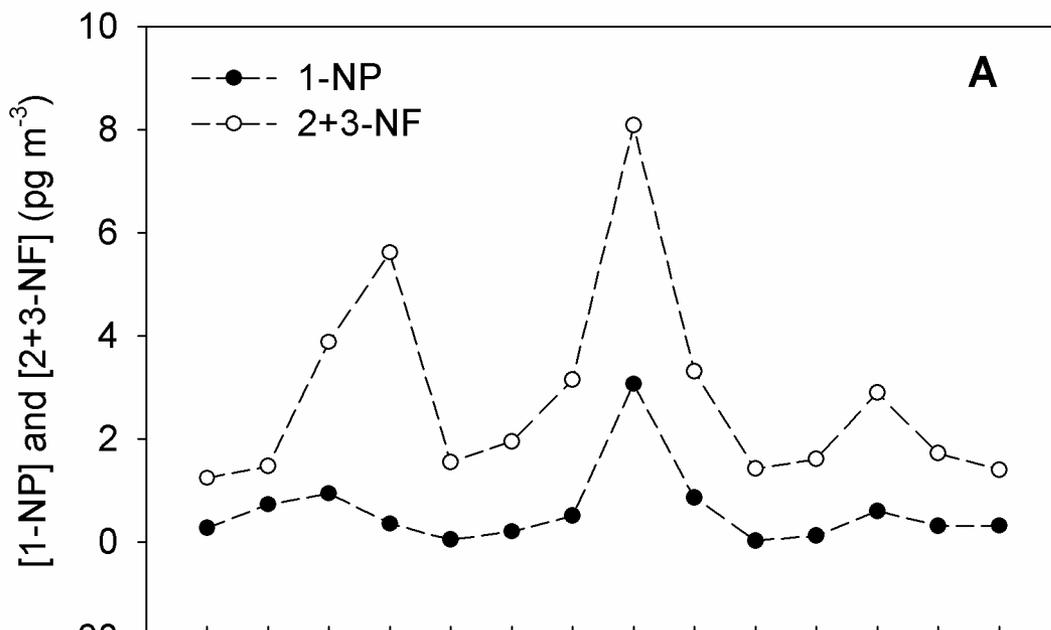
la Ciotat

10 km

TOULON

2+3-NF/1-NP





- 9-Fluorenone
- ▲ 9-Phenanthrenecarboxaldehyde
- ☆ 9,10-Anthraquinone
- △ Benzo[a]fluorenone
- △ Benzo[b]fluorenone
- ▲ Benzanthrone
- ▲ Benz[a]anthracene-7,12-dione
- 2-Nitronaphtalene
- 2+3-Nitrofluoranthene
- 1-Nitropyrene
- ⊕ 2-Nitropyrene
- ⊠ (B[ghi]P+Cor)/Σ PAHp

