Atmos. Chem. Phys. Discuss., 4, S693–S699, 2004
www.atmos-chem-phys.org/acpd/4/S693/

Atmospheric Chemistry and Physics Discussions

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.

N. Marchand et al.

Received and published: 11 May 2004

Reply to referee comments. Final response.

[1]Figures mentioned in the text are located on the following website : ftpobs.univ-bpclermont.fr/ATMOS/aerosols/Nicolas/ACPD/

General comments

We thank the three referees and Dr U. Pöschl for their comments and suggestions for the paper improvement. As we have previously answered to Dr Halsall we give here our opinion on the others comments. One objective of our paper is to study the capacity of some PAH to accurately discriminate sources. Our study focuses on the examination of relative concentrations of some PAH (BghiP, COR, BbF, BkF and CHR) well known

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in the literature as indicators of sources. Section 3 present a short review of PAH emission allowing to justify the choice of these indicators and to highlight the variability of emission data of PAH (comment of referee #1, point 3). The goal of this section is not to give an overview of field measurement as suggested by U. Pöschl (point 5). The comparison of our data with earlier studies of PAH is largely discussed in the section 4. Our argument is based on the weekly average values of relative concentration and their temporal evolution. In these conditions, the evolution on the relative concentrations in correlation with other atmospheric pollutants (EC, PM10) allows a qualitative interpretation of aerosol sources. This approach of source apportionment leads to conclusions in agreement with our knowledge of the PAH source in the two alpine valleys. In addition, the study is based on a important number of sample in comparison with most PAH field studies (from 6 to 14 depending of sampling site) and on sampling sites showing different characteristics (referee #1 point 7). As suggested by referee #1 (point 2), aerosol source apportionment can be also studied using quantitative models such as CMB or multilinear regression analysis (Kavouras et al., 2001). However, we think that this later approach requires both very reliable data of PAH emissions rates and the use of other molecular markers. Concerning emissions rates, values reported in literature for single a same source show high variability which strongly influenced the results obtained from quantitative model (See unpublished result on Marchand, 2003, http://tel.ccsd.cnrs.fr/, pp. 177-183,). The study of specific ratios such as those employed by Yunker et al. (2002) is also quite difficult due to the great variability of emissions rates of PAH (referee #1 point 2).

M. Sklorz (referee) (point 4), U. Pöschl (points 3 and 4), and referee #1 (point 2) have highlighted specific points concerning Gas/Particle partitioning and sampling artefact occurring during Şhi-volŤ collection. Thus it is necessary to clarify this aspect of PAH studies in relation with our work.

As most PAH field studies, no Şartefact-freeŤ sampling device allowing the quantification of both gaseous and particle phases have been employed. Conscious of the potential impact of sampling artefact occurring during collection, an high volume denuder device (30 m3 h-1) have been developed in parallel of the POVA program in our group (Marchand, 2003, http://tel.ccsd.cnrs.fr/, pp. 248-258, in French). In spite of the numerous studies discussing of physical aspects, it is at present impossible to correct particulate PAH values obtained with hi-vol samplers. However we have took some precautions prior to the discussion of our results

FLA and PYR were excluded from PAH total concentration (S) for the study of specific PAH relative concentrations. During our measurements although they are not the only semivolatile PAH, FLA and PYR are the only ones which show a significant correlation between their relative concentrations and temperature (figure 1). For the other most volatile PAH, BaA and CHR, (log p°L(20°C)= -6.02 and Ű6.06, respectively Ű Yamasaki et al., 1984-) no correlations between their relative concentrations and ambient temperature are observed (figure 1 [1]). Note that in Fig 1 [1], relative concentrations of these two later PAH are calculated in relation to SŠ (SŠ=S-FLA-PYR) to avoid biases due to the relation between FLA and PYR and temperature. The same observations can be made with summer results. However, due to source and photo oxidation processes effects, no global trend can be found between relative concentration (even with FLA and PYR) and temperature considering both winter and summer data sets. Considering these results, Gas/Particle partitioning and physical artefact, do not appeared as fundamental factors governing relative concentrations of CHR, BaA and heavier PAH. Consequently slight differences observed in the CHR relative concentrations between winter and summer (M. Skorltz, point 4) appear in relation with photo-oxidation processes. Indeed as shown in figure 2 [1], BaP and BaA, the most reactive PAH, present at the two sites the most important seasonal variations. BaP and BaA concentrations increase in winter by 200 and 150% with respect to SŠ increase. These seasonal variations of BaP and BaA lead to an increase of their relative concentration from 14 % in summer to 25 % in winter. Potential increase of the CHR relative concentration during winter due to gas/particle partitioning and increase of wood burning emissions is partly hidden by this phenomenon.

Another question by Referee #1 (point 2) and U.Pöschl (point 4) concerns chemical degradation of PAH occurring during collection. While this phenomenon is correctly known it is impossible to accurately correct data of O3 chemical degradation. Recently, results obtained by Tsapakis et al. (2003), even if the number of sample is quiet low, show that 27% of total PAH concentration in the particle phase can be lost by ozone degradation occurring during hi-vol sampling (sampling duration : 24h; average ozone concentration : 58 ppbv). Among PAH, BaP is one of the most reactive and O3 degradation can lead to a loss ranging from 42 to 55% of the mass. They also show that in atmosphere characterized by low O3 levels (27 ppbv), 24h hi-vol sampling do not affect substantially particulate PAH concentrations, even for BaP. During POVA intensive sampling periods O3 concentration ranged between 3 and 45 ppbv in winter and between 17 and 44 ppbv in summer (mean concentration : 21.2 ppbv during winter and 31.5 ppbv during summer). Thus, particulate PAH concentration should not be altered significantly by O3 degradation. In addition as shown in figure 3 [1], no correlations can be found between relative concentrations of BaP and O3 concentrations. Therefore, reactions between PAH and ozone occurring during the collection do not appear as a fundamental factor governing PAH concentrations during our survey.

The final version will take into account these general comments, and some part will be rewritten or added in order to clarify or improve these different points. Also, the manuscript will be careful proof reading by a native English speaker before submission of the revised version.

Specific comments

Referee #1 :

1) Efforts will be made to reduce the text. 2) See general comments. 3) We think that this short review is useful (see general comments) in agreement with the two others referees (C. Halsall and M. Sklorz). 4) Already modified in the ACPD published version. 5) Already modified in the ACPD published version. 6) see general comments. 7) see

general comments.

M. Sklorz

1) In line with comment on figure 1, we will work on another representation of the experimental area with both regional and local scale representations. 2) Main sources in each valley are described in section 2.1. We will add a short conclusions about the main PAH sources in the section 2.1 final version. With regard to wood burning sources, there is no estimation of the wood quantities burned in each valley. Official values concerning heating mode are only available at the region scale (Région Rhône Alpes). Considering these values, relative to 1996, wood burning represent 20 % of total energy used for individual heating. But this value do not take into consideration the specificities of the valleys (climate, tradition, tourist activitiesĚ). Thus it is very difficult to accurately estimates the quantities of wood burned into each valleys. Nevertheless this source is potentially important and certainly above 20% of total energy used for individual heating. 3) Text will be modified to point out more distinctly the high variability of emission data of PAH. 4) See general comments. 5) It will be corrected. 6) The question of studying the ratio BeP/BaP have been considered during the preparation of this paper. We decided not to speak about it for two essential reasons. First it did not bring new informations. BeP/BaP study confirmed interpretations relating to the concepts of distance to the sources. The second reason was that this ratio is not only influenced by atmospheric degradation processes. Source effect must not be neglected. Indeed considering Schauer et al (2001), Rogge et al (1998), Rogge et al (1993) and Fraser et al (1998) results, BeP/BaP ratios range between 0.46 to 0.94 for wood combustion and between 1.05 and 2 for vehicular sources. Interpretations of the variability of this ratio could become difficult and such discussions would make the text heavier and longer.

References

Kavouras, I.G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E.G., Von Baer, D., Oyola, P. : Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons using multivariable methods. Environ. Sci. Technol., 35, 2288-2294, 2001.

Yamasaki, H., Kuwata, K., Kuge, Y. : Determination of vapor pressure of polycyclic aromatic hydrocarbons in the super cooled liquid phase and their adsorption on airbone particulate matter. Nipon Kagaku Kaishi 8, 1324-132, 1984.

Yunker, M.B., MacDonald, R.W., Vingarzan, R., Mitchell, H., Goyette, D., Sylvestre, S. : PAHs in the Fraser River basin: a critical appraisal of PAH ratios of PAH source and composition. Organic Geochemistry, 33, 489-515, 2002.

Marchand, N.: Etude de la composante organique de lŠaérosol atmosphérique : cas de deux vallées alpines (Chamonix et Maurienne) et développement analytique. PhD thesis. Université de Savoie. (in french), 2003.

Tsapakis, M., Stephanou, E.G. : Collection of gas and particle semi-volatile organic compounds: use of an oxidant denuder to minimize PAH degradation during sampling. Atmos. Env., 37, 4935-4944, 2003.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T.: Measurement of emissions from air pollution sources. 3. C1-C29 organic compounds from fireplace combustion of wood. Environ. Sci. Technol., 35, 1716-1728, 2001.

Rogge, W.F., Hidemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T.: Sources of fine organic aerosol. 9. Pine, Oak, Synthetic Log combustion in residential fireplaces. Environ. Sci. Technol., 32, 13-22, 1998.

Rogge, W.F., Hidemann, L.M., Mazurek, M.A., Cass, G.R.: Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equiped automobiles and heavy duty diesel trucks. Environ. Sci. Technol., 27, 636-651, 1993.

Fraser, M.P., Cass, G.R., Simoneit, B.R.T. : Gas-phase and particulate-phase organic compounds emitted from motor vehicle traffic in Los Angeles. Environ. Sci. Technol.,

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32, 2051-2060, 1998.

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

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