Spatial and chemical patterns of PM₁₀ in road dust deposited in urban environment

F. Amato, M. Pandolfi, M. Viana, X. Querol, A. Alastuey, T. Moreno

*Institute of Earth Sciences "Jaume Almera", Spanish Research Council (CSIC),
C/ Luis Solé Sabarís s/n, 08028 Barcelona, Spain*

Abstract

Recent research interest has been focused on road dust re-suspension as one of the major sources of atmospheric particulate matter in an urban environment. Given the dearth of studies on the variability of the PM₁₀ fraction of road deposited sediments, our understanding of the main factors controlling this pollutant is incomplete. In the present study a new sampling methodology was devised and applied to collect PM₁₀ deposited mass from one square meter of road pavement. PM₁₀ road dust fraction was sampled directly from active traffic lanes at 23 sampling sites during a campaign in Barcelona (Spain) in June 2007. The aim of the study was to gain more insight into the variability of mass and chemistry of road dust in different urban environments, such as the city centre, ring roads, and locations nearby demolition/construction sites. The city centre showed values of PM₁₀ road dust within a range of 3-23 mg/m², whereas levels reached 24-80 mg/m² in locations affected by transport of uncovered heavy trucks. The largest dust loads were measured in the proximity of demolition/construction sites and the harbor entry with values up to 328 mg/m².

The city centre road dust profiles (%) were enriched in OC, EC, SiO₂, Fe, S, Cu, Zn, Mn, Cr, Sb, Sn, Mo, Zr, Hf, Ge, Ba, Pb, Bi, SO₄²⁻, NO₃⁻, Cl⁻ and NH₄⁺, but several crustal components such as CO₃²⁻, Ca, Ti, Na, and Mg were also considerably concentrated. Locations affected by construction and demolition activities had high levels of crustal components such as CO₃²⁻, Al₂O₃, Ca, Mg, Li, Sc, Sr, Rb and also As whereas ring roads, characterized by a higher load of uncovered heavy trucks showed an intermediate composition.

Levels of PM₁₀ components per area were also evaluated to quantify the re-suspendable amount of each element from 1 m². In the inner city environment mean values of 422 µgOC/m², 162 µgEC/m², 1363 µgCa/m², 13 µgCu/m², 12 µgZn/m², 1.9 µgSb/m² and 2.0 µgPb/m², in PM₁₀ in all cases, were registered.

Moreover the PM load at demolition/construction sites acts as a reservoir or trap for traffic-related particles, which gives rise to large amounts of hazardous pollutants, available for resuspension.

Keywords: PM₁₀ road dust; resuspension; deposition; demolition/construction impact; uncovered trucks; levels per m².

1. Introduction

As a result of the demographic growth of large European cities, urban air quality has become more and more affected by traffic-related pollutants in recent years. Several studies point to the traffic sector as a major contributor of diffuse metal emissions (EEA, 2004; Bergbäck et al., 2001; Sörme et al., 2001). Exposure to particulate matter from roadways implies an increased exposure to ultrafine particles and to PM₁₀ and PM_{2.5} emissions from tailpipes, brake wear, tire wear and road dust. However, the contributions of the last three sources to the total concentrations of metals in roadway emissions are poorly understood (Schauer et al., 2006).

Exposure to emissions from roadways has been associated with adverse health effects and linked to an increased risk of respiratory illnesses (Tsai et al., 2000; Lin et al., 2002). Künzli et al. (2000) attributed to motorized traffic half of air pollution mortality within his study and Schwartz et al. (2005) demonstrated the association between black carbon and reduced heart rate variability. Moreover, the Sb₂O₃, product of oxidation Sb₂S₃ in brake pad wear has been recognized as a possible carcinogenic by the International Agency for Research on Cancer (<http://monographs.iarc.fr/ENG/Monographs/vol47/volume47.pdf>).

Harmful substances emitted by exhausts and wear from vehicles are deposited and accumulated daily in urban dust on road pavement together with primary and secondary particles from other anthropogenic (demolition/construction, industrial stacks) and natural sources (short and long-range transport of re-suspended soils). Hence, road dust represents a hazardous carrier of toxic metals, metalloids and organic compounds which can easily be re-suspended by passing vehicles, trams and wind, resulting in an important source of atmospheric particulate matter which should be considered in environmental urban policies air pollution. However, road sampling is expensive, time consuming and dangerous. This limitation prevents emission inventory developers from obtaining a statistically valid number of samples, even less for the PM₁₀ fraction, which requires larger times of sampling.

Moreover, in Mediterranean areas the scarce and infrequent rainfall favours the accumulation of road dust on the pavement. Comparison of several European studies

(Querol et.al., 2004; Areskoug et al., 2004; Ketzel et al., 2004; Visser et al., 2001; Viana M., 2007) shows that atmospheric particulate matter in Spain was considerably enriched in mineral dust. Querol et al. (2004) found that in PM_{2.5} the highest mineral dust concentrations were recorded at urban background sites rather than at rural and sub-urban background sites. Therefore, resuspension of road dust represents also a major source of mineral dust in urban environments.

The urban dynamism around Barcelona (Spain) accounts for a high road traffic density: 36% of citizens habitually use public transport, 31% walk or bike and 33% use private vehicles. People entering the city from surrounding towns prefer private transport (52%) (<http://www.bcn.cat/transit/ca/informacio.html>). A considerable contribution to traffic density derives from motorcycles and scooters, which represent 27% of total vehicles. Moreover, in all Spain, the number of diesel powered cars has increased from 5.0 to 12.2 millions in eight years (1997-2005) whereas the number of gasoline powered vehicles fell (by 20% in the case of trucks and by 5% in the case of cars) (<http://www.dgt.es/estadisticas/estadisticas01.htm>).

In this study, we sought to improve our understanding of how the PM₁₀ fraction of road dust varies in load and chemical composition in different urban zones. To this end, we evaluated the impact of braking, demolition/construction activities and that of fugitive dust from transport by trucks. The load of PM₁₀ components per square meter was also assessed. A sampling methodology was devised and applied to collect the deposited PM₁₀ fraction directly from the road pavement at selected sampling sites, minimizing losses of particles. Furthermore this work provides useful PM₁₀ chemical profiles concerning re-suspension of fugitive dust sources for Chemical Mass Balance applications.

2. Methodology

2.1. Study area

The urban area of Barcelona (NE of Spain) covers 101 km² (Fig.1) with 1.6 million inhabitants. Such a high population concentration results in one of the highest car densities in Europe, 6.1 thousand cars per km² compared with Milan (4.4), Madrid (2.3) or Berlin (1.4). About 10% of the total area of the city is destined to asphalted pavement. The highest traffic density of the city takes place where the majority of people live and work (*Eixample*), a square-blocks area with narrow streets inducing

high exposure and canyon effect for the dispersion of pollutants. According to the data supplied by the Municipal Council of Barcelona, the number of vehicles in Barcelona in 2006 was: 616,000 cars (63.0%), 266,000 motorcycles (27.2%) and 74,000 trucks (7.6%) (<http://w3.bcn.es/fitxers/mobilitat/dadesbasiques2006.222.pdf>). Although other pollution sources, e.g. industrial activities including two gas power stations, two city waste incinerators and harbor-related emissions are located in this area, traffic constitutes the main source of air pollution (Querol et al., 2001; Perez et al., 2008).

According to earlier studies, the ambient PM₁₀ and PM_{2.5} concentrations (annual average at urban background: 2003-2006) in Barcelona were in the ranges of 39-42 and 25-29, respectively (Perez et al., 2008) with 97 daily values exceeding 50 µgPM₁₀/m³ (daily limit value). The air quality of the Barcelona metropolitan area is also affected by a complex orography that plays a key role in the atmospheric dynamics and hence in the dispersion of pollutants (Jorba et al., 2004; Jimenez et al., 2006).

In addition to the local PM emissions, Saharan dust outbreaks reach Barcelona in the order of 7–10 events per year, with the highest frequency in the summer and winter–spring periods (Rodríguez et al., 2001).

2.2. Sampling sites

With the aim of characterizing the different urban environments in the city, 23 locations were selected across the city centre, two ring roads surrounding the city core and a residential area with a high density of demolition/construction activities (Fig.1). Sampling areas were selected on the right lane of the street (Fig.2) excluding the gutter where mass is not directly re-suspended. Such a collection protocol involved the assistance of the Traffic Police for the total duration of the campaign to supervise traffic and ensure safety. The sampling campaign lasted eight days (15-22 June 2007) in order to minimize the accumulation rate. The sampling period was preceded by 3 weeks of dry weather. No precipitation was registered during the sampling days and the temperature varied between 16°C and 31°C.

Table 1 shows the main characteristics of each sampling site: traffic volume, velocity and eventual nearby fugitive crustal sources. All locations can be grouped into 4 main categories, namely, city centre, ring roads, demolition/construction and harbor activities (Table 2).

City Centre (C1-C9): this covers an area of approximately 30 km². Traffic is heavy with frequent congestions and high braking frequency. Nine sampling sites (C1-C9) were

selected inside this area. Four of them (C3, C4, C5, C6) were located along one of the busiest roads (Diagonal Avenue), which crosses the city from NE to SW, with a mean of 106,000 vehicles per day (2005, <http://www.bcn.es/estadistica/catala/index.htm>). C2, C7 and C8 are sites located at busy urban roundabouts while C1 is a less busy roundabout. C9 corresponds to an entry lane of a highway.

Ring Roads (R1-R7): approx. 120,000 vehicles per day move along two ring roads, with 80km/h speed limit and less congestion. Owing to harbor activities and the transport of residual material from demolition sites to landfills (SW of the city) the coastal ring road has a higher volume of heavy diesel traffic than the upper ring road (near the northern Collserola Range) (7.7% vs 3.9% trucks). The R7 sampling site was located at a highly polluted exit of the city at the NW end (Av. Meridiana, 132,000 veh/day, Fig.1).

Demolition/construction: a less busy area of about 1 km², located near the coastal ring road was selected to better understand the impact of urban works on inhalable fraction of road dust and its components. Four locations (W2-W5) were chosen at different distances from the hotspot (W1). The urban works had been carried out for one year before sampling and included demolition, construction of buildings and paving of sidewalks. The materials used were mainly cement, sand and tiles. Metals, tiles, and stones were frequently sawed outdoors. W6 was located next to other small works at the kerb-side of a very busy road (Meridiana Avenue).

Harbor: The commercial and touristic harbor handles 8,800 cargo vessels, 2,400 regular ferries and 690 cruises per year (<http://www.bcn.es/estadistica/catala/index.htm>). Cargo activities at the harbor, located close to urban areas are a major source of dusty materials deposited on road pavement, and consequently of atmospheric PM, mostly on a local scale. Site H1 was selected for its position at the exit of the harbor where a mean of 180 trucks per hour was estimated.

2.3. Sampling procedure and analysis

On road pavement, particles come from re-suspended soil (short and long range transport), handling of dusty materials for demolition/construction and wear of brake pads, tires and other metallic parts of vehicles as well as combustion of motors and industrial hotspots (e.g. fly ashes, Fig. 4e). As a result, the diameter of road dust particles varies in size from ultra fine to coarse.

The study of road dust re-suspension is usually performed by collecting samples directly from road pavement by sweeping sediments and either sieving (Han et al., 2007; Manno et al., 2006; Ho et al., 2003) or inducing re-suspension in the laboratory and extracting PM₁₀ through size selective inlets (Zhao et al., 2006; Chow et al., 2004). Generally these procedures and sample treatments are affected by the loss of fine and ultra fine particles owing to the difficulties of collecting all deposited material and to the electrostatic adhesion of particles to pincer/brush hairs and sieve meshes.

In order to reduce such losses during the sampling procedure, we developed a field re-suspension chamber to directly collect the re-suspended PM₁₀ fraction of road dust onto filters at sampling sites. Road sediments were aspirated from the pavement of active traffic lanes at an air flow rate of 25 l/min, using a *Becker* pump powered by a *Honda* field generator (located at some distance downwind with respect to the sampling area). Particles were immediately re-suspended in a PVC deposition chamber and the particles small and/or light enough to be carried by the air current continued their journey through the system. These particles enter a *Negretti* stainless steel elutriation filter designed to allow passage to only PM₁₀ (particles with aerodynamic diameter <10µm) grade material of average density. The particles able to penetrate this barrier were finally collected on 47 mm diameter fiber quartz or Teflon membrane filters.

Particles with aerodynamic diameter >10µm were deposited in the PVC chamber. These samples were brought to laboratory, dried for 48h at room temperature and sieved (250µm or 63µm meshes) and then analyzed by means a MALVERN MASTERSIZER E size analyzer with the aim of verifying the size selection of the sampling system. Results showed that PM₁₀ fraction was in average only 0.6% and 0.1% (in volume) of samples sieved at 250µm and 63µm, respectively.

Earlier road dust studies have not quantified or compared the load of mass collected at different sites (probably because of the absence of a sampling protocol) with the result that there are no studies on how the deposited mass of road dust <10µm varies with space. Using our method it was possible to address this issue for PM₁₀ and several components (organic carbon-OC, elemental carbon-EC, metals and metalloids, sulphate, nitrate, chlorine and ammonium). To this end, sampling was performed at all sites in a comparable surface area of 1 m² for 30 min. Moreover, for each location, three different square meters were sampled using three different filters to reduce casual errors and to collect enough samples for the required analyses: quartz fiber filters 47 mm diameter *Munktell* were used to determine the concentration of major and trace elements, OC, EC and carbonate carbon (CC) and Teflon 47 mm diameter membrane filters (1µm pore), *Schleicher & Schuell* to determine the concentration of

water soluble anions, pH and conductivity. Before sampling, quartz fiber filters were dried at 205° for 5 hours and conditioned for 48 hours at 20°C and 50% of relative humidity. Weights of blank filters were measured three times every 24 hours by a *Sartorius* LA 130 S-F microbalance (1µg sensitivity).

After sampling, filters were brought back to the laboratory for mass determination and analytical treatments. A quartz fiber filter per site was cut into two sections. Half of the filter was acid digested (5 ml HF, 2.5 ml HNO₃, 2.5 ml HClO₄) for the determination of major and trace elements and analyzed by inductively coupled plasma mass and atomic emission spectrometry (ICP–MS and ICP–AES) (Querol et al., 2001). A section of 1.5 cm² from the other half of the filter was used for the determination of OC, EC and CC by a thermal-optical transmission technique (Birch and Cary, 1996) using a *Sunset* Laboratory OCEC Analyser with the default temperature programme. Total carbon (TC) was determined as the sum of OC+EC. CC concentrations were calculated for each individual sample by manually integrating the last carbon peak before the OCEC split point. Teflon membrane filters were leached in 20 ml of bi-distilled water for the extraction of water-soluble anions and subsequent analysis by ion chromatography (IC) for sulphate, nitrate and chloride, by conventional procedure for pH and conductivity, and specific electrode for ammonium. Concentrations of Si were calculated applying the Si/Al ratio which was determined only for some samples by means a HF/aqua regia /H₃BO₃ digestion (Thompson & Walsh, 1989) and subsequent ICP-AES analyses.

Scanning Electron Microscopy (SEM) analyses were performed manually on single particles from a portion of quartz fiber filter, using a 1450 SEM (JEOL5900LV) equipped with an energy dispersive X-ray microanalysis system (EDX). Samples were carbon coated and particles were analyzed at their centre to avoid interference from adjacent particles and filter's fibers. The acquisition time of each analysis was 30 s live time, with a microscope working distance of 25 mm, accelerating voltage 20 kV, and beam current 1.00 µA.

3. Results and discussion

3.1 Load of PM₁₀ mass

The load of PM₁₀ mass fraction of road dust per m² was calculated at each location by averaging the amounts of mass collected in the three square meters sampled. Four different ranges allowed us to distinguish different features (Fig.1). Low amounts of mass (3-23 mg/m²) were found in the centre of the city (C1-C9), where traffic was very dense but almost exclusively passenger cars, motorcycles and goods vehicles. A mean

value of 9 mg PM₁₀/m² was obtained for the centre of the city. The high value of 23 mg/m² at the centre site C8 was due to the fact that this location is an important crossroads for heavy traffic towards the harbor, the industrial area of *Zona Franca* and the airport (both in the south). An interesting result was obtained for the only sampling (R1) performed at a tunnel site with a value of 13 mg/m² due to the reduced contribution from external sources.

In the second range concentration of mass per square meter was generally doubled (24-40 mgPM₁₀/m²). All sites along the coastal ring-road (R3-R6) belonged to this range. Ring roads are the main routes for uncovered heavy trucks transporting dusty materials from urban and sub-urban construction sites towards various landfills located to the SW of the city. The concentration of PM₁₀ mass deposited on the road pavement rose as traffic from uncovered heavy trucks increased.

At locations with a high density of heavy duty diesel traffic (R2 and R7) values were within the upper ranges (41-80 mg PM₁₀/m²) whereas the highest concentrations were registered at locations directly affected by public works and transport of aggregates (W-sites and H1). At W1, a demolition/construction hotspot, the mass of PM₁₀ was 328 mg/m², attributed to build up generated by the handling, loading and unloading of dusty materials. Moving progressively away from the hotspot (W1), four further sites were sampled at distances of 150 m (W2), 300 m (W3), 400 m (W4) and 480 m (W5) along the main route for trucks. The results show that the PM₁₀ mass progressively decreases with distance from the hotspot, and at 400 m the impact of these activities on PM₁₀ mass is already negligible. Values of 472, 133 and 11 mgPM₁₀/m² were measured at W2, W3 and W4, respectively. W2 registered the highest value of mass, even higher than the hotspot (W1) given that all the truck routes from the hotspot converged on this site. Transport of dusty materials by uncovered heavy trucks should therefore be taken into account in airborne PM abatement strategies. W5 was located at some distance from the truck route and not affected by too many passenger cars. Hence this site registered the lowest observed value (2.5 mg PM₁₀/m²). W6, which was affected by smaller works on the sidewalk recorded a value of 138 mgPM₁₀/m². A high value of 165 mgPM₁₀/m² was also measured at the exit of the harbor (H1) where traffic is dominated by heavy duty vehicles with a high percentage of uncovered trucks.

Therefore, exposure to airborne PM₁₀ would be much greater at W-sites, H1, and R-sites owing to the re-suspension of the deposited PM₁₀, which exceeded the concentrations at the city centre by one order of magnitude. This factor could affect the exposure to atmospheric PM, triggering dust outbreaks in the vicinity of urban works.

3.2. Chemistry

3.2.1. Chemical profiles

Table 2 shows the chemical profile of road dust obtained by averaging all 23 samples from the campaign. Results show that constituents with the highest average concentrations were Si ($37.0 \pm 21.3\%$), Ca ($12.8 \pm 4.5\%$), CO_3^{2-} ($12.4 \pm 5.3\%$) and Al_2O_3 ($8.0 \pm 2.8\%$) followed by OC ($4.5 \pm 1.4\%$), Fe ($4.0 \pm 1.7\%$), EC ($1.4 \pm 1.4\%$), K ($1.4 \pm 0.5\%$) and Mg ($1.2 \pm 0.4\%$). Averaging the concentration of trace elements in all the samples, the highest elements were found to be Ti, Zn, Ba, Cu, and Mn, with concentrations of 2743, 1104, 992, 927 and 580 $\mu\text{g/g}$, respectively. Relatively high concentrations in all road dust samples were also registered for Sr, Cr, Pb, Sn and Sb (119-230 $\mu\text{g/g}$). Moreover, considerable concentrations Zr, Rb, V, Mo and Ni (49-94 $\mu\text{g/g}$) were recorded.

The chemical results highlighted the importance of distinguishing four categories in order to shed light on how local factors influence sediment properties. Thus, we selected the 18 most representative locations and grouped them into 4 classes, depending on volume, type of traffic and additional fugitive sources (Table 2): the city centre, ring roads, demolition/construction works and harbor. The low standard deviations for concentration of every element inside each group supported the classification of sites according to the type of environment. City centre locations showed strong enrichments of OC, EC, SiO_2 , Fe, S, Cu, Zn, Mn, Cr, Sb, Sn, Mo, Zr, Hf, Ni, P, Ge, Ba, Pb, Bi, SO_4^{2-} , NO_3^- , Cl^- and NH_4^+ . Locations influenced by emission from urban works revealed the highest concentrations of CO_3^{2-} , Al_2O_3 , Ca, Mg, Li, Sc, As, Rb and Sr. Ring road profiles were characterized by an intermediate content of most of the PM_{10} components analyzed with the exception of the high levels of K, Na, Li, Ti, Rb, Pb and V. These sites were characterized by a high volume of uncovered trucks. Thus traffic-related metals were diluted with respect to the concentrations at the city centre, but they were more concentrated with respect to residential sites with construction hotspots. Other elements such as Cd, La, Ce, Co, Y, Ga, Se, W, Nb, Cs, Th and U did not show appreciable variability in the different categories.

The OC/TC ratio was on average 0.77, with a very low standard deviation among all samples, and within the range of the study by Watson and Chow (2001). The OC/EC ratio varied within the range 1.8-10.7 with average values of 3.3 for the city centre, 4.1 for ring roads and 4.5 for the demolition and construction road dust profile. The TC content (OC+EC) reached a value of 11.1% at C4 and minimum 2.8% at R3. The mean

category values of TC decreased from the city centre (7.3 %) to ring roads (5.5 %), down to the less busy roads in the proximity of building sites (5.2 %).

Sulphate content was 1.07% averaging all urban environments, but higher concentrations were registered in the city centre. Nitrate and ammonium were also low but both reached the highest values in the city centre (maximums of 0.9% and 0.6%, respectively). Probably these maximums were due to the *dilution effect* of mineral dusts at demolition/construction and ring road sites. However, the relationship between NH_4^+ and traffic remains unclear.

The concentrations (%) of major crustal components showed small differences in all the profiles. CO_3^{2-} and Ca were high at the demolition/construction sites owing to the use of aggregates (works/centre ratios were 1.4 and 1.2, respectively). Fe and S were consistently more enriched in the centre where the braking rate is high (C3, C4 and C9, Fig.4a-b-d). Although these elements could result from a variety of sources, Fe is often the major component of brake pads (Schauer et al., 2006; Adachi & Tainosho, 2004) where S is also present as barite (a common filler mineral) and several sulphurs such as Sb_2S_3 , MoS_2 and SnS (used as lubricants for semi-metallic pads). These compounds are added to brake pads to reduce friction (Fauser et al., 1999; Garg et al., 2000) and are more concentrated within the underlayer of the pads. SEM observations showed that pseudo-spherical particles of barite had a mean diameter $<1\mu\text{m}$. Sb compounds were identified only in few cases, in association with Fe-bearing particles (2-5 μm) containing also Cu, Mo, Sn, Ni and Cr (Fig.4c).

Comparison with similar studies carried out in Mexico, China and Hong Kong (Vega et al., 2001, Zhao et al., 2006, Ho et al., 2003) showed that the OC content in Barcelona was fairly low whereas the EC content showed concentrations within the range of the above studies (Table 3). No data were available for Europe and the USA. Trace element concentrations showed remarkable differences. Although some elements such as Ti, Ba and Mn were comparable with those in the literature, Cu, Sb, Zn and Mo showed marked differences (Table 3). The mean concentration of Cu in Barcelona was 5 times higher than the average of these studies but in the case of city centre it was 8 times higher. Twice as much Zn was recorded in Barcelona as in the aforementioned studies, and this enrichment increased in the city centre probably due to the high volume of diesel (Cadle et al., 1999) and two-stroke engine vehicles (Bilkis et al., 2004). In agreement with these results, Sillanpää et al. (2005) found in ambient $\text{PM}_{2.5}$ in Barcelona relatively high Cu and Zn ratios to particulate organic matter when compared with other European cities (urban background stations). Querol et al. (2007) registered the highest ambient concentrations of Cu and Sb in urban backgrounds (PM_{10} and

PM_{2.5}) with respect to industrial sites (metallurgic, petrochemical and ceramic industries). At the city centre locations in Barcelona, the concentrations of Sb and Mo were, respectively, 3.0 and 2.3 times higher than the results of Ho et al. (2003). Other components such as Mg, Fe, S, Cr, Mn, Ni, Rb, Sr and Pb were present in amounts similar to the aforementioned studies (Vega et al., 2001, Zhao et al., 2006, Ho et al., 2003), whereas concentrations of Al₂O₃, P, Ti, V, Co and Ba were relatively lower (Table 3).

Pearson's correlation coefficients between two elements were calculated to account for these high amounts of Cu, Zn, Sb and Mo. As shown in table 4 the concentrations of Sb display high correlations (>0.8) with those of Cu, Sn, Bi, Cr, Mo and Zr, good correlations with Fe, Ba, Zn, and lower but still significant correlations with Ni, Mn and EC. Furthermore, the Cu/Sb ratio was found to be very constant in all the samples regardless of any category or sampling site. This suggests that both Cu and Sb are mainly attributed to the wear of brake pads. Therefore, we may assume the Cu/Sb ratio of 7.0 ± 1.9 as a diagnostic criterion for brake wear particles. This value is at odds with the 4.26 ± 2.3 proposed by Sternbeck et al. (2002), and the 1.3 proposed by Adachi & Tainosho (2004) obtained from direct analyses of the dust in the rim of brake linings. These differences may be ascribed to the varying Cu and Sb contents of different brands of pads. Indeed, as a result of the asbestos ban, brake pads are now made from different materials (Sternbeck et al., 2002, Hjortenkrans et al., 2006). Thus brake pads used in Spain appear to contain large amounts of Cu.

Tire wear is another well known source of resuspended particulate matter, Zn being recognized as a major tracer at urban sites. Concentrations of Zn in tires vary between 1.6-1.8% (Weckwerth 2001) and are confirmed by unpublished results of our group. Furthermore, tires also contain minor concentrations of Cd, Co, Cr, Cu, Mn and Mo (Hjortenkrans et al., 2006). SEM showed that particles containing Zn were associated with Fe and Mn. Our results show that in road dust-PM₁₀, Zn had a correlation coefficient >0.8 only with Mo and >0.7 with Ba, Cr, Cu, Bi, Sn, Ni and Sb (in decreasing order) corroborating the traffic related origin of Zn with contributions from engine exhausts, tire wear and to a lesser degree brake pads.

As shown in Fig.3 Cu, Sb, Zn, Mo, Sn, Zr, Ba, Cr and Ni reached the highest concentrations at sites with braking activities (C3-C4-C9), revealing their strong link with the wear of brake pads and tires. Indeed sites C3, C4 were located at important crossroads with traffic-lights and C9 corresponds to an entry lane of a highway.

A clear correlation was found between concentrations of Ge and Cd in all the samples. ($r^2=0.90$). Both Cd and Ge often substitute Zn in sphalerite (ZnS) (Grammatikopoulos

et al., 2006). Therefore, levels of Cd and Ge in ambient PM₁₀ could probably be due to tire wear emission as well, despite the very low concentrations.

Since the ban of Pb in gasoline, Pb emissions from traffic have decreased by two orders of magnitude in Europe (see Kemp, 2002 as an example). Pb concentrations in our study were considerable (100-490 µg/g) with a slight dependence with traffic volume (Table 2 and Figure 4b) but in general lower than other studies (Vega et al., 2001, Zhao et al., 2006, Ho et al., 2003). Particles of Pb showed an oval morphology (Fig.4b - SEM) and were sometimes associated with Sn and oxygen. The Pb concentration in road dust could still be attributed to emissions from fossil fuels (Ozaki et al., 2004, Saint' Pierre et al., 2004).

3.2.2. Levels of road dust components per area

The chemical profile of the samples showed that traffic-related sources had different impacts across the city depending on the volume and type of traffic, braking frequency and urban works. Nevertheless, it is important to look at the chemical data in terms of µg/m² in order to account for load of each component. Thus it was possible to quantify the micrograms of PM₁₀-components that were available for resuspension (Table 5).

Table 5 shows the levels of major and trace elements per square meter in the city centre, which has 384 passenger cars per 1,000 inhabitants and 6,100 cars/km². Further comparative studies would be needed to find correlations between the levels of traffic-tracers per area and traffic volumes and number of dry days. Our results showed that an average concentration of 1.9 µg/m² of Sb at the city centre can be expected in contrast to the Sb emission estimated by Iijima et al. (2007), which was based on Japanese brake pads.

Levels of Sb as well as other traffic-related pollutants increased drastically near demolition and construction sites (Fig.6). Thus, the deposited crustal layer due to urban works had a considerable impact, accumulating or trapping heavy metal particles. Indeed, without any direct source of crustal dust, the build up of heavy metals dust would be reduced by rainfall and runoff waters (Robertson and Taylor, 2007). However, the accumulation of quartz, feldspars and calcite particles (often weathered and eroded under SEM observation) due to the earth handling could create a reservoir for heavy metal particles. Given that rain does not wash off fine particles if these are attached to the asphalt (Vaze et al., 2002), we may assume that the same process occurs for heavy metal particles attached to coarse crustal particles, which are less easily washed off. Hence, concentrations of Sb and Cu in PM₁₀ road dust at traffic sites that were free from direct impact of urban works varied between 0.5-3.4 µgSb/m² and 3-27 µgCu/m²

(Figures 5 and 6), whereas at sites near urban works values were within the range 7-24 $\mu\text{gSb}/\text{m}^2$ and 48-155 $\mu\text{gCu}/\text{m}^2$. Moving away from these hotspots, concentrations fell to 1.6 $\mu\text{gSb}/\text{m}^2$ and 11.0 $\mu\text{gCu}/\text{m}^2$ at W4 (at a distance of 400 m). 0.1 $\mu\text{gSb}/\text{m}^2$ and 1.0 $\mu\text{gCu}/\text{m}^2$ were registered at W5 where the traffic volume was the lowest. Therefore, in the proximity of urban works, the atmospheric concentrations of elements such as Cu, Sb, Mo, Fe, Zn could be greater due to resuspension.

The harbor site (H1) was characterized by a great accumulation of mineral dust on the road surface even though it did not register particularly high levels of Sb and Cu (4.6 and 42 $\mu\text{g}/\text{m}^2$ respectively, lower than the city centre and demolition/construction activities.). This is probably due to the fact that at this site traffic was scarce and mainly made up of old trucks.

Ring roads were characterized by a high traffic volume and a lower frequency of braking. This was reflected in relatively low concentrations of Sb and Cu (3.0 and 16.6 $\mu\text{g}/\text{m}^2$).

3.4. Source identification by factor analysis

Principal Component Analysis was applied to the chemical dataset to identify the most significant factors responsible for the variance of chemical species in PM_{10} road dust. Five factors were identified, accounting for 83% of the total variance of the whole dataset (Table 6). Although factor analysis identified two different crustal sources, soil/asphalt and demolition/construction, it could not distinguish between vehicle wear and exhaust emissions.

Factor 1 had high loadings for Cu, Mo, Sn, Sb, Cr, Zr, Zn, EC, Fe, Ba, Hf, Ni and OC. Owing to the chemical profile this factor represents the products from wear of brake pads (Sb, Cu, Mo, Fe, Sn, Ba, Zr, Hf, Zn), tires (Zn, Mo, OC), other metallic parts of cars and from motor exhaust (OC, EC, Ni, Zn, Mo). Factor 2 was dominated by Al, Ga, Li, La, K, Mg, Ti, Mn, U, V and Pb. This factor is representative of the resuspension of local soils and road pavement erosion. Factor 3 showed high loadings just for Cd and Ge. Despite its low contribution to mass, the high correlation observed between these two elements revealed that their levels in road dust (and ambient air) could be related to tire wear due to the occurrence of Cd and Ge in ZnS. Factor 4 was dominated by CO_3^{2-} , Ca and Sr. This factor was attributed to the handling of aggregates for construction and demolition activities. Factor 5 was loaded only for Na because Cl^- was not included in factor analysis, and it was identified as sea spray.

4. Conclusions

In urban areas the resuspension of road dust is an important carrier of vehicle-related pollutants in ambient PM. Nevertheless, a considerable amount of mineral dust in ambient PM₁₀ concentration is also attributed to road dust.

In this study a new sampling methodology was devised and applied in order to minimize the loss of fine and ultrafine particles. This allowed to estimate that the average load of PM₁₀ road dust able to be resuspended in the city centre of Barcelona (June 2007) was 9 mg/m². This value constitutes a useful parameter for emission factor estimation and for comparison with other scenarios. However, rainfall frequency also plays a major role in the road dust load and further investigation are needed to evaluate its impact on levels of deposited PM₁₀. Across the city centre the load of PM₁₀ road dust registered a slight variation depending on the traffic volume.

Traffic of uncovered heavy trucks played the biggest part in controlling the spatial variation of load of PM₁₀ road dust across the city, yielding concentrations between 24-80 mg/m². Demolition and construction activities within the urban area sharply increased the levels of PM₁₀ road dust (up to one order of magnitude). Nevertheless at a distance of 400 m from the hotspot, the level of PM₁₀ fell within the urban background (3-20 mg/m²).

Chemical concentrations (in %) were determined by the emission sources. City centre locations showed strong enrichments of OC, EC, SiO₂, Fe, S, Cu, Zn, Mn, Cr, Sb, Sn, Mo, Zr, Hf, Ni, P, Ge, Ba, Pb, Bi, SO₄²⁻, NO₃⁻, Cl⁻ and NH₄⁺. Locations influenced by emission from urban works revealed the highest concentrations of CO₃²⁻, Al₂O₃, Ca, Mg, Li, Sc, As, Rb and Sr. Ring road profiles were characterized by an intermediate content of most of the PM₁₀ components analyzed with the exception of the high levels of K, Na, Li, Ti, Rb, Pb and V.

Cu, Sb, Zn and Mo were sharply concentrated at locations with braking activities but in general their concentrations were much higher than similar sampling campaigns carried out in Mexico, Hong Kong and China. These differences could be attributed to the varying chemical composition of brake pads in different countries and to the advances made in brake materials. Other components such as EC, Mg, Fe, S, Cr, Mn, Ni, Rb, Sr and Pb registered values very close to the other studies, while the values of OC, Al₂O₃, P, Ti, V, Co and Ba were lower.

The cross correlation analysis applied to the chemical dataset enabled us to study associations of elements in road dust: Cu-Sb showed one of the highest correlations using all the samples. Although their content in brake pads varies between different brands and countries, we propose the Cu/Sb ratio of 7.0±1.9 as a diagnostic criterion

for brake wear particles. Cd and Ge resulted very well correlated ($r^2=0.90$) across the city, and owing to their presence in sphalerite (ZnS), were likely to be sourced by tire wear.

Deposited levels of chemical components of PM₁₀ per surface area ($\mu\text{g}/\text{m}^2$) were mainly driven by the PM load, resulting in high concentrations of crustal elements and heavy metals at locations affected by earth handling and transport. At these sites PM mass accumulation acted as a reservoir for heavy metal particles (Fe, Cu, Sb, Zn, Mo among others), making it difficult to wash off these components. Principal Component Analysis allowed us to identify five factors/sources: soil/pavement erosion, vehicle wear and exhaust, Ge/Cd occurrence in tire wear, demolition/construction activities and sea spray. Thus it was possible to distinguish between two mineral dust sources, i.e. soil/pavement erosion (tracers) and demolition/construction activities (Carbonates, Ca and Sr). Nevertheless factor analysis was not able to differentiate between wear of brake pads, tires and exhaust particles, merging these 3 sub-sources into a single factor.

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Figure captions:

Fig.1: Location of the 23 sampling sites and spatial distribution of PM_{10} road dust fraction (mg/m^2) across the city centre (C-sites), ring roads (R-sites), harbor (H1) and less busy areas with demolition/construction activities (W-sites).

Fig. 2: Sketch of sampling area for each location.

Fig. 3: Concentration of several elements at different sites: deceleration (C3, C4 and C9), urban background (C2, C5, C6, C7, C8), high velocity (R2, R3 and R5)

Fig 4: SEM observations: a) general backscattered image of a PM_{10} road dust sample where bright Fe-rich particles are clearly visible (C-sites); b) isolated Pb and Fe particles at a C-site; c) adhesion of brake metalliferous particles to mineral dust (R-site); d) Coarse pyrite (FeS_2) at a C-site; e) fly ash at a C-site; EDX spectrum of Fe-rich brake particle (point 1 in image c).

Fig.5: Spatial variability of load of available antimony ($\mu g/m^2$). Different ranges were detected for the city centre, ring roads and building activities.

Fig. 6: Impact of building activities: accumulation of brake pad-product wear in mineral dust layer.

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Fig. 6: Levels of Cu and Sb ($\mu\text{g}/\text{m}^2$) in deposited PM_{10} . At urban works sites their concentrations sharply increased when trapped within the mineral dust layer.

Table 1: List and short description of sampling sites in Barcelona (June 2007); HDD (Heavy duty diesel); UHT (Uncovered heavy trucks)

Category	Code	Location Name	Description	km/h
Centre	C1	Levant	Low Traffic-roundabout	50
	C2	Dressanes	High and slow traffic	50
	C3	Gracia	High traffic;traffic-lights	50
	C4	Valencia	Important crossroads	50
	C5	Diagonal UB	City entry-reducing velocity	50
	C6	Macia	High Traffic-roundabout	50
	C7	España	High Traffic-roundabout	50
	C8	Cerdá	High Traffic-roundabout	50
	C9	C31	Braking - entry lane for highway	80
Ring Roads	R1	Dalt S1	Tunnel-High and fast traffic	60
	R2	Dalt S4	High and fast traffic	80
	R3	Litoral S24	HDD traffic-UHT	80
	R4	Litoral S21	HDD traffic- UHT	80
	R5	Litoral pk15	HDD traffic	80
	R6	Litoral S20	HDD traffic-UHT	80
	R7	Dublin	High traffic-exit of city-UHT	50
Harbor	H1	Port	Exit of harbor-UHT	50
Demolition and Construction	W1	Provençal	Street-level works hotspot	50
	W2	Selva de Mar 1	130 m from hotspot	50
	W3	Bac de Roda	380 m from hotspot	50
	W4	Selva de Mar 2	400 m from hotspot	50
	W5	Faria	500 m from hotspot	50
	W6	Palencia	High traffic-kerbside works	50

Table 2: Average profiles of PM₁₀ fraction of road dust in four urban environments: concentration in % $\pm$ standard deviation (analytical error for harbor profile). Highest concentrations for each variable are highlighted in bold.

	Centre city	Ring Roads	Demolition and Construction	Harbour	Mean
	road dust	road dust	road dust	road dust	road dust
	8 profiles	5 profiles	4 profiles	1 profile	23 profiles
	C2-C9	R1-R3, R5, R6	W1, W2, W3, W6	H1	all
pH	6.83	6.85	7.29	7.07	6.93
Cond.	68	88	185	89	100
PM ₁₀	8.9	34.5	216	165	
OC	5.32 $\pm$ 0.99	4.18 $\pm$ 2.01	4.24 $\pm$ 1.68	na	4.52 $\pm$ 1.38
EC	1.98 $\pm$ 0.94	1.35 $\pm$ 1.03	0.99 $\pm$ 0.13	na	1.44 $\pm$ 0.83
CO ₃ ⁼	12.46 $\pm$ 5.52	9.64 $\pm$ 1.63	17.82 $\pm$ 7.45	na	12.38 $\pm$ 5.26
SiO ₂	55.09 $\pm$ 25.50	32.33 $\pm$ 5.05	29.13 $\pm$ 5.28	18.98 $\pm$ 0.95	37.00 $\pm$ 21.26
Al ₂ O ₃	8.10 $\pm$ 3.74	8.91 $\pm$ 1.39	9.93 $\pm$ 1.97	5.58 $\pm$ 0.28	7.96 $\pm$ 2.82
Ca	13.09 $\pm$ 4.75	11.71 $\pm$ 1.22	15.43 $\pm$ 3.26	23.15 $\pm$ 1.16	12.85 $\pm$ 4.50
K	1.43 $\pm$ 0.61	1.54 $\pm$ 0.24	1.50 $\pm$ 0.18	1.14 $\pm$ 0.06	1.40 $\pm$ 0.46
Na	0.45 $\pm$ 0.14	0.50 $\pm$ 0.15	0.32 $\pm$ 0.09	0.47 $\pm$ 0.02	0.42 $\pm$ 0.18
Mg	1.25 $\pm$ 0.47	1.23 $\pm$ 0.10	1.27 $\pm$ 0.18	0.82 $\pm$ 0.04	1.16 $\pm$ 0.38
Fe	5.18 $\pm$ 2.11	4.02 $\pm$ 0.66	3.83 $\pm$ 1.19	1.82 $\pm$ 0.09	4.03 $\pm$ 1.69
P	0.14 $\pm$ 0.06	0.08 $\pm$ 0.02	0.12 $\pm$ 0.03	0.07 $\pm$ 0.00	0.11 $\pm$ 0.05
S	0.54 $\pm$ 0.16	0.49 $\pm$ 0.18	0.42 $\pm$ 0.22	0.20 $\pm$ 0.01	0.46 $\pm$ 0.17
SO ₄ ²⁻	1.37 $\pm$ 0.84	1.01 $\pm$ 0.61	0.77 $\pm$ 0.78	0.37 $\pm$ 0.02	1.07 $\pm$ 0.67
NO ₃ ⁻	0.29 $\pm$ 0.32	0.13 $\pm$ 0.07	0.04 $\pm$ 0.03	0.02 $\pm$ 0.00	0.17 $\pm$ 0.21
Cl ⁻	0.54 $\pm$ 0.32	0.22 $\pm$ 0.13	0.19 $\pm$ 0.17	<LD	0.38 $\pm$ 0.26
NH ₄ ⁺	0.21 $\pm$ 0.18	0.04 $\pm$ 0.02	0.02 $\pm$ 0.01	0.02 $\pm$ 0.00	0.11 $\pm$ 0.15
Li	0.0036 $\pm$ 0.0015	0.0043 $\pm$ 0.0006	0.0042 $\pm$ 0.0005	0.0029 $\pm$ 0.0001	0.0037 $\pm$ 0.0012
Sc	0.0003 $\pm$ 0.0003	0.0005 $\pm$ 0.0004	0.0008 $\pm$ 0.0002	0.0005 $\pm$ 0.0000	0.0005 $\pm$ 0.0003
Ti	0.2882 $\pm$ 0.1207	0.3137 $\pm$ 0.0296	0.2819 $\pm$ 0.0437	0.1472 $\pm$ 0.0074	0.2743 $\pm$ 0.0921
V	0.0084 $\pm$ 0.0032	0.0100 $\pm$ 0.0014	0.0099 $\pm$ 0.0020	0.0058 $\pm$ 0.0003	0.0088 $\pm$ 0.0031
Cr	0.0237 $\pm$ 0.0105	0.0130 $\pm$ 0.0070	0.0116 $\pm$ 0.0059	0.0045 $\pm$ 0.0002	0.0154 $\pm$ 0.0095
Mn	0.0668 $\pm$ 0.0242	0.0617 $\pm$ 0.0051	0.0589 $\pm$ 0.0103	0.0327 $\pm$ 0.0016	0.0580 $\pm$ 0.0190
Co	0.0010 $\pm$ 0.0004	0.0010 $\pm$ 0.0001	0.0010 $\pm$ 0.0001	0.0005 $\pm$ 0.0000	0.0010 $\pm$ 0.0004
Ni	0.0061 $\pm$ 0.0015	0.0053 $\pm$ 0.0022	0.0042 $\pm$ 0.0018	0.0018 $\pm$ 0.0001	0.0049 $\pm$ 0.0020
Cu	0.1392 $\pm$ 0.0705	0.0771 $\pm$ 0.0622	0.0491 $\pm$ 0.0470	0.0134 $\pm$ 0.0007	0.0927 $\pm$ 0.0810
Zn	0.1533 $\pm$ 0.0440	0.1252 $\pm$ 0.0725	0.0755 $\pm$ 0.0374	0.0334 $\pm$ 0.0017	0.1104 $\pm$ 0.0707
Ga	0.0013 $\pm$ 0.0005	0.0014 $\pm$ 0.0002	0.0013 $\pm$ 0.0002	0.0008 $\pm$ 0.0000	0.0012 $\pm$ 0.0004
Ge	0.0015 $\pm$ 0.0009	0.0012 $\pm$ 0.0006	0.0003 $\pm$ 0.0002	0.0002 $\pm$ 0.0000	0.0012 $\pm$ 0.0010
As	0.0012 $\pm$ 0.0004	0.0014 $\pm$ 0.0002	0.0017 $\pm$ 0.0005	0.0011 $\pm$ 0.0001	0.0014 $\pm$ 0.0005
Se	0.0004 $\pm$ 0.0001	0.0003 $\pm$ 0.0002	0.0003 $\pm$ 0.0000	0.0002 $\pm$ 0.0000	0.0003 $\pm$ 0.0001
Rb	0.0065 $\pm$ 0.0028	0.0081 $\pm$ 0.0015	0.0081 $\pm$ 0.0013	0.0056 $\pm$ 0.0003	0.0070 $\pm$ 0.0024
Sr	0.0243 $\pm$ 0.0069	0.0210 $\pm$ 0.0033	0.0279 $\pm$ 0.0054	0.0273 $\pm$ 0.0014	0.0230 $\pm$ 0.0070
Y	0.0013 $\pm$ 0.0005	0.0014 $\pm$ 0.0001	0.0013 $\pm$ 0.0002	0.0009 $\pm$ 0.0000	0.0013 $\pm$ 0.0005
Zr	0.0125 $\pm$ 0.0042	0.0079 $\pm$ 0.0036	0.0074 $\pm$ 0.0034	0.0031 $\pm$ 0.0002	0.0094 $\pm$ 0.0048
Nb	0.0014 $\pm$ 0.0004	0.0014 $\pm$ 0.0001	0.0013 $\pm$ 0.0002	0.0008 $\pm$ 0.0000	0.0013 $\pm$ 0.0004
Mo	0.0082 $\pm$ 0.0044	0.0056 $\pm$ 0.0045	0.0036 $\pm$ 0.0038	0.0009 $\pm$ 0.0000	0.0058 $\pm$ 0.0052
Cd	0.0003 $\pm$ 0.0001	0.0003 $\pm$ 0.0001	0.0001 $\pm$ 0.0000	0.0000 $\pm$ 0.0000	0.0003 $\pm$ 0.0002
Sn	0.0248 $\pm$ 0.0140	0.0110 $\pm$ 0.0077	0.0102 $\pm$ 0.0104	0.0015 $\pm$ 0.0001	0.0144 $\pm$ 0.0121
Sb	0.0200 $\pm$ 0.0103	0.0102 $\pm$ 0.0050	0.0076 $\pm$ 0.0072	0.0015 $\pm$ 0.0001	0.0119 $\pm$ 0.0091
Cs	0.0004 $\pm$ 0.0002	0.0007 $\pm$ 0.0002	0.0005 $\pm$ 0.0001	0.0004 $\pm$ 0.0000	0.0005 $\pm$ 0.0002
Ba	0.1293 $\pm$ 0.0459	0.1113 $\pm$ 0.0238	0.0794 $\pm$ 0.0284	0.0565 $\pm$ 0.0028	0.0992 $\pm$ 0.0521
La	0.0019 $\pm$ 0.0008	0.0019 $\pm$ 0.0003	0.0020 $\pm$ 0.0003	0.0013 $\pm$ 0.0001	0.0019 $\pm$ 0.0006
Ce	0.0045 $\pm$ 0.0021	0.0044 $\pm$ 0.0008	0.0049 $\pm$ 0.0012	0.0027 $\pm$ 0.0001	0.0042 $\pm$ 0.0016
Hf	0.0004 $\pm$ 0.0001	0.0003 $\pm$ 0.0001	0.0002 $\pm$ 0.0001	0.0001 $\pm$ 0.0000	0.0003 $\pm$ 0.0002
W	0.0008 $\pm$ 0.0008	0.0009 $\pm$ 0.0004	0.0009 $\pm$ 0.0002	0.0007 $\pm$ 0.0000	0.0010 $\pm$ 0.0013

Pb	0.0225 ± 0.0100	0.0229 ± 0.0147	0.0177 ± 0.0033	0.0100 ± 0.0005	0.0195 ± 0.0100
Bi	0.0009 ± 0.0005	0.0004 ± 0.0003	0.0003 ± 0.0003	0.0001 ± 0.0000	0.0005 ± 0.0005
Th	0.0007 ± 0.0003	0.0008 ± 0.0001	0.0007 ± 0.0001	0.0005 ± 0.0000	0.0007 ± 0.0002
U	0.0002± 0.0000	0.0002 ± 0.0000	0.0002 ± 0.0001	0.0002 ± 0.0000	0.0002 ± 0.0001

Table 3: Comparison between profiles of PM₁₀ road dust fraction in different studies. (mg/m² for PM₁₀, weight % by mass for major constituents, µg/g for trace elements, DC: demolition/construction)

Sampling period	2007			1997-1998	2001	2000-2002						
	<i>Present study</i>			<i>Vega et al.2001</i>	<i>Ho et al. 2003</i>	<i>Zhao et al.2006</i>						
	Barcelona			Mexico City	Hong Kong	Tinajin	Jinan	Shijiazhuang	Taiyuan	Urumqi	Urumqi*	Yinchuan
	Centre	Ring Roads	DC									
PM₁₀	8.9	34.5	216.0	-	-	-	-	-	-	-	-	-
OC	5.3	4.2	4.2	13.9	13.9	6.9	6.4	9.8	10.9	16.0	21.0	-
EC	2.0	1.4	1.0	1.3	1.3	-	-	-	-	-	-	-
Al₂O₃	8.1	8.9	9.9	13.4	14.0	14.9	13.1	13.5	13.4	13.3	10.8	16.4
Ca	13	12	15	5	8.9	7	16	6	14	7	8	8
Mg	1.2	1.2	1.3	0.5	-	1.5	2.3	1.0	1.6	0.9	0.8	2.8
Fe	5.2	4.0	3.8	3.5	-	2.4	4.2	4.1	3.5	2.3	1.9	4.5
P	0.1	0.1	0.1	0.1	0.1	0.1	-	0.2	0.1	0.4	0.2	0.7
SO₄²⁻	1.4	1.0	0.8	0.7	0.8	4.6	3.4	2.5	7.0	1.5	1.5	7.0
NO₃⁻	0.29	0.13	0.04	0.07	0.04	0.00	0.19	0.13	0.00	0.00	0.00	0.00
Cl⁻	0.5	0.2	0.2	0.5	0.6	0.0	0.3	0.1	0.2	0.0	0.0	0.2
					0.1							
Ti	2882	3137	2819	3200	2379	6500	5520	4570	3450	4400	4200	4090
V	84	100	99	-	20	0	120	50	70	100	100	110
Cr	237	130	116	70	327	100	1020	50	170	100	100	80
Mn	668	617	589	580	1016	400	890	550	540	500	600	1030
Co	10	10	10	-	107	100	0	20	70	100	0	0
Ni	61	53	42	30	78	100	160	50	20	100	0	30
Cu	1392	771	491	140	600	100	220	80	120	100	100	130
Zn	1533	1252	755	690	5149	800	1420	810	480	200	100	120
Rb	65	81	81	50	175	-	-	-	-	-	-	-
Sr	243	210	279	310	234	-	-	-	-	-	-	-
Mo	82	56	36	-	37	-	-	-	-	-	-	-
Cd	3	3	1	-	24	-	-	-	-	-	-	-
Sn	248	110	102	-	289	-	-	-	-	-	-	-
Sb	200	102	76	-	60	-	-	-	-	-	-	-
Ba	1293	1113	794	600	1000	2400	-	1050	550	2500	1500	2010
Pb	225	229	177	350	1061	100	90	250	200	100	0	100

*heating period

Table 4: Ranges of Pearson’s coefficient values between couples of elements, across all samples

[illegible]

Table 5: Mean load of each PM₁₀ component at the city centre: major components (including Ti, Cu, Zn, Ba and Mn) (µg/m²) and trace elements (ng/m²).

µg/m ²	Mean	St. dev.	Min	Max	ng/m ²	Mean	St. dev.	Min	Max
OC	422	273	111	783	Li	351	234	115	700
EC	162	136	29	387	Sc	68	29	27	93
Al₂O₃	1503	547	473	2823	V	839	551	257	1615
Ca	1363	1029	390	3228	Cr	2179	1308	761	4607
K	141	94	47	274	Co	99	61	28	179
Na	45	32	14	113	Ni	611	368	192	1254
Mg	124	82	42	242	Ga	121	78	42	223
Fe	499	288	164	783	Ge	118	42	75	216
P	14	11	3	39	As	115	71	41	228
S	55	35	13	101	Se	41	26	0	78
SO₄²⁻	107	66	32	211	Rb	642	433	212	1202
NO₃⁻	16	12	4	41	Sr	2420	1512	666	4556
Cl⁻	43	32	16	122	Y	123	79	40	225
NH₄⁺	10	9	5	31	Zr	1161	579	440	1687
Ti	27	17	9	50	Nb	132	77	55	240
Cu	13	8	3	27	Mo	756	482	201	1578
Zn	12	7	4	22	Cd	28	9	16	39
Ba	12	7	5	24	Sn	2295	1555	549	5073
Mn	6	4	2	11	Sb	1913	1172	513	3445
					Cs	42	27	16	81
					La	191	123	59	344
					Ce	444	299	138	839
					Hf	37	16	17	52
					W	111	69	23	201
					Pb	2001	1007	689	3525
					Bi	87	56	19	186
					Th	64	41	23	117
					U	20	10	9	36

Table 6: Factor loadings for the complete dataset. Bold loadings are higher than 0.50

	Wear/exhaust	Crustal	Cd+Ge	Construction	Marine
Al₂O₃	0.10	0.96	-0.04	0.03	0.08
Ba	0.73	0.48	-0.03	0.08	0.18
Ca	-0.08	0.52	-0.15	0.70	0.13
Cd	0.12	-0.09	0.94	-0.12	-0.09
CO₃²⁻	-0.19	-0.08	-0.37	0.74	-0.29
Cr	0.92	0.20	0.17	0.01	-0.02
Cu	0.94	0.09	0.15	-0.05	0.01
EC	0.81	-0.37	-0.18	0.07	0.06
Fe	0.74	0.63	0.06	-0.01	-0.03
Ga	0.10	0.96	0.11	0.01	0.09
Ge	0.15	-0.02	0.93	-0.17	-0.02
Hf	0.71	0.33	0.53	-0.13	-0.10
K	0.13	0.94	-0.06	0.11	0.15
La	0.19	0.94	0.00	0.09	0.02
Li	-0.02	0.95	-0.03	0.08	0.10
Mg	0.25	0.90	0.04	0.15	0.15
Mn	0.54	0.80	0.06	0.04	0.05
Mo	0.92	0.18	0.06	-0.06	0.09
Na	0.04	0.51	-0.17	0.02	0.78
Ni	0.71	0.24	0.37	-0.01	0.25
OC	0.56	-0.30	0.08	0.47	0.13
Pb	0.43	0.61	-0.06	-0.17	-0.05
Sb	0.92	0.16	0.07	-0.13	-0.07
Sn	0.92	0.22	0.06	-0.02	-0.08
Sr	0.07	0.57	-0.09	0.68	0.21
Ti	0.30	0.89	0.12	-0.01	0.08
U	0.12	0.63	0.48	-0.01	0.45
V	0.43	0.62	0.23	-0.40	0.15
Zn	0.82	0.26	-0.05	0.00	0.38
Zr	0.83	0.36	0.29	-0.05	-0.14
Eigenvalue	14.5	6.3	3.0	1.4	1.1
% total variance	48.3	20.9	9.9	4.6	3.6
Cumul. Eigenvalue	14.5	20.7	23.7	25.1	26.2