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

X. Querol[1], T. Moreno[1], A. Karanasiou[1], C. Reche[1], A. Alastuey[1], M. Viana[1], O. Font[1], J. Gil[1], E. de Miguel[2], and M. Capdevila[2]

[1]Institute of Environmental Assessment and Water Research, IDAEA, CSIC, C/Jordi Girona 18–24, 08034 Barcelona, Spain
[2]Transports Metropolitans de Barcelona, TMB Santa Eulàlia, Av. del Metro s/n L'Hospitalet de Llobregat, 08902, Spain

Correspondence to: X. Querol (xavier.querol@idaea.csic.es)

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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 and winter 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 $\mu g\,m^{-3}$ $PM_{2.5}$). This is most likely due to the air conditioning system working in all carriages of the Barcelona metro during the whole year. Levels were considerably higher on the platforms, reaching mean levels of 46 and 125 $\mu g\,m^3$ 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 difficult due to the scarcity of data compared with $PM_{2.5}$. Results showed distinct PM daily cycles, with a drastic increase from 06:00 to 07:00 a.m., a diurnal maximum from 07:00 to 10:00 p.m., and marked decrease between 10:00 p.m. and 05:00 a.m. The elements with the highest enrichment were 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, the contribution of commuting by metro was estimated to account for around 10 % of the daily exposure. However, this contribution may be one order of magnitude higher when specific matals are considered. Finally, we conclude that the implementation of platform screen door systems results in reductions of both PM levels and metal concentrations. In addition an advanced optimized ventilation system gave even a much higher efficiency in reducing exposure to PM of 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 in New York and Mexico, or 3 million in London (Nieuwenhuijsen et al., 2007), making the system 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 has revealed poor air quality in the metro systems, especially concerning the levels of PM and metals (Fromme et al., 1998; Adams et al., 2001a and b; Furuya et al., 2001; Award, 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). Thus, the comprehensive reviews of the air quality in metro systems by Nieuwenhuijsen et al. (2007) and by Salma (2009) 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 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 passenger 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 and 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.

7. Wind erosion by intense air flow within the tunnels and in the platforms (Salma, 2009).

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) coincides 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 exposure to PM 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 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 the statistics of the City Council from Barcelona in 2010 walking was the dominant mode for commuting in the city (about 45 % of trips), followed by public transport (30 %), whereas 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. until midnight during weekdays 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.

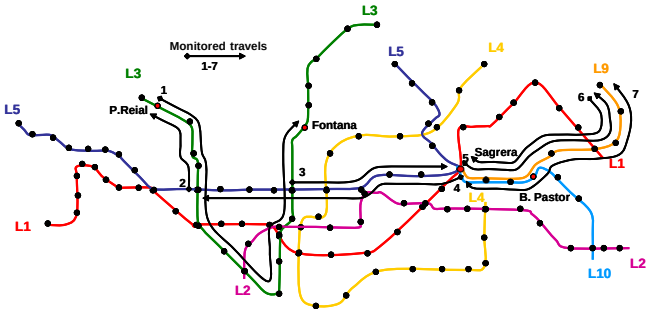

Fig. 1. Map of the Barcelona city metro system, with the location of the four stations where measurements were made on the platform, and the monitored journeys with real time measurements inside the train carriages (black lines 1 to 7).

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 new stations have also an advanced ventilation scheme. The platforms have a specific ventilation system that introduces outdoor air to renew the air throughout lateral ventilation outlets across the closed platform and that extracts the aged air through a vertical well. Furthermore, the ventilation system in the tunnels consists of vertical wells that introduce outdoor air into the tunnel.

Although braking is electric, during the approach to the platform trains of both L3 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) on L3 and in the sides of the wheels (disk brakes) in the L9 and L10 trains.

This work is the first study that presents data on levels, variability and composition of PM in the Barcelona's metro system. 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 tunnel ventilation schemes).

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 with other commuting systems.

The overall aim of this study therefore is to evaluate if the L9–L10 new metro lines, with platform screen door systems (automated systems, closed rail track and platforms, and advanced platform ventilation systems), reduce exposure to PM when compared with the conventional systems. Also to test the influence of doubling the tunnel ventilation power on air quality in the platforms.

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, Braniš (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 and UK among others, to reduce the number of accidents but also for more effective temperature and ventilation controls on the platform.

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 in 2009) and has driverless trains, 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. LT. 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. An optical counter (GRIMM 1107) and a light-scattering laser photometer (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 minute 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 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 595 and 432 are the values respectively at F-L3.

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 a number of measurements performed inside the trains. More information on these various QA/QC protocols and results is further supplied.

According to the results obtained in the study, a second measurement campaign was devised to evaluate the impact of modifying the tunnel ventilation scheme on PM levels measured on the platform at S-L9. To this end we performed PM_{10}, $PM_{2.5}$ and PM_1 measurements, as described above, during 6 to 24 February 2012.

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 (new L9) to specific transects (old 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, 20 PM_{10} and 19 $PM_{2.5}$ 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 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 from 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 diffractometer with monochromatic Cu Kα1,2 radiation ($\lambda = 1.5405$ Å) operated at 40 KV and 40 mA. 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 2 q, 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

Table 1. PM_x levels and standard deviation (std) of 5 min values ($\mu g\,m^{-3}$) 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 weighted values measured across the station.

	PM_{10}	std	$PM_{2.5}$	std	PM_1	std
Average platform Fontana 25 Jul 2011	251	67	86	8	78	7
Platform end (filter sampling site)	273	18	91	6	84	6
Average platform Fontana 27 Jul 2011	292	41	98	15	90	14
Platform end (filter sampling site)	264	20	86	7	79	6
Platform end (filter sampling site) repetition	373	11	128	4	118	4
Average platform P. Reial 26 Jul 2011	124	26	36	9	30	8
Platform end P Reial	149	32	44	10	36	8
Platform end repetition	148	18	42	10	35	7
Average platform P. Reial 29 Jul 2011	160	32	52	10	48	9
Platform end P. Reial	197	17	64	5	58	5
Average platform Bon Pastor 27 Jul 2011	87	24	21	6	18	5
Platform end B Pastor	95	11	25	2	21	1
Platform end repetition	113	4	26	1	23	1
Average platform Sagrera 25 Jul 2011	325	159	96	46	82	39
Platform end (filter sampling site)	528	8	155	1	132	1
Platform end (filter sampling site) repetition	502	11	149	0	125	1
Average platform Sagrera 27 Jul 2011	297	85	83	28	38	12
Platform end (filter sampling site)	374	43	112	15	50	5

equipped with an energy dispersive X-ray analyzer (SEM-EDX).

The data matrix obtained for the chemical analysis of around 30 components in 39 PM_{10} and $PM_{2.5}$ 12 h samples was used as a basis for a principal component analysis, PCA 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 between 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 S1 (left) 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 intercomparison exercise was performed with measurements carried out with the two optical counters at one of the measurement sites. Figure S1 (right) 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.

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. 2, measurements performed across the whole length of the platforms showed that at the S-L9 sampling site PM_x measurements were 1.4 ± 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 1.1 ± 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.

2.4 Change of ventilation schemes

The platform ventilation conditions in the new L9 are changed for winter (PW) and summer (PS) setting up by increasing the frequency of the 4 extraction fans at 25 Hz in PS mode to 3 fans at 25 Hz and 1 at 30 Hz in PW mode. In the tunnel there are 3 sequences of fans introducing outdoor

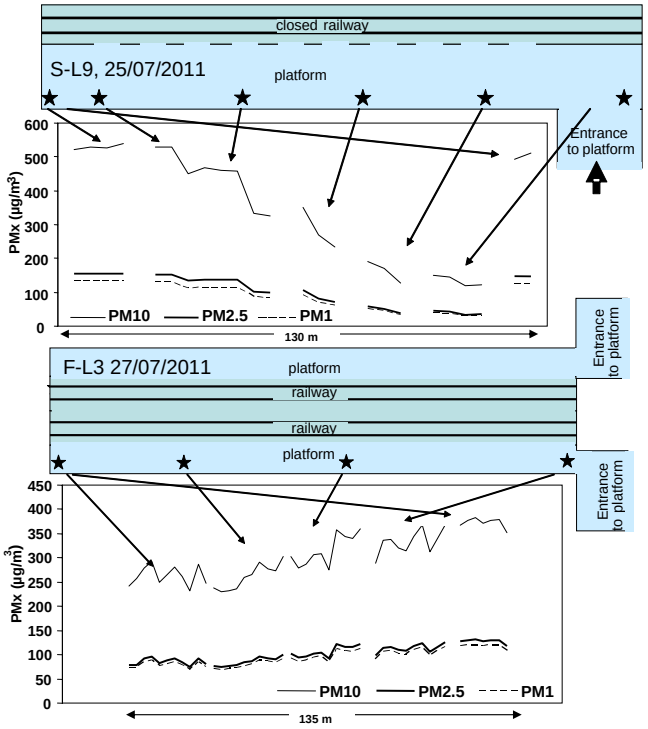

Fig. 2. Five minute PM_{10}, $PM_{2.5}$ and PM_1 levels measured along the platforms at the Sagrera (S-L9) and Fontana (F-L3) stations.

air into the tunnel that are working individually, both in summer and winter, with the difference that in summer these also work during the night. In our study we combined both platform PW and PS ventilation modes with 2 tunnel ventilation fan sequences being operative (T2) and also with only one fan system in operation (T1, as usually works every day). Thus, joining the July 2011 and February 2012 campaigns we measured PM levels at S-L9 using the following ventilation schemes: PW-T2, PW-T1, PS-T2 and PS-T1. Each ventilation scheme was maintained at least during one week.

3 Results

3.1 PM levels on platforms

Figure 3 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 with the PS-T2 ventilation scheme) were markedly lower than in the second part (PS-T1 ventilation). During 13–14 July 2011 levels increased suddenly and stayed relatively high until the end of the campaign, showing the high impact of using 2 simultaneous operation tunnel fan sequences (T2) when compared to the typical summer ventilation (PS-T1). The new measurements performed in February 2012 (Fig. 3) showed exactly the same results: no differences using PS-T1 and PW-T1, but a drastic reduction of PM levels when T2 was operating.

When PM measurements on the platforms were carried out with a time resolution of 30 s (Fig. S2) with PS-T1 ventilation scheme 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 produces such a decrease.

At both sites, during weekends PM levels were markedly lower than during week days (Figs. 3 to 5), probably due to the lower frequency of trains, as it has already been described by Johansson and Johansson (2003) for the Stockholm metro. In absence of double ventilation power in the tunnel, clear daily cycles were observed in PM_x levels at both sites (Figs. 4 and 5), with a nocturnal low from 00:00 to 05:00 a.m. LT, 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 Fig. S3). 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 from 07:00 to 10:00 a.m. on week days and from 07:00 a.m. to 01:00 p.m. on weekend days, followed by lower (but still high) levels until 10:00 p.m.. This was not coinciding with the variation of the frequency of trains (Fig. S3). PM_x levels were much lower during the night (with full summer ventilation being in operation), but doubled during the day. Finally, we also noted higher night PM_x levels at weekends and attribute this to the fact that the Barcelona metro systems works continuously from early Saturday to Sunday night.

An important finding is that during both July and February measurements, when the double ventilation power was used in the tunnels (T2), PM levels in addition to be drastically reduced varied independently of the frequency of the trains, probably because the ventilation flow prevails over the suction effect of the train arrival. Thus from 5 to 12 July 2011 the above daily pattern was not present (Fig. 5) and PM levels were relatively constant throughout the 24 h period, with slightly higher levels from 00:00 to 05:00 a.m.

Table 2 shows that mean levels of PM_{10} and $PM_{2.5}$ from gravimetric measurements from 08:30 a.m. to 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 increases up to 70 and 23 $\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$. These results indicate that the new platform design reduces PM_x exposure to metro users during waiting time. The reduction during the whole campaign reached a factor of around 2 for both PM_{10} and $PM_{2.5}$ (Table 2), whereas if only the days with double tunnel ventilation power (T2) are considered, the reduction was up to a factor of 7.2

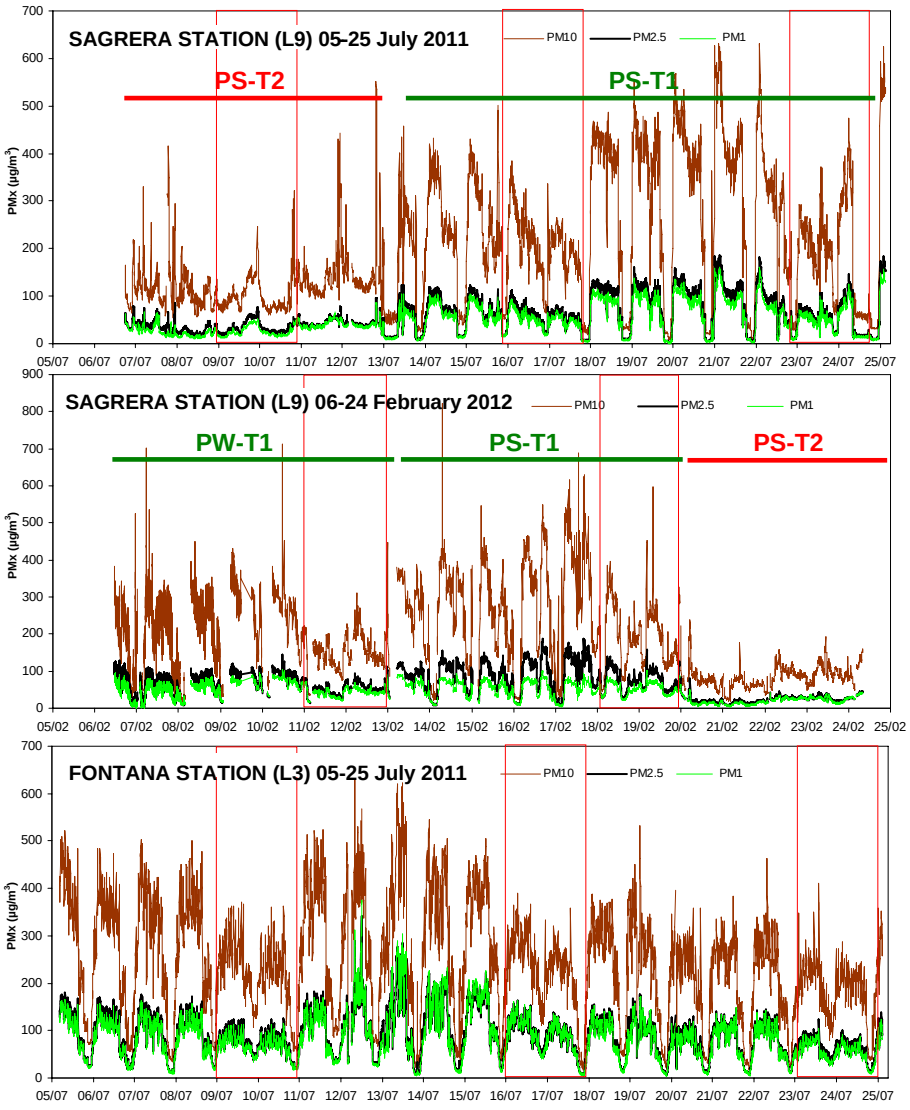

Fig. 3. Five minute PM_{10}, $PM_{2.5}$ and PM_1 levels measured at the platforms of the Sagrera (S-L9) and Fontana (F-L3) stations. Red squares indicate weekend days and time is a.m. LT). Codes PS, PW, T1 and T2 are the ventilation schemes (see methodology section).

with respect to mean values at F-L3 and of 4.2 with respect to the usual ventilation power (T1) at the S-L9 platform.

Table S1 shows the mean PM_{10}, $PM_{2.5}$ and PM_1 levels 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 were much reduced. The overall differences in mean daily $PM_{2.5}$ levels were 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.

3.2 PM levels inside the trains

Table 3 reveals that 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 m^{-3} $PM_{2.5}$, respectively. Indeed $PM_{2.5}$ levels recorded inside the trains (where most of the travelling time is spent) at L9 are considerably low, even lower than simultaneous levels of $PM_{2.5}$ recorded outdoors at urban background sites in Barcelona (18 µg m^{-3} $PM_{2.5}$). 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 probably lower than if commuting is done by buses or cars.

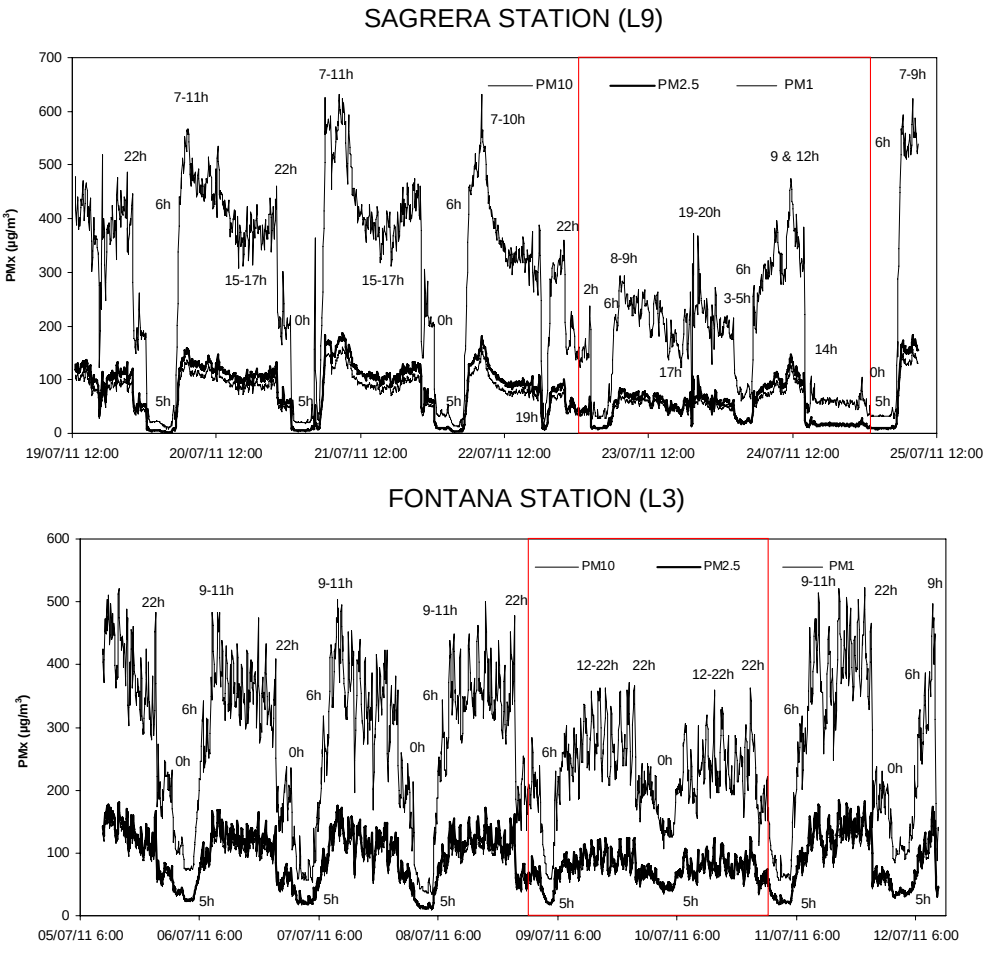

Fig. 4. Hourly PM_{10}, $PM_{2.5}$ and PM_1 levels recorded during specific days at Fontana (F-L3) and Sagrera stations (S-L9) showing very repetitive daily trends. Red squares indicate weekends.

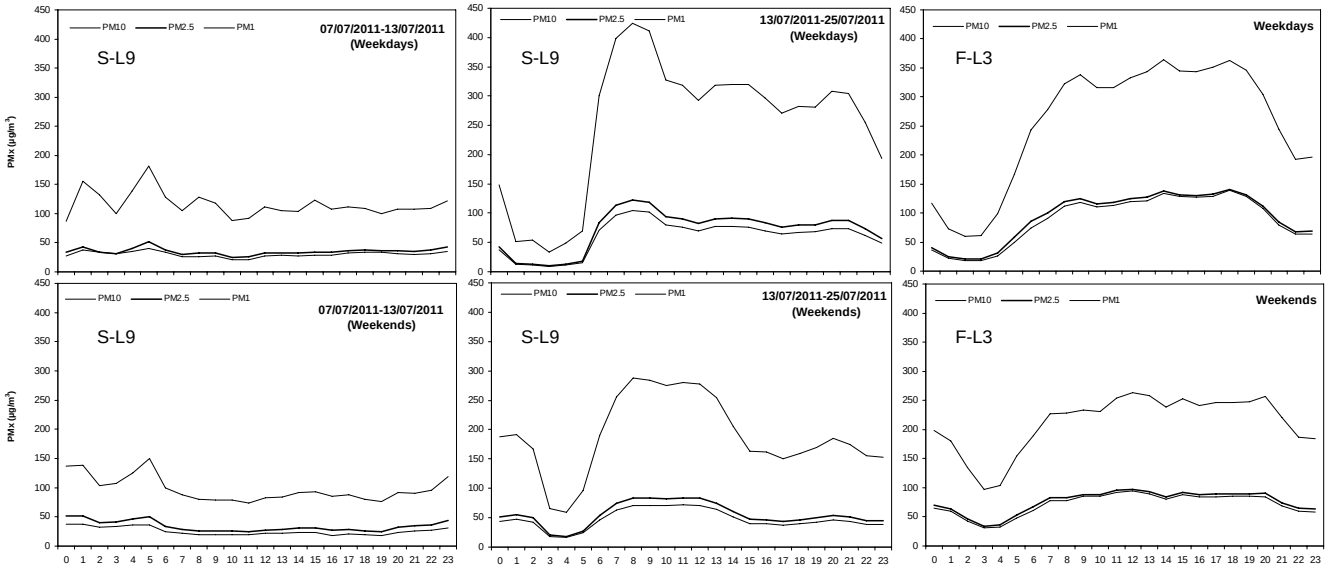

Fig. 5. Mean hourly PM_{10}, $PM_{2.5}$ and PM_1 levels recorded during the study period at Fontana (F-L3), and during the first and last measurement periods at Sagrera stations (S-L9).

Table 2. Mean levels and standard deviation (std) of PM_x ($\mu g\,m^{-3}$) from gravimetric measurements at the Sagrera (L9) and Fontana (L3) platforms from 08:30 a.m. to 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 underlined 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. PS, summer platform ventilation, T1 and T2, usual and double tunnel ventilation power.

SAGRERA L9	PM_{10}	std	$PM_{2.5}$	std	PM_{10}	std	$PM_{2.5}$	std
5–12 Jul 2011 PS-T2	64	13	**21**	**13**	45	9	**15**	**9**
13–24 Jul 2011 PS-T1	**310**	**92**	90	27	**213**	**65**	63	19
5–24 Jul 2011	206	139	65	40	145	98	46	28
FONTANA L3	PM_{10}	std	$PM_{2.5}$	std	PM_{10}	std	$PM_{2.5}$	std
5–12 Jul 2011	339	46	**115**	**16**	320	43	**108**	**15**
13–24 Jul 2011	**395**	**69**	150	27	**373**	**65**	142	26
5–24 Jul 2011	367	66	133	30	346	62	125	28

Table 3. PM_x levels and standard deviation (std) of minute values ($\mu g\,m^{-3}$) 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}	std	$PM_{2.5}$	std	PM_1	std
L3 P. Reial-Fontana (1)	52	8	17	2	16	2
L3 Sants-P. Reial rush hour (2)	100	14	32	6	30	5
L5 Diagonal-Sagrera (3)	77	14	24	4	22	4
L5 Sagrera-Sants (4)	87	21	27	7	25	6
L9 Sagrera-C Zam (5)	46	19	14	5	13	5
L9 C Zam Sagrera (6)	36	18	11	5	11	5
L9 Sagrera-C Zam-Sagrera (7)	54	16	18	5	16	5

PM measured on the S-L9 and F-L3 platforms is very coarse, with a mean $PM_{2.5}/PM_{10}$ ratio reaching 0.3 and 0.4 respectively for the whole campaign (Table S1). 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 around 0.3. 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 specific correction factors separately for PM_{10} and $PM_{2.5}$. Thus, the wide ratios measured in the previously cited studies (Fig. 6), with $PM_{2.5}/PM_{10}$ ranging from 0.3 to 0.8 both in trains and on platforms, can actually be due to differences on grain size or to artefact measurements.

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 (Figs. 7a, b, and 8). Such a laminate morphology is in agreement with an origin of mechanical abrasion between the rail track and the wheels. Older studies have shown a higher contribution of silicate particles (e.g. Sitzmann et al., 1999), but more modern results also show the prevalence of Fe-rich particles (Salma, 2009; Salma et al., 2009).

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. 7c and d), while gypsum occurs as very fine particles attached to hematite and illite surfaces (Fig. 7d). Coarse (ca. 10 µm) aggregates of calcite/dolomite and clays, and C and Fe have also been identified (Fig. 7e). 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

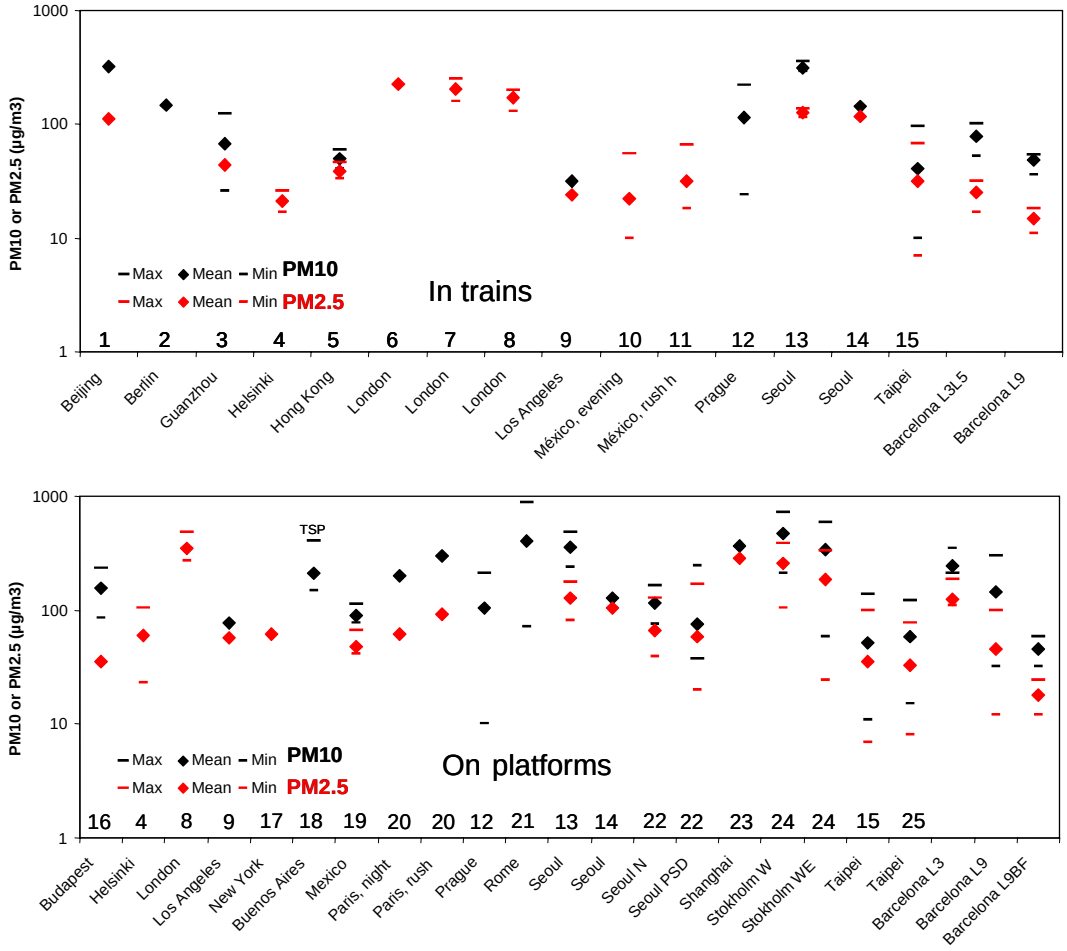

Fig. 6. Comparison of PM_{10} and $PM_{2.5}$ levels measured in trains and on platforms of worldwide metro systems with those obtained in the present study in Barcelona. W, week day, WE, weekend; L3, L5 and L9, metro lines 3, 5 and 9; BF, before the tunnel air uptake ventilation system was fully implemented. 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. (2001a); 8. Seaton et al. (2005); 9. Kam et al. (2011); 10. and 11. Gómez Perales et al. (2007); 12. Braniš (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).

F-L3 platform. Furthermore, rounded C-Fe particles generally <2.5 µm (Fig. 7f), discrete barite ($BaSO_4$) particles of around 4–5 µm (Fig. 7g), and rough-surface Fe-particles containing traces of barite and Cu (Fig. 7h) 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 mixtures of synthetic K-aluminosilicate species and vermiculite ($(Mg, Fe, Al)_3(Al, Si)_4O_{10}(OH)_2 \cdot 4H_2O$) a re also used in the manufacture of conventional brake pads.

3.4 PM speciation

Table 4 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 measurements with double tunnel ventilation power (T2). 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.

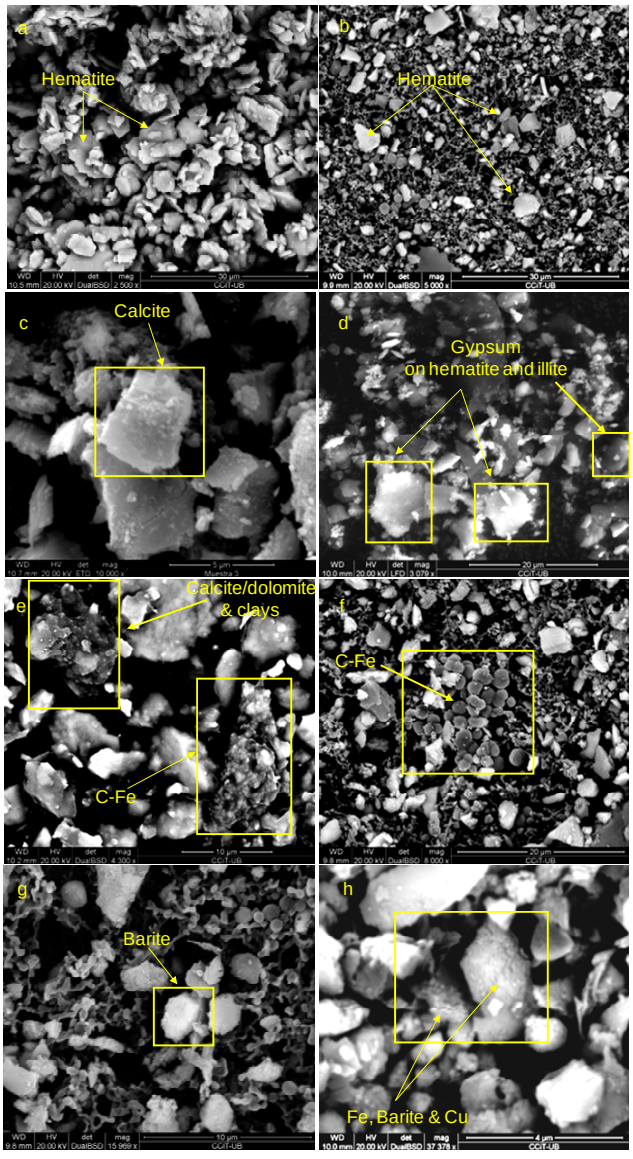

Fig. 7. SEM microphotographs and EDX spectra of PM_{10} samples collected at S-L9 and F-L3 platforms; **(a)** general view of the PM collected at S-L9 platform showing the predominance of laminate hematite from wheel/rail erosion; **(b)** general view of the PM collected at L-F3 platform showing similar 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.

As Table 4 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.

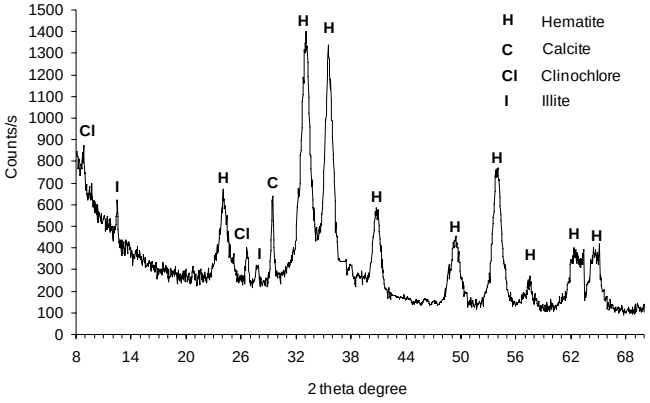

Fig. 8. XRD patterns of the >2.5 µm particles retained in the head of the $PM_{2.5}$ inlet.

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 µg m^{-3}) of $PM_{2.5}$ and 41–61 % (41–206 µg m^{-3}) of PM_{10}. This contribution was reduced by a factor of 3 (compared with S-L9 last days of the study period) and 15 (compared with F-L3), to 20 % (13 µg m^{-3}) of PM_{10} during the measurements with double tunnel ventilation power (T2) at S-L9. The high proportion of atmospheric iron present in underground steel wheel metro systems has been documented previously (Seaton et al., 2005; Adams et al., 2001a and b; Aarnio et al., 2005). Here we show that the dominant iron species is hematite (as deduced from XRD analysis). Salma et al. (2009) and Salma (2009) showed by means of Mössbauer spectroscopy, microscopy and XRD analysis that the particles in the Budapest' metro were dominantly made up of Fe-rich particles in the $PM_{2.0}$ size fraction typically consisted of aggregates of nano-sized hematite crystals that were randomly oriented, had round shapes and diameters of 5–15 nm). In addition to hematite they found, a minor fraction of the iron oxide particles also contained magnetite. Further constituents, such as ferrite, carbides and FeOOH were also identified. Magnetite was also found by Karlsson et al. (2008 and 2005) in the Stockholm subway system by XRD.

The second component in both relative and absolute abundance is carbonaceous aerosol, reaching 14–22 % (13–34 µg m^{-3}) of $PM_{2.5}$ and 13–16 % (13–53 µg m^{-3}) of PM_{10}. It is interesting to note that 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 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

Table 4. Mean levels and standard deviation (std) 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 (AUB) 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)
$\mu g\,m^{-3}$	F-L3 10 days	std	S-L9 10 days	std	F-L3 10 days	std	S-L9 first 8 days	std	S-L9 10 days	std	AUB
PM_x	155	28	90	28	339	45	64	13	100	81	21
OC	33.3	14.4	9.8	6.2	52.3	12.4	9.2	3.3	8.3	3.4	3
EC	1.2	0.8	3.2	1.4	0.3	1.0	4.6	1.5	4.4	1.4	2
OC + EC	34.5	14.7	13.0	6.0	52.7	12.6	13.8	4.4	12.7	4.5	5
ws-Cl^-	0.4	0.3	0.7	0.1	1.0	0.3	0.7	0.2	0.7	0.2	0.4
ws-NO_3^-	0.2	0.1	0.2	0.2	0.8	0.3	2.1	0.8	1.9	0.8	2.9
ws-SO_4^{2-}	2.3	0.7	2.0	0.8	5.1	0.8	6.6	1.3	5.9	1.9	3.0
ws-NH_4^+	0.3	0.1	0.4	0.2	0.6	0.2	0.9	0.2	0.8	0.3	1.7
SO_4^{2-}	2.5	0.9	2.0	0.8	9.6	3.0	6.8	1.2	6.1	1.8	3.0
Fe_2O_3	79.9	14.7	46.3	20.3	206.4	29.7	13.1	4.4	41.1	62.6	0.2
CO_3^{2-}	4.6	1.2	2.9	1.1	11.3	1.8	4.3	1.4	6.3	4.4	
Ca	1.8	0.5	1.2	0.4	4.5	0.7	1.7	0.6	2.5	1.8	0.2
Al_2O_3	1.4	0.3	0.7	0.3	3.0	0.6	1.1	0.7	1.4	0.9	0.2
Ba	2.2	0.3	0.02	0.01	5.3	0.8	0.02	0.01	0.03	0.02	0.004
Mg	0.9	0.1	0.13	0.05	2.1	0.3	0.3	0.1	0.3	0.1	0.06
CuO	0.8	0.2	0.15	0.07	2.2	0.4	0.04	0.01	0.09	0.12	0.01
MnO	0.7	0.1	0.4	0.2	1.8	0.3	0.12	0.05	0.4	0.5	0.01
ZnO	0.6	0.1	0.13	0.07	1.4	0.2	0.09	0.04	0.2	0.3	0.09
Na	0.3	0.1	0.24	0.11	0.7	0.1	0.9	0.3	0.8	0.3	0.3
K	0.10	0.1	0.08	0.07	0.6	0.1	0.5	0.2	0.5	0.2	0.2
TiO_2	0.08	0.01	0.03	0.01	0.22	0.03	0.07	0.04	0.08	0.04	0.01
Cr_2O_3	0.09	0.02	0.06	0.03	0.23	0.03	0.02	0.01	0.06	0.09	0.002
$ng\,m^{-3}$											
Sr	44	6	3	1.0	101	14	4	2	6	3	0.7
Zr	38	7	3	2	76	17	3	3	3	2	5.1
Mo	42	6	8	1.3	72	11	5	3	6	3	1.6
Sb	3	0.1	13	20	64	58	8	3	14	14	1.0
Sn	18	3	5	2	44	5	4	2	5	3	2.8
Ni	27	8	30	16	40	13	9	3	15	13	2.9
As	16	2	6	2	34	5	2	2	5	7	0.3
Pb	11	2	3	0.9	30	4	6	3	6	3	7.9
V	13	6	1.4	0.7	24	5	2	0.8	3	1.3	6.1
Co	7	2	4	0.8	15	3	11	3	10	3	0.1
P	3.2	0.6	1.3	0.5	7.9	1.0	0.7	0.2	1.4	1.6	8.4
W	2.7	0.5	1.0	0.4	4.2	1.5	1.1	0.7	1.1	0.7	0.1
Li	1.5	0.3	0.7	0.3	3.7	0.5	1.4	1.6	1.5	1.5	0.1
Hf	1.1	0.6	0.7	0.4	2.7	0.5	1.4	0.6	1.6	0.8	0.2
Rb	1.4	0.2	0.14	0.05	2.2	0.3	0.02	0.01	0.06	0.09	0.3
Nb	0.7	0.1	0.4	0.2	1.7	0.2	0.3	0.2	0.5	0.4	0.1
Ge	0.9	0.2	0.2	0.1	1.7	0.3	0.6	0.3	0.5	0.2	0.1
Ga	0.7	0.2	0.4	0.3	1.2	0.2	0.06	0.08	0.3	0.6	0.1
U	0.4	0.1	0.2	0.10	0.8	0.2	0.2	0.2	0.3	0.2	0.04
Y	0.3	0.1	0.3	0.08	0.7	0.1	0.02	0.01	0.2	0.3	0.1
Th	0.2	0.1	0.07	0.2	0.6	0.1	0.13	0.2	0.15	0.2	0.03
Ta	0.2	0.1	0.08	0.05	0.4	0.1	0.12	0.09	0.14	0.09	0.1
Cd	0.3	0.1	0.04	0.06	0.3	0.1	0.02	0.01	0.04	0.06	0.1
Bi	0.4	0.1	0.3	0.04	0.3	0.2	0.08	0.09	0.14	0.14	0.2

Table 4. Continued.

	$PM_{2.5}$				PM_{10}						$PM_{2.5}$ (outdoor)
$\mu g\,m^{-3}$	F-L3 10 days	std	S-L9 10 days	std	F-L3 10 days	std	S-L9 first 8 days	std	S-L9 10 days	std	AUB
Se	0.02	0.01	0.02	0.01	0.20	0.25	0.33	0.36	0.31	0.33	0.3
La	0.86	0.13	0.31	0.08	1.53	0.31	0.60	0.58	0.64	0.53	0.11
Ce	1.47	0.25	0.55	0.14	2.46	0.53	0.89	0.92	0.99	0.85	0.22
Pr	0.12	0.02	0.02	0.02	0.23	0.05	0.06	0.06	0.07	0.06	0.01
Nd	0.45	0.07	0.16	0.06	0.88	0.18	0.24	0.19	0.28	0.19	0.05
Sm	0.13	0.02	0.05	0.01	0.21	0.06	0.04	0.03	0.05	0.05	0.01
Gd	0.12	0.02	0.04	0.01	0.18	0.05	0.03	0.03	0.05	0.04	0.02
Dy	0.14	0.03	0.06	0.01	0.20	0.06	0.04	0.03	0.05	0.04	0.02
Er	0.06	0.01	0.02	0.01	0.10	0.02	0.02	0.01	0.03	0.02	0.02
$\mu g\,m^{-3}$											
Fe_2O_3	79.9	14.7	46.3	20.3	206.4	29.7	13.1	4.4	41.1	62.6	
Other metals	4.5	0.7	0.8	0.4	10.9	1.6	0.3	0.1	0.7	1.0	
Crustal	8.9	2.2	5.0	2.0	21.8	3.6	8.1	3.0	11.1	7.4	
SIA	2.7	0.9	2.6	1.1	6.5	1.3	9.6	2.3	8.6	3.0	
Insoluble SO_4^{2-}	0.3	0.2	<0.1	<0.1	4.5	2.3	0.2	<0.1	0.2	<0.1	
OC + EC	34	15	13.0	6.0	52.7	12.6	13.8	4.4	12.7	4.5	
Traces	0.23	0.05	0.08	0.05	0.53	0.14	0.06	0.03	0.08	0.06	
Na + Cl	0.7	0.4	0.9	0.2	1.6	0.4	1.6	0.4	1.5	0.5	
Accounted	132	34	69	30	305	52	47	14	76	79	
Unnacounted	23	4	22	4	34	11	17	6	23	15	
% Determined	85	3	76	7	90	4	73	7	76	6	

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 probably the result of a measurement artefact, more than an actual prevalence of OC versus EC. This is also supported by the clear negative correlation observed between Fe and EC contents (0.58), and the correlation between OC and Fe (0.65).

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 was 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. Wind erosion by intense air flow within the tunnels and in the platforms may also contribute to increase the levels of crustal components.

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 due to the occurrence in relatively high levels of barite (highly water-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 (5.1 $\mu g\,m^{-3}$) 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 of other sulphate species, such as sodium and calcium nitrate and sulphate, as deduced from the ion excess of sulphate+nitrate versus ammonium and XRD analysis (gypsum).

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, with this 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 1.5–1.6 $\mu g\,m^{-3}$ 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 (La to Lu), W, Bi, U and Th from 2 to 4 times higher.
- 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 usual summer ventilation (PS-T1) set up was implemented at S-L9. 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, and 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.

4 Discussion

4.1 PM levels in trains and platforms

As already mentioned several studies have 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 and b; Johansson and Johansson, 2003; Seaton et al., 2005; Braniš, 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 and Cheng and Yan, 2011; Aarnio et al., 2005; Gómez-Perales et al., 2004 and 2007; Múgica-Álvarez et al., 2012; Chan et al., 2002a and b; Kam et al., 2011; Chillrud et al., 2004) report in contrast relatively low PM levels.

Nieuwenhuijsen et al. (2007) and Salma et al. (2007) interpreted such differences in PM levels among the metro systems as 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) 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 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) reported that PM levels in underground metro stations were closely associated with the frequency at which trains run. Braniš (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 metro systems from other cities (Fig. 6, and references therein) 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 Prague; and from 129 to $407\,\mu g\,m^{-3}$ in Budapest, Paris, Seoul, Shanghai, Stockholm and Rome. Mean PM_{10} levels recorded at S-L9 during days with double tunnel ventilation power (T2) ($45\,\mu g\,m^{-3}$) 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 in the low and high range of high PM_{10} systems (145 and 346 $\mu g\,m^{-3}$, respectively).

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 and New York, 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 and Shangai. 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 the PS-T2 ventilation set up (15 $\mu g\,m^{-3}$) are even lower than in 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 PS-T2 period) and low (for the usual L9 ventilation set up) when compared with the concentration range in worldwide metro systems. At F-L3 levels may be considered as 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 $\mu g\,m^{-3}$ $PM_{2.5}$ at the new S-L9 closed platform, depending on whether all the period or the T2 ventilation period is considered, and 125 $\mu g\,m^{-3}$ $PM_{2.5}$ 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 $\mu g\,m^{-3}$ $PM_{2.5}$ 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 $\mu g\,m^{-3}$ $PM_{2.5}$ 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. 6 and Table 4) 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 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 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. 6, and references therein):

1. Mean PM_{10} levels on board of the trains ranged from 32 to 67 $\mu g\,m^{-3}$ in (from low to high): Los Angeles, Taipei, Hong Kong and Guanzhou; and from 114 to 325 $\mu g\,m^{-3}$ in Prague, Berlin, Seoul, 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 trains in the old lines, 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 and Guanzhou, 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. In Fig. 9 we show a comparison of the available published data with the results of this study.

In the Barcelona's Metro, levels of Fe averaged 144 and 55 $\mu g\,m^{-3}$ PM_{10} and $PM_{2.5}$ respectively for F-L3, and 9 $\mu g\,m^{-3}$ in PM_{10} for the first 8 days with double ventilation power (T2) at S-L9: other metal oxides such as MnO, CuO, ZnO and Cr_2O_3 decreased from 1.8 to 0.1, 2.2 to 0.1, 2.2 to 0.04 and 0.2 to 0.02 $\mu g\,m^{-3}$ for PM_{10} at F-L3 and S-L9 for the first 8 days. Levels of OC and EC reached 33 and

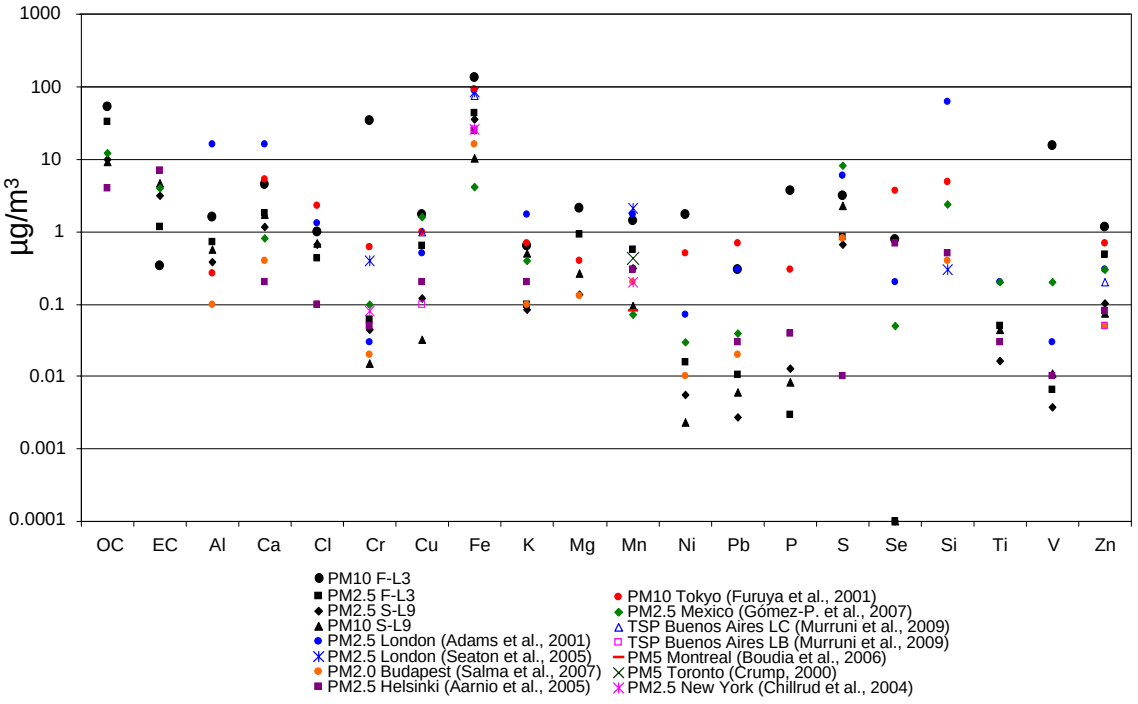

Fig. 9. Comparison of mean levels of selected components in PM_{10} and $PM_{2.5}$ obtained at Fontana (L3) and Sagrera (L9) platforms with those reported from other studies carried out in different metro systems worldwide.

1.2 µg m^{-3} in $PM_{2.5}$ for F-L3, and 9 and 5 µg 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 µg 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 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 with PS-T2 ventilation.

We were only able to find a paper with detailed PM_{10} speciation in metro systems, this showing data from the Tokyo subway system (Furuya et al., 2001). Most of the studies were carried out by analyzing $PM_{2.5}$. As shown in Fig. 9, 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 us to perform PCA using the 39 $PM_{2.5}$ and PM_{10} samples collected at both S-L9 and F-L3 platforms. The results identify the following sources/factors of PM at the Barcelona's metro (Table S2):

– 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 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.

– 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 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 closed rail tracks in platforms may make the difference.

4.3 PM exposure levels during commuting

Table S3 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 81 and 26 $\mu g\,m^{-3}$ 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 55 and 17 $\mu g\,m^{-3}$ for L9 (53 and 16 $\mu g\,m^{-3}$ for the first 8 days with doubled tunnel ventilation).

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 5 to compare the data obtained in the present study. Accordingly with the studies shown, commuting PM exposure in passenger cars reaches levels of 35–75 $\mu g\,m^{-3}$ PM_{10} and 22–83 $\mu g\,m^{-3}$ $PM_{2.5}$, comparable to those reported for metro commuting in Barcelona in July 2011: 81 and 26 $\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$. During bus commuting, $PM_{2.5}$ exposure levels reported were in the range 33–128 $\mu g\,m^{-3}$ $PM_{2.5}$ (usually being lower than 75 $\mu g\,m^{-3}$ $PM_{2.5}$), whereas during cycling/motorbike commuting were 68–88 $\mu g\,m^{-3}$ $PM_{2.5}$, being markedly higher than in the Barcelona metro. 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 5, 33–62 $\mu g\,m^{-3}$ $PM_{2.5}$, with the exception of London, 157–247 $\mu g\,m^{-3}$ $PM_{2.5}$).

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 3.9 and 1.3 $\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$, respectively. As shown in Table S3, these values are reduced if L9 is considered (2.7 and 0.8 $\mu g\,m^{-3}$). Seaton et al. (2005) reported a contribution of 17 $\mu g\,m^{-3}$ $PM_{2.5}$ for 2 h travel in the London metro, much higher than the values reported in our study for the same travelling time (2.6 $\mu g\,m^{-3}$ $PM_{2.5}$). If we assume a mean urban background concentration of 20 $\mu g\,m^{-3}$ $PM_{2.5}$ 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 $\mu g\,m^{-3}$ $PM_{2.5}$. In this case, the metro commuting contribution accounts for around 6 % of the daily exposure. More recently, Schembari et al. (2012) calculated a mean personal exposure of 26 $\mu g\,m^{-3}$ $PM_{2.5}$ 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 4), 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 to outdoor levels, depending if PM_{10} at S-L9 during the first 8 days with doubled tunnel ventilation or $PM_{2.5}$ at F-L3 are considered.
- Fe: 50–220 times, mean 221.
- Cu, Mn, Cr, Sr, Sb, As,: 4–87 times, means 24–70.
- 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.

The Enrichment Factors (EF) may be calculated by normalizing the levels of specific major and trace elements versus the content of an individual crustal component, such as Al, and this being divided by the same ratio of the mean upper crust contents (Rudnick and Gao, 2003) of the same elements. For example, the EF of arsenic may be obtained from: $EF_{As} = (As_{PM}/Al_{PM})/(As_{crust}/Al_{crust})$. If EF values are close to 1, the specific element occurs in PM in similar concentrations than in the upper crust, if EF reaches values much higher than 1, then the element is mainly supplied to PM by non crustal sources.

If EF values are calculated for the elements analyzed in the $PM_{2.5}$ from S-L9 and F-L3 platforms the following evidences were obtained:

- EF from 0.5 to 3: Ti, K, Rb, Y, REEs, Na, Mg and Sr at S-L9.
- EF from 3 to 15: Ca, Li, V, Ga, Nb, Th and Mg; Ba and Zr at S-L9; and Sr at F-L3.
- EF from 15 to 150: Mn, Cr, Co, Ni, Ge, Pb, U, W, As at S-L9 and Zr at F-L3.
- EF > 150: Fe (180), Cd (200), As at F-L3 (300), Ba at F-L3, Zn (450), Sn (450–900), Mo (450–3800), Cu (1000–2500) and Sb (7400 and 15 700).

Table 5. PM exposure levels ($\mu g\,m^{-3}$) for different commuting modes in a number of cities of the world. 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).

	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	–
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

According to these results, only from 0.5–1.1 % Fe_2O_3 may be supplied by crustal sources (mostly resuspension and erosion), the vast majority arising from mechanical abrasion of wheels, rails and brakes.

When the EFs are calculated for the outdoor $PM_{2.5}$ values of the highest EF group varied markedly:

– EF decreasing from the subway to outdoor $PM_{2.5}$: Fe (from 180 to 3), Mn (from 60 to 10), As (from 300 to 48), Ba (from 450 to 5), Cu (2500 to 275) and Sb (15 700 to 1925). The still relative high outdoor values are due to high brake and tyre dust contributions in urban air for these metals.

– EF increasing in outdoor $PM_{2.5}$: Cd (855), Zn (805), Mo (1120) and Sn (1027) also mostly supplied by industrial and traffic sources; Ni and V (48) supplied by fuel oil combustion; Na (10) from sea salt; and K (7) from biomass burning.

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 ($\times$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 ngAs 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 ngAs m^{-3} for the first 8 days only at S-L9). This represent an increase of 340, 235, 145, 40 and 20 % (180, 4, 24, 17 and 4 % for the first 8 days with higher ventilation 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 $PM_{2.5}$, 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 were 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. Results obtained in Helsinki and New York are similar to those obtained in Barcelona. However, these ratios were reduced by 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. Karlsson et al. (2005 and 2008) and Seaton et al. (2005) found that the subway particles cause much higher oxidative stress in the lung cells than outdoor urban PM in Stokholm and London, and this may be due to the high free radicals production by transition metals. Therefore, although platform exposure is relatively short, subway systems should optimize ventilation and technology to abate PM levels as much as possible.

5 Conclusions

The results of this study demonstrate that during July 2011 and February 2012 the new metro system of lines L9 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, the platform screen door system and to other design features of the platform and trains resulting on a reduction on 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 also equipped with platform screen doors.

Furthermore, the effect of doubling the power of the tunnel ventilation system at S-L9 during the first 8 days of measurements in July and in the repetition during last week of February studies is drastic in reducing ambient PM with respect to the conventional usual ventilation scheme of the tunnels. Thus with this high ventilation scheme PM levels on the platform of S-L9 were reduced by a factor of 7.2 with respect to the old F-L3 platform, and also by 4.2 with respect to the same S-L9 with the usual tunnel ventilation set up.

Furthermore, we demonstrated that the changes in the ventilation system were crucial in governing PM levels on the platform at S-L9, since using a high ventilation power resulted in levels of PM varying independently of the frequency of trains.

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 old L3. 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 $ngBa\,m^{-3}$, 5 $ngMn\,m^{-3}$, 0.6 $ngCr\,m^{-3}$ and 0.06 $ngAs\,m^{-3}$ (0.25 $\mu gFe\,m^{-3}$, 0.2 $ngBa\,m^{-3}$, 2.4 $ngMn\,m^{-3}$, 0.3 $ngCr\,m^{-3}$ and 0.01 $ngAs\,m^{-3}$ for the high tunnel ventilation period at S-L9), this accounting for an increase of 277, 235, 145, 40 and 20 % (180, 4, 24, 17 and 4 % for the high tunnel ventilation period 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 and cost evaluations are needed to implement the tunnel double ventilation scheme to drastically reduce PM levels at S-L9 platforms.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/12/5055/2012/acp-12-5055-2012-supplement.pdf.

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