Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys: Part 1: Concentrations, sources and gas/particle partitioning

A. Albinet, E. Leoz-Garziandia, H. Budzinski, E. Villenave, Jean-Luc Jaffrezo

HAL Id: insu-00375849
https://insu.hal.science/insu-00375849

Submitted on 12 Feb 2014

Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys. Part 1: Concentrations, sources and gas/particle partitioning

A. Albinet[a*], E. Leoz-Garziandia[a*], H. Budzinski[b], E. Villenave[b], J.-L. Jaffrezo[c]

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

[b] *Institut des Sciences Moléculaires (ISM), UMR 5256 CNRS, Université Bordeaux 1, 33405 Talence, France*

[c] *Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), UMR 5183 CNRS, Université Grenoble 1, 38402 Saint Martin d'Hères, France*

[*] Corresponding authors. Fax : +33 3 44 55 63 02

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

Abstract

Ambient measurements (gas + particle phases) of 16 polycyclic aromatic hydrocarbons, 17 nitrated PAHs (NPAHs) and 8 oxygenated PAHs (OPAHs) were carried out during the winter 2002-2003 and the summer 2003 in two French alpine valleys on various types of sites (traffic, sub-urban, altitude and rural). Atmospheric concentrations of these classes of compounds are of interest because they include potential mutagens and carcinogens. During both summer and winter campaigns, OPAH concentration levels were of the same order of magnitude as PAH ones while NPAH concentrations were one to two orders of magnitude lower. Total particulate PAH, OPAH and NPAH concentrations were higher in the Chamonix valley than in the Maurienne valley. A heavier pollutant accumulation process in the Chamonix valley and geomorphology promoting their dispersion seem to explain such differences. Despite reaching lower atmospheric concentrations, NPAHs seemed to account up to 20% of carcinogenic potency of particulates collected at the sites away from pollution sources. The formation of secondary compounds such as NPAHs increases significantly the carcinogenic risk at the sites away from pollution sources. Study with 2-nitrofluoranthene/1-nitropyrene ratio showed that NPAH gas phase formation was hindered in winter, and when relative contribution from primary sources was higher. Nevertheless, in winter under specific conditions, evidence of secondary NPAH formations was observed at sub-urban and traffic sites (snowfalls) and rural site (accumulation of pollutants and snowfalls). For all sampling sites, the day-time OH initiated reaction seemed to be the dominant gas phase formation pathway over the NO_3 initiated reaction. The fraction of PAHs, OPAHs and NPAHs associated with the particle phase was strongly depending on their vapour pressure and the ambient conditions.

1. Introduction and objectives

Alpine valleys represent some of the most important crossroads for international heavy-duty traffic in Europe but impact of this traffic on air quality is not well-known due to a lack of data in these complex systems. The results presented here were obtained during the research program POVA (POllution des Vallées Alpines). This study benefits of an exceptional context due to the closure of the "Tunnel du Mont Blanc" (TMB) in the Chamonix valley (Cv) for nearly 3 years after a large accident that took place in March 1999. Consequently, most heavy duty traffic in the area was diverted toward the "Tunnel du Fréjus", in the Maurienne valley (Mv). The general objective of this research program was the comparative study of atmospheric pollution in these two French Alpines valleys before and after the reopening of the TMB to heavy-duty traffic (July 2002). The program included several field campaigns, as well as 3D modelling of atmospheric emission and transport of pollutants (Brulfert et al., 2005). In this context, our specific objective was to obtain relative data on the exposure levels of the population to polycyclic aromatic hydrocarbons (PAHs) and their oxidation products, namely oxygenated and nitrated PAHs (OPAHs and NPAHs respectively), and to evaluate the influences of the combustion sources on the concentrations of these products.

PAHs are released in the atmosphere as by-products from the incomplete combustion or pyrolysis of organic matter and fossil fuel. They are extensively studied because of their potentially carcinogenic and/or mutagenic properties (IARC, 1987). PAH derivatives (NPAHs and OPAHs) have been recognised as direct-acting mutagens and carcinogens resulting more toxic than their

3

parent PAHs which require an enzymatic activation (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). NPAHs and OPAHs are either formed directly during combustion processes or in the atmosphere by both gas and heterogeneous phase reactions of PAHs induced by atmospheric oxidants (OH, NO_3, O_3) (Arey et al., 1986; Atkinson et al., 1989; Atkinson et al., 1990; Barbas et al., 1996; Environmental Health Criteria (EHC) 229, 2003; Helmig and Harger, 1994; Perraudin et al., 2007; Sasaki et al., 1997). Despite their high potential toxicity, atmospheric sources (primary or secondary) and concentrations of these PAH derivatives are well not documented.

As part of the POVA research program, two intensive field campaigns were performed in winter 2002-2003 and summer 2003. The purposes of these measurements were to characterise and to compare the occurrence of the NPAHs and OPAHs in both gas and particulate phases for various types of sites (rural, traffic, suburban and altitude) in pollution-sensitive valleys and to estimate the respective contributions of their different sources (primary and/or secondary) and their different atmospheric formation pathways.

2.   Experimental sections

2.1.   *Sampling campaigns and sites*

As part of the POVA research program, two 15-day campaigns were performed after the reopening of the TMB to the international traffic. A winter campaign took place in 2003, from January 15th to 22nd in the Cv and from January 24th to 31st in the Mv. A second campaign took place the following summer, from June 25th to July 2nd in the Mv and from July 04th to 11th in the Cv. In each valley, four sites with different characteristics were instrumented in order to study the evolution of PAH, OPAH and NPAH concentrations and reactivity (Table 1 and Fig. 1). In addition, these sampling sites were instrumented with various aerosol and/or gas samplers, including

4

continuous monitoring of NO_x, O_3, CO, PM_{10}, aerosol gravimetric measurement and size distribution, aerosol collection for chemical analysis, sampling for speciation of volatile organic compounds and meteorological data. Not all measurements were performed at every site (Table 1). The locations of the PAH sampling sites (C1 to C4 for the Cv and M1 to M4 for the Mv) are presented on Fig. 1.

2.2. Sample collection

Two types of high volume samplers (DA-80 and cascade impactor) were used to collect PAHs and their derivatives. Table 1 presents the repartition of the samplers according to the sampling sites. At sites C2 and M1 both samplers were installed in parallel.

Both ambient air particulate (on quartz filter, Schleicher & Schuell,$\varnothing$=150 mm) and gas (on PUFs polyurethane foams, Tisch Environmental, 79 mm long) phases were sampled using modified high volume samplers equipped with PM_{10} head (Model Digitel DA-80, Hegnau, Switzerland, 30 m^3 h^{-1}). Continuous 12 h samplings were performed, starting at 08:00 and 20:00 local time. Airborne particulates were also collected using high volume cascade impactors (Graseby Andersen, 35 m^3 h^{-1}). Daily 24 h samples were collected every day starting at 8:00 local time. The particles collected using this sampler were separated into seven size ranges: D_p<0.39 µm (stage 7 or back up filter), 0.39-0.69 µm (stage 6), 0.69-1.3 µm (stage 5), 1.3-2.1 µm (stage 4), 2.1-4.2 µm (stage 3), 4.2-10.2 µm (stage 2) and 10.2-50 µm (stage 1). Samples were collected on six separated fritted quartz fiber filters (Tisch Environmental, 142×149 mm), with a back up quartz fiber filter (Whatman QM-A, 203×254 mm).

Overall, 50 and 62 PUFs together with 57 and 62 total filters and twice 28 impactor samples were collected during the winter and summer campaigns, respectively. Field blanks (i.e., exposed

5

PUFs and filters without any air filtration) were collected weekly for each sampler and sampling site during both sampling campaigns.

Prior to sampling, all quartz fiber filters were burnt at 500°C for 12 h to remove any organic compounds that might be present on the filters. PUFs were pre-washed with dichloromethane using pressurised liquid extraction. After collection, filters were stored at -18°C in individual glass Petri dishes (pre-washed). PUFs were stored with their glass holder at -18°C. All samples were wrapped in aluminium foil and sealed in opaque poly bags.

2.3. Sample extraction and analysis

The complete PAH, NPAH and OPAH analytical procedures and quality assurance are presented in detail elsewhere (Albinet et al., 2006; Albinet et al., 2007b). HPLC-grade quality solvents were used and purchased from Carlo Erba SDS (Peypin, France).

Filters and PUFs were extracted with dichloromethane using pressurized liquid extraction. Consecutive impactor stages from the winter campaigns were extracted together (1 and 2, 3 and 4, etc) while those from the summer campaign were extracted individually, except for stages 1 and 2. All extracts were divided into two equal fractions, the former to determine PAHs, and the latter for NPAHs and OPAHs. 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). 16 PAHs were quantified using HPLC with fluorescence/UV detection. NPAH and OPAH concentrations were determined simultaneously using gas chromatography-mass spectrometry with negative ion chemical ionization (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

6

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 8 OPAHs were quantified (see Table S1 available in the online version). 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 m^3 ranged between 0.01 and 0.07 pg m^{-3}. OPAH detection limits for an air sample of 360 m^3 ranged between 0.01 and 2.6 pg m^{-3}.

In this paper, only results on OPAH and NPAH concentrations are discussed. Results on PAH are also take into account because they are the parent compounds of the NPAHs and OPAHs and they are considered as a base for the discussion.

3. Results and discussion

3.1. Concentrations of OPAHs and NPAHs

Table S1 (available in the online version) presents the average total (filter + PUF) OPAH and NPAH concentrations measured at each instrumented site. For the cascade impactor samples, concentrations concern only the particulate phase and were determined by summing the concentrations of all the impactor stages. Table S1 also presents, if available, the average temperature, CO, NO, NO$_x$, O$_3$, PM$_{10}$, and benzo[a]pyrene concentrations.

In general, the differences between the concentrations determined with the parallel sampling systems used were considered as negligible with regard to the variability in the analysis of particulate PAHs, OPAHs and NPAHs. Nevertheless, individual NPAH concentrations determined for the DA-80 samples during the winter period were about 3 to 4 times lower than those determined for the cascade impactor samples, for all NPAHs. The use of heating of the PM$_{10}$ sampling head in this season would seem to explain such differences (Albinet et al., 2007a).

During both summer and winter campaigns, OPAH concentration levels were of the same order of magnitude as PAHs, while NPAH were one to two orders of magnitude lower. During both, winter and summer campaigns, 9-fluorenone, 9,10-anthraquinone, and 1-naphthaldehyde were, for all types of sampling sites, the most abundant OPAHs quantitatively measured, accounting for about 20 to 70%, 10 to 60% and 10 to 40% of the total OPAH concentrations, respectively. During the winter period, benzanthrone was also a major compound. It was predominant at site C1 (where only the particulate phase was sampled), accounting for about 30% of the total OPAH concentration. 2+3-Nitrofluoranthene, 2-nitropyrene, 9-nitroanthracene and 1-nitronaphthalene were the major NPAHs in both the Cv and the Mv. Their proportion varied according to the sampling seasons. 9-Nitroanthracene and 2-nitropyrene were predominant in winter, whereas 2+3-nitrofluoranthene and 1-nitronaphthalene were prevalent in summer.

The OPAH concentration levels observed at the urban, sub-urban and rural sampling sites in both valleys were in the same range than those reported in previous studies for large agglomerations and similar sampling seasons (winter or summer) like Paris (Leoz-Garziandia et al., 2000) and Marseilles (France) (Albinet et al., 2007b); Disburg (Germany) (König et al., 1983), Portland (Ligocki and Pankow, 1989), Salt Lake City (Hawthorne et al., 1992), Houston (Wilson et al., 1995) and Boston (USA) (Allen et al., 1997); Alger (Algeria) (Yassaa et al., 2001) and Santiago (Chile) (Maria del Rosario Sienra, 2006).

Atmospheric concentrations of NPAHs such as 1-, 2-nitropyrene, 2+3-nitrofluoranthene were, for all the sampling sites except the altitude site C3, of the same order of magnitude as those reported for the cities and areas of Marseille (France) (Albinet et al., 2007b), Naples, Milan (Italy) and São Paulo (Brazil) (Ciccioli et al., 1995; Ciccioli et al., 1996), Athens (Greece) (Marino et al., 2000), Barcelona (Spain) (Bayona et al., 1994), Birmigham (England) (Dimashki et al., 2000) and for similar sampling seasons. Nevertheless, in the winter period, individual NPAH concentrations are 2

to 50 times higher than those reported by Bamford and Baker (2003) in Baltimore for urban and suburban sites.

3.2. Concentrations of PAHs, OPAHs and NPAHs: comparison of both valleys

Average Σ PAHp, Σ OPAHp and Σ NPAHp, defined as the sum of the concentrations of PAHs, OPAHs and NPAHs mainly present in the particulate phase (see Table S1 available in the online version, and section 3.6), are presented on Fig. 2. These sums comprise 10 PAHs (from benz[a]anthracene to coronene), 6 OPAHs (from 9-phenanthrenecarboxaldehyde to benz[a]anthracene-7,12-dione) and 11 NPAHs (from 2+3-nitrofluoranthene to 6-nitrobenzo[a]pyrene), respectively.

Fig. 2 indicates strong seasonal variations of concentrations between winter and summer, the former being usually one order of magnitude higher than the latter. It could be partly related to season-modulated emissions including residential heating at the first site in winter (Aymoz et al., 2006; Marchand et al., 2004; Marchand et al., 2007) but could also result to a lower degradation of this compounds link to a lower photolysis (Finlayson-Pitts and Pitts Jr, 1986) and an accumulation of pollutants due to the formation of thermal inversions very common in Alpine valleys in winter season.

Fig. 2 also indicates that, for all the time, the average concentrations are twice in the Cv (C1 and C2) than in the Mv despite much larger heavy-duty international traffic run in the latter. Therefore, heavy-duty traffic does not appear to be the fundamental parameter governing concentrations of PAHs and PAH derivatives in these areas. Ventilation is probably a key factor decreasing concentrations of pollutants in the Mv, which is wider than Cv, particularly in winter when the inversion layer formation is more relevant, leading pollutants to accumulate.

9

Differences also emerge considering the type of sampling sites. In the Cv, the C3 (2263 meters above sea level) can be considered as remote, with an absence of pollution sources, leading to very low concentrations of compounds. High concentrations observed at sites C1 (suburban) and C2 (road side) are directly in relation with the proximity of sources (traffic, wood heating…), while the rural character of site C4 and its mid-altitude (1250 meters above sea level) are probably explaining the low concentrations observed there. These differences are particularly evident in the winter season, when the very local conditions are emphasized by the air mass stability.

The low pollutant concentrations observed in the Mv compared to the Cv also show a lower variability with the site characteristics. Probably, the dispersion of pollutants can induce there a more homogeneous distribution of the pollutants all along the valley.

3.3. Carcinogenic risk

Carcinogenic risk was estimated using toxic equivalent factors (TEFs) and was calculated as:

$$Carcinogenic\ risk = \left[\sum_i [PAH]_i\ TEF_{PAH_i} + \sum_i [NPAH]_i\ TEF_{NPAH_i} \right] UR_{B[a]P} \quad (1)$$

where $[PAH]_i$ and $[NPAH]_i$ are the individual atmospheric concentrations of PAHs and NPAHs (expressed in ng m^{-3}). TEF_{PAH_i} and TEF_{NPAH_i} are the individual toxic equivalent factors of PAH and NPAH, respectively. TEFs data are obtained from INERIS for PAHs (Doornaert and Pichard, 2003) and from OEHHA (OEHHA, 2002 and 2005) for NPAHs (Table 2). To the best of our knowledge, no such data are currently available for OPAHs. B[a]P is the reference compound for TEFs of PAHs and their derivatives. The value of its TEF is normalized at 1. $UR_{B[a]P}$ is the inhalation cancer

unit risk factor of benzo[a]pyrene (=1.1 × 10^{-6} (ng m^{-3})$^{-1}$) calculated from cancer potency factors (CPFs) using the following relationship

$$UR_i = \frac{CPF_i \times 20\ m^3}{70\ kg \times CV} \quad (2)$$

where CPF$_i$ is the inhalation cancer potency factor of the compound i (equal to 3.9 (mg/kg-day)$^{-1}$ for B[a]), 20 m^3 is the reference human inspiration rate per day, 70 kg is the reference human body weight, and CV is the conversion factor from mg to ng (=1 × 10^6) (OEHHA, 2002 and 2005).

Since the gas phase PAHs and NPAHs were not sampled at all sampling sites, only compounds occurring overall in the particulate phase were taken into account (9 PAHs and 5 NPAHs: see Table 2). Further, NPAH concentrations determined with the DA-80 sampler in winter have been corrected (Albinet et al., 2007a). Results obtained for each sampling site are presented in Fig. 3.

In concordance to aerial concentrations, also the carcinogenic risk in the Cv was two times that in the Mv. In addition, the average risk is about 5 to 35 times higher during winter than during summer, except at the altitude site (C3) where it was nearly constant. The risk associated to NPAHs could reach 20% of the total risk although only five compounds reached meaningful concentrations, which remained 1 to 2 orders of magnitude lower than that of PAHs. Moreover, highest NPAH risk contributions were observed, for both winter and summer campaigns, at the altitude and rural sites C3, C4 and M1 and at the suburban site of Modane in summer period (M3). This seems to indicate that the formation of secondary NPAHs significantly increase the carcinogenic risk at sites far from direct influence of pollution sources. It follows that the determination of atmospheric concentrations of PAH derivatives is quite important for risk assessment but also further investigations are necessary to assess the carcinogenic potencies of NPAHs and especially OPAHs.

3.4. NPAHs gas phase formation vs. direct sources

Source specific ratios of NPAHs were investigated in order to assess the relative importance of primary sources versus secondary atmospheric gas phase formation, for both winter and summer periods. The ratio of 2-nitrofluoranthene to 1-nitropyrene (2-NF/1-NP) is generally used to evaluate the relative contribution of these pathways (Bamford and Baker, 2003; Ciccioli et al., 1989; Ciccioli et al., 1996; Feilberg and Nielsen, 2001; Marino et al., 2000; Zielinska et al., 1989b). 2-NF is solely produced from gas phase reactions between fluoranthene and NO_2, initiated by OH during daytime and by NO_3 during nightime (Arey et al., 1986; Atkinson et al., 1987). 1-NP has never been observed as a product from any known gas phase reaction and is therefore considered as coming essentially from direct emissions (Arey, 1998; Nielson, 1984; Paputa-Peck et al., 1983). Assuming same removal and photolysis rates for the two products (Fan et al., 1996; Feilberg and Nielsen, 2000; Kamens et al., 1994), a ratio of 2NF/1NP less than five shows a predominance of primary emission sources whereas a ratio greater than five would highlight the importance of the gas phase formation of NPAHs (Ciccioli et al., 1996).

Fig. 4 presents the 2+3-NF/1-NP ratios calculated day-by-day for all the sites except C3 where NPAH concentrations were close to the limits of quantification. It should be noted that the separation of 2- and 3-nitrofluoranthene could not be achieved with our analytical technique. Considering the relatively low proportion of 3-nitrofluoranthene relative to 2-nitrofluoranthene reported in previous studies (< 1% in Bamford and Baker, 2003 and in Zielinska et al., 1989a and <50% in Feilberg et al., 2001) we adopted conservatively an upper limit to 10 instead of 5 for the 2+3-NF/1-NP ratio, with values between these two boundaries being subjected to discussion.

In both winter and summer, the urban and sub-urban sites were clearly influenced by primary NPAH sources. By contrast, the gas-phase formation of NPAHs was evident in summer at C4 and M1, where it was favoured by both high concentrations of reactants (NO_2, NO_3 and OH) and temperature (Ciccioli et al., 1996).

Secondary NPAH formation could also be important at C1 and C2 under specific conditions. In winter, for a day-time period characterized by snowfalls, ratios observed at sites C1 and C2 were above 5 and 10, respectively. It is possible that lower photolysis during such period allows a longer life time for the secondary compounds formed in gaseous phase. Such a longer lifetime allows a larger adsorption to ambient particles where NPAHs are supposedly protected against photolysis (Atkinson and Arey, 1994) increasing the 2+3-NF/1-NP ratios.

On the average, the gas phase formation was not a major source of NPAHs at the rural site M4 where evidence for that was observed only at singular conditions during the winter period. Fig. 5 shows the day-by-day variations of Σ PAHp, Σ OPAHp and Σ NPAHp at site M4 during the winter 2002-2003 sampling campaign. During this week, three successive meteorological events were encountered: snowfall episodes, an anticyclonic period followed by a new strong snowfall period. During the anticyclonic period, the total concentrations of PAHs, OPAHs, and NPAHs increased, probably due to an accumulation process. Then, the strong snowfalls induced a decrease of the pollutant concentrations (e.g. NO_2 and PM_{10}) (Albinet et al., 2006) by wet deposition. NPAH gas phase formation was evident (2+3-NF/1-NP ratios >10) when the accumulation of primary pollutants was maximal (sample "01/27 night") and once again, when photolysis was poor (snowfalls) and sufficient NO_2 concentrations (sample "01/28 day") were observed (Fig.5).

3.5. Contribution of NPAHs from gas phase OH and NO_3 reactions

The 2-NF/2-NP ratio (2-nitrofluoranthene/2-nitropyrene) is usually used to evaluate the occurrence and the importance of the gas phase production of NPAHs from formation pathways initiated by OH and/or NO_3 (Arey et al., 1989; Atkinson and Arey, 1994; Zielinska et al., 1989b). 2-nitrofluoranthene is the major NPAH produced from the gas phase reaction of fluoranthene with OH (Arey et al., 1986) and the only nitrofluoranthene formed from the reaction initiated by NO_3

(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). Values of the ratio 2-NF/2-NP close to 10 indicate major day-time OH reactions while ratio > 100 suggests dominant night-time NO_3 formation pathways.

For all sampling sites, the 2+3-NF/2-NP ratios were consistent with the day-time OH initiated PAH nitration as predominant pathway compared to the NO_3 reaction (Fig. 6). Higher 2+3-NF/2-NP ratios in summer compared to winter suggest an increase of the reaction pathways involving the OH radical.

The 2+3-NF/2-NP ratio at rural sites was higher than at sub-urban and traffic sites. There, the concentration of NO_3 could be affected by NO freshly emitted from vehicles, which could consume NO_3 necessary for PAH nitration in night time.

3.6. PAHs, OPAHs and NPAHs gas/particle partitioning

The fraction of PAHs, OPAHs and NPAHs associated with the particle phase was strongly dependent on the molecular weight (MW) and on the ambient conditions (Fig.7). The lightest compounds (MW<202 g mol^{-1}) were detected mainly in the gas phase (>50%) whereas more than 90% of the compounds with a number of aromatic cycles $\geq$4 were detected in the particle phase for all samples and seasons.

In most cases, gas/particle partitioning of PAHs was similar in both winter and summer seasons. The special behaviour observed at the traffic site C2 was probably related to the extreme proximity of PAH emission sources (<10 m from the major road of the valley). Much larger differences were found between summer and winter for the partitioning of OPAHs and NPAHs. Due to low ambient temperature, OPAHs and NPAHs were associated overall to the particulate phase in winter at that time of the year. During summer, a wide gas/particle partitioning was observed for OPAH and

NPAH of intermediate molecular weights (206<MW<223 g mol^{-1}). Out of these compounds, only the gas/particle partitioning for 9-phenanthrenecarboxaldehyde and 3-nitrophenanthrene were correlated to the ambient temperature (Fig. 8).

4. Conclusion

During both summer and winter campaigns conducted at Cv and Mv in 2002-2003 , OPAH concentration levels were of the same order of magnitude as PAHs while NPAH concentrations were one to two orders of magnitude lower. Due to lower pollutant dispersion on average in the Cv related the geomorphology of this valley, total particulate concentrations of pollutants were higher there than in the Mv. Despite their much lower atmospheric concentrations, carcinogenic risk attributed to the NPAHs could reach 20% of the total risk to which contributed significantly secondary compounds. By looking to the 2+3-NF/1-NP ratio, the gas phase formation of 2-nitrofluoranthene was hindered in winter overall at rural sites; concurrently the importance of 1-nitropyrene increased. The 2NF/2NP ratio rates indicated that at all sampling sites, the day-time OH initiated PAH nitration was more important than reaction with NO_3 in the night. Due to more favourable meteorological conditions (sunshine and heat), 2+3-NF/2-NP ratios were higher in the Mv than the Cv. The fraction of PAHs, OPAHs, and NPAHs associated with the particle phase was strongly dependent on their vapour pressure and on the ambient conditions.

analyses, Amandine Fievet and Maxime Rouez for PAH samplings, and all of the POVA team for their general support.

References

Albinet, A.,Leoz-Garziandia, E.,Budzinski, H. and ViIlenave, E., 2006. Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography-mass spectrometry with negative ion chemical ionisation. Journal of Chromatography A 1121, 106-113.

Albinet, A.,Leoz-Garziandia, E.,Budzinski, H. and Villenave, E., 2007a. Sampling precautions for the measurement of nitrated polycyclic aromatic hydrocarbons and their derivatives in ambient air. Atmospheric Environment 41, 4988-4994.

Albinet, A.,Leoz-Garziandia, E.,Budzinski, H. and Villenave, E., 2007b. Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources. Science of the Total Environment 384, 280-292.

Allen, J. O.,Dookeran, N. M.,Taghizadeh, K.,Lafleur, A. L.,Smith, K. A. and Sarofim, A. F., 1997. Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. Environmental Science & Technology 31, 2064-2070.

Arey, J.,Zielinska, B.,Atkinson, R.,Winer, A. M.,Ramdhal, T. and Pitts Jr, J. N., 1986. The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO_x. Atmospheric Environment 20, 2239-2345.

Arey, J.,Zielinska, B.,Atkinson, R. and Aschmann, S. M., 1989. Nitroarene products from the gas-phase reactions of volatile polycyclic aromatic hydrocarbons with the OH radical and N_2O_5. International Journal of Chemical Kinetics 21, 775-799.

Arey, J., 1998. Atmospheric reactions of PAHs including formation of nitroarenes. In The handbook of environmental chemistry, PAHs and related compounds, Springer-Verlag, Ed. Berlin, Vol. 3, 347-385.

Atkinson, R.,Arey, J.,Zielinska, B.,Pitts Jr, J. N. and Winer, A. M., 1987. Evidence for the transformation of polycyclic organic matter in the atmosphere. Atmospheric Environment 21, 2261-2264.

Atkinson, R.,Aschmann, S. M.,Arey, J. and Carter, P. L., 1989. Formation of ring-retaining products from the OH radical-initiated reactions of benzene and toluene. International Journal of Chemical Kinetics 21, 801-827.

Atkinson, R.,Arey, J.,Zielinska, B. and Aschmann, S. M., 1990. Kinetics and nitro-products of gas-phase OH and NO_3 radical-initiated reactions of naphthalene, fluoranthene and pyrene. International Journal of Chemical Kinetics 22, 999-1014.

Atkinson, R. and Arey, J., 1994. Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: formation of atmospheric mutagens. Environmental Health Perspectives 102, 117-126.

Aymoz, G.,Jaffrezo, J. L.,Cozic, J.,Chapuis, D. and Maenhaut, W., 2006. Seasonal variations of PM_{10} main constituents in two valleys of the French Alps. I: EC/OC fraction. Atmospheric Chemistry and Physics Discussion 6, 6211-6254.

Bamford, H. A. and Baker, J. E., 2003. Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region. Atmospheric Environment 37, 2077-2091.

Barbas, J. T.,Sigman, M. E. and Dabestani, R., 1996. Photochemical oxidation of phenanthrene sorbed on silica gel. Environmental Science and Technology 30, 1776-1780.

Bayona, J. M.,Casellas, M.,Fernandez, P.,Solanas, A. M. and Albaiges, J., 1994. Sources and seasonal variability of mutagenic agents in the Barcelona city aerosol. Chemosphere 29, 441-450.

Brulfert, G.,Chemel, C.,Chaxel, E. and Chollet, J.-P., 2005. Modelling photochemistry in alpine valleys. Atmospheric Chemistry and Physics.

Ciccioli, P.,Cecinato, A.,Brancaleoni, E.,Draisci, R. and Liberti, A., 1989. Evaluation of nitrated polycyclic aromatic hydrocarbons in anthropogenic emission and air samples. Aerosol Science and Technology 10, 296-310.

Ciccioli, P.,Cecinato, A.,Brancaleoni, E.,Frattoni, M.,Zacchei, P. and De Castro Vasconcellos, P., 1995. The ubiquitous occurence of nitro-PAH of photochemical origin in airborne particles. Annali Di Chimica 85, 455-469.

Ciccioli, P.,Cecinato, A.,Brancaleoni, E.,Massimiliano, F.,Zacchei, P.,Miguel, A. H. and Vasconcellos, P. C., 1996. Formation and transport of 2-nitrofluoranthene and 2-nitropyrene of photochemical origin in the troposphere. Journal of Geophysical Research 101, 19567-19581.

Dimashki, M.,Harrad, S. and Harrison, R. M., 2000. Measurements of nitro-PAH in the atmospheres of two cities. Atmospheric Environment 34, 2459-2469.

Doornaert, B. and Pichard, A., 2003. Hydrocarbures aromatiques polycycliques (HAPs). Evaluation de la relation dose-réponse pour des effets cancérigènes : approche substance par substance (facteurs d'équivalence toxique-FET) et approche par mélanges. Évaluation de la relation dose-réponse pour des effets non cancérigènes : Valeurs Toxicologiques de Référence (VTR). INERIS: available at http: http://www.ineris.fr/index.php?module=cms&action=getContent&id_heading_object=1008 (french language).

Durant, J. L.,Busby Jr, W. F.,Lafleur, A. L.,Penman, B. W. and Crespi, C. L., 1996. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. Mutation Research-Genetic Toxicology 371, 123-157.

Durant, J. L.,Lafleur, A. L.,Plummer, E. F.,Taghizadeh, K.,Busby, W. F. and Thilly, W. G., 1998. Human lymphoblast mutagens in urban airborne particles. Environmental Science & Technology 32, 1894-1906.

Environmental Health Criteria (EHC) 229, 2003. Selected nitro- and nitro-oxy-polycyclic aromatic hydrocarbons. WHO Library: http://whqlibdoc.who.int/ehc/WHO_EHC_229.pdf.

Fan, Z.,Kamens, R. M.,Hu, J.,Zhang, J. and McDow, S., 1996. Photostability of nitro-polycyclic aromatic hydrocarbons on combustion soot particles in sunlight. Environmental Science & Technology 30, 1358–1364.

Feilberg, A. and Nielsen, T., 2000. Effect of aerosol chemical composition on the photodegradation of nitro-polycyclic aromatic hydrocarbons. Environmental Science and Technology 34, 789-797.

Feilberg, A.,B. Poulsen, M. W.,Nielsen, T. and Henrik Skov, 2001. Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark. Atmospheric Environment 35, 353-366.

Feilberg, A. and Nielsen, T., 2001. Photodegradation of nitro-PAHs in viscous organic media used as models of organic aerosols. Environmental Science and Technology 35, 108-113.

Finlayson-Pitts, B. J. and Pitts Jr, J. N., 1986. Atmospheric Chemistry: Fundamental and experimental techniques. Wiley-Interscience: 1097 p.

Hannigan, M. P.,Cass, G. R.,Penman, B. W.,Crespi, C. L.,Lafleur, A. L.,Busby Jr, W. F.,Thilly, W. G. and Simoneit, B. R. T., 1998. Bioassay-Directed Chemical Analysis of Los Angeles Airborne Particulate Matter Using a Human Cell Mutagenicity Assay. Environmental Science & Technology 32, 3502-3514.

Hawthorne, S. B.,Miller, D. J.,Langenfeld, J. J. and Krieger, M. S., 1992. PM_{10} high-volume collection and quantification of semi- and nonvoltile phenols, methoxylated phenols, alkanes, and polycyclic aromatic hydrocarbons from winter urban air and their relationship to wood smoke emissions. Environmental Science and Technology 26, 2251-2262.

Helmig, D. and Harger, W. P., 1994. OH radical-initiated gas-phase reaction products of phenanthrene. The Science of the Total Environment 148, 11-21.

IARC, 1987. Overall evaluations of carcinogenicity an updating of IARC monographs. Lyon, Vol. 1-42 (suppl 7).

Kamens, R. M.,Zhi-Hua, F.,Yao, Y.,Chen, D.,Chen, S. and Vartiainen, M., 1994. A methodology for modeling the formation and decay of nitro-PAH in the atmosphere. Chemosphere 28, 1623–1632.

König, J.,Balfanz, E.,Funcke, W. and Romanowski, T., 1983. Determination of oxygenated polycyclic aromatic hydrocarbons in airborne particulate matter by capillary gas chromatography and gas chromatography / mass spectrometry. Analytical Chemistry 55, 599-603.

Leoz-Garziandia, E.,Tatry, V. and Carlier, P., 2000. Sampling and analysis of polycyclic aromatic hydrocarbons (PAH) and oxygenated PAH in diesel exhaust and ambient air. Polycyclic Aromatic Compounds 20, 245-258.

Lewtas, J.,Nishioka, M. and Peterson, B., 1990. Bioassay directed fractionation of the organic extract of SRM 1649 urban air particulate and ambient matter. International Journal of Environmental Analytical Chemistry 39, 245-256.

Ligocki, M. P. and Pankow, J. F., 1989. Measurement of gas/particle distributions of atmospheric organic compounds. Environmental Science and Technology 23, 75-83.

Marchand, N.,Besombes, J.-L.,Chevron, N.,Masclet, P.,Aymoz, G. and Jaffrezo, J. L., 2004. Polycyclic aromatic hydrocarbons (PAHs) in the atmospheres of two French alpine valleys: sources and temporal patterns. Atmospheric Chemistry and Physics 4, 1167-1181.

Marchand, N.,Aymoz, G.,Jaffrezo, J. L. and Besombes, J.-L., 2007. Biomass burning indicators in the aerosol of alpine valleys. Atmospheric Environment (submitted for publication).

Maria del Rosario Sienra, M., 2006. Oxygenated polycyclic aromatic hydrocarbons in urban air particulate matter. Atmospheric Environment 40, 2374-2384.

Marino, F.,Cecinato, A. and Siskos, P. A., 2000. Nitro-PAH in ambient particulate matter in the atmosphere of Athens. Chemosphere 40, 533-537.

Nielson, T., 1984. Reactivity of polycyclic aromatic hydrocarbons toward nitrating species. Environmental Science & Technology 18, 157-163.

OEHHA, 2002 and 2005. Air toxics hot spots program risk assessment guidelines. Part II: technical support document for describing available cancer potency factors. Office of Environmental Health Hazard Assessment: available at http://www.oehha.ca.gov/air/hot_spots/pdf/TSDNov2002.pdf (p109) and http://www.oehha.ca.gov/air/hot_spots/pdf/May2005Hotspots.pdf (p8 and A-1).

Paputa-Peck, M.,Marano, R. S.,Schuetzle, D.,Riley, T. L.,Hampton, C. V.,Prater, T. J.,Skewes, L. M.,Jensen, P. H.,Ruehle, L. C.,Bosch, L. C. and Duncan, W. P., 1983. Determination of nitrated polynuclear aromatic hydrocarbons in particulate extracts by capillary column gas chromatography with nitrogen selective detection. Analytical Chemistry 55, 1946-1954.

Pedersen, D. U.,Durant, J. L.,Penman, B. W.,Crespi, C. L.,Hemond, H. F.,Lafleur, A. L. and Cass, G. R., 2004. Human-cell mutagens in respirable airborne particles in the northeastern United States. 1. Mutagenicity of fractionated samples. Environmental Science & Technology 38, 682-689.

Pedersen, D. U.,Durant, J. L.,Taghizadeh, K.,Hemond, H. F.,Lafleur, A. L. and Cass, G. R., 2005. Human cell mutagens in respirable airborne particles from the Northeastern United States. 2.

Quantification of mutagens and other organic compounds. Environmental Science & Technology 39, 9547-9560.

Perraudin, E.,Budzinski, H. and Villenave, E., 2007. Identification and quantification of primary ozonation products of phenanthrene and anthracene adsorbed on silica particles. Atmospheric Environment in press.

Sasaki, J.,Aschmann, S. M.,Kwok, E. S. C.,Atkinson, R. and Arey, J., 1997. Products of the Gas-Phase OH and NO_3 Radical-Initiated Reactions of Naphthalene. Environmental Science & Technology 31, 3173-3179.

Schuetzle, D., 1983. Sampling of vehicle emissions for chemical analysis and biological testing. Environmental Health Perspectives 47, 65-80.

Wilson, N. K.,McCurdy, T. R. and Chuang, J. C., 1995. Concentrations and phase distributions of nitrated and oxygenated polycyclic aromatic hydrocarbons in ambient air. Atmospheric Environment 29, 2575-2584.

Yassaa, N.,Meklati, B. Y.,Cecinato, A. and Marino, F., 2001. Organic aerosols in urban and waste landfill of Algiers metropolitan area: Occurrence and sources. Environmental Science & Technology 35, 306-311.

Zielinska, B.,Arey, J.,Atkinson, R.,Ramdahl, T.,Winer, A. M. and Pitts Jr, J. N., 1986. Reaction of dinitrogen pentoxide with fluoranthene. Journal of American Chemical Society 108, 4126-4132.

Zielinska, B.,Arey, J.,Atkinson, R. and Wiener, A. M., 1989a. The nitroarenes of molecular weight 247 in ambient particulate samples collected in southern California. Atmospheric Environment 23, 223-229.

Zielinska, B.,Arey, J.,Atkinson, R. and McElroy, P. A., 1989b. Formation of methylnitronaphthalenes from the gas-phase reactions of 1- and 2-methylnaphthalene with OH

radicals and N_2O_5 and their occurrence in ambient air. Environmental Science & Technology 23, 723-729.

Table 1

Characteristics of the sampling sites and parameters measured

Site	Abbreviation	Type	Latitude	Longitude	Altitude (m.a.s.l.)	PAH samplers	
						DA-80	Impactor
Chamonix Valley							
Clos de l'Ours	C1	Suburban	45.9143	6.86019	1034		X
Les Bossons	C2	Traffic	45.9067	6.84505	1042	X	X
Plan de l'Aiguille	C3	Altitude	45.9013	6.88650	2263	X	
Argentière	C4	Rural	45.9865	6.92957	1250	X	
Maurienne Valley							
Tigny	M1	Rural	45.4303	6.28550	441	X	X
Orelle	M2	Suburban	45.2101	6.56670	1134	X*	
Modane	M3	Suburban	45.2036	6.66720	1094		X
Sollières	M4	Rural	45.2564	6.80870	1373	X	

* Only in summer 2003.

Site	CO	NO$_x$	O$_3$	VOCs	PM$_{10}$	EC/OC	POM	T	P	WS, WD
Chamonix Valley										
C1		X	X	X	X	X	X	X	X	X
C2		X	X		X			X		
C3		X	X	X	X	X	X	X		
C4	X	X	X					X	X	X
Maurienne Valley										
M1	X	X	X					X	X	X
M2		X	X	X	X	X	X	X	X	X
M3	X	X	X	X	X	X	X			
M4		X	X	X	X	X		X		

VOCs: volatile organic compounds; EC: elemental carbon; OC: organic carbon; POM: partial speciation of the particulate organic matter; T and P: atmospheric temperature and pressure; WS: wind speed; WD: wind direction.

Supplementary Table 1

Average results for total (filter + PUF) OPAH (ng m^{-3}), NPAH (pg m^{-3}), benzo[a]pyrene (ng m^{-3}) concentrations and associated particulate fraction, T (°C), CO, NO, NO$_2$, PM$_{10}$ and O$_3$ concentrations (µg m^{-3}) for the winter and summer campaigns in both valleys

	C1[a] (n=7)		**C2** (n=14)			**C3[a]** (n=7)		**C4** (n=9)			**M1** (n=14)			**M3[a]** (n=7)		**M4** (n=13)		
	Mean	(SD)	Mean	(SD)	% Filter	Mean	(SD)	Mean	(SD)	% Filter	Mean	(SD)	% Filter	Mean	(SD)	Mean	(SD)	% Filter
T (°C)	-3	(2)	-3	(2)	-	-3	(2)	-0	(2)	-	1	(3)	-	-	-	-4	(4)	-
NO (µg m^{-3})	47	(25)	72	(38)	-	4	(3)	1	(1)	-	11	(9)	-	3	(3)	2	(1)	-
NO$_2$ (µg m^{-3})	56	(8)	52	(10)	-	7	(3)	9	(5)	-	32	(11)	-	34	(11)	10	(6)	-
PM$_{10}$ (µg m^{-3})	22	(4)	24	(11)	-	4	(1)	-	-	-	-	-	-	8	(4)	9	(5)	-
CO (µg m^{-3})	-	-	-	-	-	-	-	437	(761)	-	396	(169)	-	868	(115)	-	-	-
O$_3$ (µg m^{-3})	10	(8)	19	(11)	-	79	(3)	61	(11)	-	25	(16)	-	69	(29)	51	(20)	-
Benzo[a]pyrene (ng m^{-3})	1.88	0.76	2.81	(1.28)	100	0.01	0.01	0.16	(0.14)	100	0.85	(0.41)	100	0.68	(0.71)	0.76	(1.10)	100
OPAHs (ng m^{-3})																		
1-Naphthaldehyde	0.18	(0.16)	7.82	(7.36)	9	0.16	(0.78)	2.38	(1.19)	9	3.08	(3.74)	1	0.59	(0.37)	1.68	(1.63)	12
9-Fluorenone	0.67	(0.37)	11.23	(4.33)	43	0.19	(0.13)	1.54	(1.48)	47	4.10	(1.97)	12	2.79	(1.58)	2.53	(2.15)	53
9-Phenanthrenecarboxaldehyde	0.31	(0.12)	0.43	(0.16)	100	0.01	(0.01)	0.04	(0.02)	100	0.18	(0.14)	86	0.28	(0.18)	0.16	(0.14)	100
9,10-Anthraquinone	1.42	(0.49)	3.60	(1.09)	99	0.15	(0.08)	0.57	(0.37)	100	1.77	(1.49)	93	2.76	(1.71)	2.36	(2.74)	99
Benzo[a]fluorenone	0.84	(0.19)	1.59	(0.67)	100	0.17	(0.15)	0.43	(0.43)	100	0.45	(0.26)	99	0.79	(0.90)	0.63	(1.03)	100
Benzo[b]fluorenone	0.86	(0.23)	1.49	(0.64)	100	0.18	(0.22)	0.36	(0.33)	100	0.44	(0.23)	100	0.65	(0.78)	0.60	(1.00)	100
Benzanthrone	1.71	(0.59)	2.05	(0.95)	100	0.15	(0.29)	0.26	(0.17)	100	0.69	(0.33)	100	0.87	(0.91)	0.48	(0.82)	100
Benz[a]anthracene-7,12-dione	0.27	(0.06)	0.55	(0.18)	100	0.13	(0.19)	0.22	(0.25)	100	0.29	(0.13)	100	0.29	(0.31)	0.45	(0.83)	100
NPAHs (pg m^{-3})																		
1-Nitronaphthalene	13.1	(6.4)	185.7[b]	(135.0)	14	0.4[b]	(0.7)	51.0[b]	(33.4)	6	40.7[b]	(36.6)	6	5.3	(3.9)	25.5[b]	(22.0)	19
2-Nitronaphthalene	8.9	(3.9)	66.2[b]	(46.7)	15	0.1[b]	(0.1)	23.8[b]	(13.6)	4	28.5[b]	(24.9)	3	3.9	(2.6)	14.8[b]	(12.2)	12
2-Nitrofluorene	1.2	(1.1)	1.1[b]	(0.4)	100	nd	-	0.1[b]	(0.2)	50	0.1[b]	(0.2)	100	0.6	(0.7)	0.2[b]	(0.6)	100
9-Nitroanthracene	502.6	(147.9)	85.3[b]	(60.0)	100	1.7[b]	(3.1)	10.3[b]	(8.5)	97	145.1[b]	(102.2)	88	327.6	(221.5)	114.7[b]	(184.5)	98
9-Nitrophenanthrene	20.9	(12.9)	4.3[b]	(1.7)	94	0.1[b]	(0.1)	0.7[b]	(0.9)	91	1.6[b]	(1.4)	72	4.9	(3.7)	0.5[b]	(0.2)	96
3-Nitrophenanthrene	40.8	(8.6)	9.3[b]	(2.2)	100	0.1[b]	(0.1)	1.1[b]	(1.0)	100	5.5[b]	(1.8)	92	14.0	(9.8)	3.4[b]	(4.3)	100
2+3-Nitrofluoranthene	260.8	(161.2)	167.5[b]	(168.8)	98	1.3[b]	(1.4)	18.7[b]	(17.0)	98	101.8[b]	(59.8)	100	277.2	(322.6)	80.8[b]	(146.8)	100
4-Nitropyrene	48.0	(14.3)	20.8[b]	(24.8)	98	2.1[b]	(2.1)	4.5[b]	(1.7)	86	4.6[b]	(2.1)	100	20.5	(14.4)	6.5[b]	(7.1)	99
1-Nitropyrene	186.9	(58.5)	53.7[b]	(25.7)	100	2.4[b]	(2.6)	9.9[b]	(6.1)	97	24.8[b]	(21.9)	100	70.0	(53.6)	10.8[b]	(7.6)	100
2-Nitropyrene	659.6	(167.1)	186.2[b]	(67.7)	99	14.8[b]	(38.2)	70.4[b]	(46.4)	91	72.3[b]	(32.9)	99	257.3	(357.3)	70.4[b]	(110.7)	100
7-Nitrobenz[a]anthracene	90.1	(47.2)	12.6[b]	(13.9)	100	0.2[b]	(0.5)	1.5[b]	(1.8)	98	22.0[b]	(22.7)	100	49.5	(48.0)	16.5[b]	(43.7)	100
6-Nitrochrysene	2.8	(1.2)	0.5[b]	(0.2)	100	0.0[b]	(0.1)	0.2	(0.1)	83	0.5[b]	(0.4)	100	1.4	(2.7)	0.6[b]	(0.6)	100
1,3-Dinitropyrene	30.4	(9.0)	17.4[b]	(12.4)	100	nd	-	1.7[b]	(2.3)	100	4.2[b]	(2.3)	100	20.3	(27.1)	4.0[b]	(8.1)	100
1,6-Dinitropyrene	0.2	(0.3)	nd	-	-	nd	-	1.2[b]	(1.9)	100	6.5[b]	(4.2)	100	0.1	(0.1)	1.8[b]	(1.7)	100
1,8-Dinitropyrene	85.7	(29.5)	30.6[b]	(18.2)	100	nd	-	4.6[b]	(3.7)	100	12.0[b]	(5.0)	100	30.7	(34.6)	10.1[b]	(16.5)	100
6-Nitrobenzo[a]pyrene	13.0	(3.9)	4.3[b]	(2.8)	100	0.1[b]	(0.1)	0.2[b]	(0.3)	100	6.5[b]	(4.2)	100	5.4	(7.1)	9.2[b]	(26.6)	100

Winter 2002-2003

Supplementary Table 1 (continued)

	Summer 2003																					
	C1[a] (n=7)		C2 (n=14)			C3 (n=7)			C4 (n=14)			M1 (n=14)			M2 (n=11)			M3[a] (n=7)		M4 (n=14)		
	Mean	(SD)	Mean	(SD)	% Filter	Mean	(SD)	% Filter	Mean	(SD)	% Filter	Mean	(SD)	% Filter	Mean	(SD)	% Filter	Mean	(SD)	Mean	(SD)	% Filter
T (°C)	16	(3)	17	(6)	-	12	(4)	-	15	(6)	-	25	(6)	-	21	(5)	-	21	(4)	18	(6)	-
NO (µg m⁻³)	5	(1)	42	(23)	-	0	(0)	-	1	(0)	-	1	(1)	-	1	(1)	-	4	(4)	0	(0)	-
NO$_2$(µg m⁻³)	16	(6)	33	(10)	-	1	(1)	-	6	(2)	-	8	(5)	-	10	(7)	-	13	(6)	5	(2)	-
PM$_{10}$ (µg m⁻³)	16	(7)	27	(13)	-	14	(6)	-	-	-	-	-	-	-	27	(14)	-	29	(15)	30	(18)	-
CO (µg m⁻³)	-	-	-	-	-	-	-	-	181	(27)	-	188	(85)	-	-	-	-	324	(71)	-	-	-
O$_3$ (µg m⁻³)	62	(18)	62	(21)	-	113	(20)	-	84	(31)	-	120	(36)	-	97	(23)	-	93	(24)	99	(25)	-
Benzo[a]pyrene (ng m⁻³)	0.04	(0.03)	0.12	(0.13)	100	0.01	(0.00)	100	0.04	(0.03)	69	0.03	(0.05)	100	0.05	(0.07)	100	0.03	(0.02)	0.05	(0.05)	78
OPAHs (ng m⁻³)																						
1-Naphthaldehyde	0.30	(0.02)	1.11	(0.74)	8	nd	-	-	3.53	(10.36)	1	0.33	(0.41)	0	0.34	(0.24)	30	0.07	(0.05)	0.30	(0.32)	29
9-Fluorenone	0.62	(0.02)	1.77	(0.55)	8	0.16	(0.11)	2	0.41	(0.36)	13	0.61	(0.69)	9	0.96	(0.51)	7	0.11	(0.07)	0.47	(0.45)	10
9-Phenanthrenecarboxaldehyde	0.07	(0.00)	0.06	(0.04)	65	0.00	(0.00)	92	0.01	(0.01)	69	0.02	(0.01)	68	0.02	(0.01)	35	0.00	(0.00)	0.01	(0.00)	61
9,10-Anthraquinone	1.59	(0.04)	0.97	(0.52)	68	0.05	(0.02)	99	0.26	(0.17)	85	0.47	(0.36)	58	0.37	(0.22)	63	0.34	(0.13)	0.13	(0.09)	75
Benzo[a]fluorenone	0.33	(0.02)	0.23	(0.28)	98	0.00	(0.00)	95	0.03	(0.02)	93	0.08	(0.14)	83	0.05	(0.03)	86	0.02	(0.02)	0.03	(0.01)	82
Benzo[b]fluorenone	0.19	(0.02)	0.26	(0.40)	99	0.01	(0.00)	99	0.02	(0.02)	96	0.09	(0.18)	99	0.04	(0.03)	97	0.02	(0.02)	0.03	(0.02)	94
Benzanthrone	0.02	(0.00)	0.29	(0.48)	99	0.00	(0.00)	100	0.02	(0.02)	97	0.06	(0.09)	99	0.04	(0.03)	95	0.00	(0.00)	0.05	(0.03)	99
Benz[a]anthracene-7,12-dione	0.22	(0.03)	0.15	(0.27)	98	0.00	(0.00)	100	0.02	(0.02)	98	0.13	(0.30)	98	0.04	(0.03)	90	0.02	(0.02)	0.02	(0.01)	96
NPAHs (pg m⁻³)																						
1-Nitronaphthalene	0.3	(0.3)	55.5	(31.0)	5	0.1	(0.1)	10	15.0	(38.2)	6	25.6	(29.7)	13	27.4	(36.0)	4	1.7	(1.3)	12.5	(18.9)	2
2-Nitronaphthalene	0.2	(0.1)	21.2	(10.2)	1	0.4	(0.3)	0	6.8	(15.1)	1	14.3	(13.3)	1	16.4	(16.3)	1	0.4	(0.2)	6.8	(9.4)	1
2-Nitrofluorene	0.2	(0.4)	4.3	(3.5)	27	0.5	(1.1)	100	0.2	(0.6)	34	4.1	(7.2)	81	4.8	(4.4)	22	0.8	(2.0)	0.7	(0.5)	100
9-Nitroanthracene	7.6	(2.3)	22.4	(10.0)	69	0.4	(0.1)	98	4.0	(5.1)	53	22.2	(18.4)	44	11.3	(9.1)	69	11.5	(7.0)	2.8	(2.7)	75
9-Nitrophenanthrene	0.2	(0.1)	0.3	(0.2)	62	0.0	(0.0)	100	0.2	(0.4)	31	0.1	(0.1)	25	0.0	(0.1)	87	0.5	(0.3)	0.0	(0.0)	100
3-Nitrophenanthrene	1.2	(0.4)	2.8	(1.5)	69	0.1	(0.1)	55	0.9	(1.0)	98	4.1	(4.7)	28	2.9	(2.4)	32	2.2	(1.4)	0.6	(0.3)	57
2+3-Nitrofluoranthene	10.1	(9.7)	29.7	(24.8)	68	1.8	(1.3)	100	7.1	(11.1)	55	63.1	(45.4)	99	22.8	(20.4)	86	16.6	(10.4)	3.1	(2.2)	100
4-Nitropyrene	0.3	(0.2)	2.8	(4.3)	100	0.0	(0.0)	100	0.1	(0.1)	100	0.2	(0.6)	100	0.1	(0.1)	91	0.4	(0.4)	0.1	(0.1)	100
1-Nitropyrene	2.8	(0.9)	7.7	(4.8)	92	0.6	(0.5)	100	0.7	(0.4)	92	4.7	(5.1)	99	6.5	(7.2)	79	6.5	(5.8)	0.8	(0.7)	100
2-Nitropyrene	5.2	(5.8)	27.7	(35.8)	100	0.7	(0.5)	100	4.0	(3.4)	100	8.8	(15.0)	92	1.8	(2.2)	94	15.1	(10.0)	0.9	(1.1)	100
7-Nitrobenz[a]anthracene	0.5	(0.4)	2.1	(4.3)	100	nd	-	-	0.1	(0.3)	100	0.3	(0.5)	100	0.7	(1.1)	100	0.6	(0.8)	0.1	(0.3)	100
6-Nitrochrysene	0.0	(0.0)	1.2	(1.5)	61	0.3	(0.7)	100	nd	-	-	1.0	(2.0)	83	2.4	(1.8)	60	1.5	(3.8)	0.2	(0.3)	100
1,3-Dinitropyrene	0.2	(0.3)	2.1	(5.0)	100	nd	-	-	nd	-	-	0.6	(2.2)	100	nd	-	-	0.6	(0.7)	nd	-	-
1,6-Dinitropyrene	0.0	(0.0)	0.0	(0.0)	100	nd	-	-	nd	-	-	nd	-	-	nd	-	-	nd	-	nd	-	-
1,8-Dinitropyrene	0.4	(0.7)	10.1	(23.6)	100	nd	-	-	0.4	(0.7)	100	0.4	(1.6)	100	0.2	(0.5)	100	1.1	(0.9)	0.3	(0.6)	100
6-Nitrobenzo[a]pyrene	0.1	(0.1)	0.9	(1.2)	100	0.2	(0.1)	100	0.1	(0.2)	100	0.3	(0.7)	100	1.0	(1.6)	100	1.4	(1.9)	0.9	(1.2)	100

[a] Concentrations determined with cascade impactor (only particulate phase).

[b] NPAH concentrations determined in winter with DA-80 sampler could be 3 to 4 times higher (see Albinet et al., 2007a for more details)

nd: not detected

Table 3

PAH and NPAH toxic equivalent factors (TEFs)

Compounds	TEFs
PAHs[1]	
Benz[a]anthracene	0.1
Chrysene	0.01
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Benzo[a]pyrene	1
Dibenz[a,h]anthracene	1
Benzo[g,h,i]perylene	0.01
Indeno[1,2,3,c,d]pyrene	0.1
Coronene	0.001
NPAHs[2]	
1-Nitropyrene	0.1
4-Nitropyrene	0.1
6-Nitrochrysene	10
1,6-Dinitropyrene	10
1,8-Dinitropyrene	0.1

[1] data from Doornaert and Pichard (2003).

[2] data from OEHHA (2002 and 2005).

Figure Captions

Fig. 1. Map of the Alpine area of the POVA research program and location of the sampling sites in the Chamonix and the Maurienne valleys.

Fig. 2. Average Σ PAHp, Σ OPAHp and Σ NPAHp during winter 2002-2003 and summer 2003 field campaigns according to the sampling site (see the Results and discussion section for details). The errors bars show the standard deviation from the weekly average concentration.

¤ Concentrations determined with cascade impactor.

* NPAH concentrations determined in winter with DA-80 sampler could be 3 to 4 times higher (see Albinet et al., 2007a for more details).

Fig. 3. Total carcinogenic risk calculated from atmospheric concentrations of 9 PAHs and 5 NPAHs mainly associated to the particulate phase.

* NPAH concentrations determined by DA-80 sampler in winter have been corrected by a factor of 3.6 (Albinet et al., 2007a).

Fig. 4. 2+3-Nitrofluoranthene/1-Nitropyrene ratios (2+3-NF/1-NP) for air samples collected in the Chamonix and Maurienne valleys during winter 2002-2003 and summer 2003 sampling campaigns (Imp: cascade impactor sampler). Gray triangles and rounds represent the average ratios over the full weeks.
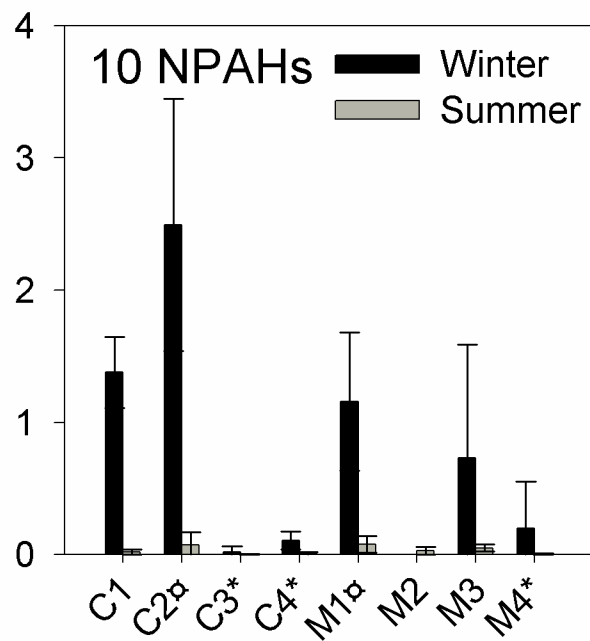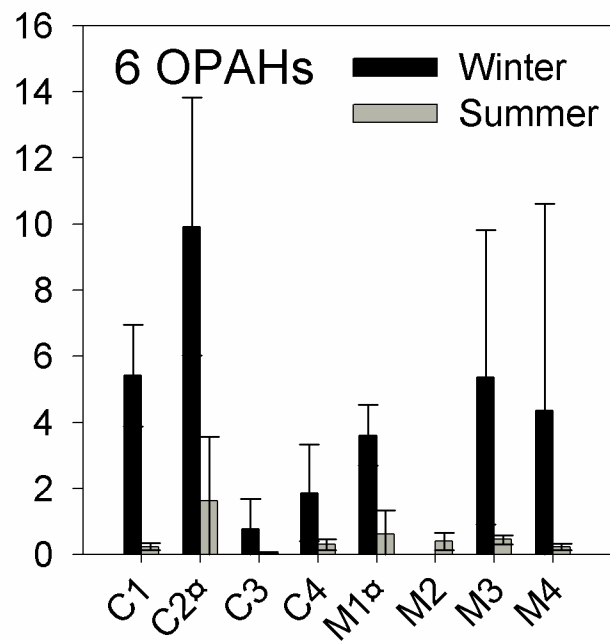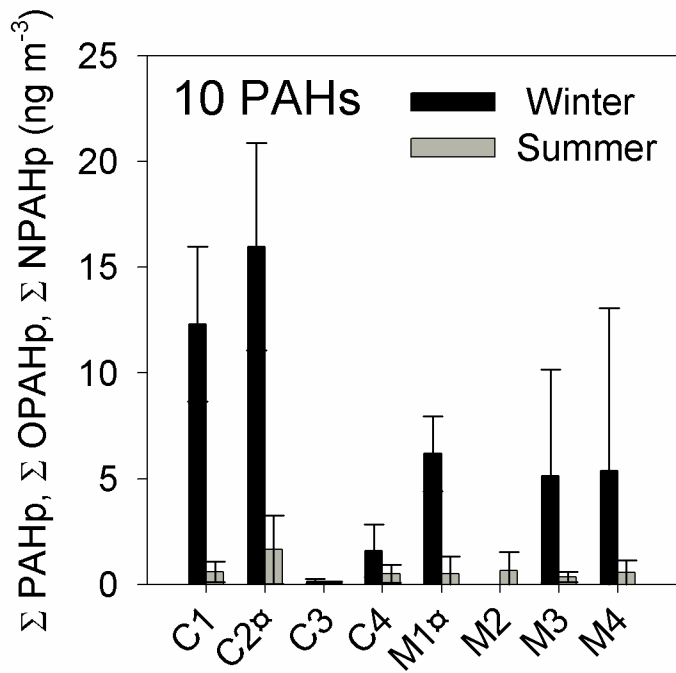
Fig. 5. Weekly variations of the 2+3-Nitrofluoranthene/1-Nitropyrene ratio (2+3-NF/1-NP), Σ PAHp, Σ OPAHp, Σ NPAHp and NO_2 concentrations at the rural site of Sollières (M4) during the winter 2002-2003 sampling campaign (see the Results and discussion section for details).
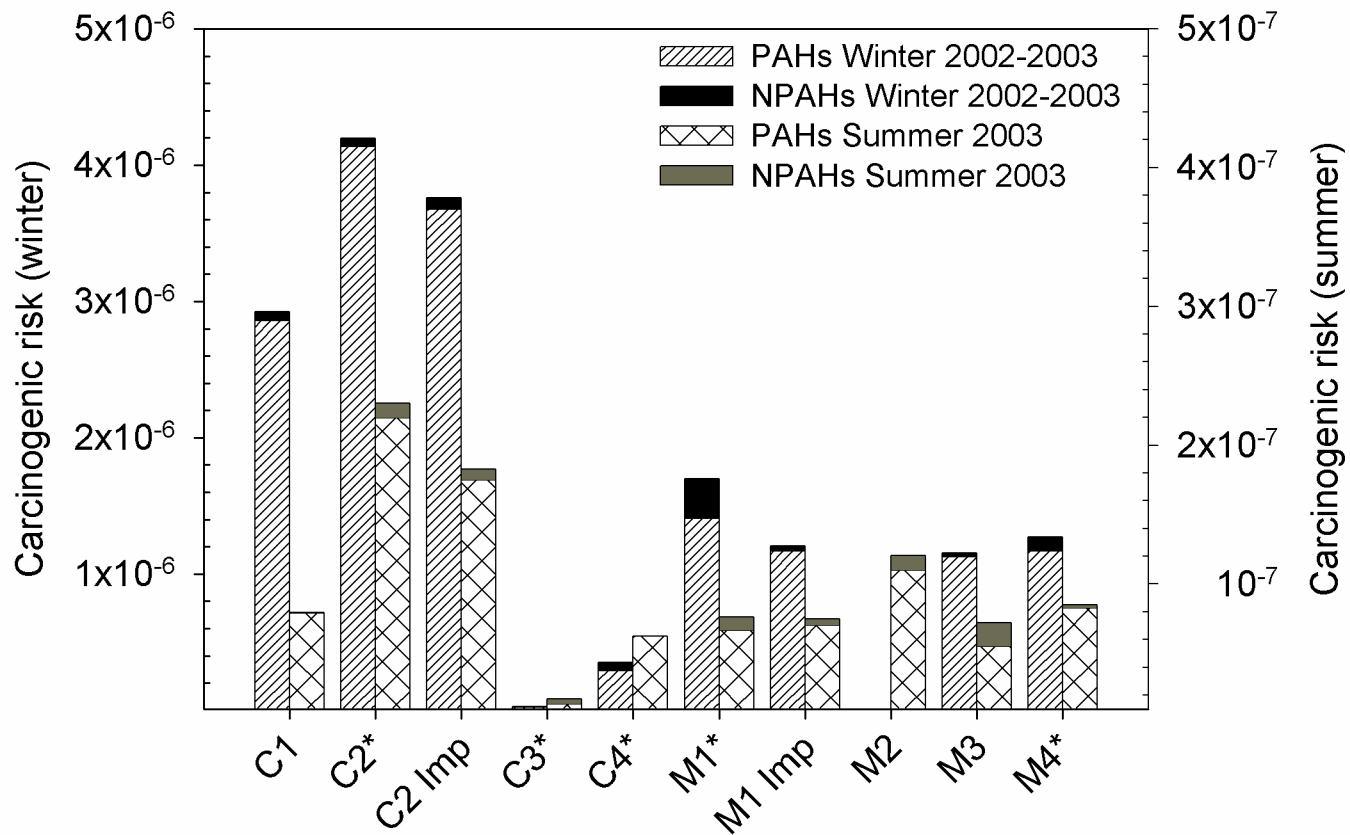
Fig. 6. 2+3-Nitrofluoranthene/2-Nitropyrene ratios (2+3-NF/2-NP) for air samples collected in the Chamonix and Maurienne valleys during winter 2002-2003 and summer 2003 sampling campaigns (Imp: cascade impactor sampler).
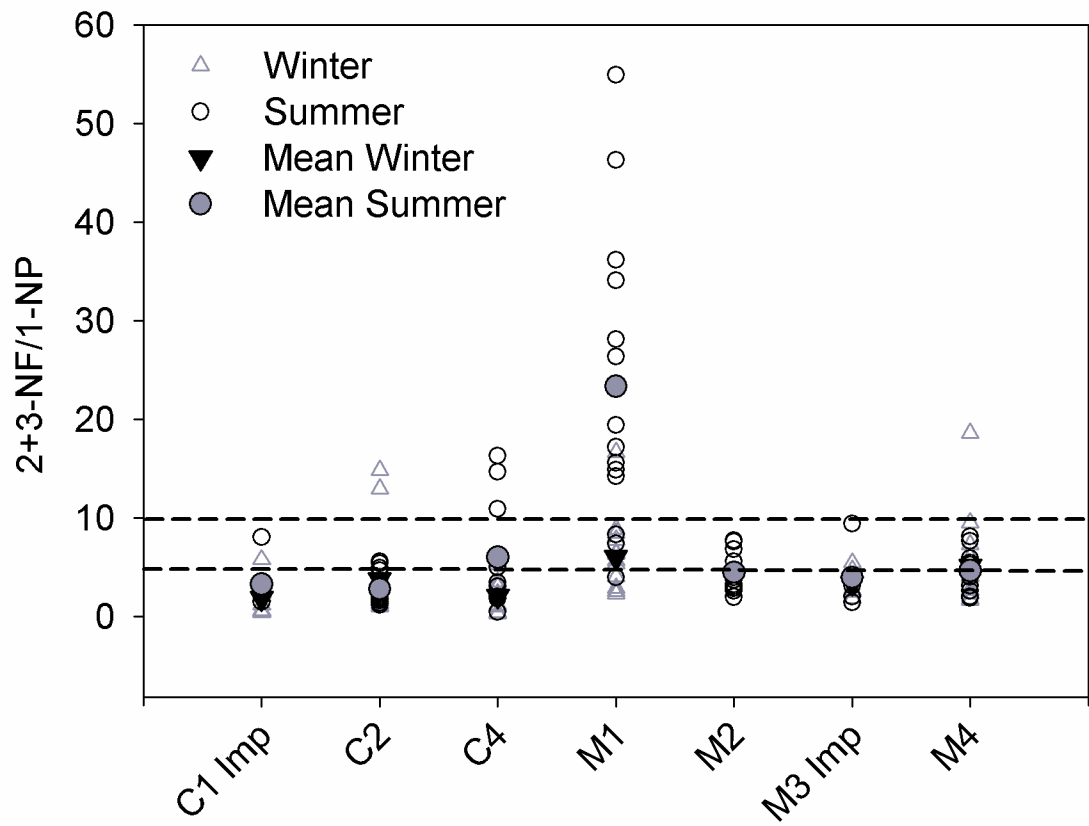
Fig. 7. PAH, OPAH and NPAH particulate fractions according to their molecular weight for the winter 2002-2003 and summer 2003 sampling campaign (all sampling sites taking into account).
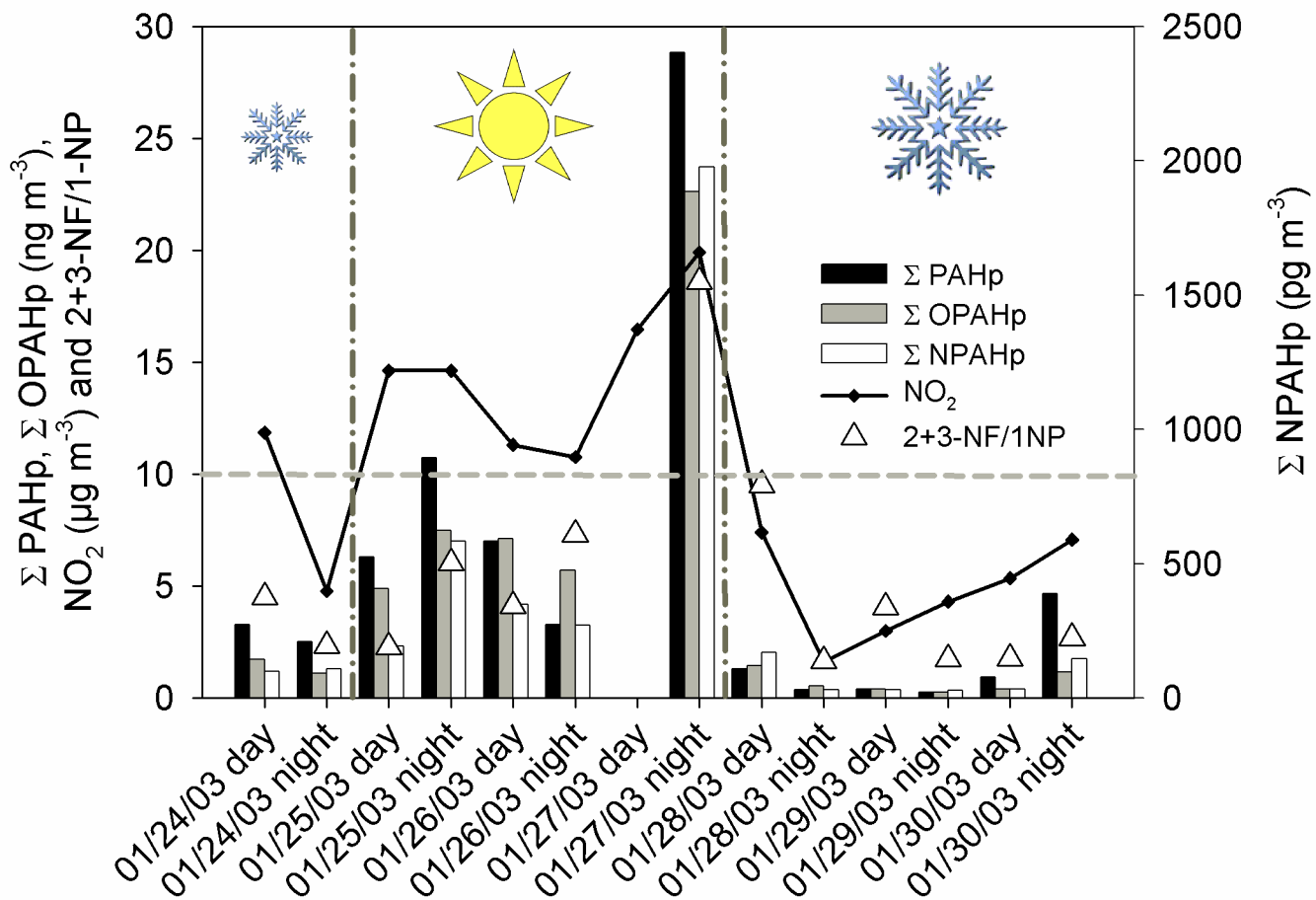
Fig. 8. Fraction of 9-phenanthrenecarboxalehyde and 3-nitrophenanthrene in particulate phase according to the ambient temperature during the summer period (results from all sampling sites taken into account).
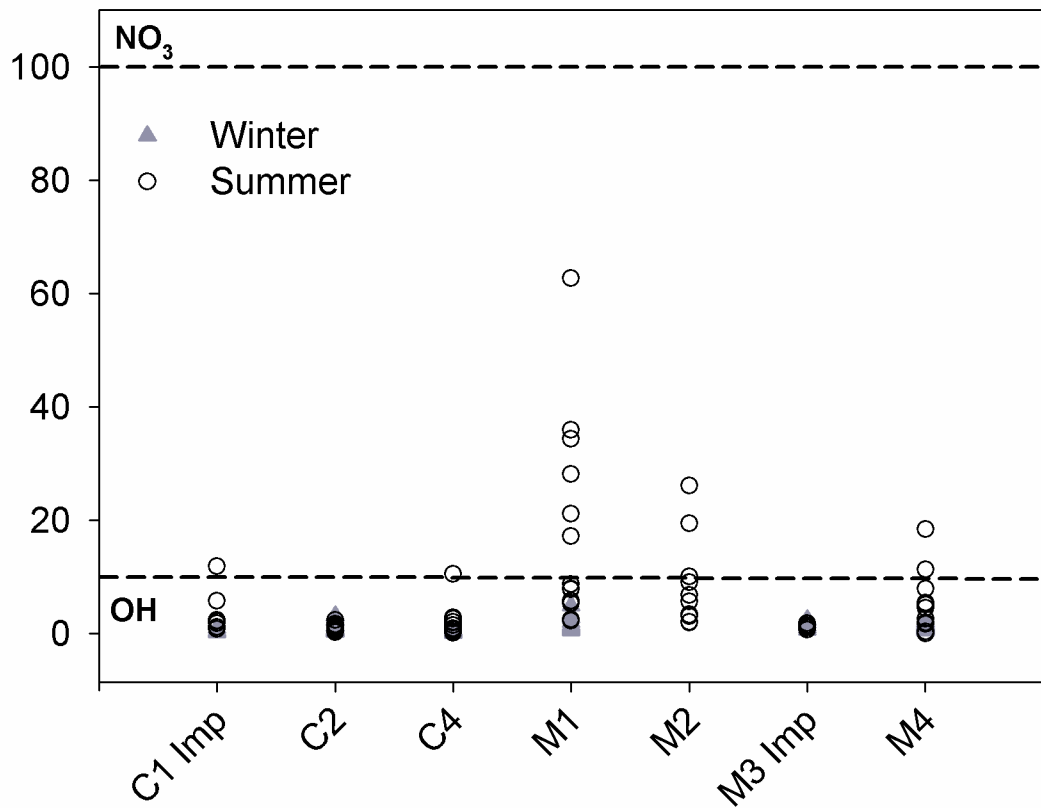
9-Phenanthrenecarboxaldehyde (MW=206)

$y = -0.02x + 1.23$
$R^2 = 0.43$

3-Nitrophenanthrene (MW=223)

$y = -0.03x + 1.45$
$R^2 = 0.50$
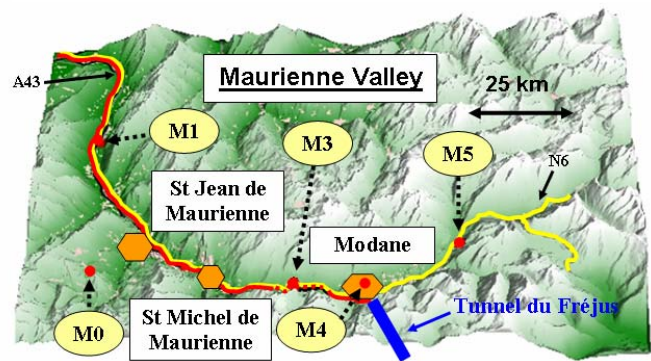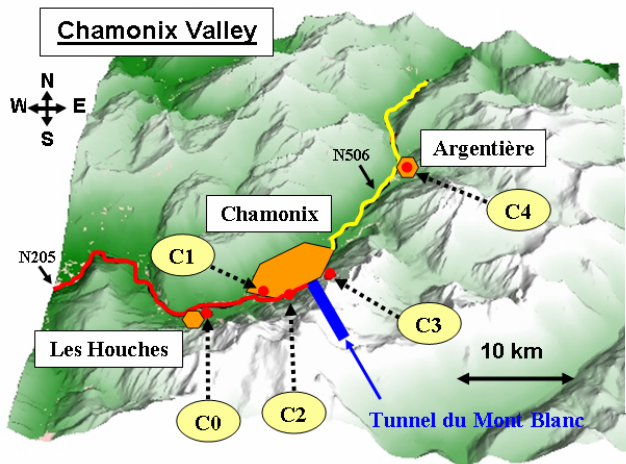
Fraction in particulate phase

External temperature (°C)