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Variability of levels and composition of PM_{10} and $PM_{2.5}$ in the Barcelona metro system

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Abstract

From an environmental perspective, the underground metro system is one of the cleanest forms of public transportation in urban agglomerations. Current studies report contradicting results regarding air quality in the metro systems: whereas some reveal poor air quality, others report PM levels which are lower or of the same order of magnitude than those measured in traffic sites above ground level. The present work assesses summer indoor air quality and passenger exposure in the Barcelona metro, focusing on PM levels and their metal contents. In addition, the impact on indoor air quality of platform screen door systems (automated systems consisting of closed rail track and platforms) is evaluated, to determine whether these systems reduce passenger exposure to PM when compared with conventional systems (open tracks and platforms). In the Barcelona metro, PM levels inside the trains in summer are amongst the lowest reported for worldwide metro systems (11–32 $\mu PM_{2.5}\,m^{-3}$). This is most probably due to the air conditioning system working in all carriages of the Barcelona metro during the whole year. On the platforms, levels were considerably higher, reaching mean levels of 59 and 88 $\mu gPM_{2.5}\,m^{-3}$ in the new (L9) and old (L3) lines, respectively. PM_{10} data are also reported in the present study, but comparison with other metro systems is more difficult due to the scarcity of data compared with $PM_{2.5}$. Results showed clear PM daily cycles, with a drastic increase from 06:00 to 07:00 a.m., a diurnal maximum from 07:00 a.m. to 10:00 p.m., and marked decreases between 10:00 p.m. and 05:00 a.m. The elements with the highest enrichment are those associated with wheel or brake abrasion products (Ba, Fe, Cu, Mn, Cr, Sb, As, Mo, Co, Sr, among others). Laminar hematite (Fe_2O_3) was the dominant particle type, being mainly originated by mechanical abrasion of the rail track and wheels. Regarding passenger exposure to PM inside the metro system, the contribution of commuting by metro was estimated to account for around 10 % of the daily exposure. Finally, we conclude that the implementation of platform screen door systems results in reductions of both PM levels and metal concentrations, but in addition an advanced optimized ventilation system gave even a much

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higher efficiency in reducing PM exposure to metro commuters. Combining these two features PM exposure levels in the platforms may be reduced down by a factor of 7 with respect the old subway lines in Barcelona.

1 Introduction

1.1 Metro systems and air quality

All air quality plans in European cities incentivise the use of public transport as an effective tool for the abatement of atmospheric emissions from the transport sector in urban agglomerations (Nagl et al., 2007). One of the most "clean" forms of public transport is the underground metro system. This is due to the following: (a) the system is usually based on electric trains (with low emissions); (b) it can transport a large number of passengers, up to nearly 7 million passengers/day in the case of Tokyo, nearly 5 million day^{-1} in New York and Mexico, or 3 million in London (Nieuwenhuijsen et al., 2007), and consequently the system is energetically and environmentally efficient; and (c) underground transport favours a more fluid traffic on the surface, with correspondingly less congestion.

However, a number of studies have revealed poor air quality in the metro systems, especially concerning the levels of PM and metals (Frome et al., 1998; Adams et al., 2001a, b; Furuya et al., 2001; Award et al., 2002; Seaton et al., 2005; Johansson and Johansson, 2003; Karlsson et al., 2005; Aarnio et al., 2005; Cheng et al., 2008; Ye et al., 2010; Cheng and Yan, 2011; Kam et al., 2011, among others). However, this is not the case for all systems. In the comprehensive review of the air quality in metro systems by Nieuwenhuijsen et al. (2007) it is demonstrated that several studies (e.g. London, Helsinki, Stockholm) have reported higher levels of PM in the metro when compared with other commuting systems or with street canyons. In contrast, other publications have shown PM levels measured at metro systems to be lower or of the same order of magnitude than those measured in traffic sites above ground

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level (Nieuwenhuijsen et al., 2007). Such differences have been attributed to different ventilation and air conditioning systems, as well as variations in wheel materials and braking mechanisms.

Despite the fact that PM levels may be relatively high, population exposure to PM levels during commuting, including metro systems, cannot be evaluated by comparison with ambient air quality standards. Commuting in large urban agglomerations takes place mostly across air pollution hotspots. Thus, during private car, bus, cycling or even pedestrian commuting, travellers are exposed to high levels of traffic pollutants due to the proximity to emission sources. Also during metro commuting, abrasion, sparking and resuspension products may cause high exposure levels to PM higher or lower than those reached during surface commuting (Adams et al., 2001a; Chan et al., 2002a, b; Aarnio et al., 2005; Gómez-Perales et al., 2007; Tsai et al., 2008). Furthermore, commuters spend a small proportion of their time in transport, whereas most air quality standards are devised for longer exposure periods, such as annual or daily periods.

The main PM emission sources affecting indoor levels in metro systems are as follows:

1. Mechanical abrasion of rail/wheel and brakes and from the catenary (overhead line equipment).
2. Resuspension of material caused by air turbulence in the stations and tunnels.
3. PM emitted during night-time maintenance works, including use of traction fuel oil engines, construction works and welding dust.
4. Cleaning activities.
5. Surface air uptake from the surface, usually highly polluted by urban emissions.
6. Sporadic incidents, such as flooding of tunnels with high sediment waters, and fires.

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The summary of results on metro systems compiled by Nieuwenhuijsen et al. (2007), and other studies such as Salma et al. (2007), Kam et al. (2011) and Ho et al. (2012) coincide in concluding that:

1. Rubber wheel systems cause less PM pollution than steel wheel systems.
2. Electric braking systems produce less PM emissions than conventional brake pads.
3. Air conditioning in trains drastically reduces the PM exposure inside the carriages, where most of commuting time is spent.
4. Newer metro systems usually have lower PM exposure levels due to the implementation of newer technologies, including better ventilation systems and platform screen door systems.

1.2 The Barcelona's metro system

Barcelona city (north-eastern Spain) has a population of 1.6 million inhabitants rising to 4.5 million for the entire catchment metropolitan area. Its red line (L1) started operating in 1924 (after London, Budapest, Paris, Stockholm, Madrid, among others). After this first line, the green (L3), blue (L5), yellow (L4), purple (L2), bright green (L11) and very recently the new L9 and L10, have progressively been built from 1928 to 2010.

According to statistics from the Barcelona City Council, commuting in the city in 2010 was dominated by walking (about 455 of the trips), followed by public transport (30 %) and while the car accounted for close to 10 % of all trips and cycling around 2 %. The Barcelona metro absorbs a very important part of the urban commuting load, transporting around 1.25 million passengers on workdays (around 50 % of the city's public transport). The most frequent average time spent is 35 min (approx. 10.2 km round trip).

The total length of the underground system is 102.6 km, consisting of 140 train stations (Fig. 1). Trains run from 05:00 a.m. in the morning until midnight during weekdays

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and Sundays, and for 24 h on Saturdays, with a frequency between 2 and 15 min, depending on the day (weekend or weekday) and time of day. Trains from all lines are equipped with an efficient air conditioning system that works continuously throughout the year, but with higher intensity in the summer period.

The system has the following type of stations:

a. Two platforms in the same tunnel with the two rail tracks in the centre running in parallel, one for each direction.

b. Two platforms separated by a middle wall, or built in different tunnels.

c. The new L9 and L10 stations have single platforms in different tunnels and the platform is separated from the rail track by a wall with mechanical doors that are opened simultaneously with the train doors (known as platform screen door systems). The system is automatic, with computer controlled driving system that optimises speeds, braking and stopping processes. The platforms also have a specific ventilation system that channels the convective dynamics caused by the train approach to renew the air throughout lateral ventilation outlets across the closed platform. This ventilation system consists of 2 vertical wells with 2 outdoor inlets that introduce outdoor air into the tunnel from 07:00 a.m. to 10:00 p.m. local time. The tunnel air is channelled towards the ventilation inlets by the train circulation, and subsequently introduced on the platform throughout the lateral ventilation outlets. This system allows air renovation on the platform, but also produces convective dynamics in the tunnel that may cause the resuspension of tunnel dust and the subsequent arrival of this dust to the platforms.

Furthermore, although braking is electric during the approach to the platform, trains of both L3–L5 and L9–L10 systems use pneumatic braking after deceleration to a certain velocity to finally stop in the station. To this end both systems use asbestos-free brake linings, being in the front of the wheel (brake shoes) in L3 and L5 and in the sides of the wheels (drum brakes) in the L9 and L10 trains.

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This work is the first study that presents data on levels, variability and composition of PM in the Barcelona's metro system and was performed during summer. The main objectives of the study are to:

1. Measure and interpret temporal variations in PM_{10}, $PM_{2.5}$ and PM_1 levels on platforms and train carriages, comparing the old L3 and new L9 line (with platform screen door systems and new and advanced platform ventilation systems).
2. Evaluate differences in chemical and mineralogical composition of PM_{10} and $PM_{2.5}$ measured at these 2 different lines.
3. Evaluate the commuting exposure levels for PM_{10}, $PM_{2.5}$ and their chemical components for the 2 types of metro lines, and compare them to other commuting systems.

The overall aim of this study therefore is to evaluate if the L9–L10 new metro system, with platform screen door systems (automated systems closed rail track and platforms, and advanced platform ventilation systems), reduces exposure to PM when compared with the conventional systems.

Very few studies have been published on reducing PM levels in metro systems. Johansson and Johansson (2003) evaluated the effect of washing railways and walls in tunnels on abatement of PM levels at the Stockholm underground, identifying a decrease of around 13 % of the $PM_{2.5}$ levels on the platforms. Salma et al. (2007) attributed the relatively low PM levels in Budapest metro to the effect of tunnel washing (twice in a year). Furthermore, Branis (2006) also measured low levels of PM_{10} in the Prague underground immediately after a complete clean up and reconstruction. Very recently, Ho et al. (2012) showed that the installation of platform screen doors in a Seoul subway station reduced mean PM_{10} and $PM_{2.5}$ levels in around 15 %. As reported by these authors, platform screen door systems have already been installed in a number of metro systems of US, Canada, Brazil, Japan, Denmark, UK, among others, to reduce the number of accidents, but also for more effective temperature and ventilation controls on the platform.

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2 Methodology

2.1 Sampling and measurements

2.1.1 Platform measurements

Two highly contrasting underground stations within the Barcelona metro system were selected for air quality measurements, these being Sagrera L9 (S-L9) and Fontana L3 (F-L3) stations (Fig. 1). Whereas Fontana station belongs to one of the oldest underground lines in the system, Sagrera is part of the youngest, most technologically advanced line (opened 2009) and has driverless trains and platform screen door systems separating rail track from the platform, and advanced platform ventilation systems. The following instruments were placed at the far end of the platform at the train entry point, and were in operation in each station from 5 to 25 July 2011:

1. A high volume sampler (30 $m^3\,h^{-1}$) MCVPM1025, equipped with quartz microfiber filters (Pallflex) and programmed to sample PM_{10} or $PM_{2.5}$ from 08:30 a.m. to 08:30 p.m. During the first 10 days a PM_{10} inlet was used, whereas in the last 11 days the inlet was substituted by a $PM_{2.5}$ one.

2. Two optical counters: GRIMM 1107 and DustTrak DRX TSI were used for real-time measurements of levels of PM_{10}, $PM_{2.5}$ and PM_1 performed on a continuous basis with 5 min resolution during the study period. From 5 to 12 July 2011 the GRIMM counter was measuring at S-L9 station and the DustTrak at F-L3, whereas from 12 to 25 July, the instruments were exchanged.

Sporadically (on 25–29 July 2011), PM levels were systematically measured at different points on the platform in order to evaluate the representativeness of the PM measurements carried out in the sampling sites (located at one end of the platform due to safety and logistic reasons). These measurements were carried out with optical counters using resolution times from 5 min to 30 s starting at the sampling sites

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and continuing at different distances across the platforms, with a final repetition at the starting point. In the case that a spatial gradient is found this final repetition is crucial to verify if such trend is attributable to temporal or spatial gradients.

A limitation for the evaluation of the efficiency of the design of the new L9 concerning abatement of PM levels is the fact that the frequency of vehicles is very different in the two lines. Thus, a frequency of 354 and 279 trains per day during week and weekend days is reached at S-L9, whereas these values reach 595 and 432, respectively at F-L9. Levels of PM_{10} and $PM_{2.5}$ provided by both GRIMM and DustTrak monitors were corrected against the in situ and simultaneous gravimetric measurements of PM_{10} and $PM_{2.5}$ obtained with the high volume samplers. Levels of PM_1 were corrected using the factors obtained for $PM_{2.5}$. In addition, a GRIMM-DustTrak intercomparison was done during measurements performed in a number of train measurements. More information on these various QA/QC protocols and results is further supplied.

2.1.2 Train measurements

During 25, 27 and 29 July 2011, real time measurements of PM_{10}, $PM_{2.5}$ and PM_1 levels were obtained from within trains of metro lines L3, L5 and L9 over different travel distances, varying from the whole line (L9) to specific transects (L3 and L5). Figure 1 shows the seven monitored journeys during which measurements were carried out both in continuous mode and on a 30 s resolution time mode. Both GRIMM and DustTrak monitors were transported in bags and placed on the knees of passengers sitting on train seats in the middle of carriages approximately equidistant from the doors. Air uptake inlets were placed at shoulder height.

2.2 Sample treatment and chemical and mineralogical analyses

After sampling, PM_{10} and $PM_{2.5}$ filters, previously heated at 200 °C, were stabilized at 20 °C and 50 % relative humidity before weighing. This procedure was repeated 24 h later, with samples being stabilized again under the same conditions and re-weighed

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several times. Once the PM_{10} and $PM_{2.5}$ ambient levels were obtained by gravimetric measurements, the filter samples were treated for chemical analysis with the following procedure:

1. A fraction of each filter of approximately 150 cm^2 was acid digested (HF HNO_3:$HClO_4$, 5:2.5:2.5 ml), kept at 90 °C in a Teflon reactor for 6 h, driven to dryness and re-dissolved with 2.5 ml HNO_3 to make up a volume of 50 ml with Milli-Q grade water. This treated fraction was then chemically analysed by using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES: IRIS Advantage TJA Solutions, THERMO) for determination of major and certain trace elements, and by using Mass Spectrometry (ICP-MS: X Series II, THERMO) for the trace elements. For quality control of the analytical procedure a small amount (approx. 5 mg) of the NIST 1633b (fly ash) reference material loaded on a similar fraction of blank quartz filter was also analyzed.

2. Another fraction of filter of about 75 cm^2 was water leached with de-ionized water (30 g of Milli-Q grade water) to extract the soluble fraction. The solution obtained was analyzed by ion chromatography for determination of Cl^-, SO_4^{2-}, and NO_3^-, and by specific electrode for NH_4^+.

3. A third portion of filter was used for the analysis of organic (OC) and elemental carbon (EC) by means of thermo-optical methods by means of a laboratory OC-EC Sunset instrument using the protocol EUSAAR-2 (Cavalli et al., 2010).

Laboratory blank filters were analyzed following the same methodology and concentrations were subtracted to those found for the samples in order to calculate the ambient concentrations. Concentration uncertainties were estimated as described by Escrig et al. (2009).

To identify major mineral species present in PM, the coarse fraction retained in the $PM_{2.5}$ cut off inlets collected at S-L9 and F-L3, was analyzed by means of X-ray powder diffraction (XRD). XRD patterns were collected using a Bruker D8 Advance diffractometre with monochromatic Cu Kα1,2 radiation (λ = 1, 5405) operated at 40 KV and 40 mA.

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The primary parallel X-ray beam was generated by a Göbbel mirror and the scattered beam was analyzed by a Sol-X detector with the following scanning parameters: from 4 to 60° of 2q, a step size of 0.05° and time per step of 3 s. The particle resolved composition and morphology were investigated by a Quanta 200 Scanning electron Microscope equipped with an energy dispersive X-ray analyzer (SEM-EDX).

The data matrix obtained for the chemical analysis of around 30 components in approximately 40 PM_{10} and $PM_{2.5}$ 12 h samples was used as a basis for a principal component analysis carried out in order to identify factors or sources contributing to the load of PM_{10}, $PM_{2.5}$ and their constituents. To this end the STATISTICA software package was used and varimax normalization was applied.

2.3 Comparability of PM measurements

As described above data on PM_{10} and $PM_{2.5}$ levels obtained with the two optical counters (DustTrak and GRIMM) were corrected with correction factors obtained from the comparison with in situ and simultaneous gravimetric measurements performed at the two sampling sites with high volume samplers. Thus, at the two sites from 5 to 14 July 2011, the high volume sampler was equipped with a PM_{10} inlet, whereas from 15 to 25 July 2011 a $PM_{2.5}$ inlet was used. This provided enough in situ $PM_{2.5}$ and PM_{10} measurements to correct real-time and continuous measurements. PM_1 levels were corrected with the same correction factors obtained for $PM_{2.5}$. Figure 2 (bottom) shows an example of such comparison for $PM_{2.5}$ levels measured with one of the optical counters (DustTrak in this case). This procedure ensures the comparability of the PM_x data obtained with the two optical counters at the two measurement sites. Furthermore, an inter-comparison exercise was performed with measurements carried out with the two optical counters at one of the measurement sites. Figure 2 (top) shows very good results from such as an intercomparison of $PM_{2.5}$ levels performed on a minute resolution by means of the two types of optical counters after correction against high volume data.

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As stated above, sampling sites at both S-L9 and F-L3 platforms were located at the platform end, at the train arrival side, mainly for security reasons. As shown in Table 1 and Fig. 3, measurements performed across the whole length of the platforms showed that at the S-L9 sampling site PM_x measurements were 1.442 ± 0.2 times higher than the mean levels of the whole platform. In the case of F-L3, levels at the sampling site were only 1.06 ± 0.2 times higher. In other L9 and L3 platforms measured (Palau Reial L3 and Bon Pastor L9) PM_x levels at the platform end were 1.2 ± 0.1 higher compared with mean levels. This indicates that levels measured at the S-L9 sampling site are probably around 40 % higher than the exposure levels of travellers waiting elsewhere along the platform, whereas at F-L3, measurements are only 6 % higher. These factors are very similar for all three PM size fractions measured.

3 Results

3.1 PM levels on platforms

Figure 4 shows the variation of PM_x levels (5 min resolution) measured on the platforms of the S-L9 and F-L3 stations. The results show that at S-L9 site the PM_x levels during the first part of the campaign (7–12 July 2011) were markedly lower than in the second part. During 13–14 July 2011 levels increased suddenly and stayed relatively high until the end of the campaign. This increase was coincident with the final setting of the summer air ventilation scheme. Thus, from 13 July 2011 ventilation of the platform at S-L9 was carried with higher flow speeds (also inside the tunnels where ventilation was not carried out before), more air propulsion engines being working and with ventilation being still active from 12:00 a.m. to 05:00 a.m. (stop in winter). The ventilation is being carried out along lateral outlets, which introduce outdoor air In this system outdoor air is introduced from surface ventilation wells, flowing through specific channels that reach the lateral outlets along the platform. Another indoor extraction well is extracting aged air to the surface. This continuously renovates the air on the platform, but also

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convective dynamics inside the tunnel caused by train circulations may cause resuspension that favours the transport of sedimented dust into the platform when doors are opened and though not sealed parts of the platform. Such a change in the ventilation of the platform may have caused the increase in PM_x levels. The ventilation system is very complex and with the data available is not possible to identify the specific features of settings causing such a large difference in PM levels. Further studies are in progress to investigate it. At F-L3 PM_x levels remained relatively constant throughout the study period, as did operation conditions.

Although we recognize that the changes in the ventilation system were crucial in governing PM levels on the platform at S-L9, due to the fact that during the first period the ventilation system was being tested for implementation and a large number of variables were not completely controlled, we can not obtain definite conclusions on the conditions that accounted for the low PM levels in the first implementation stage. Currently a number of measurement campaigns are being carried out at S-L9 to deeply evaluate the different ventilation conditions on the PM levels.

When PM measurements on the platforms were carried out with a time resolution of 30 s (Fig. 5) the data clearly show that the arrival of the train causes a decrease on PM levels on the platform of both stations. Ventilation of the platforms by the air flux and suction caused by train arrival probably cause such a decrease.

At both sites, during weekends PM levels were markedly lower than during week days (Figs. 4 and 6), probably due to the lower frequency of trains. This has already been described by Johansson and Johansson (2003) for the Stockholm metro.

Clear daily cycles were observed in PM_x levels at both sites (Figs. 6 and 7), with a nocturnal low from 12:00 to 05:00 a.m., a drastic increase from 06:00 to 07:00 a.m., a diurnal maximum from 07:00 a.m. to 10:00 p.m., and marked decreases at 10:00 p.m. and 12:00 a.m. (when frequency of trains was reduced at both sites, Supplement S1). In addition to these general temporal trends, more subtle differences were also noted. Thus whereas at F-L3 high PM_x levels were recorded constantly throughout the day, at S-L9 distinct peaks in concentration were measured during 07:00–10:00 a.m.

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on week days and 07:00 a.m.–01:00 p.m. on weekend days, followed by lower (but still high) levels until 10:00 p.m. This is not coinciding with the variation of the frequency of trains (S1). In the first period of measurement at S-L9, when levels of PM_x where markedly lower (5–13 July 2011), the above daily pattern was not present (these values not being included in Fig. 6). PM levels were relatively constant throughout the 24 h period, with slightly higher levels from 12:00 to 05:00 a.m., probably due to the night stop of ventilation during this pre-summer ventilation set up. In the last study period, PM_x levels were much lower during the night (with full summer ventilation being in operation), but doubled during the day. Finally, we also note higher night PM_x levels recorded at weekends and attribute this as due to the fact that the Barcelona metro systems works continuously from early Saturday to Sunday night.

Table 2 shows that mean levels of PM_{10} and $PM_{2.5}$ from gravimetric measurements from 08:30 a.m.–08:30 p.m. were much higher at F-L3 (346 and 125 $\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$ respectively) than at S-L9 (145 and 46 $\mu g\,m^{-3}$). If only the sampling period for 5–12 July is considered (before the change in ventilation), levels at S-L9 were 45 and 15 $\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$, whereas the average for the whole first 10 days increase up to 70 and 23 $\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$. These results evidence that the new platform design reduces PM_x exposure to metro users during waiting time. This reduction during the whole campaign reached a factor of around 2 for PM_{10} and $PM_{2.5}$ respectively (Table 3) whereas if only the first 8 days are considered, the reduction reaches a factor of 7.2 with respect to mean F-L3 and 4.2 with respect the full summer ventilation at the same S-L9 platform.

Table 3 shows the mean PM_{10}, $PM_{2.5}$ and PM_1 levels as recorded with the real-time instruments (with the pertinent corrections from comparison with gravimetric data). In this case levels are lower than those reported in Table 2 for 08:30 a.m. to 08:30 p.m. period, given that during the night PM emissions are much reduced. The overall differences in mean daily $PM_{2.5}$ levels are still maintained, with a factor of 2.0 to 3.4 times lower levels in the new S-L9 with respect to the old F-L3 platform, depending on the period (first 8 days or whole period) considered.

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3.2 PM levels inside the trains

Table 4 reveals how PM_x levels measured inside trains during different journeys and timing along lines L9 and L3 were markedly lower (by a factor of 5) than those measured at the platforms. In general $PM_{2.5}$ levels measured during travelling along line L9 are lower than those measured for L5 and L3, with mean values for each of these lines being 11–18, 24–27, and 17–32 µg $PM_{2.5}$ m^{-3}, respectively. Indeed $PM_{2.5}$ levels recorded inside the trains (where most of the travelling time is spent) at L9 are in fact especially low, even lower than simultaneous levels of $PM_{2.5}$ recorded outdoors at urban background sites in Barcelona (18 µg$PM_{2.5}$ m^{-3}). Even the highest $PM_{2.5}$ levels measured during train travel along the other older lines (L5 and L3, 27–32 µg m^{-3}) are most probably lower than if commuting is done by bus or by car.

PM measured on the S-L9 and F-L3 platforms is very coarse, with a mean $PM_{2.5}/PM_{10}$ ratio reaching 0.29 and 0.37 respectively for the whole campaign (Table 3). The slightly coarser pattern of S-L9 may be due to the influence of resuspension caused by the specific ventilation system of the last study period. Inside the trains the ratio $PM_{2.5}/PM_{10}$ remains remarkably constant within the range 0.30–0.33. Comparison of the $PM_{2.5}/PM_{10}$ ratios measured in this study with worldwide values is difficult due to the following factors: (a) in several studies only PM_{10} or $PM_{2.5}$ is measured, (b) some studies use optical counting devices for measurements without intercomparison and correction with gravimetric data; (c) other studies correct the measurements of PM_{10} and $PM_{2.5}$ by comparison with other real time (Beta or TEOM) or gravimetric measurements, but applying the same factor to both PM fractions. Only a few studies apply correction factors specifically for PM_{10} and $PM_{2.5}$. Thus we cannot be sure that the wide ratios measured in the previously cited studies (Fig. 8), with $PM_{2.5}/PM_{10}$ ranging from 0.3 to 0.8 both in trains and on platforms, are actually due to differences on grain size or to artefact measurements. In any case, it seems that a 0.3–0.4 ratio is the most commonly reported in metro systems.

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3.3 PM mineralogy

Laminar hematite (Fe_2O_3) is the dominant mineral particle at both new (S-L9) and old (F-L3) platforms as deduced from XRD and SEM-EDX analysis (Fig. 9a and b, and Fig. 10). Such a laminate morphology is in agreement with an origin of mechanical abrasion between the rail track and the wheels.

Besides hematite, calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), clinochlore ($(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$), quartz ($SiO_2$), illite (a clay mineral, $(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$) and traces of gypsum ($CaSO_4$ $2H_2O$) were also detected by XRD and SEM-EDX in the PM fractions collected at S-L9 platform. Calcite, dolomite, and illite generally occur as discrete particles (Fig. 9c and d), while gypsum occurs as very fine particles attached to hematite and illite surfaces (Fig. 9d). Coarse (ca. 10 µm) aggregates of calcite/dolomite and clays, and C and Fe have also been identified (Fig. 9e). The resuspension by air turbulence of deposited material within the tunnel is the most probable source of the mentioned mineral species, whereas the formation of aggregates may be attributed to sporadically high moisture conditions or floodings.

In addition to the aforementioned major occurrence of laminate hematite, halite (NaCl), quartz, and dolomite were also detected by XRD in the samples collected in the F-L3 platform. Furthermore, rounded C-Fe particles generally <2.5 µm (Fig. 9f), discrete barite ($BaSO_4$) particles of around 4–5 µm (Fig. 9g), and rough-surface Fe-particles containing traces of barite and Cu (Fig. 9h) occur frequently in the PM fractions at F-L3 platform. Fusion produced by sparking at the catenary and subsequent fast quenching may account for the formation of spherical C-Fe particles. The mechanical abrasion of brake pads is probably the source of the discrete barite and also the rough-surface Fe-Barite particles, typical components of conventional brakes systems. More randomly, K-aluminosilicate particles with traces of barite and Cu were also detected at F-L3 platform. These particles may also arise from abrasion of brake pads since synthetic K-aluminosilicate species are also used in the manufacture of conventional brake pads.

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3.4 PM speciation

Table 5 summarizes the mean concentrations of levels of the 54 species analysed in PM_{10} and $PM_{2.5}$ at both S-L9 and F-L3 platforms during the study period, and the mean levels of these components at S-L9 during the first 8 days of the campaigns, before the summer ventilation set up was fully implemented. It is important to note that some components may be present in higher mean levels in $PM_{2.5}$ than in PM_{10} at S-L9, this having been caused by the fact that during the first 10 days PM_{10} was sampled, whereas during the last 10 days (with full summer ventilation set up implemented and higher PM levels) $PM_{2.5}$ samples were collected.

As Table 5 shows, the sum of all the components allowed determining from 73 to 88 % of the PM mass. The remaining mass being probably water molecules (moisture, formation and crystallization water) and some heteroatoms that were not analysed.

Fe_2O_3 is the dominant species present in both PM_{10} and $PM_{2.5}$ at both new (S-L9) and old (F-L3) platforms, as deduced from the XRD analysis and chemical speciation results, this oxide comprising 51–52 % (46–80 $\mu g\,m^{-3}$) of $PM_{2.5}$ and 41–61 % (41–206 $\mu g\,m^{-3}$) of PM_{10}. This contribution was reduced by a factor of 3 (compared with S-L9 last study period) and 15 (compared with F-L3) to 20 % (13 $\mu g\,m^{-3}$) of PM_{10} during the first 8 days of measurements at S-L9 when the ventilation system worked adequately. The high proportion of atmospheric iron present in underground steel wheel metro systems PM has been documented previously (Seaton et al., 2005, Adams et al., 2001a, b; Aarnio et al., 2005), although here we provide what we believe to be the first identification of the dominant iron species as hematite (as deduced from XRD analysis).

The second component in both relative and absolute abundance is carbonaceous aerosol, reaching 22–14 % (13–34 $\mu g\,m^{-3}$) of $PM_{2.5}$ and 13–16 % (13–53 $\mu g\,m^{-3}$) of PM_{10}. It is interesting to note that the levels of this component of PM were not lower during the first 8 days, compared with the final period at S-L9. Thus, levels of carbonaceous components not only did not decrease during the period with higher ventilation, but even slightly increased. Concerning the OC and EC contributions, although

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we measured EC and OC separately with a thermo-optical method, it is possible that Fe_2O_3 may act as a catalyser for EC oxidation at relatively low temperatures when the Fe_2O_3/EC ratio is very high (Chow et al., 2004). In this case, EC would be detected as OC by the thermo-optical method. Thus, with the Fe contents present in our samples, the high OC/EC ratios obtained in the study are very probably the result of a measurement artefact, more than an actual prevalence of OC versus EC. This is also supported by the clear anti-correlation observed between Fe and EC contents, and the correlation between OC and Fe.

Levels of the crustal component (Al_2O_3+CO_3^{2-}+Ca+K+Mg+TiO_2) are double in F-L3 with respect S-L9 (9 to 5 and 22 to 11 $\mu g\,m^{-3}$ for $PM_{2.5}$ and PM_{10}, respectively), but accounting in both cases for 6 % of $PM_{2.5}$ and 7–11 % of PM_{10}. In both stations, the crustal component is dominated by quartz, calcite and clay minerals (illite) as deduced from XRD analysis. This points to infiltrated outdoor dust resuspension, construction dust, or dry and resuspended mud introduced by convective dynamics during the air uptake from outdoor into the tunnel and subsequent channelling of wind flows to the platform throughout the lateral ventilation outlets.

Levels of water-soluble sulphate were very similar at both F-L3 and S-L9, with mean values close to 2 and 6 $\mu g\,m^{-3}$ for $PM_{2.5}$ and PM_{10}, respectively. However, levels of bulk sulphate (calculated from the bulk S content measured in the acidic solution by ICP-AES) were much higher than those of water soluble sulphate (measured in a water leachate with HPLC) in the case of the F-L3 station. This is very probably due to the occurrence in relatively high levels of barite (highly insoluble $BaSO_4$) in the coarse ($PM_{2.5-10}$) fraction at this station. Thus, whereas at S-L9 levels of Ba are <0.03 $\mu g\,m^{-3}$ at both $PM_{2.5}$ and PM_{10}, at F-L3, these reach values of 2 and 5 $\mu g\,m^{-3}$ in $PM_{2.5}$ and PM_{10}, probably related to differences in composition of brake pads of the trains of L3 and L9. Barite is very often used as a bulk material (as mineral filler) for the fabrication of brakes in trains and road vehicles (Sternbeck et al., 2002; Aarnio et al., 2005). In fact this 5 $\mu g\,m^{-3}$ coarse Ba represents 4.5 $\mu g\,m^{-3}$ of coarse insoluble sulphate, which is exactly the difference between the levels of PM_{10} water soluble sulphate (6.1 $\mu g\,m^{-3}$)

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and total sulphate (9.6 $\mu g\,m^{-3}$) in F-L3.

Nitrate levels were very similar, with 0.2 and 0.8–1.9 $\mu g\,m^{-3}$ for $PM_{2.5}$ and PM_{10}, respectively. Both sulphate and nitrate levels fall in the range of typical summer outdoor levels in Barcelona, whereas in winter, sulphate levels are markedly reduced and nitrate slightly increased (Pérez et al., 2008).

Levels of ammonium clearly correlate with water soluble sulphate at both S-L9 and F-L3 ($R^2 = 0.81$ and 0.66). For nitrate, the correlation with ammonium levels is still evident, but lower than for sulphate ($R^2 = 0.36$ and 0.33). The results suggest the occurrence of ammonium sulphate, and ammonium nitrate (the main modes of occurrence of sulphate and nitrate in outdoor conditions), but also the occurrence of other sulphate species, such as sodium and calcium nitrate and sulphate, as deduced from the ion excess of sulphate+nitrate versus ammonium and the XRD analysis.

Conversely to most of the PM components analyzed, levels of secondary inorganic aerosols (SIA, sulphate + nitrate + ammonium) in PM_{10} were slightly higher (34 to 48 %) in S-L9, than in F-L3, and this is probably reflecting a better outdoor air uptake for ventilation in the new metro station. Thus this outdoor PM component, accounts for 2–3 % of $PM_{2.5}$ at both stations, but for 2 and 9 % of PM_{10} in F-L3 and S-L9, respectively.

Levels of sodium+chloride reached similar levels at both stations (0.7–0.9 and 1.6–1.5$\mu g\,m^{-3}$ for $PM_{2.5}$ and PM_{10}).

Concerning the levels of trace elements, much higher mean levels in PM_{10} were measured at F-L3 with respect to S-L9. The following grouping of elements was obtained according to the degree of their enrichment in the former versus the later:

- Ba is enriched in PM_{10} at F-L3 near 200 times with respect S-L9.
- Hf, Cu, Mo, Sr, Zr, 40 to 10 times higher.
- Mg, Mn, Fe, Zn, Cu, Ni, As, Sn, Ta, Pb, from 5 to 9 times higher.
- Al, Ca, Ti, Cr, Li, Ga, Ge, Sb Y, Nb, Cd, REEs, W, Bi, U and Th from 2 to 4 times higher.

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– Na, K, V, Se, Rb, similar levels at both stations.

In the case of levels of trace elements in $PM_{2.5}$, the above differences were reduced, probably due to the fact that $PM_{2.5}$ was carried out at the 2 sites during the last 10 days of the campaign, when with full summer ventilation set up was implemented at S-L9 and higher resuspension was produced. However, despite this, important differences were present:

– Ba levels are still 100 times higher at F-L3.

– Sr, Mo, Hf, As, 10-15 times.

– Mg, Cu, Zn, Zr and Ta, 5–8 times.

– Al, Fe, Ca, Mn Cr, Ti, Li, V, Co, Ni, Ga, Ge, Rb, Y, Nb, Cd, Sn, REEs, W, Pb and Bi 1.2 to 6 times.

– Similar (<1.2) levels K, Na, Se, Th and U.

As previously stated, for other components, both the type and composition of brakes from the L3 and L9 trains, the better air-recirculation in the new stations of L9 and the platform screen door system, may account for these differences. Elements with similar concentrations are those introduced in the metro system mostly from outdoor air (Na, K, Se, V, among others).

It is also interesting to note the high levels of As measured in $PM_{2.5}$ at F-L3 ($13\,ng\,m^{-3}$) compared with S-L9 ($1.4\,ng\,m^{-3}$). This is probably associated with the occurrence of this element as an impurity in brakes, railway or catenary metallic components.

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4 Discussion

4.1 PM levels in trains and platforms

As already mentioned a number of studies reported high PM levels in a number of metro systems, such as Berlin, London, Stockholm, Prague, Roma, Beijing, Budapest, Seoul, Paris and Shanghai (Fromme et al.,1998; Adams et al., 2001a, b; Johansson and Johansson, 2003; Seaton et al., 2005; Branis, 2006; Ripanucci et al., 2006; Li et al., 2007; Salma et al., 2007; Kim et al., 2008; Park and Ha, 2008; Raut et al., 2009; Ye et al., 2010). Other studies performed in metro systems, such as Tokyo, Taipei, Helsinki, México, Hong Kong, Guanzhou, Los Angeles and New York (Furuya et al., 2001; Cheng et al., 2008; Cheng and Yan, 2011; Aarnio et al., 2005; Gómez-Perales et al., 2004, 2007; Mugica-Álvarez et al., 2012; Chan et al., 2002a, b; Kam et al., 2011; Chillrud et al., 2004) report relatively low PM levels.

Nieuwenhuijsen et al. (2007) and Salma et al. (2007) interpreted that such differences in PM levels among the metro systems may be due to the abrasion of railways and catenary metal, and to braking systems. The former study also showed that the old metro systems, some of them founded in the late XIX or early XX centuries, had worse ventilation that the new systems; this being reflected in higher PM levels in the older systems. Furthermore, Nieuwenhuijsen et al. (2007) also demonstrated that the lowest PM levels were recorded in metro systems with trains equipped with rubber or rubber/steel wheels (Montreal, México, Tokyo and Hong Kong). Finally, they also implicated the air conditioning implemented in a number of metro systems such as New York, Tokyo, Washington, Hong Kong, and Guanzhou, as a possible factor favoring low PM levels in trains. Johansson and Johansson (2003) also reported that PM levels in underground metro stations are closely associated with the frequency at which trains run. Branis (2006) and Cheng et al. (2008) suggested that outdoor air quality may also significantly influence low PM levels metro systems through ventilation systems.

When comparing the data obtained at S-L9 and F-L3 platforms in this study with published data from the metro systems from other cities (Fig. 8, and references therein)

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the following observations may be made:

1. Mean PM_{10} levels on the platform range from 51 to 103 $\mu g\,m^{-3}$ in (from low to high) Taipei, Los Angeles, México and probably (as deduced from $PM_{2.5}$ levels) Helsinki, New York and Prague; and from 129 to 407 $\mu g\,m^{-3}$ in Budapest, Paris, Seoul, Shanghai, Stockholm, Rome and probably London. Mean PM_{10} levels recorded at S-L9 during 8 days before the change of ventilation (45 $\mu g\,m^{-3}$) fall in the low range of the lowest PM_{10} metros. If the whole measuring period is considered then PM_{10} levels at S-L9 and F-L3 fall, respectively, in the low and high range of high PM_{10} systems (145 and 346 $\mu g\,m^{-3}$).

2. Mean $PM_{2.5}$ levels on the platform measured in these previous studies range from 33 to 62 $\mu g\,m^{-3}$ in Taipei, Budapest, Mexico, Los Angeles, Helsinki, New York, and probably Prague; from 93 to 129 $\mu g\,m^{-3}$ in Paris and Seoul; and from around 200 to 375 $\mu g\,m^{-3}$ in London, Stockholm, Shangai and probably Rome. The mean levels of $PM_{2.5}$ attained for the whole study period at the S-L9 platform (46 $\mu g\,m^{-3}$) are slightly lower than those reported recently by Ho et al. (2012) for a Seoul subway station equipped with platform screen doors (58 $\mu g\,m^{-3}$).

3. Mean $PM_{2.5}$ levels recorded during measurements at S-L9 during 8 days before the change of ventilation to full summer set up (15 $\mu g\,m^{-3}$) are even lower than the lowest $PM_{2.5}$ metros. If the whole period is considered $PM_{2.5}$ levels at S-L9 still fall in the range of the lowest $PM_{2.5}$ metros, and F-L3 in the middle $PM_{2.5}$ systems (46 and 125 $\mu g\,m^{-3}$, respectively). Thus, we may qualify $PM_{2.5}$ levels recorded in the S-L9 as very low (for the first 8 days period) and low (for the whole period) when compared with the usual concentration range in worldwide metro systems. At F-L3, levels may be considered intermediate.

PM levels are much elevated on the platforms, being around 3-4 times higher than in trains, with mean levels of 46 and 18 $\mu g PM_{2.5}\,m^{-3}$ at the new S-L9 closed platform, depending on whether all the period or the first 8 days are considered, and

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125 µg$PM_{2.5}$ m^{-3} at the old open F-L3 platform (Table 2). Furthermore, additional measurement campaigns carried out at two additional platforms (Table 1) showed mean levels of 44 µg$PM_{2.5}$ m^{-3} at Palau Reial (a relatively new station added to the L3 line which has open platforms with the two direction platforms isolated one from the other by a wall), and 23 µg$PM_{2.5}$ m^{-3} at Bon Pastor (new and closed platform from L9, similar to S-L9). Thus, PM levels measured on the platforms in the Barcelona metro in July 2011 are also in the lowest range reported for metro systems worldwide (Fig. 8 and Table 5) in the case of the newer metro stations, whereas levels at the older L3 stations fall in the low range for high PM old metro systems. Reasons for this differentiation are probably related to:

1. New and optimized L9 ventilation systems that although in full summer setting cause resuspension of dust, yield lower PM levels than in L3 platforms.
2. The closure of the platforms in the new L9 stations, where the automatic platform doors open and close simultaneously with the doors of the train and isolate the platform from the pollution of the tunnels.
3. New free driver L9 train with optimal speeds and braking systems.
4. The separation of the 2 different opposite platforms in the L3 stations made in an intermediate growth stage of the metro system such as Palau Reial station, also yielded relatively low levels of PM. If these two platforms are not isolated, as it is the case for F-L3, both emissions from railway abrasion and brakes, and the resuspension of dust are higher since the trains from the two opposite directions emit PM into the same space.
5. The F-L3 platform has a slightly curved shape and railway and brake abrasion emissions may be higher.
6. Although in both cases electric braking is used, in the case of F-L3 the final braking is carried out with frontal brake pads, whereas in S-L9 this is done with lateral

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pads (similarly to disc braking systems in cars).

As for the measurements performed on the platforms, the following evidences were obtained when comparing the data obtained on PM levels measured in the trains from our study and the data published from worldwide metro systems (Fig. 8, and references therein):

1. Mean PM_{10} levels on board of trains ranged from 32 to 67 $\mu g\,m^{-3}$ in (from low to high): Los Angeles, probably (as deduced from $PM_{2.5}$ levels) Helsinki, México, Taipei, Hong Kong and Guanzhou; and from 114 to 325 $\mu g\,m^{-3}$ in Prague, Berlin, Seoul, probably London, and Beijing. Mean PM_{10} levels measured in the trains of L9 (48 $\mu g\,m^{-3}$) fall in the range of the lowest PM_{10} metro systems, but also in the case of L3 and L5 (79 $\mu g\,m^{-3}$).

2. Mean $PM_{2.5}$ levels on board of trains ranged from 21 to 44 $\mu g\,m^{-3}$ in Helsinki, México, Los Angeles, Taipei, Hong Kong, Guanzhou, and probably Prague; probably from around 60 to 90 $\mu g\,m^{-3}$ in Berlin; and from 112 to 250$\mu g\,m^{-3}$ in Beijing, Seoul and London. Mean $PM_{2.5}$ levels measured in the trains of L9 (15 $\mu g\,m^{-3}$) fall below the range of the lowest $PM_{2.5}$ metro systems. For L3 and L5 summer $PM_{2.5}$ levels also fall in the range of the lowest $PM_{2.5}$ metros (25 $\mu g\,m^{-3}$).

3. Probably air filtering by air conditioning systems intensively operating in summer in the trains is responsible for the low PM levels measured in both new (L9) and old (L3 and L5) metro lines in Barcelona.

4.2 PM speciation

There are only a few studies on PM speciation carried out in metro systems. We show a comparison of the available published data with the results of this study in Fig. 11. Adams et al. (2001a, b) measured mean levels of 87, 63, 16, 16, 1.7, 0.3 $\mu g\,m^{-3}$ for Fe, Si, Al, Ca, Mn and Zn in $PM_{2.5}$ in the London metro platforms. Seaton et al. (2005)

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measured in the same metro system levels of 57–115, 2–4, 08–3.4 and 0.2–0.7 $\mu g\,m^{-3}$ of Fe, Si, Mn and Cr in $PM_{2.5}$. Furuya et al. (2001) measured also very high levels of metals in the Tokyo metro, with mean levels of 94, 5, 5, 1, 0.7, 0.6 and 0.3 $\mu g\,m^{-3}$ for Fe, Ca, Si, Cu, Ni, Zn and Cr in PM_{10}. Aarnio et al. (2001) measured lower metal levels in the Helsinki metro, but still much higher than typical outdoor concentrations. Thus, mean $PM_{2.5}$ levels of 25, 0.3, 0.2 and 0.2 $\mu g\,m^{-3}$ of Fe, Mn, Ca and Cu were reported. Levels of OC and EC reached 7 and 4 $\mu g\,m^{-3}$ in $PM_{2.5}$. Similar levels were also reported in the New York metro system by Chillrud et al. (2004), with 26, 0.2 and 0.1 $\mu g\,m^{-3}$ of Fe, Mn and Cr; and by Salma et al. (2007) in Budapest underground, with 16 $\mu gFe\,m^{-3}$, 0.4 $\mu g\,m^{-3}$ of Ca and Si, 0.1–0.2 $\mu g\,m^{-3}$ of Al, Mn and Cu, and 0.01–0.05 $\mu g\,m^{-3}$ of Ni, Cr and Zn in PM2.0. In the Buenos Aires underground, Murruni et al. (2009) reported levels of Fe, Cu and Zn in TSP reaching 40–110, 0.4–1.2, and 0.1–0.2 $\mu g\,m^{-3}$ in the more polluted C line, and 8–46, 0.05–0.2, and 0.05 in the less polluted line B. In the Toronto Metro levels of 0.43 $\mu g\,m^{-3}$ of Mn in $PM_{2.5}$ were reported. In the case of the Mexico metro system (Gómez Perales, 2004, 2007) levels of Fe, Si, Cu, Ca, Zn, Mn and Cr in $PM_{2.5}$ reached, 4, 1.6, 2.4, 0.8, 0.3, 0.1 and 0.1 $\mu g\,m^{-3}$, respectively. In this case OC and EC levels reached around 12 and 4 $\mu g\,m^{-3}$, respectively. This higher (OC+EC)/Fe ratio is probably due to the rubber type wheel system used in Mexico. However, levels of elements such as Cu were still at relatively high levels.

In the Barcelona's Metro, levels of Fe ranged from 144 and 55 $\mu g\,m^{-3}$ in PM_{10} and $PM_{2.5}$ respectively, for F-L3 to 9 $\mu g\,m^{-3}$ in PM_{10} for the first 8 days at S-L9, whereas levels of Mn, Cu, Zn and Cr decreased from 0.6 to 0.1, 0.5 to 0.03, 0.5 to 0.08 and 0.1 to 0.02 $\mu g\,m^{-3}$ for the same periods and PM sizes. Levels of OC and EC reached 33 and 1.2 $\mu g\,m^{-3}$ in $PM_{2.5}$ for F-L3 and 9 and 5 $\mu g\,m^{-3}$ in PM_{10} for the first 8 days at S-L9. Levels of Ca and Al were around 1.7 and 0.7 $\mu g\,m^{-3}$, respectively, for the two sites, periods and PM sizes. According to these results, levels of metals are intermediate between the London and Helsinki metro systems for metals in the case of the old F-L3 platform, but much lower than in most metro systems in the case of the first 8 sampling

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days at S-L9 (Fig. 9). In the case of Fe, only the Mexico metro (with rubber wheel trains) recorded lower levels than the S-L9 station at Barcelona during the first 8 days of sampling.

We were only able to find a paper on with detailed PM_{10} speciation in metro systems, the one showing data from the Tokyo subway system by Furuya et al. (2001). Most of the studies were carried out by analyzing $PM_{2.5}$. As Shown in Fig. 1, F-L3 registered very similar levels to those from Tokyo subway.

In the present study a larger number of elements were analyzed when compared with the previously referenced speciation studies. This allowed applying a Principal Component Analysis using the nearly 40 $PM_{2.5}$ and PM_{10} samples collected at both S-L9 and F-L3 platforms. The results allowed the identification of the following sources/factors of PM at the Barcelona's metro (S1):

- Factor 1 (64 % of the variance) contains elements with 0.9 to 0.6 factor loadings (from the highest to the lowest): Cu, Ba, Sr, Sn, Mo, Pb, Mg, OC+EC, Ti, Zn, Co, Ni, As, Cd, W, PM_x, Al, Mn, Li, REEs, S, Cr, V. Since, several of these elements are typically associated with brake emissions, and PM is present with a high factor loading, this group of elements probably represents the emissions from brake abrasion with a particularly high impact on PM levels at F-L3, and much lower influence at S-L9, the latter having platforms with closed rail tracks. Probably, the much higher concentrations measured at F-L3 with respect to S-L9 for elements such as Ba (100 times higher) Mo (15 times), Sr (15 times) As (10 times) and Cu (5 times) are caused by differences in the composition of frontal and lateral-disc brake pads used in each line.

- Factor 2 (15.3 % of the variance) contains elements with 0.9 to 0.6 factor loadings (from the highest to the lowest): NO_3^-, Na, NH_4^+, K, SO_4^{2-}, Se, V; and anti-correlated with U (factor loading -0.7). This factor probably represents the outdoor contribution to the platform ambient air. Since PM has a low factor loading, this factor probably has very low influence on the variability of PM on the platforms.

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– Factor 3 (4.7 % of the variance) contains elements with 0.8 to 0.6 factor loadings (from the highest to the lowest): Fe, Ca, Cr, Th, PM_x, Sb, Mn, Rb, Al. Since Fe is the element with higher factor loading, this group of elements probably represents the wheel-rail abrasion products, but also resuspension emissions, as deduced from the relatively high factor loadings of Ca, Th, Al and Rb, typical crustal components. Most of these elements are present in higher concentrations at F-L3 by a factor of 2 compared with S-L9. Again, the platforms with closed rail tracks may make the difference.

4.3 PM exposure levels (commuting)

Table 6 shows data from the calculation of the PM exposure for a metro commuting travel of 30 min in the train and 5 min on the platform. Mean exposure during this travel would reach 83 and 27 $\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$, respectively, as deduced from the calculation of the mean concentrations according to the time spent in the train and platforms. These values are reduced to 60 and 19 $\mu g\,m^{-3}$ for L9 (53 and 16 $\mu g\,m^{-3}$ for the first 8 days at S-L9).

Since data on PM exposure during different commuting modalities in Barcelona is not available for comparison, an assessment on PM exposure levels from different cities and transport modes is shown in Table 7 to compare the data obtained in the present study.

Int Panis et al. (2010) obtained mean exposure commuting levels of PM_{10} for passenger cars and bicycles in Belgian cities ranging from 35 to 75, and 42 to 78 $\mu gPM_{10}\,m^{-3}$, respectively. In Dublin, McNabola et al. (2008) reported mean exposure levels reaching 83, 88, 128 and 63 $\mu gPM_{2.5}\,m^{-3}$ for car, bike, bus and pedestrian commuting. Fondelli et al. (2008) measured exposure levels during commuting by bus and taxi in Florence in the range of 33 to 75 and 20 to 70 $\mu gPM_{2.5}\,m^{-3}$, respectively.

$PM_{2.5}$, $PM_{3.5}$ or PM_4 exposure levels in passenger cars in London, Houston, and Manchester reached from 35 to 42 $\mu g\,m^{-3}$ (Morandi et al., 1988; Adams et al., 2001a,

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b; Gee et al., 1999; Gee and Raper, 1999). $PM_{2.5}$ exposure during bus commuting reached mean levels of 39 $\mu g\,m^{-3}$ in London (Adams et al., 2001), but 338 $\mu gPM_4\,m^{-3}$ in Manchester (Gee et al., 1999; Gee and Raper, 1999). Cycling commuting in London and Manchester reached 30 $\mu gPM_{2.5}\,m^{-3}$ and 54 $\mu gPM_4\,m^{-3}$, respectively but 135 $\mu gPM_{3.5}\,m^{-3}$ in Southampton (Adams et al., 2001; Bevan et al., 1991; Gee et al., 1999; Gee and Raper, 1999). Taxi commuting reached 33 $\mu gPM_{2.5}\,m^{-3}$ in London according Pfeifer et al. (1999).

Tsai et al. (2008) measured mean motorcycle commuting exposure levels in Taipei of 113, 68 and 48 $\mu g\,m^{-3}$ for PM_{10}, $PM_{2.5}$ and PM_1, respectively. For car commuting exposure levels reached 42, 22 and 16 $\mu g\,m^{-3}$, but time was the longest. For bus commuting levels reached 70, 39 and 31 $\mu g\,m^{-3}$ for PM_{10}, $PM_{2.5}$ and PM_1.

Metro commuting exposure levels (Table 7) reached 50 and 33 $\mu g\,m^{-3}$, respectively, for PM_{10} and $PM_{2.5}$ in Hong Kong (Chan et al., 2002a), and 67 and 44 $\mu g\,m^{-3}$ in Guanzhou (Chan et al., 2002b). In Taipei exposure levels reached 65, 35 and 26 $\mu g\,m^{-3}$, respectively for PM_{10}, $PM_{2.5}$ and PM_1 (Tsai et al., 2008), similar levels to the 33 $\mu gPM_{2.5}\,m^{-3}$ reported for México by Gómez-Perales et al. (2007), lower to those obtained for New York (62 $\mu g\,m^{-3}$, Chillrud et al., 2004) and another study carried out in México (61 $\mu gPM_{2.5}\,m^{-3}$, Gómez-Perales et al., 2004), and much lower than those reported by Seaton et al. (2005) in London (157–247 $\mu gPM_{2.5}\,m^{-3}$).

Accordingly with the studies shown, commuting PM exposure in passenger cars reaches levels of 35–75 $\mu gPM_{10}\,m^{-3}$, 22–83$\mu gPM_{2.5}\,m^{-3}$, comparable levels to the ones reported for metro commuting in Barcelona in July 2011: 83 and 27 $\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$. $PM_{2.5}$ exposure levels during bus and cycling/motorbike commuting in these studies reached 33-128 (most of them in the range 39–75 $\mu gPM_{2.5}\,m^{-3}$) and 68–88 $\mu gPM_{2.5}\,m^{-3}$, respectively, markedly higher than in the Barcelona metro (27 $\mu gPM_{2.5}\,m^{-3}$). Finally, the mean levels of $PM_{2.5}$ exposure during metro commuting in Barcelona obtained in the present study are also lower than most of the exposure levels in worldwide metro systems (Table 7, 33–62 $\mu gPM_{2.5}\,m^{-3}$, with the exception of

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London, 157–247 $\mu g PM_{2.5}\, m^{-3}$).

Our results also show that for the study period, a return travel of 35 min duration (70 min in total) contributes to the mean 24 h exposure with 4.0 and 1.3 $\mu g\, m^{-3}$ for PM_{10} and $PM_{2.5}$, respectively. As shown in Table 6, these values are reduced if L9 is considered (2.9 and 0.9 $\mu g\, m^{-3}$). Seaton et al. (2005) reported a contribution of 17 $\mu g PM_{2.5}\, m^{-3}$ for 2 h travel in the London metro, much higher than the values reported in our study for the same travelling time (2.6 $\mu g PM_{2.5}\, m^{-3}$). If we assume a mean urban background concentration of 20 $\mu g PM_{2.5}\, m^{-3}$ for Barcelona (Pérez et al., 2008) equivalent to the urban background exposure, the metro commuting contribution accounts for around 13 % of the daily exposure. However, Jacquemin et al. (2007) evidenced that mean $PM_{2.5}$ personal exposure of 50 citizens with cardiovascular problems in Barcelona reached around 45 $\mu g PM_{2.5}\, m^{-3}$. In this case, the metro commuting contribution accounts for around 6 % of the daily exposure. More recently, Schembari et al. (2012) obtained a mean personal exposure of 26 $\mu g PM_{2.5}\, m^{-3}$ for 53 pregnant women in Barcelona. In this case, the metro commuting contribution accounts for around 10 % of the daily exposure.

When comparing the levels of the $PM_{2.5}$ components analyzed in this study with those reported by Pérez et al. (2008) for their mean levels in outdoor urban background $PM_{2.5}$ at Barcelona (Table 5), the following groups of components can be considered according their metro/outdoor enrichment ratios:

- Ba is enriched 5–2000 times, with a mean of 270 times, in the metro $PM_{2.5}$ compared outdoor levels, depending if PM_{10} at S-L9 during the first 8 days or $PM_{2.5}$ at F-L3 are considered, respectively.
- Fe: 50–220 times, mean 221.
- Cu: 4–80 times, mean 50.
- Mn: 11–87 times, mean 70.

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- Cr: 10–40 times, mean 35.
- Sr: 4–59 times, mean 31.
- Sb: 9–30 times, mean 32.
- As: 7–44 times, mean 24.
- Mo, Co, W, Li, Ge, Ga and Th: 10–20 times.
- PM, OC + EC, Ca, Al, Mg, Zn, Ti, Zr, Sn, Ni, Hf, Rb, Nb, U, Y, Ta and REEs: 3–9 times.
- Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Na, K, Pb, V, P, Cd, Bi and Se: 0.1–1 times.

The elements with the highest enrichment are those associated with wheel or brake abrasion products (Ba, Fe, Cu, Mn, Cr, Sb, As, Mo, Co, Sr, among others) included in factor 1 and 3 from the PCA. Furthermore, the most of the components with a low metro/outdoor ratio coincide with those included in factor 2 of the PCA attributed to the outdoor contribution.

In the present study we calculated the contribution to daily exposure of a number of elements that have been found largely enriched in the metro particles compared to outdoor $PM_{2.5}$. Thus, calculated contributions to $PM_{2.5}$ daily exposure from a return 35 (×2) minutes journey reach: 0.5 µgFe m^{-3}, 10 ngBa m^{-3}, 5 ngMn m^{-3}, 0.6 ngCr m^{-3} and 0.06 ng As m^{-3} (0.25 µgFe m^{-3}, 0.2 ngBa m^{-3}, 2.4 ngMn m^{-3}, 0.3 ngCr m^{-3} and 0.01 ng As m^{-3} for the first 8 days at S-L9). This estimates increases of 340, 235, 145, 40 and 20 % (180, 4, 24, 17 and 4 % for the first 8 days at S-L9) compared to outdoor based exposure of Fe, Ba, Mn, Cr and As respectively.

Aarnio et al. (2005) in Helsinki found that although the metro commuting contributed only to 3 % of the daily $PM_{2.5}$ exposure, for some metals this contribution was very high, close to 200 and 60 % of the outdoor levels in the case of Fe and Mn, respectively. In this case the metro Fe levels in $PM_{2.5}$ were around 300 times higher than in outdoor

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$PM_{2.5}$, and those of Mn, Cu, Ni, Ti and Cr from 10 to 100 times. Chillrud et al. (2005) measured levels of Fe, Cr and Mn from 100 to 250 times higher in the New York subway than in outdoor. Levels of Cu, Al, Sn, Ag, Sb and As where 10–25 times higher; those of Ti, Ca, Sc, Be, Na, Zn, K, Pb, Cs, Co, Mn and Cd from 3 to 9 times higher; and those of La, V, Se SO_4^{2-} and Tl similar or lower than outdoor. Both results obtained in Helsinki and New York are similar to those obtained in Barcelona. However, these ratios were reduced to a factor of 2 for most of these elements in the case of the Mexico City subway (Múgica-Álvarez et al., 2012), probably as a result of the wheel type used.

5 Conclusions

The results of this study demonstrate that during July 2011 the new metro system of lines L9 and 10 in the Barcelona city subway was able to reach ambient particulate pollution lower than in the conventional system (L3) by a factor of 2 to 3, which is probably attributable to the advanced ventilation set up, to the platform screen door system and other design features of the platform and trains which, reduce the contribution of metallic abrasion dust to ambient PM on the platform. The levels of $PM_{2.5}$ attained for the whole study period in the S-L9 platform are of the same order of those reported recently by Ho et al. (2012) for a Seoul subway station equipped with platform screen doors.

The full summer ventilation set up implemented from 13 July at S-L9 produces a high air renovation rate, but also higher convective dynamics may cause the resuspension of dust. The ventilation system is very complex and with the data available is not possible to identify the specific features causing the large differences in PM levels measured. Further studies are in progress to investigate it. In any case, during the first 8 days of measurements, without this summer ventilation set up being fully implemented, the reduction of ambient PM with respect to the conventional L3 line reached a factor of 7.2, but also of 4.2 with respect to the full summer ventilation operation settings at the same S-L9.

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While recognize that the changes in the ventilation system were crucial in governing PM levels on the platform at S-L9, due to the fact that during the first period the ventilation system was being tested for implementation and a large number of variables were not completely controlled, we can not obtain definite conclusions on the conditions that accounted for the low PM levels in the first implementation stage. Currently a number of measurement campaigns are being carried out at S-L9 to deeply evaluate the different ventilation conditions on the PM levels.

Although during the approach to the platform braking is electric, trains of both old (L3–L5) and new (L9–L10) systems use pneumatic braking after deceleration to a certain velocity to finally stop on the platform. Both systems use asbestos-free brake linings, but these are frontal to the wheel in L3 and L5 and lateral in the L9 and L10 trains. The different composition of brake pads of these braking systems is responsible for much higher levels (by factors from 5 to 200) of specific metals, such as Ba, As, Sr, Mo, Cu, among others, in the conventional line 3. Low metal specifications for brake pads would reduce considerably exposure to metals of commuters.

The chemical speciation of PM allowed identifying 3 major sources of particles in the metros system: (a) brake wear; (b) outdoor air introduced into the metro; (c) metal wear.

The mineralogical characterization by means of SEM and XRD permitted to identify the presence of laminar hematite (Fe_2O_3) as the dominant particle, being mainly originated by mechanical abrasion of the rail track and wheels.

Levels of PM inside trains of the Barcelona city subway are amongst the lowest reported for worldwide metro systems. This is most probably due to the air conditioning system working in all carriages of the Barcelona metro.

Our results also evidence that for the study period, a return travel of 35 min duration (70 min in total) could contribute to the mean 24 h exposure with 4.0 and 1.3 $\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$, respectively. These values are reduced if L9 is considered (2.9 and 0.9 $\mu g\,m^{-3}$). This may increase daily personal exposure to $PM_{2.5}$ in around 10 %. The calculated contributions to $PM_{2.5}$ daily exposure reach: 0.5 $\mu gFe\,m^{-3}$, 10 $ngBa\,m^{-3}$,

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5 ngMn m^{-3}, 0.6 ngCr m^{-3} and 0.06 ng As m^{-3} (0.25 µgFe m^{-3}, 0.2 ngBa m^{-3}, 2.4 ngMn m^{-3}, 0.3 ngCr m^{-3} and 0.01 ng As m^{-3} for the first 8 days at S-L9), this accounting for an increase of 277, 235, 145, 40 and 20 % (180, 4, 24, 17 and 4 % for the first 8 days at S-L9) when compared to the outdoor based exposure of Fe, Ba, Mn, Cr and As respectively. Such mean levels of $PM_{2.5}$ exposure during metro commuting in Barcelona are also lower than most of the exposure levels in worldwide metro systems. Both PM levels and metal concentrations are clearly reduced in the case of the new L9 with respect the L3, but also research is needed to optimize the full summer ventilation scheme to avoid increasing PM levels at S-L9 platforms.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/6655/2012/acpd-12-6655-2012-supplement.pdf.

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Table 1. PM_x levels ($\mu g\,m^{-3}$) measured across the platforms at different metro stations from L9 and L3 lines. Mean data of the sampling sites (at the platform end) are also reported for comparison with the mean ponderate values measured across the station.

	PM_{10}	$PM_{2.5}$	PM_1
Platform Fontana 25/07/2011	252	89	80
Sampling site	253	89	82
Platform Fontana 27/07/2011	292	98	90
Sampling site	264	86	79
Sampling site repetition	373	128	118
Platform P. Reial 26/07/2011	124	36	30
Platform end P Reial	149	44	36
Platform end repetition	148	42	35
Platform P. Reial 29/07/2011	160	52	48
Platform end P. Reial	197	64	58
Platform Bon Pastor 27/07/2011	87	21	18
Platform end B Pastor	95	25	21
Platform end repetition	113	26	23
Platform Sagrera 25/07/2011	297	83	38
Sampling site	374	112	50
Platform Sagrera 27/07/2011	328	97	83
Sampling site	528	155	132
Sampling site repetition	429	127	108

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Table 2. Mean levels of PM_x from gravimetric measurements at the Sagrera (L9) and Fontana (L3) platforms from 08:30 a.m.–08:30 p.m. Values highlighted in bold are deduced from gravimetric PM_{10} or $PM_{2.5}$ by applying $PM_{2.5}/PM_{10}$ ratios of the respective sampling period. The italic data in the right hand of the table are the levels corrected by factors of 1.42 and 1.06 to represent the exposure across the whole S-L9 and F-L3 platforms, respectively, as explained in the methodology section.

SAGRERA L9	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
5–11/07/2011	64	**21**	*45*	***15***
5–14/07/2011	100	**33**	*70*	***23***
15–25/07/2011	**310**	90	***213***	*63*
5–25/07/2011	206	65	*145*	*46*
FONTANA L3	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
5–14/07/2011	339	**115**	*320*	***108***
15–25/07/2011	**395**	150	***373***	*142*
05–25/07/2011	367	133	*346*	*125*

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Table 3. Mean levels of PM_x from real time 24 h day^{-1} measurements at the Sagrera (L9) and Fontana (L3) platforms. The italic data in the right hand of the table are the levels corrected by factors of 1.42 and 1.06 to represent the exposure across the whole S-L9 and F-L3 platforms, respectively, as explained in the methodology section.

SAGRERA L9	PM_{10}	$PM_{2.5}$	PM_1	PM_{10}	$PM_{2.5}$	PM_1	$PM_{2.5}/PM_{10}$
7–12/07/2011	117	37	30	*82*	*26*	*21*	0.32
13–25/07/2011	241	69	68	*169*	*48*	*41*	0.29
7–25/07/2011	201	59	49	*142*	*41*	*35*	0.29
FONTANA L3	PM_{10}	$PM_{2.5}$	PM_1	PM_{10}	$PM_{2.5}$	PM_1	$PM_{2.5}/PM_{10}$
7–12/07/2011	258	90	84	*244*	*84*	*79*	0.35
13–25/07/2011	229	87	83	*216*	*82*	*78*	0.38
7–25/07/2011	239	88	83	*225*	*83*	*79*	0.37

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Table 4. PM_x levels ($\mu g\,m^{-3}$) measured inside trains during different journeys across lines 9, 5 and 3. Numbers in brackets refer to trips marked in Fig. 1.

Monitored travel (number in Fig. 1)	PM_{10}	$PM_{2.5}$	PM_1
L3 P. Reial-Fontana (1)	52	17	16
L3 Sants-P. Reial rush hour (2)	100	32	30
L5 Diagonal-Sagrera (3)	77	24	22
L5 Sagrera-Sants (4)	87	27	25
L9 Sagrera-C Zam (5)	46	14	13
L9 C Zam Sagrera (6)	36	11	11
L9 Sagrera-C Zam-Sagrera (7)	54	18	16

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Table 5. Mean levels of PM, and analyzed components in PM_{10} and $PM_{2.5}$ at Fontana (L3) and Sagrera (L9) platform sites from 5 to 24 July 2011. ws, water soluble; SIA, secondary inorganic aerosols. Annual urban background levels of $PM_{2.5}$ components reported for Barcelona by Pérez et al. (2008) are also shown for comparison.

	$PM_{2.5}$		PM_{10}			$PM_{2.5}$ (outdoor)
$\mu g\,m^{-3}$	FONTANA 10 days	SAGRERA 10 days	FONTANA 10 days	SAGRERA first 8 days	SAGRERA 10 days	Urban backgd.
PM_x	155	90	339	64	100	21
OC	33	10	52	9	8	3
EC	1.2	3	0.3	5	4	2
OC+EC	34	13	53	14	13	5
ws-Cl^-	0.4	0.7	1.0	0.7	0.7	0.4
ws-NO_3^-	0.2	0.2	0.8	2.1	1.9	2.9
ws-SO_4^{2-}	2.3	2.0	5.1	6.6	5.9	3.0
ws-NH_4^+	0.3	0.4	0.6	0.9	0.8	1.7
SO_4^{2-}	2.5	2.0	9.6	6.8	6.1	3.0
Fe_2O_3	80	46	206	13	41	0.2
CO_3^{2-}	5	3	11	4	6	
Ca	1.8	1.2	5	1.7	3	0.2
Al_2O_3	1.4	0.7	3	1.1	1.4	0.2
Ba	2.2	0.02	5	0.02	0.03	0.004
Mg	0.9	0.13	2.1	0.3	0.3	0.06
CuO	0.8	0.15	2.2	0.04	0.09	0.01
MnO	0.7	0.4	1.8	0.12	0.4	0.01
ZnO	0.6	0.13	1.4	0.09	0.2	0.09
Na	0.3	0.2	0.7	0.9	0.8	0.3
K	0.10	0.08	0.6	0.5	0.5	0.2
TiO_2	0.08	0.03	0.22	0.07	0.08	0.01
Cr_2O_3	0.09	0.06	0.23	0.02	0.06	0.002

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Table 5. Continued.

	$PM_{2.5}$		PM_{10}			$PM_{2.5}$ (outdoor)
	FONTANA 10 days	SAGRERA 10 days	FONTANA 10 days	SAGRERA first 8 days	SAGRERA 10 days	Urban backgd.
ng m^{-3}						
Sr	44	3	101	4	6	0.7
Zr	42	8	72	5	6	5.1
Mo	38	3	76	3	3	1.6
Sb	27	30	40	9	15	1.0
Sn	18	5	44	4	5	2.8
Ni	16	6	34	2	5	2.9
As	13	1.4	24	2	3	0.3
Pb	11	3	30	6	6	7.9
V	7	4	15	11	10	6.1
Co	3	1.3	8	0.7	1.4	0.1
P	3	13	64	8	14	8.4
W	3	1.0	4	1.1	1.1	0.1
Li	1.5	0.7	3.7	1.4	1.5	0.1
Hf	1.4	0.1	2.2	0.1	0.1	0.2
Rb	1.1	0.7	2.7	1.4	1.6	0.3
Nb	0.9	0.2	1.7	0.6	0.5	0.1
Ge	0.7	0.4	1.2	0.1	0.3	0.1
Ga	0.7	0.4	1.7	0.3	0.5	0.1
U	0.4	0.3	0.3	0.1	0.1	0.04
Y	0.4	0.2	0.8	0.2	0.3	0.1
Th	0.3	0.3	0.7	0.02	0.2	0.03
Ta	0.3	0.04	0.3	0.02	0.04	0.1
Cd	0.2	0.1	0.4	0.1	0.1	0.1
Bi	0.2	0.1	0.6	0.1	0.1	0.2
Se	0.02	0.02	0.2	0.3	0.3	0.3

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Table 5. Continued.

	$PM_{2.5}$		PM_{10}			$PM_{2.5}$ (outdoor)
$ng\,m^{-3}$	FONTANA 10 days	SAGRERA 10 days	FONTANA 10 days	SAGRERA first 8 days	SAGRERA 10 days	Urban backgd.
La	0.86	0.31	1.53	0.60	0.64	0.11
Ce	1.47	0.55	2.46	0.89	0.99	0.22
Pr	0.12	0.02	0.23	0.06	0.07	0.01
Nd	0.45	0.16	0.88	0.24	0.28	0.05
Sm	0.13	0.05	0.21	0.04	0.05	0.01
Gd	0.12	0.04	0.18	0.03	0.05	0.02
Dy	0.14	0.06	0.20	0.04	0.05	0.02
Er	0.06	0.02	0.10	0.02	0.03	0.02
$\mu g\,m^{-3}$						
Fe_2O_3	80	46	206	13	41	
Other metals	4	0.8	11	0.3	0.7	
Crustal	9	5	22	8	11	
SIA	3	3	6	10	9	
OC+EC	34	13	53	14	13	
Traces	0.2	0.1	0.5	0.1	0.1	
Na+Cl	0.7	0.9	1.6	1.6	1.5	
Accounted	132	69	300	46	76	
Unnacounted	24	21	39	17	24	
% Determined	85	76	88	73	76	

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Table 6. Calculation of PM exposure levels for a metro commuting travel of 30 min in the train and 5 min on the platform.

Mean Platforms	PM_{10}	$PM_{2.5}$	
$\mu g\,m^{-3}$	346	125	Fontana L3
	142	44	Palau Reial L3
	150	43	Bon Pastor L9
	145	46	Sagrera L9
	196	65	Mean
Mean in trains	PM_{10}	$PM_{2.5}$	
	79	25	L3–L5
	45	14	L9
	65	20	Mean
$\mu g\,m^{-3}$ supplied to daily exposure			
Platform	PM_{10}	$PM_{2.5}$	
5min	1.2	0.4	Fontana L3
	0.5	0.2	Palau Reial L3
	0.5	0.1	Bon Pastor L9
	0.5	0.2	Sagrera L9
	0.7	0.2	Mean
Train	PM_{10}	$PM_{2.5}$	
30 min	1.6	0.5	L3–L5
	0.9	0.3	L9
	1.3	0.4	Mean
$\mu g\,m^{-3}$ total contribution Platform and train × 2 (return) to daily exposure			
35 min	PM_{10}	$PM_{2.5}$	
	2.9	0.9	L9
	5.0	1.6	L3–L5
	4.0	1.3	Mean Barcelona Metro
PM exposure ($\mu g\,m^{-3}$) during metro commuting 35 min (5 min in platform and 30 min in train)			
	PM_{10}	$PM_{2.5}$	
	60	19	L9
	103	34	L3–L5
	83	27	Mean Barcelona Metro

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Table 7. PM exposure levels for different commuting modes in a number of cities of the world.

	Car	Bus	Pedestrian	Motorbike	Cycle	Taxi	Metro
Mexico							
$PM_{2.5}$ [1]	–	70	–	–	–	–	61
$PM_{2.5}$ [2]	–	51	–	–	–	–	33
Houston							
$PM_{3.5}$ [3]	35	–	–	–	–	–	–
New York							
$PM_{2.5}$ [4]	–	–	–	–	–	–	62
London							
$PM_{2.5}$ [5]	–	–	–	–	–	33	246
London							
$PM_{2.5}$ [6]	36	39	–	–	30	–	202
Southampton, UK							
$PM_{3.5}$ [7]	–	–	–	–	135	–	–
Manchester, UK							
PM_{4} [8,9]	42	338	–	–	54	–	–
Belgian cities							
PM_{10} [10]	35-75	–	–	–	42-78	–	–
Dublin							
$PM_{2.5}$ [11]	83	128	63	–	88	–	–
Florence							
$PM_{2.5}$ [12]	–	33-75	–	–	–	20-70	–

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Table 7. Continued.

	Car	Bus	Pedestrian	Motorbike	Cycle	Taxi	Metro
Munich							
PM_{10} [13]	–	137	–	–	–	–	–
Taipei							
PM_{10} [14]	42	70	–	113	–	–	65
$PM_{2.5}$ [14]	22	39	–	68	–	–	35
PM_{1} [14]	16	31	–	48	–	–	26
Hong Kong							
PM_{10} [15]	–	97	–	–	–	58	50
$PM_{2.5}$ [15]	–	71	–	–	–	–	33
Guanzhou							
PM_{10} [16]	–	156	–	–	–	104	67
$PM_{2.5}$ [16]	–	123	–	–	–	89	44
Barcelona Mean							
PM_{10}	–	–	–	–	–	–	83
$PM_{2.5}$	–	–	–	–	–	–	27
PM_{1}	–	–	–	–	–	–	25
Barcelona L9							
PM_{10}	–	–	–	–	–	–	60
$PM_{2.5}$	–	–	–	–	–	–	19
PM_{1}	–	–	–	–	–	–	16

[1] Gómez-Perales et al. (2004); [2] Gómez-Perales et al. (2007); [3] Morandi et al. (1988); [4] Chillrud et al. (2004); [5] Pfeifer et al. (1999); [6] Adams et al. (2001); [7] Bevan et al. (1991); [8] Gee et al. (1999); [9] Gee and Raper (1999); [10] Int Panis et al. (2010); [11] McNabola et al. (2008); [12] Fondelli et al. (2008); [13] Praml and Shierl (2000); [14] Tsai et al. (2008); [15] Chan et al. (2002a); [16] Chan et al. (2002b).

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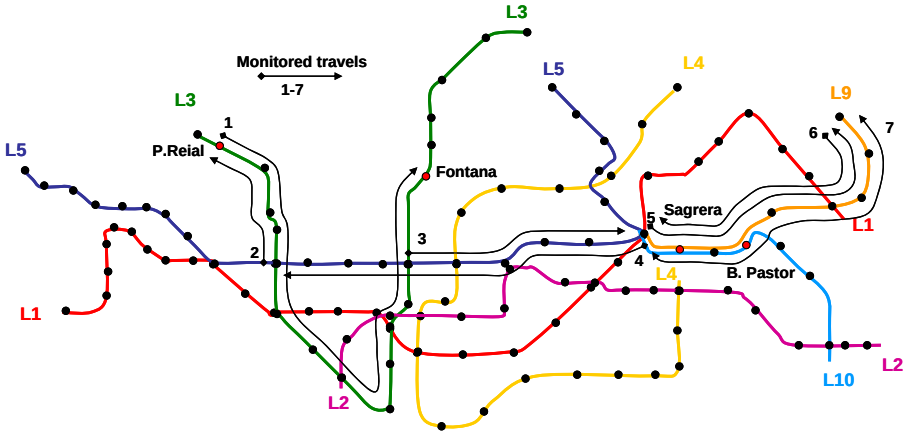

Fig. 1. Map of the Barcelona city metro system, with the location of the four stations where measurements were made on the platform, and the monitored routes with real time measurements inside the train carriages (black lines 1 to 7).

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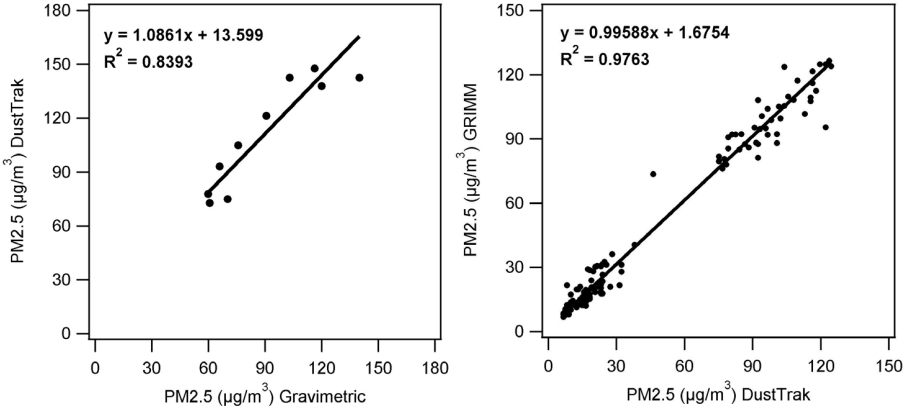

Fig. 2. Left: comparison of $PM_{2.5}$ levels measured with one of the optical counters (DustTrak in this case) and high volume samplers (gravimetry). Right: comparison of measurements of $PM_{2.5}$ levels performed on a minute resolution by means of the two types of optical counters after correction against high volume data.

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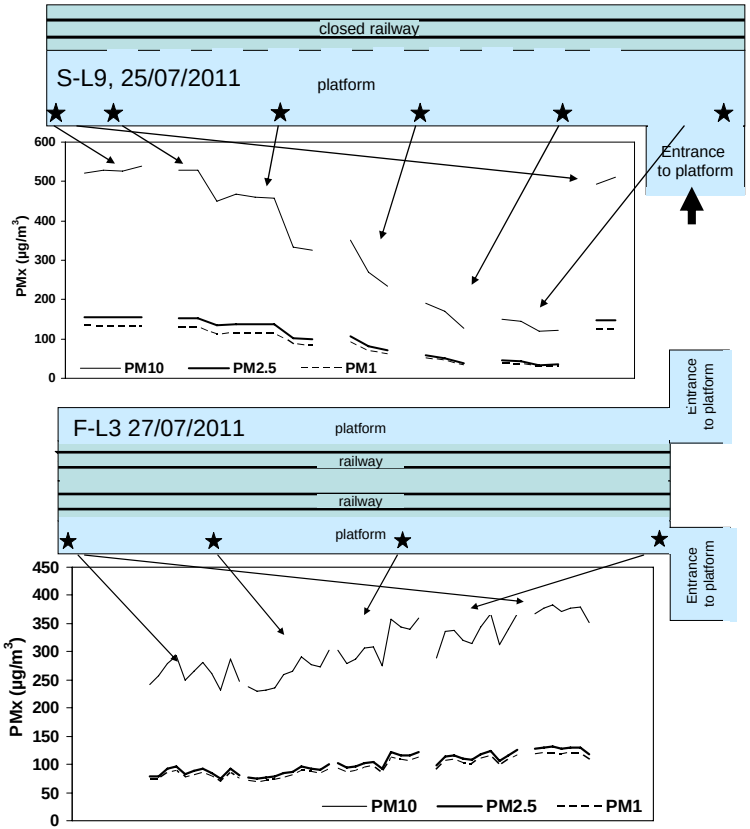

Fig. 3. Five minute PM_{10}, $PM_{2.5}$ and PM_1 levels measured along the platforms at the Sagrera (S-L9) and Fontana (F-L3) stations.

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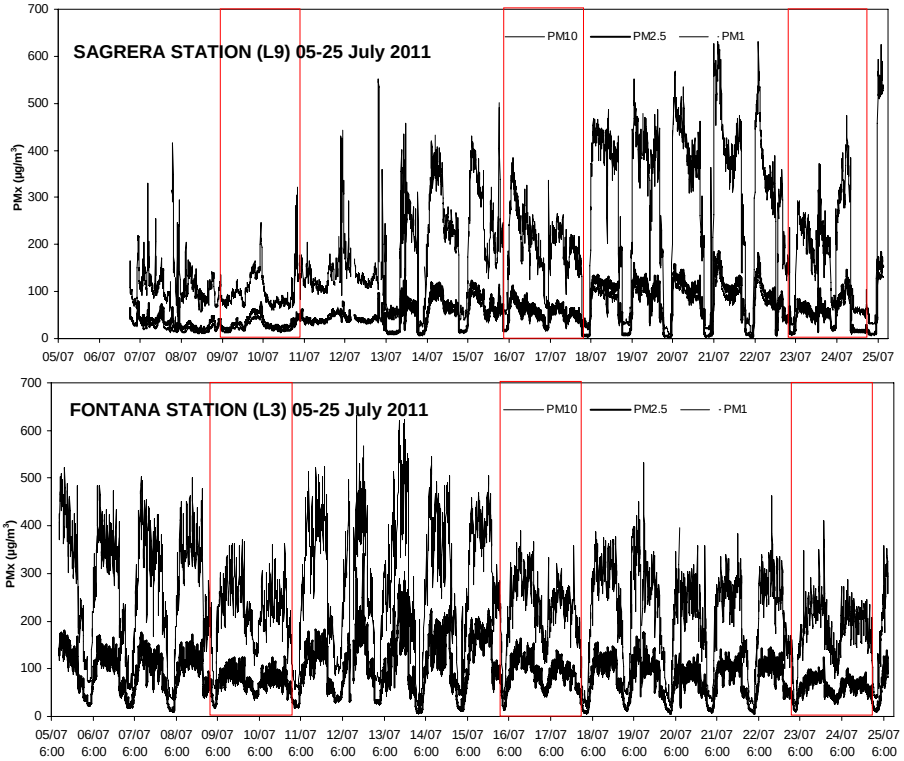

Fig. 4. Five minute PM_{10}, $PM_{2.5}$ and PM_1 levels measured at the platforms of the Sagrera (S-L9) and Fontana (F-L3) stations. Red squares indicate weekend days and time is a.m. local time.

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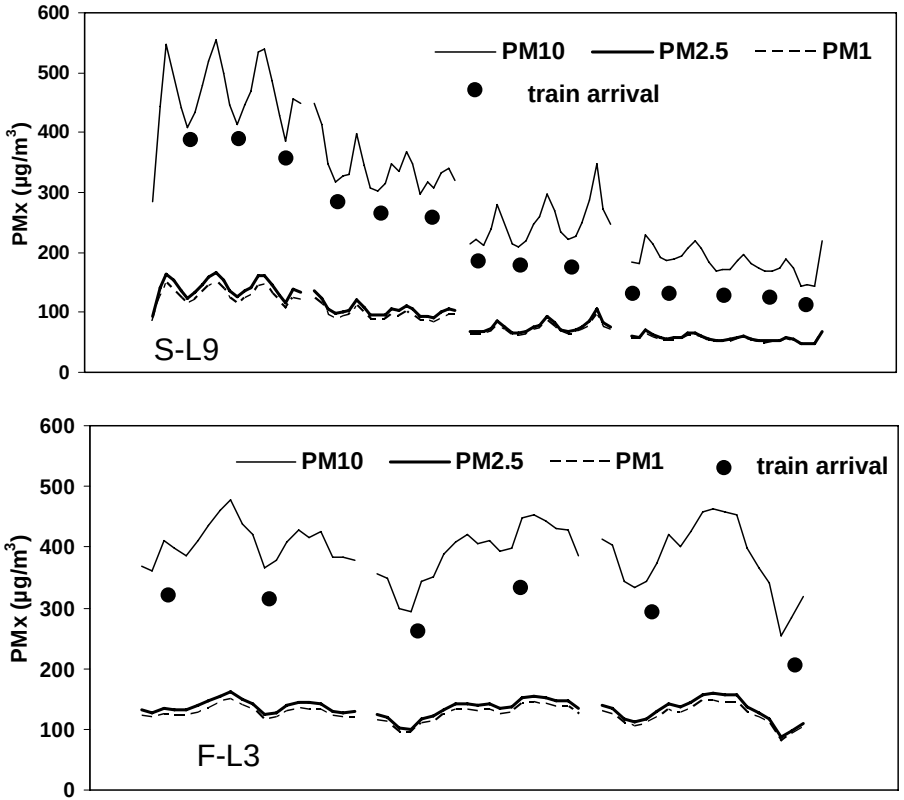

Fig. 5. Levels of PM_{10}, $PM_{2.5}$ and PM_1 measured across the platforms at the Sagrera (S-L9) and Fontana (F-L3) stations using 30 s time resolution. Data clearly show that the arrival of the train (black dots) causes a decrease on PM levels on the platform at both stations. Horizontal axe: distance to end of platform.

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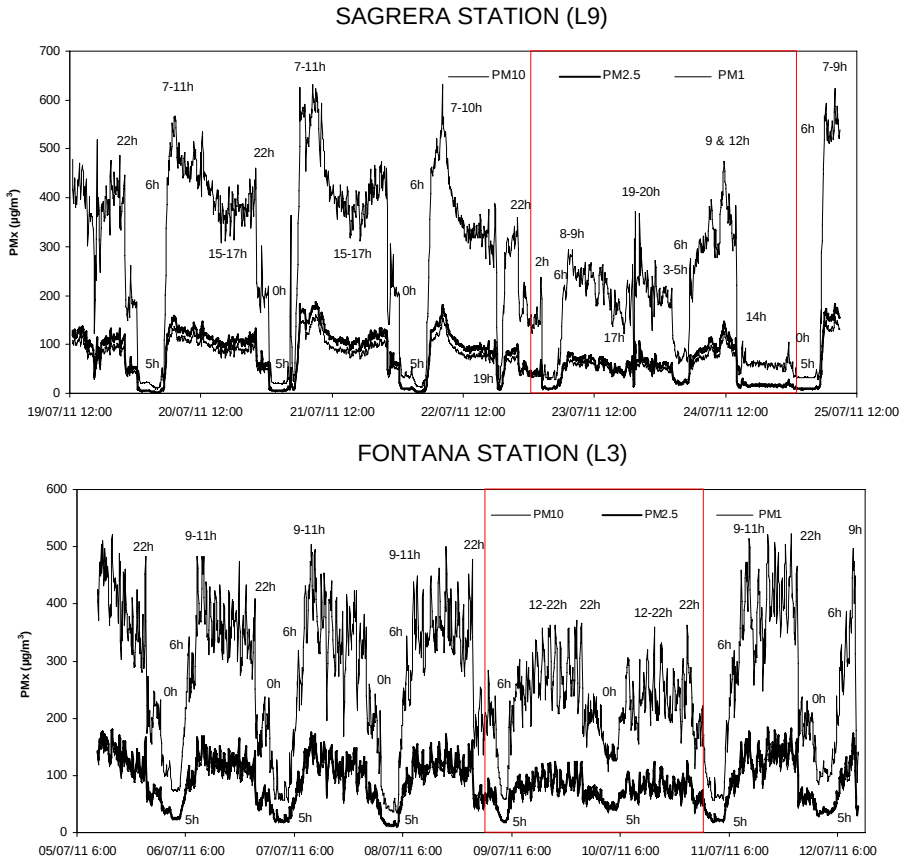

Fig. 6. Hourly PM_{10}, $PM_{2.5}$ and PM_1 levels recorded during specific days at Fontana (F-L3) and Sagrera stations (S-L9) showing very repetitive daily trends. Red squares indicate weekends.

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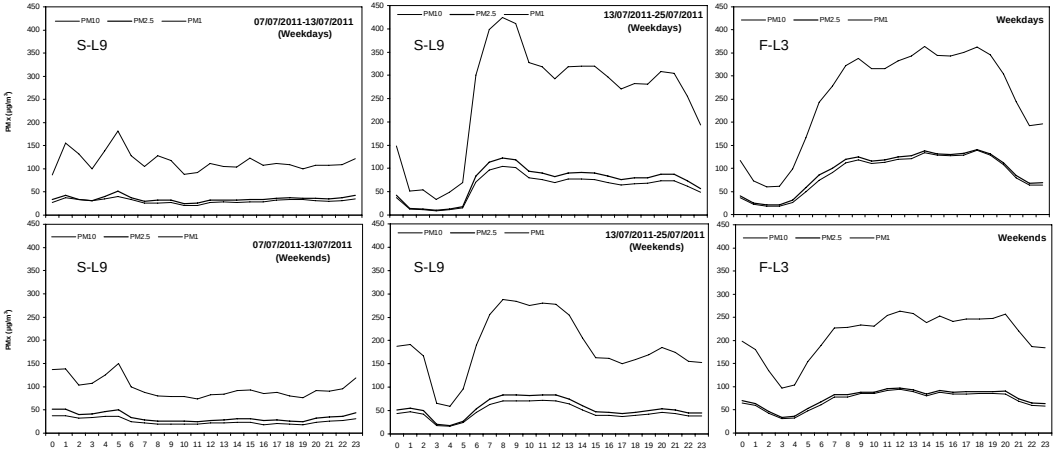

Fig. 7. Mean hourly PM_{10}, $PM_{2.5}$ and PM_1 levels recorded during the study period at Fontana (F-L3), and during the first and last measurement periods at Sagrera stations (S-L9).

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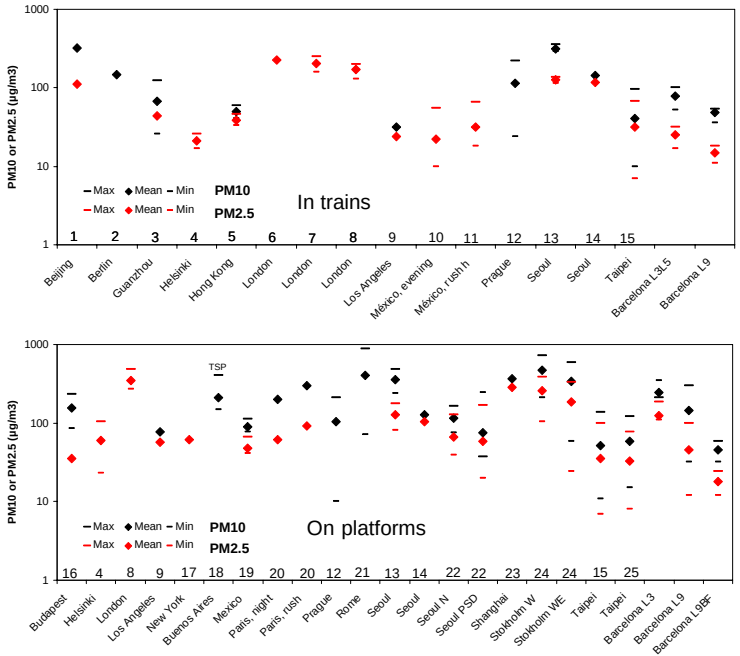

Fig. 8. Comparison of PM_{10} and $PM_{2.5}$ levels measured in trains and on platforms of worldwide metro systems with those obtained in the present study in Barcelona. W, week, WE, weekend; L3, L5 and L9, metro lines 3, 5 and 9; BF, before the tunnel air uptake ventilation system was fully implemented. 1, Li et al. (2007); 2, Fromme et al. (1998); 3, Chan et al., (2002b); 4, Aarnio et al. (2005); 5, Chan et al. (2002a); 6. Pfeifer et al. (1999); 7, Adams et al. (2001); 8, Seaton et al. (2005); 9, Kam et al. (2011); 10 and 11, Gómez Perales et al. (2007); 12, Branis (2006); 13, Kim et al. (2008); 14, Park and Ha (2008); 15, Cheng et al. (2008); 16, Salma et al. (2007); 17, Chillrud et al. (2004); 18, Murruni et al. (2009), in this case total suspended particles (TSP); 19, Múgica-Álvarez et al. (2012), Raut et al. (2009); 21, Ripanucci et al. (2006); Ho et al. (2012) N and PSD standing for without and with platform screen doors; 23, Ye et al. (2010); 24, Johansson and Johansson (2003); 25, Cheng et al. (2011).

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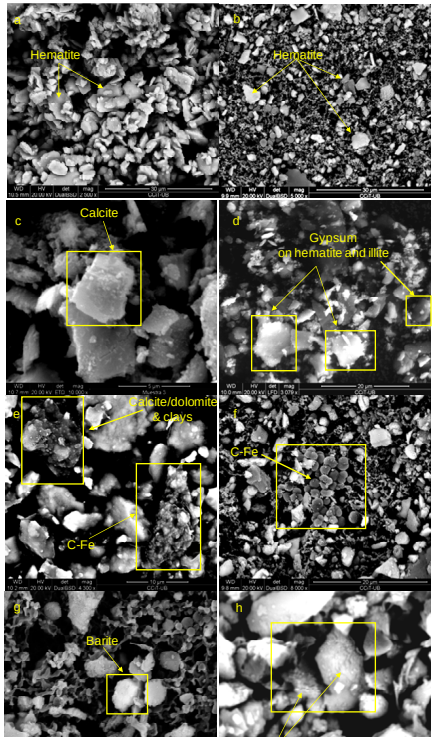

Fig. 9. SEM microphotographs and EDX spectra of PM fractions collected at S-L9 and F-L3 platforms; **(a)** general view of the PM collected at S-L9 platform showing the predominance of laminate hematite from wheel/rail erosion; **(b)** general view of the PM collected at L-F3 platform showing similar grains but also the occurrence of rounded and rough particles; **(c)** discrete calcite crystal (4–5 µm), at S-L9; **(d)** traces of fine gypsum on hematite and illite surfaces at S-L9; **(e)** aggregates of calcite/dolomite, clays and C-Fe at S-L9; **(f)** detail of rounded and melted C-Fe particles <2.5 µm at L-F3; **(g)** discrete barite particle (4–5 µm) from brake pads erosion; and **(h)** rough-surface Fe particles with traces of Barite and Cu arising from friction between wheels and brake pads.

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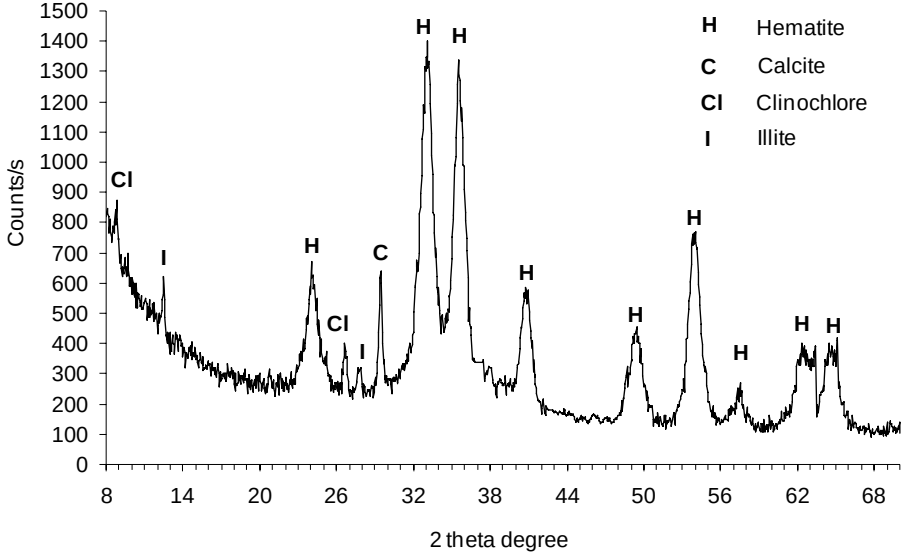

Fig. 10. XRD patterns of the >2.5 µm retained in the head of the $PM_{2.5}$ inlet.

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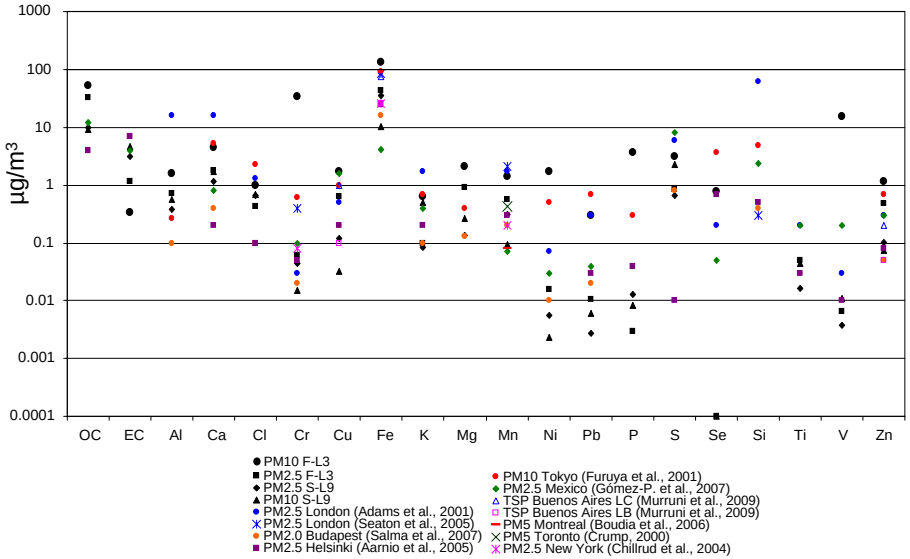

Fig. 11. Comparison of mean levels of selected components in PM_{10} and $PM_{2.5}$ obtained at Fontana (L3) and Sagrera (L9) platforms with those reported from other studies carried out in different metro systems worldwide.

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