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Spatial variability of trace elements and sources for improved exposure assessment in Barcelona

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HIGHLIGHTS

- Trace and major elements PM_{10} and $PM_{2.5}$ concentrations at 20 sites in Barcelona.
- Ba, Cr, Cu, Fe, Mn, Mo, Pb, Sn, Zn and Zr in higher concentrations at traffic sites.
- Spatial variations related to non-traffic sources observed for specific elements.
- Sources: road traffic, fueloil combustion, sulphate, industry, mineral, marine.
- Improved exposure assessment to be exploited by epidemiological studies.

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ABSTRACT

Trace and major elements concentrations in PM_{10} and $PM_{2.5}$ were measured at 20 sites spread in the Barcelona metropolitan area (1 rural background, 6 urban background, 13 road traffic sites) and at 1 reference site. Three 2-week samples per site and size fraction were collected during 2009 using low volume samplers, adding a total of 120 samples. Collected samples were analysed for elemental composition using Energy Dispersive X-ray fluorescence (XRF). EC, OC, and hopanes and steranes concentrations in $PM_{2.5}$ were determined. Positive Matrix Factorisation (PMF) model was used for a source apportionment analysis. The work was performed as part of the ESCAPE project.

Elements were found in concentrations within the usual range in Spanish urban areas. Mineral elements were measured in higher concentrations during the warm season, due to enhanced resuspension; concentrations of fueloil combustion elements were also higher in summer. Elements in higher concentration at the traffic sites were: Ba, Cr, Cu, Fe, Mn, Mo, Pb, Sn, Zn and Zr. Spatial variations related to non-traffic sources were observed for concentrations of Br, Cl, K, and Na (sea salt origin) and Ni, V and S (shipping emissions), which were higher at the coastal sites, as well as for Zn and Pb, higher at sites closer to industrial facilities.

Five common sources for PM_{10} and $PM_{2.5}$ were identified by PMF: road traffic (with tracers Ba, Cr, Cu, Fe, Mo and Zn); fueloil combustion (Ni and V); secondary sulphate; industry (Pb and Zn); and mineral source (Al, Ca, Mg, Si, Sr and Ti). A marine aerosol source, a mixture of sea salt with aged anthropogenic aerosols, was found only in PM_{10}. EC, hopanes and steranes concentrations correlate strongly with the PM_{10} road traffic source contributions, being hence all attributed to the same source. OC may arise from other sources in addition to road traffic and have a high contribution of secondary OC.

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Significant spatial and temporal variation in the $PM_{2.5}$ and PM_{10} elemental composition was found. Spatial patterns differed per element, related to the main source. The identified source contributions can be used in health studies of source-specific particles.

1. Introduction

Exposure to air pollution has adverse health effects, including increased mortality and morbidity (Cohen et al., 2005; Perez et al., 2009; Zanobetti and Schwartz, 2009). Most of the health studies are based on ambient measurements taken at a single sampling point in a city, but the pollutants concentrations may vary across the city (Hoek et al., 2002; Minguillón et al., 2012b; Mangia et al., 2013). Therefore, accounting of the spatial variability within a city would allow an improved exposure assessment, which could have an important impact on the effect estimates (Setton et al., 2010; Kloog et al., 2013). This variability may differ between cites due to differences in urban structure, vehicle fleet composition and fuel types. Moreover, current estimates of the European health impact of ambient particulate matter (PM) are primarily based on exposure–response relationships established in studies from North America. Hence the need of studies on recent and current exposures in Europe using refined exposure assessment tools is clear.

The ESCAPE project (European Study of Cohorts for Air Pollution Effects, www.escapeproject.eu) aims to investigate long-term effects on human health of exposure to air pollution in Europe. The overall strategy is to efficiently utilise health and confounder data from existing European cohort studies by adding air pollution exposure assessment, focussing on spatial variation of long-term average ambient PM, PM composition and NO_x concentrations in a number of European cities.

The present study focuses on the city of Barcelona, as one of these cities. Barcelona city has a high traffic density in comparison to other European cities, a large proportion of diesel vehicles, and a specific geography and city design, with abundant semi-tall buildings and relatively narrow streets leading to the known street canyon effect (Mirzaei and Haghighat, 2012). Several studies on the air quality of Barcelona, including PM source apportionment, have been carried out (Querol et al., 2001; Amato et al., 2009a; Perez et al., 2009; Pérez et al., 2010). Nevertheless, they do not cover the spatial variation of ambient pollutants and source contributions. Knowing the spatial distribution of the contribution of different sources of ambient PM and not only the ambient pollutants concentrations may be a useful tool to identify the location of the sources and to better understand how the emissions are transported through the city. Therefore, the present study aims at evaluating the pollution by particulate matter in Barcelona and its chemical composition in terms of spatial and temporal variability, and at identifying the main PM sources and studying the spatial variation of their contributions.

2. Methods

2.1. Sampling sites, schedule and instrumentation

There is a well-defined methodology followed during the ESCAPE study regardless of the specific area of study (www.escapeproject.eu/manuals/) and detailed methods can be found elsewhere (Eeftens et al., 2012). For the exposure assessment, 20 sites were selected in Barcelona, together with a reference site (Fig. 1, Table S1). From those, 6 sites were classified as urban background (UB), 13 sites were traffic sites (TR), 1 site was considered rural background (RB) and the reference site was located in an urban background area.

PM_{10} and $PM_{2.5}$ samples were collected for three periods of 14 days per site in the cold, warm and one intermediate temperature season during 2009. The sampling was done 15 min every 2 h, so that a 42-h sample was collected over the 14-days sampling period. Due to the limited amount of samplers, the sampling was performed simultaneously at four sites at a time. The reference site was instrumented similar to the other sites and two-weeks samples were taken during the whole period.

PM samples were collected using Harvard impactors at a flow rate of 10 L per minute on 37 mm Andersen 2 μm pore size Teflon filters. The air flow was measured using rotameters before and after sampling, excluding samples with a start or end flow below 8 L per minute. Filters were weighed following the ESCAPE weighing protocol (www.escapeproject.eu/manuals/). For extended $PM_{2.5}$ characterisation, additional samples were collected on quartz filters (QMA, Whatman).

2.2. Chemical analysis and quality control

Collected PM_{10} and $PM_{2.5}$ samples (on Teflon filters) were analysed for elemental composition using Energy Dispersive X-ray fluorescence (XRF). Methods are described by De Hoogh et al. (2013). Briefly, forty-eight elements were measured in Cooper Environmental Services, Portland USA. For quality control, NIST reference material (SRM 1228 and SRM 987) was analysed and repeated analysis of a multi-elemental quality control standard (Multi 30585) were performed. Furthermore replicate analyses of

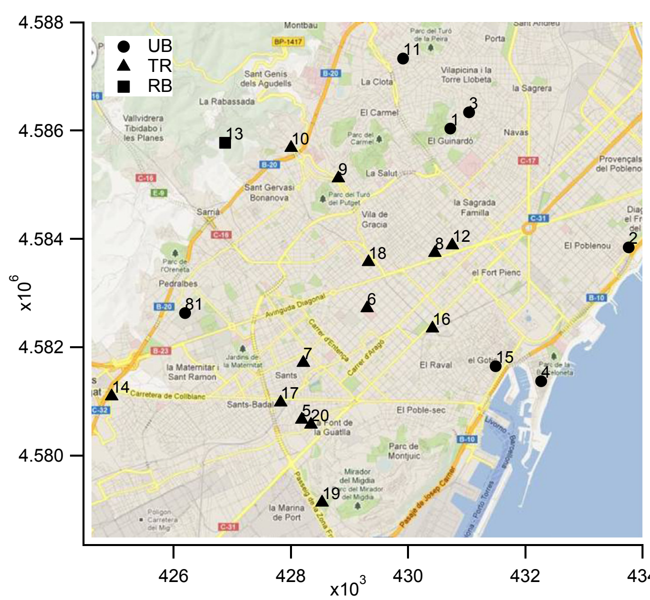

Fig. 1. Map of the Barcelona metropolitan area with the location of the monitoring sites with the corresponding identification numbers (ID). UB: urban background; TR: traffic; RB: rural background. *Y* and *X* axis are UTM coordinates. Site 81 is the reference site.