Anthropogenic influenced mineral dust ambient fine particles at an urban site in Barcelona (Spain)

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Mineral dust is a contributor of the global aerosol budget, with arid regions as principal sources. IPCC (2007) gives a best estimate of the direct mineral dust radiative forcing (RF), with the highest uncertainty in the radiative balance estimations being associated to mineral dust for both its direct and indirect effects. In addition, differentiating the anthropogenic influenced dust has important implications for health effects. Thus, several factors related to the estimation of mineral dust optical properties keep unresolved, including the anthropogenic contribution. The differentiation in the origin of the mineral dust burden is then urgent on the climate debate and a better understanding on the airborne dust properties is needed.

1. Scope and aims of the study

The Saharan desert is a major source of mineral dust in the western Mediterranean cities although mineral dust from road resuspension, industrial and other human activities is also important. The dust load favours certain heterogeneous chemical reactions in the atmosphere, increasing the complexity of the urban aerosol picture.

The aim of this study was to improve the identification of anthropogenic dust in the $PM_{2.5}$ collected in Barcelona during the "Determination of the sources of atmospheric Aerosols in Urban and Rural Environments in the western Mediterranean" (DAURE) campaign. To achieve this purpose, samples for microscopy analysis were taken at different times of the day during a winter local episode in Barcelona (25-28 February 2009) dominated by atmospheric stability. The study focused on quantifying the diurnal variations of mineral dust range and associated properties such as size, morphology and chemical composition at an individual particle level by Computer Controlled Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy techniques (CCSEM/EDS). Particles were firstly grouped into different clusters based on the elemental composition and secondly, on morphological basis. The abundance and size distributions of the different groups are explained in the discussion.

2. Methods

2.1 Sample collection

The monitoring site was located at the University Campus (urban background station, 41°23'24"N, 02° 6'58"E , 80 masl) in the western side of Barcelona, close to one of the main traffic roads of the city, the Diagonal avenue. A total of 13 samples for microscopy analysis were collected at morning (7-8 h UTC), noon (11-13 h UTC), afternoon (15-19 h UTC), and evening times (19-22 h UTC) during 4 consecutive days (25-28 February 2010). Particle loading was optimized by varying the sampling time intervals from 30 minutes to 2 hours based on the $PM_{2.5}$ concentration levels continuously recorded by a GRIMM-1107 optical monitor at the time of sampling. Particles were collected into polycarbonate filters (PC filters, Millipore®, 0.2 µm pore size) with a single stage cascade impactor with 2.4 µm of cut-off size, working at 0.6 $m^3 \cdot s^{-1}$. Samples were mounted in aluminum stubs for SEM analysis and carbon coated to avoid particle looses.

Days of sampling, February 25th to 28th were associated to high-pressure conditions over Barcelona, stability of air that favored the accumulation of pollutants and regional pollution influencing the area, thus high $PM_{2.5}$ concentrations were recorded during these days. On the February, 28^{th} a Saharan dust outbreak was detected affecting the northeastern part of the Iberian Peninsula. The study area was under its influence although this episode was not very intense.

2.2 Microscopy analysis

A Personal SEM® (ASPEX PSEM®) with a totally automated CCSEM system was used to obtain size, morphology and elemental composition of 22,700 particles. The specific limitations of the technique as well as the details of the procedure can be found in Coz et al. (2008). The EDS analyzer coupled to the PSEM allowed to obtain the relative concentration of 18 elements (C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ba, Pb). Particle size (D_p) was quantified by the diameter of a circle with equivalent particle surface. Compactness (D_p/D_{max}) was used to describe particle morphology. The mass estimate was done using as in Coz et al. (2010).

The study focused into the major chemical groups involving anthropogenic influenced origin, but also typical from natural soil resuspension and Saharan outbreaks including: (1) silicates, (2) calcium carbonates, and (3) iron and titanium oxides. Particles were classified into these different clusters based on ratios between the relative elemental compositions following the rules proposed in Coz et al. (2009).

2.3 Quantification of the anthropogenic influenced dust

Based on the work by Moreno et al. (2009) from the elements analyzed in this work, Si, Al, K, Na, Ca, and Ti (generally associated with felsic silicates), are the commonest geological elements in ambient particle matter. On the other hand, some industrially proposed tracers included in this work are Zn, Pb, Cu and Mn. In addition to these anthropogenic tracers, V, Cr and Ni have been also included in the classification as anthropogenic-related metals. Since interesting elements such as Ca, Fe or Ti are frequently found in both crustal and anthropogenic dust, particle morphology has also been used to differentiate between both origins. The resulted rules for the classification are:

- *Iron/Titanium oxides*: classified as anthropogenic-related if the morphological compactness > 0.90 (type I). Iron oxides from industrial processes are typically close to the sphericity as well as titanium oxides from paints. If particles of this type contain industrially or fuel combustion heavy metal tracers, they classified as type II.
- *Calcium carbonates*: Particles within this group containing industrially or fuel combustion heavy metal tracers are classified as being anthropogenic influenced.
- *Silicates*: Particles within this group containing Ca or/and Fe (and any other anthropogenic tracer) and a morphological compactness > 0.90 are classified as anthropogenic influenced (type I). This group also includes the spherical aluminosilicates (SAS) or fly-ashes typical from industrial sources involving coal combustion. Particles not in Type I containing industrially or fuel combustion tracers are classified as being anthropogenic influenced (type II).

3. Results

The average inferred from the daily (9-21 h UTC) $PM_{2.5}$ chemical mass balance for "crustal" matter was of 10.7% ± %1.2 (by mass). $PM_{2.5}$ during the periods sampled for microscopy ranged from 23 to 60 $\mu g \cdot m^{-3}$. Silicates were the predominant group, comprising nearly half of the $PM_{2.5}$ mass amongst the three groups. Calcium carbonates and heavy metal oxides comprised 22% and 28% respectively but varied with the period of sampling. Heavy metal oxides were especially abundant in the samples taken during the morning period whereas calcium carbonates had slightly higher concentrations during the mid-day hours.

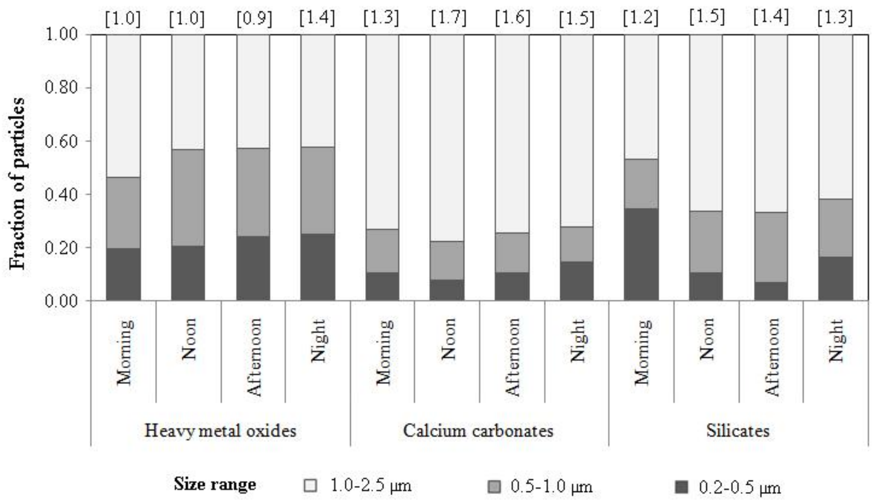

Figure 1. Fraction of particles in the 0.2-0.5 µm (dark grey), 0.5-1.0 µm (medium grey), 1.0-2.5 µm (light grey) in each cluster and period. Particle mean size placed in the top of the bar in brackets.

Table 1. Anthropogenic influenced iron and titanium oxides fraction (by number from the total in each cluster and size range).

Cluster	Size range (μm)	Anthropogenic Influenced fraction							
		Type I				Type II			
		Morning	Noon	Aftern.	Night	Morning	Noon	Aftern.	Night
Titanium oxides	1-2.5	0.55	0.29	0.57	0.45	0.27	0.49	0.43	0.45
	0.5-1	0.60	0.27	0.38	0.38	0.20	0.45	0.63	0.31
	0.2-0.5	0.00	0.20	0.33	0.00	0.75	0.62	0.67	0.78
Iron oxides	1-2.5	0.24	0.29	0.31	0.24	0.60	0.49	0.48	0.58
	0.5-1	0.30	0.27	0.31	0.30	0.49	0.45	0.47	0.45
	0.2-0.5	0.26	0.20	0.26	0.26	0.61	0.62	0.62	0.56

3.1 Metal oxides

Metal oxides are associated to the smallest particle sizes independently of the sampling time of the day with mean sizes close to the micrometer (Figure 1). Around 50% of the particles within the heavy metal oxides group fall into the submicrometric range, but despite this abundance by size, their presence in this size range turns into less than 3% by mass. The high proportion of heavy metal compounds found in the fine range is of special importance since the smallest particles are more suitable to cause higher damage in the respiratory system due to a deeper penetration into the lung tissues. Heavy metal oxides presented very specific morphologies that facilitate particle disruption down to few nanometers of size. Anthropogenic influenced iron and titanium oxides present smaller average diameters than the rest of the particles in the group. This anthropogenic influenced fraction is extremely high in the fine range for both clusters (from 70% to nearly 100% for the titanium oxide particles and from 73 to 88% in the case of the iron oxide particles, Table 1). Spherical oxides (type I) seem to be distributed within all the size ranges, excepting by the absence of titanium oxides in the 0.2-0.5 μm size range during the morning and night periods. On the other hand mixtures of silicates and heavy metal oxides with soot are frequent in this 0.2-0.5 μm size range. The fraction of both iron and titanium oxides mixed with heavy metal compounds has a tendency to increase for smaller particles as it also happens with the calcium carbonate and silicate clusters.

3.2 Anthropogenic influenced calcium carbonate

Calcium carbonate is a typical component of road soil resuspension and construction dust generally associated with the coarse fraction.

Table 2. Anthropogenic influenced calcium carbonate fraction.

Cluster	Type	Size range (μm)	Anthropogenic Influenced fraction			
			Morning	Noon	Afternoon	Night
Calcium carbonates	II	1-2.5	0.24	0.24	0.22	0.16
		0.5-1	0.29	0.40	0.43	0.35
		0.2-0.5	0.27	0.65	0.80	0.62

The fraction of most common carbonates, calcite and dolomite, may dramatically vary in natural soils depending on the geological setting of the region. It can also be a component of some Saharan dust intrusions. Barcelona belongs to the calcareous lithographic region of Spain (Coz et al., 2010), and thus the topsoil composition as well as the emitted resuspended dust would be expected to be enriched with these components even in the fine range. In this study, calcium carbonate mainly falls into the 1-2.5 µm size range, with only around 20% of the particles falling into the submicrometric range (Figure 1). As expected, calcium carbonates present the highest mean sizes for the same periods amongst the rest of the clusters, with average diameters between 1.3-1.7 µm (Coz et al., 2010). There is a high variability in the fraction of calcium carbonate particles containing heavy metal compounds that ranges from 0.16 to 0.80 depending on the time of the day and size range analyzed (Table 2), with the smallest size range beings the one presenting the highest variability with fractions between 0.27 and 0.80. Higher fractions in particles between 0.2-0.5 µm after the morning traffic peak might be associated to a larger state of mixture in non deposited particles or to a larger non traffic influence but to construction works.

All the heavy metal elements are present in the three size groups with the exception of Pb, whose presence is nearly inexistent. Calcium carbonate particles containing heavy metals (such as …) are also associated to higher contents in other elements such as Fe, Al, Si, P or S than those without heavy metals. This difference is highly important for elements such as Na, Cl or Ti that are from 2-4 times the element/Ca ratio (by atomic weight) in anthropogenic influenced carbonates with respect to the non influenced ones. This difference is specially marked in the 0.2-0.5 µm size range. Mg is slightly higher in calcium carbonate particles larger than 0.5 µm with anthropogenic influence (~1.25 times) but higher than 2 times for particles between 0.2 and 0.5 µm. Anthropogenic influenced calcium carbonates are associated to smaller sizes than the rest of the particles in the group.

3.3 Anthropogenic influenced silicate

As calcium carbonates, silicates are typical components of road and natural soil resuspension and construction dust, and are also present in industrial and traffic emissions. Aluminosilicates are typically the footprint of Saharan incursions into the Iberian Peninsula. This difference is especially high in the samples associated to the morning traffic peak in which nearly 40% of the silicates are smaller than 0.5 µm.

Table 3. Anthropogenic influenced silicate fraction (by number within each size range).

Cluster	Size range (µm)	Anthropogenic Influenced fraction							
		Type I				Type II			
		Morning	Noon	Aftern.	Night	Morning	Noon	Aftern.	Night
Silicates	1-2.5	0.12	0.16	0.14	0.13	0.21	0.25	0.19	0.26
	0.5-1	0.12	0.23	0.12	0.13	0.20	0.20	0.28	0.35
	0.2-0.5	0.05	0.10	0.05	0.02	0.32	0.41	0.39	0.64

Table 3 presents the results for the anthropogenic influenced fraction for Types I and II. Type I, mainly comprised of aluminosilicates are mainly over 500 nm of size. On the other size, the fraction influenced by heavy metal compounds presents larger fractions in particles smaller than 500 nm independently of the daytime period. All the groups in Table 3 are associated to smaller average diameters than non anthropogenic ones. The relative content of metals such as Ti, Fe or Ba is more than double in the smaller sizes for anthropogenic influenced particles, and they also have much higher relative contents (2-3 times) of P and Cl.

4. Conclusions

The study of individual atmospheric particles including iron and titanium oxides, calcium carbonates and silicates frequently associated to a natural origin (soil resuspension or Saharan dust incursions), has exhibited a very variable anthropogenic influence in the fine range of particulate matter ($PM_{2.5}$), depending on the group and size range. Mineral particles with anthropogenic influence seemed characterized by a more complex mixture of minerals and heavy metal compounds, always associated to smaller average sizes than the rest of the particles in the same group. These mixtures were especially frequent in the smaller sizes (0.5 μm), and presented much higher relative contents of elements such as Na, P, S, Cl, or K, depending on the type of particle. Results like these exhibit the importance of approaching a quantification and characterization of mineral dust from anthropogenic origin in order to assess their specific effects on climate change and human health.

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