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Discriminating the regional and urban contributions in the North-Western Mediterranean: PM levels and composition

Jorge Pey*, Xavier Querol, Andrés Alastuey

Institute of Environmental Assessment and Water Research, IDÆA-CSIC, Temporary address: C/Lluis Solé i Sabaris, s/n, 08028, Barcelona, Spain

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A B S T R A C T

Simultaneous measurements of the PM concentration levels and chemical composition of atmospheric aerosols at a regional background (RB) and an urban background (UB) site, located in the same geographic region, allowed for the determination of their urban and regional contributions. In the specific case of the North-Western region of the Mediterranean the RB amount has been quantified in 18, 13 and 12 μg m^{-3} for PM_{10}, $PM_{2.5}$ and PM_1, respectively, whereas the UB contribution reached 22, 13 and 8 μg m^{-3}, respectively. The UB contributions in the Western Mediterranean are much higher than those observed in other European regions; especially concerning the coarse fraction. The high loads of road dust in the urban areas across the Mediterranean may account for these large differences.

The urban contributions are extremely enriched in Ca, Fe, Sb, Sn, Cu, Zn, being the main tracers of the road dust, with concentrations up to 6–8 times higher than those at the RB. Elemental carbon and nitrate are mainly derived from direct vehicular emissions. Some industrial tracers (Mn, Pb, Bi) are also enriched in the urban area. The evaluation of the Cu/Sb, Cu/Zn, Cu/Cd and Cu/Pb ratios and the high enrichment of these trace elements versus the Upper Crustal Composition average values corroborates the importance of the road-traffic emissions in the study area, also influencing the RB.

The supplementary results from a suburban site in the Balearic Islands and the evaluation of the V/Ni ratios evidence the strong signature of fuel-oil combustion processes, which is a general characteristic of the Mediterranean aerosols.

1. Introduction

Natural and anthropogenic sources contribute to the atmospheric aerosol cocktail around the world. Health, climatic and environmental effects demand investigation on atmospheric aerosols. Several epidemiological studies link increases in mortality and morbidity with atmospheric pollution in general but, in many cases, with atmospheric aerosols in particular (Dockery and Stone, 2007). The health effects of PM_x are likely to depend on several factors, including the size and composition of the particles (Franklin and Schwartz, 2007; Pérez et al., 2008, 2009). It is clear that different components of PM_x may have diverse health impacts, and although, increased PM-mass concentration is related with increased mortality and morbidity, it is still unclear which specific components should be abated to diminish the health effects from ambient aerosols.

Furthermore, the climatic effects of atmospheric aerosols are now under exhaustive investigation due to the public concern about climatic change. It is known that atmospheric aerosols play an important role on climate (IPCC, 2007), heating or cooling the atmosphere as function of its composition, contributing to creating or destroying clouds, among others. Nevertheless, several questions remain open including the future scenarios and the role of the complexity of the aerosols as a whole in a given area. The study of the size distribution, the chemical composition, the mass/number concentration, the atmospheric processes and the emission sources appears to be necessary to carry out these climatic studies.

Regional background (RB) sites are ideal locations to study the atmospheric aerosols in a regional context, where they will be controlled mainly by the meteorological conditions rather than local sources. Consequently, these sites are needed for the evaluation of climatic effects of the atmospheric aerosols. The research in this kind of environments has raised importance in Europe in the last years owing to the creation of the European research network EUSAAR (European Supersites for Atmospheric Aerosol Research) composed by 20 RB monitoring sites, which includes the Montseny site, used in this study.

On the other hand, great part of the population lives in urban agglomerations where local anthropogenic emissions from road transport, industry, residential and domestic sources prevail.

* Corresponding author. Tel.: +34 934095410; fax: +34 934110012.
E-mail address: jorge.pey@idaea.csic.es (J. Pey).

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Severe pollution episodes may occur as a consequence of the meteorological conditions and the air pollutant emissions, which may have negative health effects. The quantification of the contributions of the local sources is the only way to discriminate between the local and the regional atmospheric pollutant concentrations. For this reason, the quantification of the urban contributions in a given city requires of a RB site in the same region.

This work integrates the measurements and interpretations carried out in two type of monitoring sites, RB and urban background (UB), located in the same region, the NW Mediterranean. The aim of this study is to quantify the UB and RB contributions of different aerosol components. The comparison between the aerosols composition in the study region with the average composition of the Upper Continental Crust may help to identify those sources influencing the urban background, and those affecting the whole region.

2. Methodology

2.1. Study area

The region selected for this study is located in the North-Eastern Spain, in the province of Barcelona. This region may be considered as representative of the NW Mediterranean. Two monitoring sites were selected, one RB (Montseny) and one UB highly influenced by traffic emissions (Barcelona-CSIC). The NE part of the Iberian Peninsula is a region highly populated, mostly concentrated in the Barcelona metropolitan area (around 4 million of inhabitants and a very dense traffic in the central area, around 6100 vehicles per km^2 compared with 1500–2000 vehicles per km^2 in most European cities), several industrial zones, power plants, and important highways crossing the area in all directions. In this situation, anthropogenic emissions are of a high importance and make this region one of the most polluted in Spain.

The intricate topography of the region in combination with the particular atmospheric dynamics of the Western Mediterranean (Millán et al., 1997; Rodríguez et al., 2001) makes this region very interesting for the study of the atmospheric aerosols. The location of the monitoring sites, the main anthropogenic activities, and geographic characteristics are shown in Fig. 1.

2.2. Monitoring sites

The Barcelona-CSIC site is located in the city of Barcelona, 68 m. a.s.l., and 150 m from Diagonal Avenue, one of the busiest roads. This site represents the UB conditions, influenced by significant traffic and industrial emissions (Pérez et al., 2008a). According to Pérez et al. (2008a), the mean annual levels of PM_{10}, $PM_{2.5}$ and PM_1 at this site varied from 39 to 42, 25–29 and 18–21 $\mu g\ m^{-3}$, respectively. The number of exceedances of the daily limit value of 50 $\mu g\ m^{-3}$ of PM_{10} ranged from 58 to 104 in the period 2003–2008, with the highest number in 2006.

The Montseny site is situated 50 km NNE of Barcelona, at 720 m. a.s.l., in a forested natural park declared as Biosphere reserve by UNESCO in 1978. This site represents the RB conditions in the NE of Iberia (Pérez et al., 2008b). Currently, the Montseny and 19 other RB sites constitute the EUSAAR (European Supersites for Atmospheric Aerosol research) network. Pérez et al. (2008b) reported mean levels (2002–2007) of PM_{10}, $PM_{2.5}$ and PM_1 of 17, 13 and 11 $\mu g\ m^{-3}$, respectively.

2.3. Instruments and measurement schedule

PM-mass concentrations were continuously monitored, on hourly basis, at both sites using GRIMM laser spectrometers (model 1107 at Montseny and 1108 at Barcelona-CSIC). These instruments provide real-time concentrations of the number of particles in different grain sizes from 0.3 to 20 μm, which are converted to mass concentrations (PM_{10}, $PM_{2.5}$ and PM_1) by applying specific algorithms. The PM-mass concentrations were corrected with the factors obtained at each site from the comparison between real-time and gravimetric measurements.

PM_{10} and $PM_{2.5}$ were sampled at each site (collected during continuous sampling periods of 24-h) with a frequency of two samples per week and fraction by using high-volume instruments (at a flow of 30 $m^3\ h^{-1}$) MCV-CAV and DIGITEL-DH80. These instruments were set up with identical DIGITEL inlets for PM_{10} and $PM_{2.5}$.

2.4. Filter analysis and chemical determination

PM_{10} and $PM_{2.5}$ sampling was effectuated on quartz fibre filters Schleicher and Schuell (QF20 150 mm). Previously, the filters were

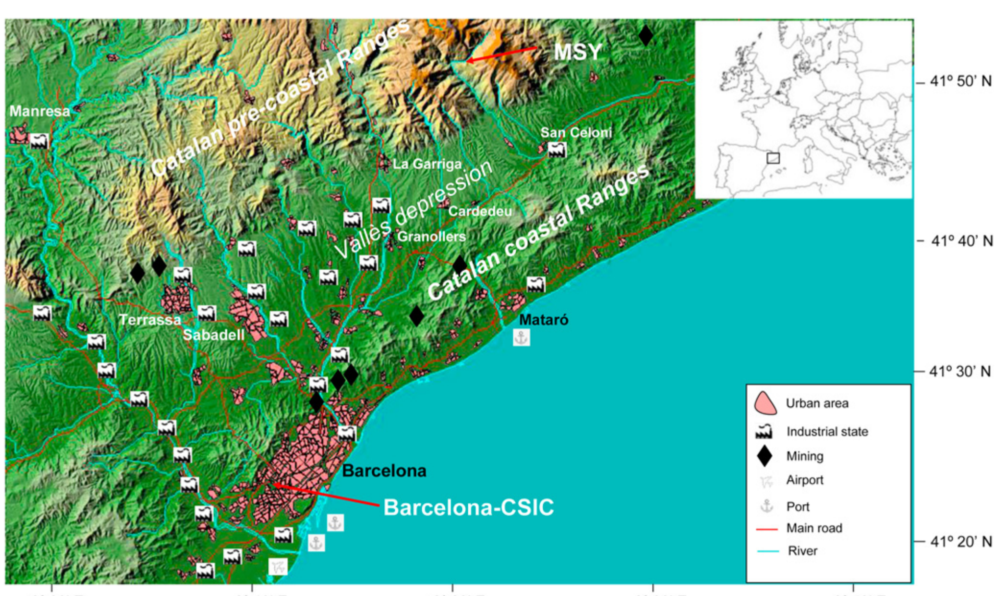

Fig. 1. Map of the study area, showing the monitoring sites (Barcelona-CSIC, UB; and MSY, RB).