Within-city variability as a tool for source apportionment of trace elements. Application to the Barcelona metropolitan area

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Trace and major elements concentrations in PM_{10} and $PM_{2.5}$ were measured at 20 sites spread in the Barcelona metropolitan area (6 urban background sites, 13 road traffic sites and 1 rural background site). Three 2-week samples per site and size fraction were collected during 2009 using low volume samplers, adding a total of 120 samples. Additionally, a reference site was instrumented similar to the other sites and was used for seasonal correction of the data. Collected samples were analyzed for elemental composition using Energy Dispersive X-ray fluorescence (XRF). The work was performed as part of the ESCAPE project, which aims to investigate long-term effects on human health of exposure to air pollution in Europe.

Elements were found in concentrations within the usual range in Spanish urban areas (Querol et al., 2008). Some elements, such as Al, Na, Ni, S and V were recorded in higher concentrations during the warm period (spring+summer) with respect to the cold period (autumn+winter). Al is associated with mineral matter, which is higher during the warm season due to enhanced soil resuspension due to drier conditions. Na is associated with sea salt, with a typical higher contribution in summer. Ni and V are associated with fueloil combustion, with a contribution typically higher during the warm season. S is assumed to be present as sulphate, higher in summer and lower in winter due to its temperature-dependent particle-gas equilibrium.

Elements found in higher concentration at the traffic sites were: Ba, Cr, Cu, Fe, Mn, Pb, Sn, and Zn, which can then be attributed to the influence of road traffic (including road dust resuspension). On the contrary, some other elements did not show any significant difference between traffic sites and urban background sites, indicating a more regional behaviour: Al, Ca, Cl, K, Mg, Na, Ni, P, Rb, S, Si, Sr, and V.

Some spatial variability, not related to the type of site, was observed for some elements. Thus, Cl and Na concentrations were higher at the sites close to the coastal line, whereas concentrations diminished with increasing distance to the coast, evidencing the sea spray origin of these two species. Ni and V concentrations were highest at the site closest to the port, pointing to the influence of the ship emissions on the ambient concentrations of these two elements (Figure 1 shows average V concentrations as an example). The spatial variation of some other elements needs to be further investigated to be able to conclude on a specific origin.



Figure 1. Average vanadium concentrations in PM_{10} at the Barcelona sites during 2009.

On average, the SiO₂/Al₂O₃ ratio was 3.4 in PM_{2.5} and 3.6 in PM₁₀, ranging from 3.0 to 3.7 in PM_{2.5} and from 3.3 to 3.9 in PM₁₀ as averages for each of the sites. No significant differences were found for different type of sites indicating that the sources affecting the urban background sites, the traffic sites and the regional background site are either the same or they have the same SiO₂/Al₂O₃ ratio. This experimental ratio will be very useful for future studies, since SiO₂ concentrations had to be estimated based on Al₂O₃ concentrations in several air quality studies, due to the impossibility of analyzing SiO₂ in quartz fibre filters.

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Querol, X., Alastuey, A., Moreno, T., et al. (2008). *Atmos. Environ.* **42**, 3964-3979.