An annual study of organic atmospheric aerosol from a rural site of Madrid (Spain)

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Abstract. The organic fraction of aerosols was characterized in two particulate matter fractions, PM2.5 and PM10 from a rural site of Madrid, since April 2004 to March 2005. Aerosol-associated n-alkanes, polycyclic aromatic hydrocarbon (PAH), alcohols and acid compounds were measured in order to evaluate its seasonal variability and sources. An analytical protocol has been developed; samples were Soxhlet extracted, cleaned-up by silica gel column chromatography and subsequently analyzed by gas chromatography mass spectrometry (GC-MS). Polar compounds were previously derivatised with BSTFA. Samples studied contain *n*-alkanes ranged from C_{14} to C_{40}, thirteen PAHs from acenaftene to Benz(ghi)perilene have been quantified, and several polar compounds, as alcohols, fatty acids, and some secondary organic aerosol components, mainly some products of degradation of a-pinene. Moreover, distinct seasonal profiles were detected in both particulate fractions studied.

Key Words: Atmospheric Aerosol, Chemical Composition, Organic Compounds, PM10 / PM2.5

INTRODUCTION

The European Directive 1999/30/CE settles down maximum values of different atmospheric pollutants, between which total particulate matter is. The purpose of this Directive was to reduce their concentrations and therefore preventing and/or reducing its effects over environment and human health. In addition, the IPCC (Intergovernmental Panel on Climate Change, 1995) emphasized over the adverse impact on human health and environment produced by atmospheric aerosols. Nevertheless, within the particulate matter of atmospheric aerosol, the organic fraction is less studied and understood than the inorganic one, so it is going to be more difficult diminish its concentration.

On the other hand, within atmospheric aerosols, rural aerosols are the less studied. Nowadays, data sets of concentrations reached by organic compounds in urban areas are going to be available. Chemical composition of rural aerosol is mainly conducted by biogenic origin, with a lower anthropogenic contribution. In fact, a study about composition in a rural area is of particular interest for the understanding of background of atmospheric pollution.

OBJETIVE

This work is aimed at identify several compounds of organic fraction of atmospheric aerosol collected in a rural area of Madrid (Spain) for a period of one year. There have been simultaneous studied two different fractions, PM10 and PM2.5.

EXPERIMENTAL PART

Sampling and Organic Analysis

An annual campaign took place in Chapineria, a little town situated in the south-west of the city of Madrid, collecting simultaneously two different fractions, PM2.5 and PM10. Sampling was performed using two high-volume samplers and was collected over quartz filters, previously calcinated.

Samples were Soxhlet extracted with a mixture of dichloromethane/acetone (3:1). Later, extracts were concentrated and cleaned-up by silica gel column chromatography and four fractions were obtained, alkanes, PAHs, alcohols and acids respectively. Polar compound were derivatised with BSTFA and analyzed by GC-MS, as same as alkanes, whereas PAHs were submitted to HPLC with florescence detection.

Target Compounds

It has been analyzed more than 50 organic compounds. In order to facilitate the study, these compounds were divided in four different families:

(a) aliphatic hydrocarbons (C_{14} – C_{40} n-alkanes, phytane and pristine)
(b) polycyclic aromatic hydrocarbons (Acenaphthene, Fluorene, Phenanthrene, Fluoranthene, , Benz(a)anthracene, Chrysene, Benzo(b)Fluoranthene, Pyrene, Anthracene, Benzo(k)Fluoranthene, Benzo(a)Pyrene, Dibenz(a,h)anthracene, Benzo(g,h,i)perilene)
(c) alcoholic compounds (C_{12} – C_{26} alcohols)
(d) acids compounds (C_9-C_{28} fatty acids, oleic, linoleic, pinic, pinonic, norpinonic, azelaic acids)

RESULTS AND DISCUSSION

Table 1 shows minimum, maximum and mean values of total concentration of particulate matter in both fractions together its seasonal variability.

In all seasons the mean mass concentrations of PM2.5 and PM10 was slightly lower than that measured in a urban area, for example the extent work of Ling-Yan in Beijing during 2002 (Ling-Yan *et al.*, 2006), where mean values raise 66-78 $\mu g/m^3$ for PM2.5 and the work of Chan (Chan *et al.*, 2005) for PM2.5 and PM10 fractions. Therefore, an explication of this fact was the lower anthropogenic contribution in the rural area. In addition, values measured for PM2.5 and PM10 were similar to that collected in a rural area of Portugal (Alves *et al.*, 2001).

The PM2.5 fraction showed more seasonal variability than PM10 fraction. The highest values for two fractions were reached during last days in September; corresponding with intrusion episode from Sahara.

Table 1: Minimun, maximum and mean values for PM10 and PM2.5 during the sampling period

	PM2,5 (μg/m^3)			PM10 (μg/m^3)		
	Min	**Max**	**Mean**	**Min**	**Max**	**Mean**
Spring	4,7	22,4	13,3	8,2	57,1	26,0
Summer	3,1	28,0	27,1	12,8	94,9	34,1
Autumn	4,2	37,3	18,3	5,9	109,5	34,1
Winter	6,9	64,1	21,8	11,4	87,3	37,0

Aliphatic and Aromatic Hydrocarbons

The first fraction analyzed contains *n*-alkanes ranged from C_{14} to C_{40}. *n*-alkane C_{29} usually showed the highest values in both fractions. It was remarkable the odd to even predominance mainly in PM10 fraction. Moreover in PM10 fraction, CPI and %WNA values were higher during summer than in winter, due to plants emits less amount of matter in winter than in summer and spring.

In relation with PAHs, thirteen compounds were evaluated in PM10 and PM2.5 samples. The annual average concentrations of each individual PAH in the rural area were within a range of 1 – 1500 pg/m^3 in PM10 fraction and 1 – 600 pg/m^3 in PM2.5 fraction. Benzo(ghi)perilene, Benzo(a)chrisene and Pirene were the most abundant PAH compounds identified in both fractions. The seasonal variability was 5-6 times higher during winter compared to summer in PM10 and PM2.5 fractions.

Polar Compounds

Eighteen alcoholic compounds, within the range of C_{12} to C_{30}, were identified and quantified in both fractions studied with a maximum concentration of 200 ng/m^3. CPI and %WNA values confirm the biogenic contribution to aerosol.

Last fraction contains acidic compounds. There have been identified fatty acids comprised between nonanoic and octacosanoic acid with mean values in PM2.5 fraction of 50.8 ng/m^3, 170.3 ng/m^3, 208.7 ng/m^3 and 139.9 ng/m^3 for spring, summer, autumn and winter respectively. Moreover, some unsaturated fatty acids and three degradation products of a-pinene were quantified in both fractions. In the same way as alcohols, CPI and %WNA values confirm the biogenic contribution to atmospheric aerosol.

Seasonal Variability

For organic compounds, unlike which it happens for total concentration of particulate matter, the seasonal variability was more pronounced in PM10 samples (Figure 1). It is remarkable the fact in PM10 fraction; acids average concentration low 40 % since summer to winter, however n-alkanes and PAHs increased a lot. This variability appears

in PM 2.5 fraction slightly, only *n*-alkanes and PAHs increase its average concentrations and acids diminish it.

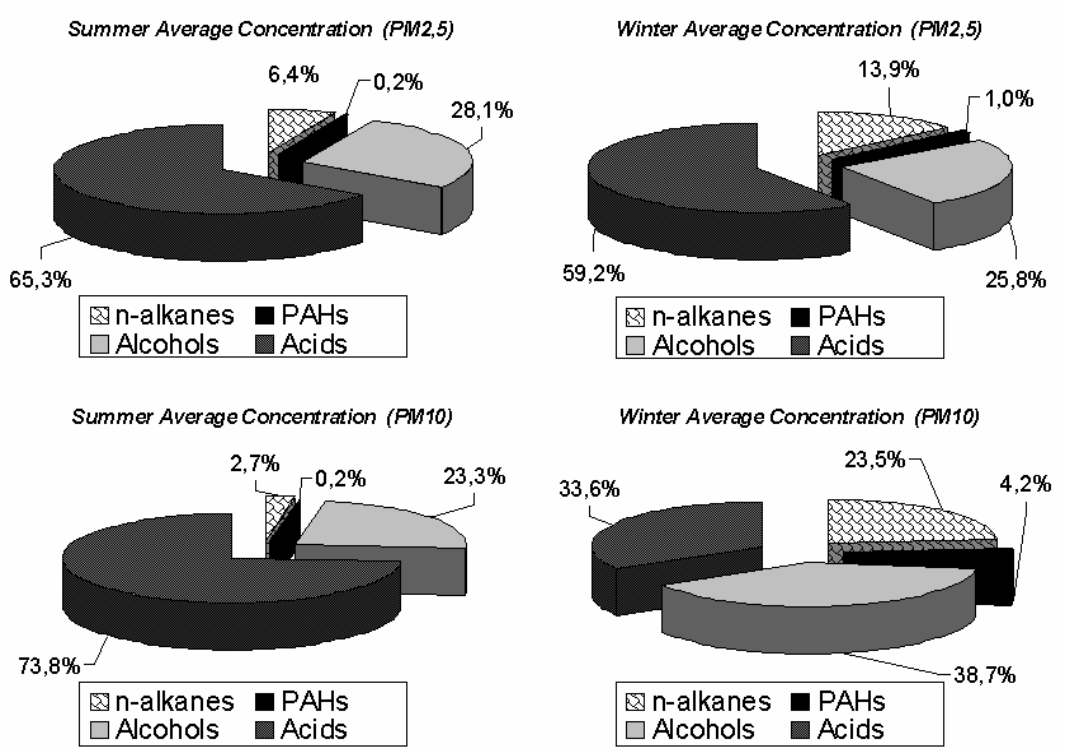

Figure 1: Average concentration of the four families of compounds studied in both fractions during winter and summer

Variability of PAH in samples studied may be due to increase of fossil fuel combustion for domestic heating during winter, meanwhile acids variability was due to lower biogenic emissions by plants during winter.

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