

Mineralogy and Geochemistry of Inhalable Road Dust Particles in Three European Cities

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INTRODUCTION.

As a result of the demographic growth of large European cities, urban air pollution has become increasingly affected by traffic-related emissions in recent years. A large part of the road traffic emissions comes from the so-called non-exhaust sector. This comprises several mechanical processes that emit inhalable particles while vehicles are travelling, including wear of brakes, tyres and road pavement but mainly involving the resuspension of deposited particles due to wheel-generated turbulence.

The environmental burden of the non-exhaust particles is high for several reasons: i) brakes and road dust particles may contain components such as heavy metals, PAHs and sulphides (IARC, 1989, Schauer et al., 2006); ii) due to their coarse-size (above 2.5 µm), non-exhaust particles have a large impact on the PM mass and therefore are responsible of most of the exceedances measured in cities (EEA, 2010); iii) concern over this PM component is increasing because no abatement strategies are currently underway to combat non-exhaust emissions.

The present study aims to investigate the spatial and chemical properties of road sediments below 10 µm in three contrasting European urban environments: a densely populated major coastal Mediterranean city (Barcelona, Spain; 1.6 million inhab.), a much smaller Southern European city (Girona, Spain: 95,000 inhab.), and a moderate sized Central European city (Zürich, Switzerland: 380,000 inhab.).

METHODS.

A total of 39 samples were obtained

from the three cities. 23 of them were collected in the city centers: 8 in Zürich, 9 in Barcelona and 6 in Girona. 16 extra samples were collected in special interest sites of Barcelona: ring roads, harbour and construction sites.

A field resuspension chamber was developed for this special purpose directly vacuuming in situ the resuspended fraction < 10 µm of road dust onto filters (Amato et al., 2009). Road sediments are vacuumed from the pavement of active traffic lanes, particles are immediately resuspended in a methacrylate deposition chamber and the particles small and/or light enough to be carried by the air current continued their journey through the system (Fig. 1). These particles enter a Negretti stainless steel elutriation filter designed to only allow passage to particles <10 µm. The particles able to penetrate this barrier are finally collected on 47 mm diameter fiber quartz or Teflon membrane filters, while particles with aerodynamic diameter >10 µm are deposited in the methacrylate chamber and along the elutriation filter.

In this study, sampling was performed at all sites in a comparable surface area of one square meter (1 m²) for 30 minutes. For each location, three different square meters were sampled using three different filters to reduce casual errors and to collect enough sample for the required analyses: two quartz fiber filters 47 mm diameter Munktell were used to determine the loading of major and trace elements, OC and EC and one Teflon 47 mm diameter membrane filters (1 µm pore) Schleicher & Schuell to determine the loading of water-soluble ions. Using our method it was then possible to quantify the load of road dust <10 µm per unit area and through the chemical speciation, also of road dust components <10 µm (OC, EC, metals, sulfate, nitrate, chloride and ammonium) (Amato et al., 2009).

Mineralogy of samples was investigated by means of XRD analyses on a second batch of samples collected simultaneously to the first one. Due to the high mass sample required for XRD analysis, these samples were not particles <10µm but total sediments, collected by pincer brushing on the gutter zone. XRD analyses were



fig 1. Sampling sites.

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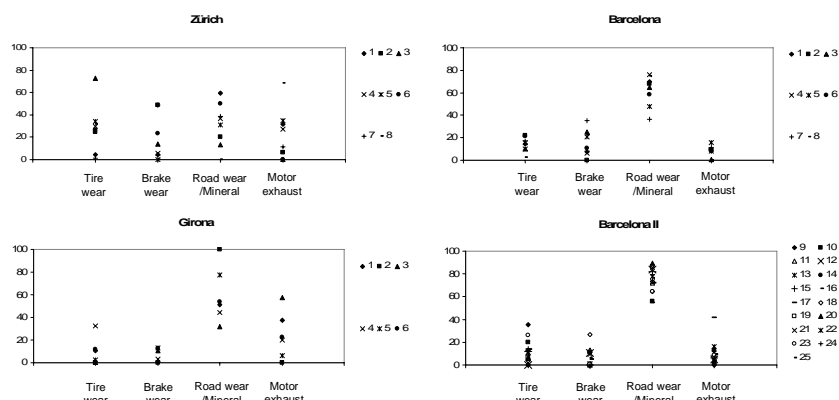


fig 2. Source contributions to road dust levels <10 µm.

performed in a Bruker D-5005 diffractometer. Results were obtained using CuKα radiation, a wavelength of $\lambda = 1.5405 \text{ \AA}$ and a secondary graphite monochromator. Analytical conditions were step size of 0.05° (with 3 s timing per step), 40 kV and 30 mA.

RESULTS AND DISCUSSION.

Loadings of road dust <10 µm from the 8 sites sampled in Zürich range from 0.2-1.3 mg m⁻², with an average of 0.7±0.3 mg m⁻², making this site the least contaminated (in terms of road dust) of the 3 under study. The loading range in Girona starts where the one of Zürich ends, with a range of 1.3-7.1 mg m⁻² and an average of 3.5±2.4 mg m⁻². By far the most polluted site in terms of road dust <10µm mass loading is Barcelona, where a range of 3.7-23.1 mg m⁻² and an average of 8.9±6.5 mg m⁻² were recorded.

A clear increase of absolute loadings (µg m⁻²) was found for OC, EC, Fe, Cr, Mn, Cu, Zn, Mo, Sn, Sb, Cs, Ba, W, Pb and Bi, together with traffic intensity, revealing the existence of some relationship between number of vehicles and loadings of (deposited) specific pollutants below 10µm.

XRD results reveal a mineralogy which in all three groups of samples is dominated by quartz, alkali feldspars, carbonate and phyllosilicates (clay minerals). Minor phases identified in some samples include iron oxides (hematite, magnetite), Na-carbonate, talc, and Fe-Mg amphibole. Quartz is the most common mineral in all the Zürich samples, as well as in most of those analysed from Girona and Barcelona. This is likely to be a road pavement-related signature, given the abundance of granite stones in all pavements of

sampling roads. The exceptions to this are two sites in Girona (C/Barcelona and Plaça Espanya) and one site in Barcelona Harbor (Dressanes), where the content of carbonate minerals (calcite and dolomite) exceeds that of quartz. Apart from these three exceptions, the combined content of calcite and dolomite form the second most common group of minerals after quartz. Calcite is more common than dolomite, especially in Barcelona where dolomite content is always low. Alkali feldspars (both albite and K-feldspar) comprise the third largest rock forming mineral group, with albite always being the more abundant of the two. Again, their presence is strongly related to road pavement eroded particles. The albite content of the samples collected at construction sites is especially high, and may derive from dust produced from a number of construction materials such as sand, aggregates or cutting of natural stones. The phyllosilicate mineral assemblage detectable using XRD includes illite, muscovite, chlorite (clinochore), kaolinite, and palygorskite. Of these, illite (a K-Fe bearing clay mineral) is the most frequently present, presumably representing resuspended soil materials derived from the geological weathering of felsic silicates (usually feldspar). The white mica muscovite is much less common than illite, but is clearly present in most of the Barcelona samples, especially in that collected at the construction work site (where illite content is unusually low), again probably recording the anthropogenic use of building materials. Finally Fe-oxides and talc might be locally related to brake wear and catalyst (only for talc, www.luzenac.com/ceramics.htm).

The most immediately obvious differences between the sites are the

high relative abundance of OC+EC and NO₃⁻, and the low amounts of crustal silicates at Zürich compared with Barcelona.

Barcelona samples are relatively enriched in crustal elements, notably Ti, Rb, Sr, Cs, and the lanthanoid elements La and Ce. In contrast, Zürich PM is appreciably more contaminated by anthropogenic metals. Averaged levels of Cu, Mo, Co, Zr, Ni, Sb, As, Nb, Zn and Cr are all over 40% higher in Zürich than in Barcelona. This metal enrichment is further demonstrated by Fig. 2 which compares the data with the composition of the upper continental crust, normalising each value to Al. The trace metals/metalloids that are most obviously enriched with respect to the Upper Continental Crust are Cd, Sb, As, Mo, Sn, Ni, Pb, Cu, Zn, Ba. Of these, Sb, Mo, Sn, Ni, Cu and Zn are most prominently enriched in Zürich, a distinctive signature attributed mainly to the influence of traffic contamination. Vanadium showed pretty constant concentrations except in Barcelona, where the site closer to the harbour showed twice as much Vanadium. A Positive Matrix Factorization was performed on this unique dataset including loadings from the three urban environments. Four factors were identified: namely Road wear/Mineral (traced by typical crustal species: Al, Ca, Fe and V, probably related to the bitumen of asphalt), Vehicular Exhaust (EC and OC), Brake wear (Fe, Cu, Zn, Cr, Sn and Sb) and Tire Wear (OC, S and Zn). Source contributions are depicted for any single sample in Fig. 2.

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