Available online at www.sciencedirect.com
ScienceDirect
Atmospheric Environment 42 (2008) 1677–1691
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

# Partitioning of major and trace components in $PM_{10}$–$PM_{2.5}$–$PM_1$ at an urban site in Southern Europe

N. Pérez, J. Pey, X. Querol*, A. Alastuey, J.M. López, M. Viana

*Institute of Earth Sciences 'Jaume Almera', CSIC, C/Lluis Solé i Sabarís s/n, 08028 Barcelona, Spain*

Received 1 August 2007; received in revised form 13 November 2007; accepted 19 November 2007

**Abstract**

Partitioning of major and trace components in $PM_{10}$–$PM_{2.5}$–$PM_1$ at an urban site in Barcelona (Spain) in the Western Mediterranean was studied in the period 2005–2006. Particular attention was paid to the partitioning of mineral matter and to the evidence of possible interactions of mineral matter with other pollutants (gaseous pollutants and secondary PM). The results showed a high contribution of mineral matter (mainly anthropogenic, but sporadically associated with African dust outbreaks) in levels of both $PM_{10}$ and $PM_{2.5}$. A high proportion of nitrate was also present in the coarse fractions as a result of the interaction of mineral matter with gaseous pollutants. As at most urban sites in Europe, sulphate and carbonaceous aerosols are mainly present in the finer PM fractions. The $PM_{1-2.5}$ fraction resembled that of $PM_{10}$ in composition. The chemically unaccounted fraction (mostly bounded water) had also a fine grain size, probably because of the fine size of the hygroscopic aerosol components. The data series follow an increasing trend for $PM_1$ levels (and less clearly for $PM_{2.5}$) from 1999 to 2006, whereas no trend is observed for $PM_{10}$.

The contributions of African dust and regional soil resuspension to the annual $PM_{10}$ levels has been estimated in around 1–2 and 2–3 $\mu g\,m^{-3}$ in this part of Spain. The African dust outbreaks accounted for around 15–20 exceedances of the European daily $PM_{10}$ limit value.

Finally, the data obtained were compared with data from selected European sites to highlight major differences in levels and speciation of PM.


*Keywords:* Atmospheric particulate matter; Speciation; Urban; Pollution; Mineral dust; Saharan dust

## 1. Introduction

Atmospheric particles are emitted from a wide variety of anthropogenic and natural sources, and consequently their physical and chemical properties may vary widely. In accordance with the atmospheric sciences, the fine PM mode includes particles $<1\,\mu m$ ($PM_1$; Whitby, 1978; Wilson and Suh, 1997). This is due to the fact that most particles in the coarse fraction ($>1\,\mu m$) are primary and generated by mechanical processes (such as mineral dust and sea spray). Coarse secondary particles may also be found (Wakamatsu et al., 1996; Querol et al., 1998), due to chemical interaction of gases with primary particles of crustal or marine origin (most $>1\,\mu m$). In the fine fraction ($PM_1$) particles may be primary (such as diesel soot), or secondary formed from

*Corresponding author. Fax: +34 93411 0012.
*E-mail address:* xavier.querol@ija.csic.es (X. Querol).

1352-2310/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2007.11.034

gaseous precursors by nucleation or by condensation on existing particles.

According to health experts, the PM fraction $<100\,\mu m$ ($PM_{100}$) is known as inhalable PM. The PM fraction $<10\,\mu m$ ($PM_{10}$) is known as the thoracic fraction since it is able to enter the thoracic airways. Finally, there is a finer size fraction ($PM<4\,\mu m$ or $PM_4$) that could penetrate the conductive airways of the tracheobronchial tree that distributes the inhaled air to the gas-exchange airways in the lungs. This fraction is known as respirable PM (US-NIOSH—National Institute for Occupational Safety and Health, Centres for Disease Control and Prevention-guidelines). However, in air quality $PM_{10}$ and $PM_{2.5}$ ($PM<2.5\,\mu m$ or alveolar fraction) are usually selected as monitoring parameters in worldwide environmental standards. Thus, in air quality, the coarse fraction is considered the one between 2.5 and 10 μm ($PM_{2.5-10}$), whereas $PM_{2.5}$ is considered the fine fraction. This particular size discrimination is due to the fact that fine and coarse particles generally have distinct sources and formation mechanisms. However, as stated above, for the atmospheric scientific community these PM size ranges are not related to the formation mechanism. US-EPA (2004) states: 'Over the years, the terms fine and coarse, as applied to particles, have lost the precise meaning given in Whitby's (1978) definition. In any given article, therefore, the meaning of fine and coarse, unless defined, must be inferred from the author's usage…. Fine particles and $PM_{2.5}$ are not equivalent terms.'

In addition to the local and regional anthropogenic PM emissions, both the levels and composition of ambient air PM depend on climatology (mainly temperature, humidity, photochemistry, resuspension of soil particles, rain scavenging potential, re-circulation of air masses, dispersive atmospheric conditions) and on the geography (mainly proximity to the coast, topography, soil cover and proximity to arid zones) of a given region. Therefore, wide variations in PM levels and characteristics may be expected when considering different European regions such as the Southern Mediterranean, Eastern European or Scandinavian countries with very different climatologic and geographical patterns. Diverse environmental conditions and PM source characteristics may condition size partitioning of the PM components. Thus, a high load of PM mineral matter in dry regions of the EU may favour interaction with gaseous pollutants and give rise to a high proportion of coarse secondary PM (Harrison and Pio, 1983) when compared with wet and cold regions. Likewise, warm conditions may favour the partitioning of atmospheric pollutants towards the gaseous phases, which in turn may also interact with the coarse components and increase the secondary coarse PM load (Harrison and Kito, 1990; Wakamatsu et al., 1996).

This study focuses on the chemical speciation of $PM_{10}$, $PM_{2.5}$ and $PM_1$ during a 1-year period (October 2005–October 2006) at an urban site in Barcelona (North-eastern Spain), with special emphasis on mineral matter in order to better understand: (a) the mean partitioning of major and trace PM components, (b) the seasonal variations and (c) their source origin. Furthermore, $PM_{10}$ and $PM_{2.5}$ 1999–2006 data and other PM data from prior studies carried out in Barcelona are also considered to support interpretations.

Data on levels and speciation of $PM_1$ in Europe are very scarce, especially in Southern Europe. Pakkanen et al. (2003) furnished data on $PM_1$ samples in Helsinki; Spindler et al. (2004, 2006) in a rural area of Germany; and Putaud et al. (2002), Vecchi et al. (2004), Giugliano et al. (2005) and Ariola et al. (2006) in different sites of Italy. The results of the partitioning of PM components in the $<1$, 1–2.5, and 2.5–10 μm fractions in the study area (highly dust polluted) may help to yield further insight into the influence of mineral matter on the different PM grain size fractions, and to provide evidence of possible interactions of mineral matter with other pollutants (gaseous pollutants and secondary PM pollutants).

## 2. Methodology

### 2.1. Sampling and measurements

The PM monitoring site in Barcelona (North-eastern Spain) selected for this study is an urban background station (Barcelona-CSIC) exposed to road traffic emissions from the Diagonal Avenue (approximately 150 m distance), one of the largest avenues in the city. The monitoring station is located on the roof (two storeys) of the Institute of Earth Sciences "Jaume Almera". The levels of $PM_{10}$, $PM_{2.5}$ and $PM_1$ were measured continuously by means of a laser-spectrometer dust monitor (Grimm Labortechnik GmbH & Co. KG; models 1107 and 1108). Twenty-four hour samples of $PM_{10}$, $PM_{2.5}$ and $PM_1$ were simultaneously collected on quartz micro-fibre filters (Schleicher and Schuell;