

**Polycyclic aromatic  
hydrocarbons in the  
atmosphere of two  
French alpine valleys**

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# Polycyclic aromatic hydrocarbons in the atmosphere of two French alpine valleys: Temporal trends and examination of sources

**N. Marchand<sup>1,\*</sup>, J. L. Besombes<sup>1</sup>, N. Chevron<sup>1</sup>, P. Masclet<sup>1</sup>, G. Aymoz<sup>2</sup>, and J. L. Jaffrezo<sup>2</sup>**

<sup>1</sup>LCME, ESIGEC, Université de Savoie, 73376 le Bourget du Lac, France

<sup>2</sup>LGGE, CNRS, Université Joseph Fourier, 24 rue Molière, 38402 St. Martin d'Hères, France

\*Now at: LaMP, CNRS, Université Blaise Pascal, 14 avenue des Landais, 63177 Aubière, France

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Correspondence to: N. Marchand (n.marchand@opgc.univ-bpclermont.fr)

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## Abstract

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. As part of the program “Pollution des Vallées Alpines” (POVA), we performed two sampling surveys of PAHs in two sensitive valleys: the Chamonix and the Maurienne Valleys, between France and Italy. Sampling campaigns were performed during summer 2000 and winter 2001, both periods taking place during the closure of the “Tunnel du Mont-Blanc”. The objectives of this paper are first to describe the relations between PAH concentrations, external parameters (sampling site localization, meteorological parameters, sources), and the aerosol characteristics, including its carbonaceous fraction (OC and EC). The second objective is to study the capacity of the PAH profiles to accurately discriminate the different emissions sources. Temporal evolution of relative concentration of individual PAH (CHR), and PAH groups (BghiP+COR and BbF+BkF) are studied in order to discriminate wood combustion, gasoline, and diesel emissions, respectively. The results show that during both seasons the total particulate PAH concentrations were higher in the valley of Chamonix, despite the stopping of the international traffic through the Chamonix valley. Seasonal cycles, with higher concentrations in winter are also stronger in this valley. During winter, particulate PAH concentration can reach very high levels ( $155 \text{ ng.m}^{-3}$ ) in this valley during cold anticyclonic periods. Sources examination shows the impact of heavy duty traffic in the Maurienne valley and of gasoline vehicles in the Chamonix Valley during summer. During winter, Chamonix is characterized by the strong influences wood combustion in residential fireplaces, even if temporal evolution of specific PAH ratios are uneasy to interpret. Information on sources given by PAH profiles can only be considered as qualitative.

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## 1. Introduction

Alpine valleys are unique transportation pathways in Europe, and a small number of corridors support a large traffic of heavy duty trucks. This traffic, added to local emissions, can induce high levels of pollutants in these deep valleys subjected to specific atmospheric dynamic in mountainous area (Prévôt et al., 2000). The results presented here were obtained during the program “Pollution des Vallées Alpines” (POVA). This program focuses on atmospheric chemistry in the two transit corridors between France and Italy: the Chamonix and Maurienne Valleys (Fig. 1). This study benefits from an exceptional context, with the “Tunnel du Mont Blanc” in the Chamonix valley being closed for nearly 3 years after a large accident in March 1999. Consequently, most heavy duty traffic in the area was taking place through the “Tunnel du Fréjus”, in the Maurienne valley. This traffic was as large as that expected in 2010 (in 2001, 7428 vehicles per day including 4244 trucks, on average). The general objectives of the POVA program are the comparative studies of atmospheric pollution and the modeling of atmospheric emissions and transport in these two French alpine valleys before and after the reopening of the “Tunnel du Mont Blanc” to heavy duty traffic. The program includes several field campaigns, associated with 3D modeling. In this context, our specific objectives are to obtain a better knowledge of the particulate pollution in the alpine valley and to estimate the respective influences of the main aerosol sources.

Investigations on the carbonaceous fraction of aerosol can bring information on their nature and sources. This fraction is composed of many compounds which constitute the organic carbon (OC) and elemental carbon (EC) (Penner and Novakov, 1996). Within the organic carbon, the Polycyclic Aromatic Hydrocarbons (PAH) are well representative of atmospheric pollution. Due to their low natural emission (Dachs et al., 1996; Nikolaou et al., 1984), PAH are good tracers for anthropogenic inputs in atmosphere. They are mainly formed during incomplete combustions or pyrolysis of organic materials. Thus, they result from combustions of oil derivatives, coals, natural gas, biomass and household wastes (Besombes et al., 2001). In addition, because of their

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potential carcinogenic effects (IARC 1983, 1987), PAH are now regarded as priority pollutants by both the United States Environmental Protection Agency and the European Community.

In urban and suburban environment, the PAH main sources are vehicular emissions and domestic heating (Simoneit, 2002; Nikolaou et al., 1984; Rogge et al., 1996; Li and Kamens, 1993), the contribution of the later increasing significantly during winter (Schauer and Cass, 2000; Carrichia et al., 1999; Pistikopoulos et al., 1990a; Nielsen, 1996). Studies on the PAH chemical signatures are performed for more than 30 years. Owing to large changes in emissions ratios and chemical profiles between each of these sources, PAH have tentatively been used for their discrimination and apportionment capability in air quality studies (Khalili et al., 1995; Li and Kamens, 1993; Pistikopoulos et al., 1990a; Nielsen, 1996; Aceves and Grimalt, 1993; Harrison et al., 1996). However, very great variability is observed in the emission ratios of PAH. Therefore, it is generally difficult to quantify the impact of several sources based on PAH only. Our study takes place in a simpler context, with fewer source types than in urban environment. It is therefore interesting to evaluate our ability to resolve these sources with PAH profiles in the valleys.

As part as the POVA program, two intensive field campaigns were performed in summer 2000 and winter 2001. After a section summarizing current knowledge on PAH emissions by anthropogenic sources, we are discussing our results in terms of comparisons of the concentrations and of the PAH profiles between seasons and valleys. The objectives of our study are first to describe the relations between PAH concentrations, external parameters (sampling site localization, meteorological parameters, sources) and the aerosol characteristics, including its carbonaceous fraction (OC and EC). The second objective is to study the capacity of the PAH profiles to accurately discriminate sources.

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## 2. Experimental section

### 2.1. Sampling campaigns and sampling sites

Fig. 1 presents the morphology of the two valleys investigated. The Chamonix valley, about 17 km in length, is surrounded by mountains reaching between 3000 and 4800 m above sea level (m a.s.l.). It is characterized by some of the steeper sidewalls in the Alps. The valley floor, oriented SW–NE and at about 1000 m a.s.l., is very narrow, not exceed 1.5 km in most places. The Maurienne valley is much longer (roughly 130 km) and wider (up to several km at some places). The narrowest part (less than 1 km) is located in the Orelle pass (M2). The surrounding peaks varies between 2500 and 3800 m a.s.l., and the valley floor increases from 550 m a.s.l. (in Saint Jean de Maurienne, M5) to 1340 m a.s.l. (in Sollières, M3). The lower section of the valley, from the beginning of the valley to Orelle, is approximately oriented NW–SE. A second section, from Orelle (M2) to the upper part is roughly oriented SW–NE.

The two valleys are among the most important European north-south routes across the Alps. Each valley allows a direct connection between France and Italy with highways in their respective tunnels. Since the closure of “Tunnel du Mont-Blanc”, the traffic in the Chamonix Valley is essentially linked to local and tourism activities, and mostly due to personal vehicles (2% only of light duty trucks for local delivery and tourism buses, on average). During the period June 2000–April 2002, the traffic density was about 13300 vehicle per day ( $\text{veh d}^{-1}$ ) on average, with a maxima at about 30000  $\text{veh.d}^{-1}$  during August on national road 205 (N205). The weekly traffic showed also a slight maximum on Saturday, in relation with the tourist activity. It should be noticed that 50.1% of personal vehicles are using diesel fuel in France (value for the year 2000).

In the Maurienne valley, the traffic is distributed on a main road (N6) and the highway (A43). The personal vehicle traffic was on the order of 6000  $\text{veh.d}^{-1}$  during our study, with a small maximum on weekends. The heavy duty traffic essentially takes place on the highway with about 3000 trucks. $\text{d}^{-1}$  on average. It reaches its maximum on Wednesdays (6000 trucks. $\text{d}^{-1}$ ), with a minimum on Sundays ( $<1000$  trucks. $\text{d}^{-1}$ ).

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Industrial activities are only taking place in the Maurienne valley, with some chemical and metallurgic plants located near the main towns in the valley (Saint Jean -M5- and Saint Michel de Maurienne).

As part of the POVA program, two 15-days campaigns were performed while the international traffic was stopped in the Chamonix valley. A summer campaign took place in 2000, on 14–21 August in the Chamonix valley and on 22–29 August in the Maurienne valley. A winter campaign took place in 2001, on 16–22 January in the Chamonix valley and on 25–31 January in the Maurienne valley. In each valley, five sampling sites were instrumented with various aerosol or gas samplers, including automatic analyzers for NO<sub>x</sub>, ozone, and PM<sub>10</sub>, and aerosol collection for chemical analysis. All of these measurements were not performed at all sites. The locations of these sites (C1 to C5 and M1 to M5 in the valleys of Chamonix and Maurienne, respectively) are presented on Fig. 1. PAH were collected at two sites in each valley during winter: Le Clos de l'Ours (C1) and Les Houches (C2) for the Chamonix valley, and Modane (M1) and Orelle (M2) for the Maurienne valley. During summer, PAH were collected at one site per valley only: Le Clos de l'Ours (C1) and Modane (M1). These last two sites are located in suburban areas, while the sites at Les Houches and Orelle are more rural, being located several hundred meters away from the main roads in each valley.

## 2.2. Sample collection and analysis

The sampling and analytical procedures for the determination of PAH atmospheric concentrations are described in details by Besombes et al. (2001). Briefly, airborne particulates were collected by high volume samplers (50 m<sup>3</sup>.h<sup>-1</sup> on average) on pre-cleaned glass fiber filter (GF/F Whatmann filter, 210×270 mm). Sampling duration at all sites was 24 h (starting at 08:00 LT) during the summer campaign and 12 h (starting at 08:00 and 20:00 LT, respectively) during the winter campaign. After collection, filters were stored at cold temperature (−4°C) in aluminum sheets sealed in polyethylene bags, until analysis.

Samples were soxhlet extracted for 3h (BUCHI B-811) with a mixture of

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dichloromethane and cyclohexane (2/1 v/v). PAH analyses were performed by reversed phase high performance liquid chromatography on a Vydac C18 column (length 25 cm, granulometry 5 $\mu$ m and internal diameter 4.5 mm) with a ternary elution gradient (methanol, water acetonitrile). All solvents were degassed using helium sparging to eliminate possible oxygen quenching during fluorescence. PAH were identified and quantified by UV fluorescence at variable excitation and emission wavelengths. With this method, the following 11 PAH were determined quantitatively: fluoranthene (FLA), pyrene (PYR), chrysene (CHR), benzo[a]anthracene (BaA), benzo(e)pyrene (BeP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[ghi]perylene (BghiP), indeno(1,2,3-cd)pyrene (IP), and coronene (COR). The overall analytical and sampling errors were estimated between 18 and 41%, depending on the PAH considered (Marchand, 2003).

Measurements for NO<sub>x</sub> (Thermo Environmental Instruments 42C) and PM<sub>10</sub> (TEOM1400A, R and P) were conducted on a 15 min basis at the same sites. Parallel sampling for EC and OC analysis were conducted with open face filters on a 4 or 6 h basis, according to the site and the season. We used QMA quartz filters (47 mm), pre fired for 1 h at 800°C in order to lower the blank levels. Filters were kept and transported by packs of 20 in leak proof glass jars before sampling. After sampling, they were stored at -18°C in individual Petri slides wrapped up in aluminum foil in sealed bags, until analysis. Analyses for OC and EC took place at INW, Gent, Belgium, using a thermo-optical method on a Sunset Lab analyzer (Birch and Carry, 1996). The temperature ramp uses four steps up to 870°C under pure helium for the quantification of OC, and four steps up to 900°C with a mixture of 98% He + 2% O<sub>2</sub> for that of EC. Arithmetic means were used to calculate 12 or 24 h average concentrations for the time steps of the PAH sampling.

### 3. A short review of studies on PAH emissions

A very large literature is dealing with emissions of PAH by various anthropogenic combustion sources. As mentioned previously, residential heating with wood fires, as well as vehicular emissions are considered the main sources in urban and suburban environments. Table 1 summarises some of the emissions rates of total PAH presented in the literature.

Wood combustion, as a domestic heating source, plays an important role for organic carbon (OC) emissions. Schauer et al. (1996) and Schauer and Cass (2000) calculated, for an urban environment (in Los Angeles), an annual average contribution of wood combustions to the ambient OC ranging between 5 and 22% (year 1982), with maxima between 30 and 65% during winter months (result for the year 1996). With a ratio PAH/OC higher in the emissions of wood combustions than in the vehicular emissions (Table 1), wood combustion in residential areas can represent one of the most important PAH source (Li and Kamens, 1993). This is corroborated by very high PAH emission rates (ranging between 4 and 14 mg.kg<sup>-1</sup> of burned wood), 1 to 3 orders of magnitude larger than those calculated from vehicular emissions (Table 1). The later range between 0.01 and 0.07 mg.kg<sup>-1</sup> for recent gasoline powered light vehicles, and between 0.25 and 1.4 mg.kg<sup>-1</sup> for heavy duty trucks.

As can be seen with the large standard deviation in these values, it remains very difficult to estimate precisely the emission rates, due to the great number of parameters influencing them. In the case of vehicular emissions, the most important parameter on the variability of the emissions rates is the engine temperature. Indeed, Combet et al. (1993) highlighted a PAH emission 20 times larger during cold start than during warm use for gasoline light vehicles (average of 10 vehicles on slow urban cycle). This difference between cold start and warm use also exists for diesel vehicles, but to a lesser extent (with a factor of 1,5 only, for an average of 20 vehicles). Fabrication year as well as mean velocity also influence very significantly PAH emissions rates (Combet et al., 1993). The use of catalytic converter decreases the quantities of emitted PAH by

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a factor ranging between 20 and 1000 (Schauer et al., 2002; Rogge et al., 1993; Paturel et al., 1996). Finally, the composition of the fuel, especially their concentration in PAH, also influences the quantities emitted in the atmosphere (Marr et al., 1999; Mi et al., 1998; Rogge et al., 1993). For gasoline light vehicles, Marr et al. (1999) highlighted a strong correlation between chemical composition and PAH emissions rates, underlining the importance of unburned fuel as a important PAH source. For diesel vehicles, it is the composition of the engine oil that seems to be the important factor in PAH emission (Schauer et al., 2002).

In the case of residential heating, combustion conditions (temperature, moisture, availability in oxygen) largely influence emission rates, as do the nature of the fuel (wood type, presence of foliage) (Standley and Simoneit, 1987; Jenkins et al., 1996). Jenkins et al. (1996) report that smoldering combustions emit 4–5 times more PAH than flaming combustions.

With the whole range of PAH more or less emitted by each type of sources, many studies focused over the last 30 years on the determination of PAH chemical profiles as fingerprints of these sources (Li and Kamens, 1993). It led to many observations in the emissions ratios that can be considered source specific.

First of all, gasoline vehicular emissions are characterized by PAH with higher molecular weight than those measured in diesel exhaust. It is particularly the case for BghiP and COR (Rogge et al., 1993; Miguel et al., 1998; Miguel and Pereira, 1989), and seems to be in relation with the engine operating temperatures (Rogge et al., 1993; Combet et al., 1993; Schauer et al., 2002). Combet et al. (1993) showed that BghiP emission rates were approximately 55% higher during warm driving cycles than during cold driving cycles. The same result is obtained for the IP, but to a lesser extent (increase of 25% only). These results are also in line with the study of Marr et al. (1999), showing a direct correlation between fuel and exhausts compositions for gasoline vehicles. In this study, only the BghiP shows emission rates clearly higher than those extrapolated from the fuel composition. This result suggests pyrosynthetic formation processes within the engine, a process requiring strong temperatures (Marr

et al., 1999; Combet et al., 1993). Thus, gasoline emissions are characterized by an abundance in BghiP and COR (Nielsen, 1996; Li and Kamens, 1993; Rogge et al., 1993).

For diesel vehicles, Marr et al. (1999) did not highlighted any correlation between fuel and exhaust compositions. This result suggests the importance of unburned lubricating oil emissions and that of internal formation processes. Taking into account relative abundances in heavy PAH, significantly weaker for diesel vehicles than for gasoline vehicles, engine oil rejections seem to be an important factor in diesel exhausts. This same process is also suggested for hopanes emissions (Schauer et al., 2002). Finally, Combet et al. (1993) did not observe any modification of the PAH chemical signature according to the engine temperatures. Diesel emissions are usually distinguished from gasoline emissions by greater relative concentrations in BbF, BkF and CHR (Li and Kamens, 1993; Hering et al., 1984; Li et al., 1996; Duran et al., 2001; Rogge et al., 1993).

PAH chemical signatures of wood combustion aerosols also show an important proportion of CHR and of BbF and BkF, but to a lesser extent than in diesel emissions. In the study of Rogge et al. (1998), CHR represents 70% by mass of a selection of 9 particulate PAH emitted during oak combustion, with an high emission rate of 2.8 mg.kg<sup>-1</sup>. However, for the same wood and in equivalent conditions (residential fireplace), the data reported by Schauer et al. (2001) leads, on the same basis of 9 HAP, to a contribution in CHR significantly lower (30%; emission rate: 0.75 mg.kg<sup>-1</sup>). As in the case of diesel emissions, high molecular weight PAH (BghiP, IP and COR) show weak contributions to total PAH emissions. They are not emitted at all during hard wood combustions (Oros and Simoneit, 2001b; Schauer et al., 2001), but are more abundant during soft wood combustions (Oros and Simoneit, 2001a; Schauer et al., 2001). However, they were measured (particularly COR) during bush (Freeman and Catell, 1990) and savannas fires (Mascllet et al., 1995).

Separating profiles resulting from diesel and wood combustions emissions is thus relatively uneasy on the basis of PAH only. In case of multiple sources, it seems nec-

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essary to consider correlations with other tracers, and not only absolute values of a relative PAH contributions, to obtain an accurate estimation of the impact of these anthropogenic sources.

## 4. Results and discussion

### 4.1. Average total concentrations and seasonal variations

The total PAH concentration (called  $\Sigma$  represents the sum of the individual concentrations of the following 11 PAH: FLA, PYR, BaA, CHR, BeP, BbF, BkF, BaP, BghiP, IP and COR.  $\Sigma'$  is obtained by excluding FLA and PYR from  $\Sigma$ . FLA and PYR are present in the atmosphere in the particulate and in the gas phase (at  $T = 20^\circ\text{C}$   $C_{\text{particles}}/C_{\text{gas}} = 0.36\%$  and  $5.6\%$  for FLA and PYR, respectively (Seinfeld and Pandis, 1998)). While they are the most abundant PAH in our series, with combined relative contribution to  $\Sigma$  lose to 50% on average, their strong dependency to gas-particle partitioning with temperature could lead to large uncertainties in ratios to total PAH essentially linked to atmospheric conditions, not sources. It is therefore useful to compare both  $\Sigma$  and  $\Sigma'$  in order to evaluate this artefact. Table 2 presents all the results for the 2 seasons and all sites, for the average concentrations of  $\Sigma$ ,  $\Sigma'$ ,  $\text{PM}_{10}$ , EC, OC, and for temperature over each campaign. All of the following observations pertains to  $\Sigma$ , but they are virtually the same when  $\Sigma'$  is considered.

The general levels of PAH concentrations ( $0.7\text{--}1.3 \text{ ng}\cdot\text{m}^{-3}$  during summer and  $3.5\text{--}47.6 \text{ ng}\cdot\text{m}^{-3}$  during winter, Table 2) are of the same order of magnitude than those observed in large European cities such as Munich (Kiss et al., 1998), Rome (Cecinato et al., 1999 ; Menichini et al., 1999), Naples (Caricchia et al., 1999), London (Dimashki et al., 2001) or Paris (Pistikopoulos et al., 1990a) despite the much lower population in the valleys. During summer (for all sites) and during winter (at M1, M2 and C2), the concentrations are comparable to those in moderate polluted urban areas. These concentrations at the suburban area of Chamonix (C1) during winter ( $47.6 \text{ ng}\cdot\text{m}^{-3}$ ) are

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representative of very strongly polluted atmospheres.

Several factors regulate the concentrations of PAH and their evolution in the valleys. The impact of the proximity of the sampling sites from potential sources is underlined by the differences between sub-urban sites (M1 and C1) and more rural sites (M2 and C2), with concentrations about 2.5 time higher in the former, for both valleys (Table 2). It underlines the role of local emissions sources, as opposed to transport from the outside of the valleys, for the PAH concentrations.

Strong seasonal variation can also be observed at both suburban sites M1 and C1. The increase in  $\Sigma$  is larger in the valley of Chamonix, with a winter/summer ratio of 36, than in the valley of Maurienne, where the winter/summer ratio is about 14. These seasonal variations are usually observed with a ratio winter/summer ranging between 4 and 10 (Carrichia et al., 1999; Menichini et al., 1999; Dörr et al., 1996; Harrisson et al., 1996; Halshall et al., 1994; Aceves and Grimalt, 1993; Kiss et al., 1998). They can be explained by the conjunction of several processes. First, it results from additional emissions, particularly with residential heating as a new source in winter. This is clearly seen in the evolution of the ratio  $\Sigma/PM_{10}$  between seasons, with values about 30 times higher in winter than in summer in both valleys, indicative of a stronger impact of combustion sources on the composition of aerosols during winter. Second, seasonal variability can be linked with the shift of the gas/particles partitioning toward the particulate phase, induced by the temperature decrease (Pankow and Bildeman, 1992). This decrease is rather large in our case, with, for example, average temperatures of 18.0°C and -2.5°C over the sampling weeks in Chamonix (Table 2), in summer and winter, respectively. Third, degradation processes are less pronounced in winter, leading to some accumulation of reactive compounds. It can be illustrated by considering the evolution of BaP concentrations, one of the most reactive PAH in the particulate phase (Kamens et al., 1990). In our case, BaP presents the strongest winter/summer ratio (57 at C1 and 44 at M1) of all PAH considered, confirming the impact of the degradation processes on the seasonal variations of the total concentration. Finally, a last factor concerns the changes in atmospheric dynamic, especially the formation of in-

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versions layers. Formation of inversions layers is not specific to mountainous systems but they are more frequent and stronger in this type of environment where direct sunshine can be very limited in winter due to steep-sided valleys (Anquetin et al., 1999). All of these reasons can probably explain the larger amplitude of seasonal variations observed at our sites compared to that in large cities in flat/low altitude areas.

Both seasons are also characterized by stronger PAH concentrations in the valley of Chamonix (1.3 and 47.6 ng.m<sup>-3</sup> at C1 during summer and winter, respectively) than in the valley of Maurienne (0.7 and 9.7 ng.m<sup>-3</sup> at M1 during summer and winter, respectively), despite very large heavy duty international traffic in the later. Average  $\Sigma$  ratios between the two valleys are close to 2 and 5 during summer and winter, respectively. Therefore, heavy duty traffic does not appear like the fundamental parameter governing the PAH concentrations. The influences of other sources and of the dilution and dispersion processes seem preponderant. With this respect, the larger ventilation in the much wider Maurienne Valley is most probably one of the key factor decreasing concentrations with dispersion.

Figure 2 presents the average ratio of each PAH measured to  $\Sigma'$ , for all sites and seasons. None of these profiles is fundamentally different from the others, indicative of some permanency of the sources in the valleys. Nevertheless, some changes can be highlighted, showing some evolution of the main sources according to the valley or the season. Average values of the specific contributions of BghiP+COR, BbF+BkF, and CHR to  $\Sigma'$  are presented in Table 2. It shows that the first of these ratio (indicative of the impact of emissions from gasoline powered vehicles) is much larger in the suburban area of the Chamonix valley (22–28% at C1) than in the Maurienne Valley (13% at M1 and 15% at M2), or in rural area of the Chamonix valley (12% at C2). This impact is about the same at all of these later sites. It decreases significantly between summer and winter at C1 (Table 2).

The second of these ratios (indicative of emissions from diesel vehicles, with some implication of wood burning) shows only small differences between sites and seasons. However, higher values are systematically measured in the Maurienne Valley, where

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all the cases show the same proportion (24–25%). This ratio shows more variability in the Chamonix valley with higher values during summer than winter (22 and 18% at C1, respectively), and higher values at the rural site C2 (23%) than at the suburban one (18% at C1). Therefore, differences between valleys are more marked at the suburban sites (M1 and C1), especially during winter. A first approach for the interpretation of these results would lead to consider diesel vehicles sources as main PAH source in the Maurienne Valley, even in winter when domestic heating is a potential important PAH source. For the Chamonix Valley, winter decrease of BF contribution at C1 would be the consequence of the strong influence of gasoline vehicles emissions, while differences observed between C1 and C2 could be explained by a stronger relative impact of wood burning sources at the rural site.

Such an interpretation is in good agreement with results obtained with  $\text{CHR}/\Sigma'$  ratios. As mentioned in Sect. 3, CHR is strongly emitted by wood combustion but shows also significant emission rate from diesel sources. During summer, no biomass fires or agricultural fires have been observed. Thus, differences in  $\text{CHR}/\Sigma'$  ratio between C1 (15%) and M1 (21%) at that time is indicative of the larger influence of diesel vehicles exhaust in the Maurienne Valley. The larger ratios in the rural sites in winter in both valleys (16 and 19% at M2 and C2, respectively and 14% at C1 and M1) is also on line with stronger influences of wood burning at these sites.

Further insights in these hypotheses can be gained by considering other anthropogenic indicators such as EC, OC, NO, and by studying temporal evolutions of the concentrations during the sampling periods.

## 4.2. Temporal evolutions

### 4.2.1. Summer campaign

Figure 3 presents the evolution of daily total concentration of PAH ( $\Sigma$  for sites C1 and M1 during the summer campaign, together with the evolution of concentrations of NO and NO<sub>2</sub>. This figure also presents the variations of the ratios  $(\text{BghiP}+\text{COR})/\Sigma'$  and

$(BbF+BkF)/\Sigma'$ .

The total PAH concentrations in the Chamonix Valley are rather constant throughout the week, except on Friday (18 August) and Sunday (20 August) when maximum and minimum values are measured, respectively. On Sunday, the lower activity near the sampling site can explain the decrease in concentration, as it is usually observed for primary pollutants such as NO (Fig. 3). The sharp increase of concentrations on Friday is also characterized by the higher concentration of NO and the higher relative concentrations of heavy PAH (BghiP and COR) (Fig. 3). At the same time, wind speed and direction measured at the local meteorological station also indicate very light winds at ground. Thus, the strong increase in PAH concentration is related to an increase in vehicular emissions near the sampling site magnified by limited dispersion/dilution processes.

From a more general point of view, Fig. 3 shows strong covariations between  $\Sigma$ , NO and the ratio  $(BghiP+COR)/\Sigma$  at the suburban site of the Chamonix Valley (C1) during the overall period, while the contribution of Benzofluoranthenes (BbF+BkF) is nearly constant. Therefore, gasoline emissions appear to be the main source of PAH in the Chamonix Valley, confirming the interpretation proposed with average values. Further analysis shows that the Pearson correlation coefficient between  $\Sigma$  and NO ( $r = 0.93$ ) is better than that calculated between  $\Sigma$  and  $NO_2$  ( $r = 0.69$ ). Thus, the influence of proximity sources appears preponderant. In addition, we observe strong correlations between  $\Sigma$ , EC and OC ( $\Sigma$  vs OC :  $r = 0.93$ ;  $\Sigma$  vs. EC :  $r = 0.79$ ), but no correlations between the organic fraction and  $PM_{10}$  ( $\Sigma$  vs.  $PM_{10}$  :  $r = -0.1$  ; OC vs.  $PM_{10}$  :  $r = 0.14$ ). These results suggest an external mixing of the particles making up the  $PM_{10}$  mass, and an organic fraction strongly influenced by primary anthropogenic sources.

Total concentrations show more variability in the Maurienne Valley (Fig. 3). The higher  $\Sigma$  are obtained on Saturday (26 August ) and Sunday (27 August). However, these two days were also characterized by a strong episode of Saharan dust associated with anthropogenic inputs, most probably with an origin from the heavily industrialized Torino area in Italy, as discussed in Colomb et al. (2002). We will not discuss it

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further here. Except for these 2 days, the higher PAH concentrations are observed on Wednesdays (23 and 30 August). As mentioned in Sect. 2.1, it is the day of maximum heavy duty traffic on the highway in the valley, with 6000 trucks on average. These concurrent maxima are therefore in good agreement with the discussion on average values, indicating a large impact of diesel emission in the Maurienne Valley. However, the temporal variations of PAH ratios show some discrepancies with this first interpretation. While the contribution of BF to  $\Sigma'$  is higher than those of BghiP and COR, total PAH concentrations are more correlated to the later ratios (Fig. 3). Therefore, the variations of PAH concentrations seem to be linked to changes in the gasoline source, with a constant impact of diesel sources. Further work is needed to reconcile these two sets of observations. Finally, as opposed to the Chamonix Valley,  $\Sigma$  are not correlated in the Maurienne Valley neither with NO ( $r = -0.32$ ) nor NO<sub>2</sub> ( $r = -0.38$ ) (Fig. 3). This situation shows the efficient dispersion mechanisms between sources and sampling sites in this valley at that time of the year.

#### 4.2.2. Winter campaign

Figures 4 and 5 present the temporal evolutions of the total PAH concentrations together with the evolution of NO for each of the 12 hours sampling periods, at the suburban sites (C1 and M1) and rural sites (C2 and M2), respectively. These figures also present the variation of the ratios (BghiP+COR)/ $\Sigma'$ , (BbF+BkF)/ $\Sigma'$  and CHR/ $\Sigma'$ .

In the Chamonix Valley, temporal evolutions of  $\Sigma$  show strong variability all along the week at the two sites. This variability can partly be explained by the variation of meteorological parameters. During the first part of the campaign, from 16–18 January (period 1), anticyclonic conditions prevailed with low temperature ( $-4.5^{\circ}\text{C}$  on average) and low wind speed. Concentrations of PAH up to  $150\text{ ng}\cdot\text{m}^{-3}$  are recorded at that time. Afterwards, from 19–22 January (period 2), different meteorological conditions occur with more disturbed weather, higher temperatures ( $-1.5^{\circ}\text{C}$  on average) and higher wind speed. These conditions allow a better dispersion of the particles, leading to lower PAH concentrations. The influence of meteorological conditions can also be highlighted by

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correlations between  $\Sigma$  and others parameters such as EC, OC and  $PM_{10}$  concentrations. Table 3 presents the correlations between  $\Sigma$ ,  $PM_{10}$ , OC, EC, and NO at the two sites for both meteorological periods. At site C1, the correlations between all these parameters are very strong during the 2 periods (ranging from 0.6 to 0.98). High correlations between  $\Sigma$ , EC, and NO are relatively usual in source areas, while such a result between  $\Sigma$  and  $PM_{10}$  is rather unusual ( $r = 0.971$  and  $0.956$  during period 1 and period 2, respectively). PAH are mainly associated with submicron aerosol (Venkataraman and Friedlander, 1994; Schnelle-Kreis et al., 2000; Aceves and Grimalt, 1993; Pistikopoulos et al., 1990b), a size range that generally represents only a small fraction of the  $PM_{10}$  mass balance. Since PAH are primary anthropogenic compounds, such correlations indicate that  $PM_{10}$  concentrations result essentially from primary anthropogenic emissions, with marginal inputs of natural aerosol. This is in good agreement with the very large contribution of EC to  $PM_{10}$  (20% on average) during these periods.

There are further differences between the two meteorological periods. First, the correlations between  $\Sigma$ , EC, and NO are lower during period 1 than at during period 2 at the suburban site (C1) (Table 3), suggesting an "older" aerosol during the anticyclonic period. Also, despite similar correlation coefficients between  $\Sigma$  and  $PM_{10}$ , their ratio varies between the two periods (Fig. 6) at that site: an accumulation of pollutants is again suggested during period 1, with larger relative concentrations of PAH in the  $PM_{10}$ . Second, the same characteristics are also seen at the rural site C2 during period 1, despite much lower concentrations: strong correlations (Table 3) between all the parameters and a ratio  $\Sigma/PM_{10}$  identical to that at the suburban site suggest a contaminated air mass at the scale of the valley. During the second part of the sampling week, all of these correlations significantly decrease at C2, indicative of a smaller direct impact of the emissions sources for this rural site in perturbed meteorological conditions. During this period, PAH concentrations and 12h average  $PM_{10}$  concentrations present low variability, preventing accurate calculation of their ratio (Fig. 6).

In the Maurienne valley, two meteorological periods can also be observed. A first period (period 3), from 25–27 January, is characterized by a disturbed episode with some

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precipitations and relatively strong NE-SW winds. During the last part of the campaign, from 28–31 January (period 4), anticyclonic conditions prevailed with low temperatures and low wind speed mainly orientated SW-NE. As opposed to the valley of Chamonix, the total PAH concentrations in the Maurienne valley do not show very large evolutions between these two periods (Figs. 4 and 5). Further, no significant correlations are observed at site M1 between  $\Sigma$ , EC, or  $PM_{10}$  (NO was not measured at that site) for any of the periods. It may indicate the complexity of the sources contributing to  $PM_{10}$  at that site. At Orelle (rural site M2), no significant correlations are observed during period 3 while strong correlations appear during period 4 (Table 4) between  $\Sigma$ , EC, NO, and  $PM_{10}$ , indicative of the impact of local combustion sources in these conditions.

Therefore, under winter conditions, the strong PAH levels observed in the two valleys, and especially in the Chamonix Valley, are generated by internal sources. Under these specific conditions, the study of the capability of PAH to discriminate sources is particularly interesting. In the Chamonix valley, the ratios  $BF/\Sigma'$  and  $CHR/\Sigma'$  show good covariations at the two sites, especially at the rural site (Fig. 5). It can be postulated that BF and CHR are emitted in a predominant way by the wood combustion source. The importance of this source is confirmed by the presence in large quantities of guaia-cyl and syringyl derivatives in our samples. These compounds come from the thermal breakdown of lignin and are indicators of wood combustions (Nolte et al., 2001). These results will be discussed in a future publication.

In the Maurienne valley where mixing sources and important dilution/dispersion processes have been highlighted, the study of temporal evolution of these three PAH ratio is more than complex. No correlation are observed between  $BF/\Sigma'$ ,  $CHR/\Sigma'$ ,  $(BghiP+COR)/\Sigma'$ , and  $\Sigma$  (Figs. 4 and 5) underlining the influence of multiples sources and processes governing PAH concentrations. Examinations of these specific ratios are therefore insufficient to describe PAH sources.

## 5. Conclusions

The study of PAH concentrations and speciation in the context of these alpine valleys bring in several interesting pieces of information. First, it shows the large impact of local sources to the contamination of the atmosphere. This impact is much larger in winter than in summer, with an increasing contribution of local combustion sources to the formation of PM<sub>10</sub>. This increase for one season to the other is larger than generally observed in other type of environment. It is partly due to additional sources, but is also very much enhanced by local meteorology. All of these conditions can lead to PAH concentrations in the range of several tens of ng.m<sup>-3</sup>, comparable to those observed in large cities. The current levels show that it will be challenging to meet potential new EU standards in this environment. The current proposition of directive is based on a target value of 1 ng.m<sup>-3</sup> on annual average for BaP, while the UK government Expert Panel on Air Quality Standard has set a UK air quality standard at 0.25 ng.m<sup>-3</sup> for the same species (Dimashki et al., 2001).

Second, our results show that PAH concentrations were higher in the valley of Chamonix Valley than in the Maurienne Valley, in a context of no international heavy duty traffic in the former. This sensitivity is probably connected both to the morphological differences of these valleys, with more ventilation in the wider Maurienne Valley, and to the importance of wood combustion sources in the Chamonix Valley. It will be interesting to compare these results for the second sets of field campaigns proposed in the POVA program, undertaken with the "Tunnel du Mont Blanc" reopen to international traffic.

Third, one goal of this study was also to investigate the ability of PAH to discriminate the different combustion sources, in an environment simpler than large urban areas. Examinations of the relative concentrations of several PAH (BghiP, COR, BbF, BkF, and CHR) and of their evolutions provide a qualitative interpretation of aerosol sources that is in general agreement with our knowledge of these sources in the valleys. However, differences remain small (between valleys, sites, and seasons). Considering the vari-

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ability of the different relative emission rates proposed in the literature, the use of PAH alone in a quantitative study (using a CMB approach, for example) on the influence of sources seems rather dubious. Further work in this direction is in progress, using other molecular markers, including wood combustion tracers.

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**Table 1.** Emission rates of PAH [ $\mu\text{g.kg}^{-1}$ ] for different sources.

| PAH ( $\Sigma$ ) <sup>a</sup>                        | Emission rate<br>( $\mu\text{g.kg}^{-1}$ ) | $\Sigma$ /OC<br>(%) | Observations   | Reference                  |
|--|--|---------------------|--|----------------------------|
| <b>Vehicular sources</b>                             |  |                     |  |                            |
| <i>Gasoline</i>                                      |  |                     |  |                            |
| Catalysed–equipped light vehicles                    | 8.1 <sup>‡</sup> (0.7) <sup>b</sup>        | 0.02                | Average of 9 vehicles (1986–1994) <sup>d, e</sup>        | Schauer et al. 2002        |
| Catalysed–equipped light vehicles                    | 350 (26) <sup>c</sup>                      | 2.8                 | Average of 7 vehicles (1977–1983) <sup>d, e</sup>        | Rogge et al. 1993          |
| Light vehicles                                       | 72.5 <sup>†</sup>                          | -                   | Calculated from tunnel measurements<br>(San Francisco. ) | Miguel et al. 1998         |
| <i>Diesel</i>  |  |                     |  |                            |
| Heavy duty trucks                                    | 240 (60.2) <sup>b</sup>                    | 0.5                 | Average of 2 heavy duty trucks<br>(1987) <sup>d, e</sup> | Rogge et al. 1993          |
| Heavy duty trucks                                    | 1403 <sup>†</sup>                          | -                   | Calculated from tunnel measurements<br>(San Francisco)   | Miguel et al. 1998         |
| <b>Wood combustion in residential<br/>fireplaces</b> |  |                     |  |                            |
|  | 13700 <sup>‡</sup>                         | 2.5                 | Pine   | Schauer et al. 2001        |
|  | 6900 <sup>‡</sup>                          | -                   | Pine   | Rogge et al. 1998          |
|  | 5000 <sup>‡</sup>                          | 1.7                 | Oak  | Schauer et al. 2001        |
|  | 4900 <sup>‡</sup>                          | -                   | Oak  | Rogge et al. 1998          |
|  | 3700 <sup>‡</sup>                          | 1                   | Eucalyptus   | Schauer et al. 2001        |
| Coal   | 950.10 <sup>3</sup>                        | 82                  | Average of 4 coal ranks                                  | Oros and Simoneit.<br>2000 |

<sup>a</sup>: Total concentration of the following 11 PAH in the particulate phase ( $\Sigma$ ): FLA. PYR. BaA. CHR. BeP. BbF.

BkF. BaP. BghiP. IP. COR ; <sup>‡</sup>:  $\Sigma$  without COR ; <sup>†</sup>:  $\Sigma$  without COR and BeP ;

<sup>b</sup>: In parentheses values refer to  $\mu\text{g.km}^{-1}$  emission rates report by authors : conversion into  $\mu\text{g.kg}^{-1}$  is carried out while considering as density of gasoline and diesel respectively 743 and 830  $\text{g.L}^{-1}$  (Miguel et al., 1998). The fuel consumption taken into account are 8.5  $\text{km.L}^{-1}$  for gasoline powered light vehicles (Miguel et al., 1998) and 12  $\text{km.L}^{-1}$  for heavy duty trucks (Rogge et al., 1993) ; <sup>c</sup>: conversion into  $\mu\text{g.kg}^{-1}$  is carried out while considering as fuel density 743  $\text{g.L}^{-1}$  and as fuel consumption 9.9  $\text{km.L}^{-1}$  (Rogge et al., 1993)

<sup>d</sup>: Vehicles year of fabrication ; <sup>e</sup>: FTP ( Federal Test Procedure) procedure : urban cycle.

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**Table 2.** Averages results on  $\Sigma$ ,  $\Sigma'$ , EC, OC, PM<sub>10</sub>, T and PAH relative concentrations for the summer and winter campaigns in the two valleys, respectively.

|  | Summer                        |                 | Winter          |                   |                 |                   |
|--|-------------------------------|-----------------|-----------------|-------------------|-----------------|-------------------|
|  | M1 <sup>(c)</sup>             | C1              | M1              | C1                | M2              | C2                |
| $\Sigma$ <sup>(a)</sup> (ng.m <sup>-3</sup> )  | 0.7 (0.3), n=6 <sup>(d)</sup> | 1.3 (0.4), n=9  | 9.7 (4.0), n=11 | 47.6 (42.4), n=14 | 3.5 (1.2), n=12 | 18.4 (19.1), n=13 |
| $\Sigma'$ <sup>(b)</sup> (ng.m <sup>-3</sup> ) | 0.3 (0.2)                     | 0.7 (0.3)       | 6.4 (2.5)       | 22.8 (16.7)       | 2.3 (0.7)       | 8.8 (8.6)         |
| PM10 (μg.m <sup>-3</sup> ) <sup>(e)</sup>      | 18.9 (14.0)                   | 28.0 (4.2)      | 12.9 (5.1)      | 24.3 (12.8)       | 12.6 (7.3)      | 13.1 (5.1)        |
| EC (μg.m <sup>-3</sup> )                       | nd <sup>(f)</sup>             | 2.0 (0.7), n=27 | 1.5 (0.6), n=41 | 4.8 (3.2), n=41   | 0.7 (0.4), n=42 | 1.3 (0.8), n=41   |
| OC (μg.m <sup>-3</sup> )                       | nd                            | 9.6 (3.2), n=27 | 7.4 (2.3), n=41 | 13.7 (5.3), n=41  | 4.2 (2.0), n=42 | 12.2 (4.8), n=41  |
| T°C <sup>(e)</sup>                             | 15.3 (3.1)                    | 18.0 (1.4)      | -1.0 (2.3)      | -2.5 (2.8)        | -0.7 (2.6)      | -3.3 (2.7)        |
| (BghiP+COR)/ $\Sigma'$                         | 13% (3)                       | 28% (4)         | 13% (5)         | 22% (5)           | 15% (3)         | 12% (6)           |
| (BbF+BkF)/ $\Sigma'$                           | 25% (3)                       | 22% (2)         | 24% (5)         | 18% (3)           | 24% (3)         | 23% (3)           |
| CHR/ $\Sigma'$                                 | 21% (3)                       | 15% (2)         | 14% (4)         | 14% (4)           | 16% (2)         | 19% (5)           |

<sup>a</sup> : Sum of all PAH; <sup>b</sup> : Sum of all PAH except FLA and PYR; <sup>c</sup> : Excluding Saharan dust episode (see text);

<sup>d</sup> : average value (standard deviation), n=number of samples; <sup>e</sup> : TEOM (R&P) measurements, data acquisition frequency : see text ; <sup>f</sup> : not determined

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**Table 3.** Pearson correlation coefficients between  $\Sigma$ , PM<sub>10</sub>, OC, EC and NO at sites C1 and C2 (Valley of Chamonix) during winter. Meteorological periods are described in the text. Pearson coefficients calculated with 6 and 8 points for periods 1 and 2, respectively.

| C1       |          |       |       |       |    |
|----------|----------|-------|-------|-------|----|
| Period 1 | $\Sigma$ | PM10  | OC    | EC    | NO |
| $\Sigma$ | 1        |       |       |       |    |
| PM10     | 0.971    | 1     |       |       |    |
| OC       | 0.966    | 0.956 | 1     |       |    |
| EC       | 0.783    | 0.779 | 0.833 | 1     |    |
| NO       | 0.654    | 0.578 | 0.678 | 0.933 | 1  |
| C2       |          |       |       |       |    |
| Period 2 | $\Sigma$ | PM10  | OC    | EC    | NO |
| $\Sigma$ | 1        |       |       |       |    |
| PM10     | 0.956    | 1     |       |       |    |
| OC       | 0.971    | 0.953 | 1     |       |    |
| EC       | 0.933    | 0.946 | 0.936 | 1     |    |
| NO       | 0.921    | 0.900 | 0.925 | 0.979 | 1  |

| C2       |          |       |       |       |    |
|----------|----------|-------|-------|-------|----|
| Period 1 | $\Sigma$ | PM10  | OC    | EC    | NO |
| $\Sigma$ | 1        |       |       |       |    |
| PM10     | 0.986    | 1     |       |       |    |
| OC       | 0.912    | 0.962 | 1     |       |    |
| EC       | 0.783    | 0.861 | 0.937 | 1     |    |
| NO       | 0.885    | 0.873 | 0.747 | 0.570 | 1  |
| C2       |          |       |       |       |    |
| Period 2 | $\Sigma$ | PM10  | OC    | EC    | NO |
| $\Sigma$ | 1        |       |       |       |    |
| PM10     | 0.525    | 1     |       |       |    |
| OC       | 0.640    | 0.871 | 1     |       |    |
| EC       | 0.519    | 0.674 | 0.667 | 1     |    |
| NO       | 0.647    | 0.659 | 0.509 | 0.587 | 1  |

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**Table 4.** Pearson correlation coefficients between  $\Sigma$ ,  $PM_{10}$ , OC, EC, and NO at site M2 (Maurienne Valley) during the winter campaign. Meteorological periods are described in the text. Pearson coefficients calculated for 5 and 7 points for periods 3 and 4, respectively.

### M2

| <i>Period 3</i> | $\Sigma$ | <i>PM 10</i> | <i>OC</i> | <i>EC</i> | <i>NO</i> |
|-----------------|----------|--------------|-----------|-----------|-----------|
| $\Sigma$        | 1        |              |           |           |           |
| PM 10           | 0.128    | 1            |           |           |           |
| OC              | 0.928    | 0.833        | 1         |           |           |
| EC              | 0.318    | 0.650        | 0.647     | 1         |           |
| NO              | 0.197    | -0.120       | 0.519     | 0.904     | 1         |

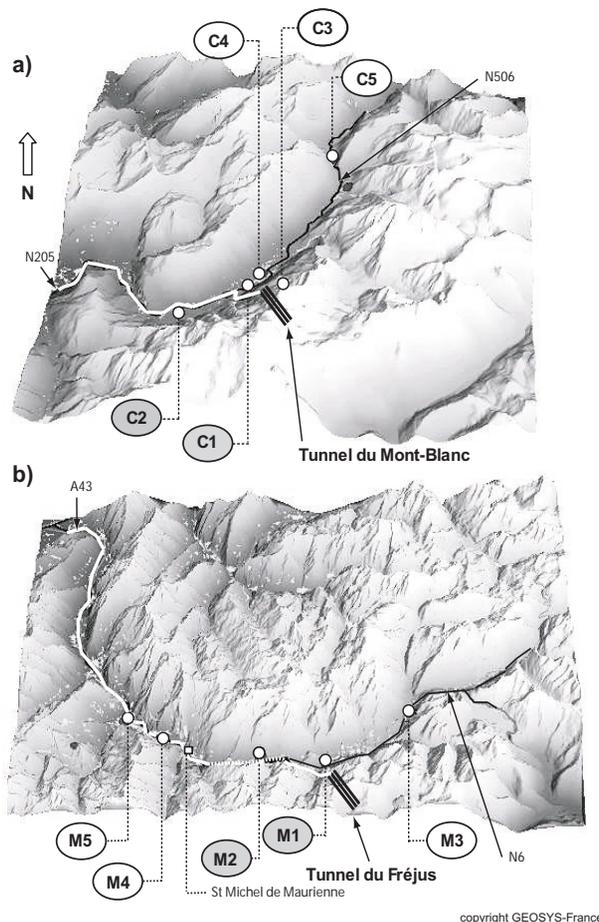
| <i>Period 4</i> | $\Sigma$ | <i>PM 10</i> | <i>OC</i> | <i>EC</i> | <i>NO</i> |
|-----------------|----------|--------------|-----------|-----------|-----------|
| $\Sigma$        | 1        |              |           |           |           |
| PM 10           | 0.886    | 1            |           |           |           |
| OC              | 0.696    | 0.940        | 1         |           |           |
| EC              | 0.685    | 0.866        | 0.931     | 1         |           |
| NO              | 0.812    | 0.928        | 0.890     | 0.753     | 1         |

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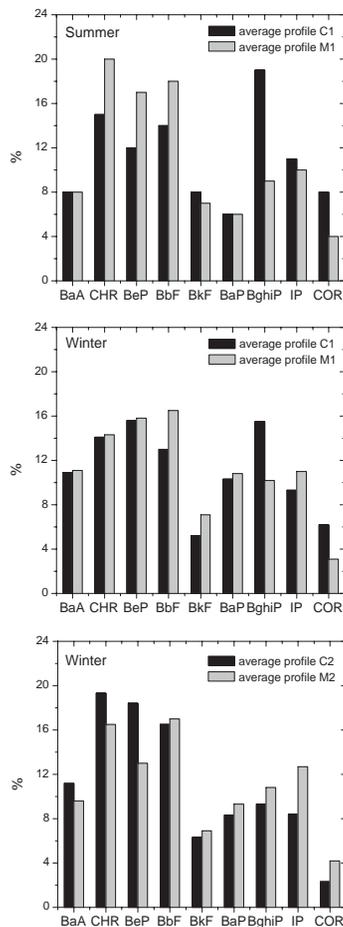


**Fig. 1.** Map of the two alpine valleys, **(a)** Chamonix Valley, and **(b)** Maurienne Valley, and sampling sites during the summer 2000 and winter 2001 campaigns, respectively. Shaded points (C1, C2 and M1, M2) represent sites instrumented for PAH sampling.

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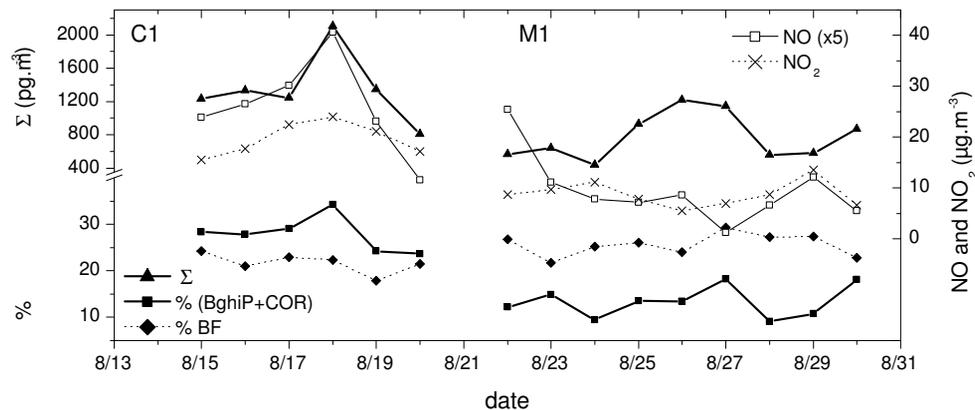


**Fig. 2.** Average PAH chemical profiles. Relative concentrations are calculated for the ratio of individual PAH with the total PAH concentration  $\Sigma'$ .

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**Fig. 3.** Evolution of  $\Sigma$ , NO (x5) and NO<sub>2</sub> concentration, relative concentration of BghiP+COR, and of BF (BbF+BkF) during the summer campaign at C1 and M1 sites.

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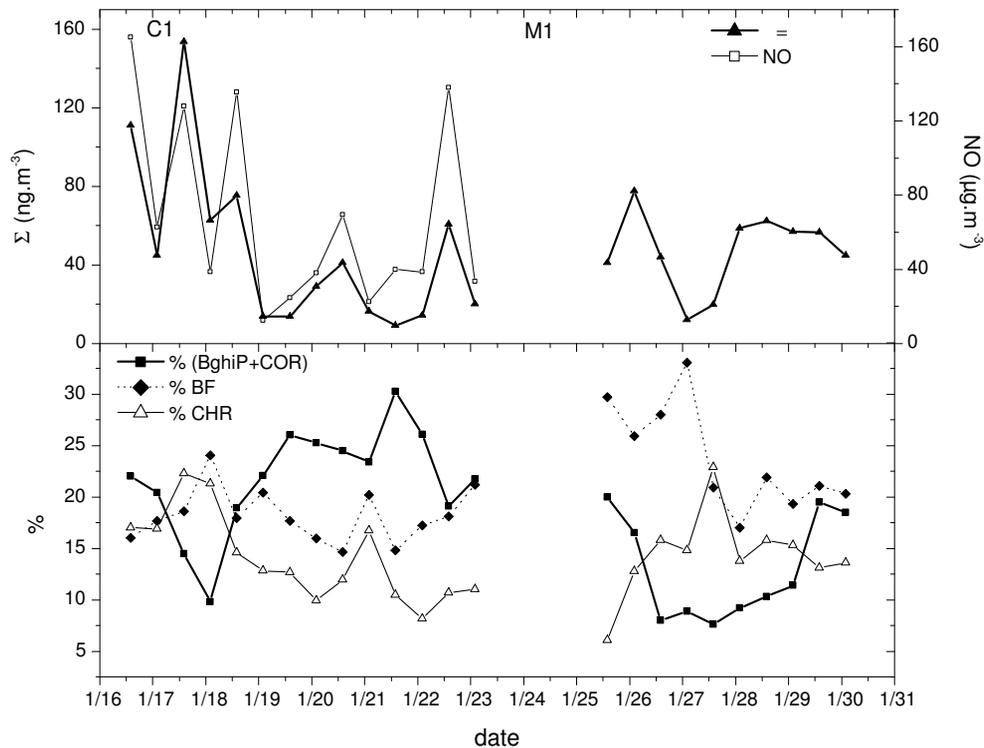
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**Fig. 4.** Evolution of  $\Sigma$  and NO concentrations and of relative concentrations of BghiP+COR, of BF (BbF+BkF) and of CHR at C1 and M1 during the winter campaign.

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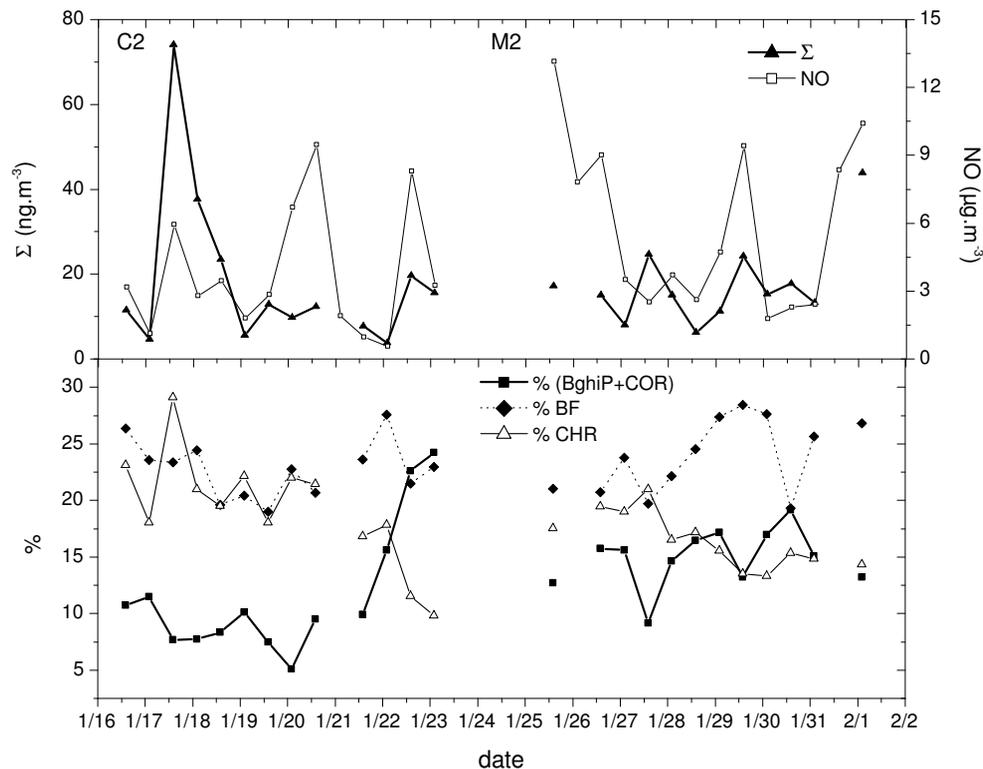
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**Fig. 5.** Evolution of  $\Sigma$  and NO concentrations and of relative concentrations of BghiP+COR, of BF (BbF+BkF) and of CHR at C2 and M2 during the winter campaign. For M1 and M2,  $\Sigma$  is multiplied by 5.

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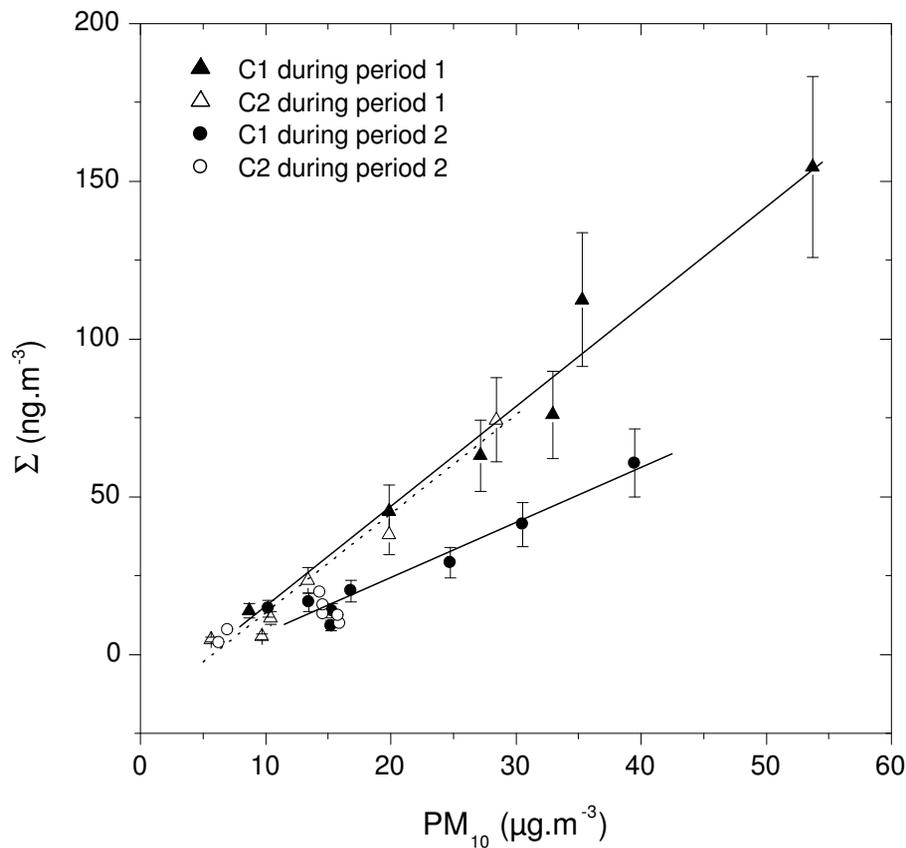
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**Fig. 6.** Correlations between the total PAH concentrations and PM<sub>10</sub> obtained in the Chamonix valley for the two sampling sites during the winter campaign.

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