

Interactive comment on “Polycyclic aromatic hydrocarbons in the atmosphere of two French alpine valleys: Temporal trends and examination of sources” by N. Marchand et al.

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First, we would like to thank Dr C. Halsall for his useful comments that will allow improvement of the paper. The revised manuscript will incorporate several suggestions made by the referee. Here are answers to every comments made by Dr C. Halsall.

Section 3 (and Table 1): The emission rates of PAH presented in Table 1 concern PAH in the particulate phase, as mentioned in the foot-notes. The data reported in the text also refer to particulate emissions of PAH. We will add a sentence in the revised manuscript to fully clarify this point.

Section 4.1: We suggest that the strong seasonal variation in PAH concentrations can be explained by the conjunction of several processes. One of them concerns the lower degradation in winter, without ruling out an increase of PAH emission during this sea-

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son. However, as suggested by the referee, other reactive PAH such as B(a)A also presents a great winter/summer ratio (51 at C1 and 30 at M1). These values are the strongest values measured after the B(a)P. The other PAH are characterized by winter/summer ratio in the range of 21 to 43 at C1 and 7 to 21 at M1. This seems to favour an hypothesis related to reactivity more than one linked to sources.

P10 and Fig 2 : Figure 2 is necessary to illustrate that the average PAH profiles do not allow to accurately discriminate the PAH sources. Indeed, this figure shows that no statistical differences for most of PAH in profiles is observed, while the sampling sites are characterized by different sources and conditions (rural or urban sites, winter or summer). Consequently, the study of sources apportionment must be improved taking into consideration both the contribution of specific PAH (CHR) or PAH groups (BghiP+COR, BkF+BbF) and their evolution. However, in the revised manuscript, standard deviations will be added to the figure 2, and more detailed comments will be made in the text.

P11 Para 1. We will rewrite this paragraph in order to clarify this point. Independent t-test have been performed to evaluate the differences in means between sites and seasons for relative concentrations of the three PAH or PAH groups markers used to discriminate sources. All values discussed in the text can be considered as statically different ($p\text{-level} < 0.05$). We will precise this point in the revised version. Thus, seasonal and spatial variations of these ratios provide suitable information on the influence of PAH sources. For example, during winter in the valley of Chamonix, higher contributions of B(b/k)F and CHR are observed at the rural site (C2) than at the suburban site C1 (18 and 23% for B(b/k)F and 14 and 19% for CHR at C1 and C2, respectively). At the same time, the BghiP+COR contributions are higher at the suburban site C1 (22% at C1 and 12% at C2). Considering CHR and, to a lesser extend, B(b/k)F as indicators of wood burning sources, and BghiP+COR as an indicator of gasoline sources, theses results show both the larger influence on aerosol composition of gasoline exhaust at C1 and a stronger impact of wood burning at C2.

In summer, the biomass burning source can be neglected since no fires have been

observed during the sampling period. The CHR and B(b/k)F contributions are then indicative of influence of diesel emissions. In these conditions, the comparison of the two suburban sites (M1 and C1) show higher contribution of CHR and B(b/k)F at M1, and stronger contribution of BghiP+COR at C1. Consequently, these results are in line with a higher influence of diesel vehicle source at M1 than at C1.

Section 4.2 P12, para 1: A correlation between sum-PAH and NO could not be systematic even if these compounds are both primary pollutants. Considering the short life time of NO, the strong correlation observed in the Chamonix valley shows the preponderance of PAH proximity sources. A correlation with NO₂ would have underline influences of more remote sources.

P12, para 2: The Saharan dust event observed during the summer campaign is largely discussed in Colomb et al. (2002) and Aymoz et al. (2004). We do not want to develop the discussion of this specific event in this paper, as it only concerns two of our samples. We use the term "Saharan dust associated with anthropogenic input" because this period of southerly winds is characterized by large increase of dust tracers (large particles, soluble calcium, PM₁₀) immediately followed by an increase of chemical species of anthropogenic origin (sulfate, small particles, some VOCs), most probably from the Torino area in Italy.

P12, para 2 : In order to fully understand this part we will replace the sentence by : "While the contribution of BF to sum-PAH is higher than those of B(ghi)P and COR, total PAH concentrations are more correlated to the ratio (B(ghi)P+COR)/S. Therefore, the variations of PAH concentrations seem to be linked to changes in the gasoline source, with a constant impact of diesel sources".

Section 4.2.2 P14, para 1. At site C2, PAH and PM₁₀ present low variability during period 2. In these conditions, the ratio PAH/PM₁₀ is not describing a large range of concentrations, limiting the precision on the determination of the slope, even if a correlation coefficient can be calculated. Therefore, period 2 is included in Figure 5 for

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each sampling site but the curve is not drawn for C2.

Figure 5: We think that the correlations are significant when considering the analytical errors in PAH concentrations indicated on Figure 5, in spite of the fact that only few points are available. As suggested by the referee similar plot are obtained using organic carbon (OC). This is illustrated by the strong correlation observed between PM10 and OC at each site and for the two periods. The correlations between OC and S confirms that aerosols in Chamonix valley result from anthropogenic emissions in winter.

General comments :

The manuscript will be careful proof reading before submission of the revised version. In line with comment on figure 1, we will also work on another representation of the experimental area.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 887, 2004.

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