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# Particulate matter concentrations, physical characteristics and elemental composition in the Milan underground transport system

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## HIGHLIGHTS

► PM10 levels in subway stations were studied and its elemental composition determined.
► OPC's were used to determine size distributions.
► PM10 concentrations were greater than in ambient air by up to a factor of 8.
► Source contributions were estimated on the platform and mezzanine levels.
► PM10 levels were largely due to local sources such as brake, wheel and cable wear.

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## ABSTRACT

An extensive measurement campaign was conducted in the Milan subway system in order to investigate PM10 concentrations, to determine its physical and elemental composition, its origins, and to attempt to quantify source contributions. The Milan subway system includes three lines and stations typically consist of two underground levels: an intermediate floor (mezzanine) where the turnstiles for accessing the platform are located, and a platform level, one floor down. Measurements were performed in two stations for each line, and both microenvironments (platform and mezzanine) were investigated in all cases. PM10 samples were collected at all twelve sites over three daily periods for nine consecutive days at each site. Particle number concentrations were also measured with Optical Particle Counters (OPC) and size-number distributions were determined. X-ray fluorescence analysis was also performed on the samples to determine element concentrations. The results indicate PM sources related with train operations as the dominant impact on particulate concentrations. Average weekday PM10 concentrations between 105 and 283 $\mu g\ m^{-3}$ were observed at the platform level, while average ambient concentrations of 36 $\mu g\ m^{-3}$ were observed. Fe, Ba, Sb, Mn and Cu were found to be significantly enriched. Metal particles, occurring mostly in the range of diameters between 1 and 5 μm, and therefore likely originating from mechanical processes, account for most of the PM10 mass at the platform level. Wheel, brake and track wear are found to contribute 40–73% of total PM10 mass and electric cable wear (Cu and Zn oxides) 2%–3%. Concentrations measured on the mezzanine levels are intermediate between those found in ambient air and on the platform level, with average daytime PM10 values ranging from 50 to 80 $\mu g\ m^{-3}$. The situation observed on the mezzanine can well be described through an appropriate mixing of ambient and platform level air. A decreasing, albeit still significant, impact from internal sources is observed, with particulate from wheel, brake and track wear contributing an average of 2–25%, and electric cable wear 0.5–1.2%, to total PM10 mass.



## 1. Introduction

Ambient PM10 concentrations exceeding the limits set by the European air quality Directive (European Commission, 2008) are a major concern in the Milan metropolitan area, but individual exposure to particulate matter can be strongly influenced by indoor levels, as most people spend 80–90% of their time in a variety of indoor environments. In urban areas, transport-related microenvironments can be of concern when evaluating population exposure to particulate matter (Adams et al., 2001; Gómez-Perales et al., 2007).

Prior studies in the subway lines of several cities throughout the world indicate, with few exceptions, that particulate matter (PM)

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concentrations significantly higher than those measured in ambient air are generally found in these environments. Elevated PM concentrations have been found in the subway systems of Barcelona (Querol et al., 2012), Berlin (Fromme et al., 1998), Boston (Levy et al., 2000), Budapest (Salma et al., 2007, 2009), Buenos Aires (Murruni et al., 2009) Helsinki (Aarnio et al., 2005), London (Adams et al., 2001), Los Angeles (Kam et al., 2011), Mexico City (Gómez-Perales et al., 2004, 2007), Rome (Ripanucci et al., 2006), New York (Chillrud et al., 2004, 2005), Paris (Raut et al., 2009), Prague (Braniš, 2006), Seoul (Kim et al., 2008; Jung et al., 2010), Shanghai (Xiaojiang et al., 2010), Stockholm (Johansson and Johansson, 2003), and Tokyo (Furuya et al., 2001). However, results are not always directly comparable because of differences in measurement methods, time averages, chemical and size characterization of particulate matter, the type of environment investigated and duration of the measurements (Nieuwenhuijsen et al., 2007). Some of these studies have also investigated particulate matter composition (Aarnio et al., 2005; Salma et al., 2007; Murruni et al., 2009; Chillrud et al., 2004, 2005), and metals such as Fe, Cu, Ba, and Mn, were found to be significantly enriched in comparison with typical outdoor levels. It has been suggested that these elements originate from the mechanical wear of rails, electric cables, brake pads, and wheels, but the contribution of such sources has not been quantified. A pedestrian exposure study performed in Milan also gives indications of elevated particle mass concentrations in subway stations (Lonati et al., 2011).

Based on the information available, measurements of particulate levels in the Milan subway system were performed to provide data and information for a possible exposure study and to determine the contributing sources for the purpose of identifying possible abatement measures.

Milan is served by three subway lines, at different depths, with different tunnel sizes, and different train frequencies. The underground system is a heavily used mode of transportation, carrying almost one million passengers on a weekday. In all three subway lines, two main types of environments are connected with the subway system: a first underground level (mezzanine), where cafes, newspaper kiosks, sometimes small shops, and the station controller (transport company employee) are located; and the track-level station (platform level), one floor down. Both types of locations were investigated in two different stations for each of the three subway lines. In order to gather information on the relationship between pollutant levels and the characteristics of the sites investigated, the measurements were extended to all three subway lines and to different stations and microenvironments with different characteristics (amount of mixing with external air, depth, connections with the upper level, size and shape of the station itself and the tunnels, number of trains in transit).

A comprehensive study of PM10 levels, and its physical and chemical characteristics was performed with continuous measurements over a significant length of time (nine days at each site); local particulate sources were identified and their contributions quantified. A simple method was also applied to estimate the respective contributions of outdoor and platform level air to the mezzanine floor air quality.

Since airborne particulate matter is an heterogeneous mixture with chemical and physical characteristics dependent on the originating sources and other environmental factors, particulate matter in a closed underground environment with local particulate emission sources is likely to be qualitatively different from that typically found in ambient air. As a consequence, mass concentrations might not correlate with possible health effects in the same way as in the case of urban particulate matter. Number and size distribution and chemical composition (Harrison and Yin, 2000; Riley et al., 2002; Davidson et al., 2005; Valavanidis et al., 2008) can therefore be useful metrics for an evaluation of personal exposure in such microenvironments. Particle number and size distributions were therefore also measured in each site and elemental composition of the samples was determined.

## 2. Experimental methodology

### 2.1. Sampling sites

The Milan subway system is a heavily used mode of transportation within the city and between the city and nearby towns. The M1 (Red) line was inaugurated in 1964 and extends over a total length of 28 km and 38 stations; the M2 (Green) line was inaugurated in 1969, and is 35 km long with 33 stations; the M3 (Yellow) line was inaugurated in 1990, and is 13 km long with 17 stations.

All three lines were investigated in this work. Two stations in the urban area were selected for each line, based on their different characteristics: Duomo and Porta Venezia on the Red line (R), Piola and Cadorna on the Green line (G) and Duomo and Crocetta on the Yellow line (Y). In all cases, measurements were performed both on the mezzanine level and on the platform at the track-level. The architecture of the stations and tunnels is different for each station: two separate tunnels with a central platform in Piola, one wide tunnel with two tracks in Duomo-R, Porta Venezia and Cadorna, a single narrow tunnel with one track in Duomo-Y and Crocetta. The mezzanine at Duomo is large and several shops are located there, as in Cadorna where it is also connected to a railway station; the others are smaller. Duomo and Cadorna are connecting stations between the Red and the Yellow Lines and the Red and the Green Lines, respectively. In all stations an air exchange system guarantees at least eight air changes per hour, through natural ventilation and forced extraction. The characteristics of the stations and the measurement periods are summarized in Table 1 and train operations are summarized in Table 2.

**Table 1**
Characteristics of the subway stations where measurements were performed and of the external area by the station entrance according to Directive 2008/50/CE.

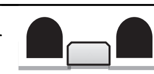
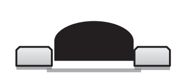
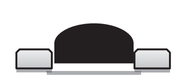
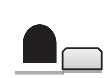
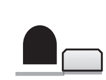
| Subway line/ station | Measurement period | Tunnel type | Plaform depth | Ambient station classification |
|---|---|---|---|---|
| Green Line – Piola | 23 Mar–2 Apr |  | −13 m | Urban traffic |
| Green Line – Cadorna | |  | −8 m | Urban traffic |
| Red line – Duomo | 8–19 Apr |  | −10 m | Urban background |
| Red line – Porta Venezia | |  | −9 m | Urban traffic |
| Yellow line – Duomo | 19–30 Apr |  | −23 m | Urban background |
| Yellow line – Crocetta | |  | −20 m | Urban traffic |

**Table 2**
Number of train passages for the three subway lines.

| | Green line (Piola and Cadorna) | Red line (Duomo-R and Porta Venezia) | Yellow line (Duomo-Y and Crocetta) |
|---|---|---|---|
| Total number of trains on a weekday | 545 | 638 | 225 |
| Maximum number of trains per hour | 51 | 57 | 20 |
| Total number of trains on Saturdays | 389 | 532 | 183 |
| Maximum number of trains per hour – Saturdays | 24 | 34 | 12 |
| Total number of trains on Sundays | 297 | 362 | 161 |
| Maximum number of trains per hour – Sundays | 18 | 24 | 11 |

For comparison purpose, outdoor ambient concentrations were obtained from the regional air quality monitoring network stations of Milano-Verziere (kerb site) and Milano-Pascal (urban background site).

A map indicating the positions of the sampling sites is shown in Fig. 1.

### 2.2. Monitoring instruments and sampling campaigns

#### 2.2.1. PM10 measurements

PM10 samples were collected with low-volume TECORA Skypost samplers with a flow rate of 2.3 $m^3$ $h^{-1}$ according to the EN 12341 (European Standard, 1998). PTFE membrane filters with PMP support rings were used, to allow for analysis with energy dispersive X-ray fluorescence method (ED-XRF). Routine maintenance on the samplers (inlet cleaning and calibration of pump flow) was performed at the beginning of each sampling campaign.

Gravimetric PM10 samplers were used to collect three samples per day, one spanning the night hours, with no train service (24:00–6:00), and two for the daytime (6:00–15:00 and 15:00–24:00). The filters were weighed, after being equilibrated for at least 48 h in a drier, using a six-digit Sartorius M3P microbalance. Changes in temperature and relative humidity in the weighing room were monitored and the weighing operations were carried out in relatively constant conditions.


**Fig. 1.** Map indicating the position of the sampling sites.

In the regional air quality monitoring sites, daily measurements are performed with continuous PM10 beta gauge monitors: an Environment MP101M at the Milano-Verziere station, where 1-h average concentrations are also available, and an OPSIS SM200 at the Milano-Pascal station.

#### 2.2.2. Optical Particle Counter measurements

Continuous particulate number measurements with an Optical Particle Counter (OPC) were also performed during each sampling campaigns. Therefore, four OPC's were in use at the same time: two Grimm 107, which detect particles with size greater than 0.25 μm and classify them into 31 size classes, and two Con.Tec. DustMonit, which detect particles with diameter greater than 0.30 μm and classify them into 8 size classes. All instruments were laboratory tested before the campaign, by running them in parallel in ambient air. The Pearson coefficients for the correlations between any two number concentration series were found to be between 0.97 and 1.00.

The optical response of an OPC to different types of particles can vary significantly (Chen and Lin, 2010) as, according to Mie theory, the amount of light scattered from a particle of a given size depends on its refraction index, i.e. on the particle chemical composition. Moreover, the calibration factors used by OPC's to estimate mass concentrations are derived in typical urban outdoor conditions (Grimm and Eatough, 2009), where particulate matter is qualitatively very different from that found in the subway environment. For these reasons mass concentrations directly generated by the OPC's were not always well correlated with those obtained from the gravimetric measurements ($R^2$ coefficients between 0.128 and 0.861 depending on station and sampling period). The approach of using a single factor to correct OPC's mass concentrations is therefore clearly inadequate in this case.

PM10 average 1-h mass concentrations were therefore recalculated from number concentrations $C_{num}$, by assuming spherical particles, and deriving $\rho_i$ coefficients, with dimension of a density, for each size class from the following expression:

$$C_m = \sum_{i=1}^{n} \rho_i \cdot C_{num_i} \cdot \frac{\pi d_i^3}{6} \cdot \varepsilon_i$$

where $C_m$ is the mass concentration measured with the gravimetric method during train operation and at nighttime, $\varepsilon_i$ is the sampling efficiency as described in UNI EN 12341:1998 (European Standard, 1998), and $d_i$ is the average particle diameter for size class $i$ (Colombi et al., 2012).

Considering $\rho_i$ to be dependent on particle diameter, its value was assumed constant within each of three size clusters (<1 μm, 1–5 μm, and >5 μm) identified by applying cluster analysis to hourly number concentrations (hierarchical cluster analysis of autoscaled data, Pearson $R$ coefficient as similarity index, centroid method of classification). The $\rho_i$'s were obtained by minimizing the sum of the deviations between each of the measured and calculated values of $C_m$ (least-square method).

Values of $\rho_i$ between 0.24 g m$^{-3}$ and 20 g m$^{-3}$ were calculated, depending on size class, time of day (day/night) and site. These coefficients should not be taken as an actual particle density, and large variations are to be expected, as they must account for a number of factors in addition to actual different physical densities, such as the fact that real particles are not spherical, that the geometric diameter is different from the light-scattering diameter measured by an OPC, and that the $\varepsilon_i$ coefficients are defined for aerodynamic, not light-scattering, diameters.

Mass concentrations calculated from OPC numerical concentrations according to the method described above were then validated by correlating them with gravimetric concentrations, and $R^2$ coefficients were obtained between 0.857 and 0.972.

#### 2.2.3. Elemental analysis

The analysis of trace elements was performed with a Panalytical Epsilon5 Energy Dispersive X-Ray Fluorescence (ED-XRF) system to determine the concentrations of elements with $Z > 11$. The instrument uses a polarized X-ray beam that allows for a significant reduction of spectral background. The system was calibrated with a set of Micromatter standards and tested with NIST 2782.

## 3. Results and discussion

### 3.1. Mass concentrations

Average mass concentrations for the three daily periods were determined with the gravimetric samplers. Some outliers were identified and associated with occasional, mostly nighttime, maintenance or cleaning operations, and therefore were not included in the analysis. The resulting concentrations were compared with ambient PM10 levels measured at the Milano-Verziere, a downtown location about one hundred meters from the Duomo subway station. PM10 concentrations are consistently higher on the platform level than on the mezzanine level, and both are higher than in ambient air. Diurnal and weekly cycles are observed, with higher concentrations during train operation hours than during the night, and lower levels on weekends than on weekdays. Daily averages, maximum and minimum PM10 values, and standard deviations for all sites are summarized in Tables 3 and 4 for weekdays and weekends respectively. As an example, Fig. 2 shows the trends measured in the Piola station. Station depth appears to affect

**Table 3**
PM10 mass concentrations in μg m$^{-3}$ for weekdays.

| Green line | | Piola | | Cadorna | | Milano-Verziere |
|---|---|---|---|---|---|---|
| 23 Mar–2 Apr | | Platform | Mezzanine | Platform | Mezzanine | Ambient |
| Daytime | Min | 137 | 38 | 58 | 34 | 12 |
| | Average | 187 | 74 | 105 | 80 | 38 |
| | Max | 235 | 117 | 183 | 139 | 67 |
| | St. Dev. | 34 | 25 | 31 | 27 | 16 |
| Nighttime | Min | 26 | 15 | 21 | 19 | 12 |
| | Average | 67 | 45 | 53 | 54 | 33 |
| | Max | 107 | 88 | 79 | 77 | 59 |
| | St. Dev. | 28 | 25 | 22 | 23 | 17 |
| Red line | | Duomo-R | | Porta Venezia | | Milano-Verziere |
| 8–19 Apr | | Platform | Mezzanine | Platform | Mezzanine | Ambient |
| Daytime | Min | 106 | 45 | 82 | 38 | 19 |
| | Average | 182 | 73 | 108 | 61 | 36 |
| | Max | 227 | 104 | 163 | 98 | 70 |
| | St. Dev. | 34 | 19 | 26 | 17 | 16 |
| Nighttime | Min | 68 | 27 | 28 | 29 | 20 |
| | Average | 121 | 57 | 60 | 58 | 33 |
| | Max | 151 | 121 | 95 | 85 | 50 |
| | St. Dev. | 29 | 30 | 24 | 24 | 12 |
| Yellow line | | Duomo-Y | | Crocetta | | Milano-Verziere |
| 19–30 Apr | | Platform | Mezzanine | Platform | Mezzanine | Ambient |
| Daytime | Min | 205 | 29 | 234 | 48 | 28 |
| | Average | 264 | 50 | 283 | 76 | 36 |
| | Max | 299 | 66 | 327 | 107 | 44 |
| | St. Dev. | 26 | 11 | 22 | 17 | 5 |
| Nighttime | Min | 82 | 47 | 69 | 46 | 29 |
| | Average | 103 | 63 | 87 | 58 | 42 |
| | Max | 155 | 80 | 104 | 72 | 57 |
| | St. Dev. | 24 | 13 | 13 | 9 | 11 |

**Table 4**
PM10 mass concentrations in μg m$^{-3}$ for weekends.

| Green line | | Piola | | Cadorna | | Milano-Verziere |
|---|---|---|---|---|---|---|
| 23 Mar–2 Apr | | Platform | Mezzanine | Platform | Mezzanine | Ambient |
| Daytime | Min | 89 | 38 | 57 | 37 | 10 |
| | Average | 119 | 74 | 73 | 53 | 23 |
| | Max | 153 | 117 | 88 | 68 | 33 |
| | St. Dev. | 31 | 25 | 13 | 13 | 10 |
| Nighttime | Min | 53 | 15 | 47 | 52 | 31 |
| | Average | 61 | 45 | 99 | 102 | 34 |
| | Max | 70 | 88 | 151 | 153 | 37 |
| | St. Dev. | 12 | 25 | 74 | 71 | 4 |
| Red line | | Duomo-R | | Porta Venezia | | Milano-Verziere |
| 8–19 Apr | | Platform | Mezzanine | Platform | Mezzanine | Ambient |
| Daytime | Min | 65 | 35 | 44 | 25 | 13 |
| | Average | 137 | 63 | 71 | 47 | 25 |
| | Max | 174 | 81 | 112 | 99 | 65 |
| | St. Dev. | 38 | 15 | 22 | 25 | 17 |
| Nighttime | Min | 41 | 30 | 32 | 29 | 18 |
| | Average | 96 | 54 | 45 | 50 | 34 |
| | Max | 198 | 74 | 65 | 89 | 52 |
| | St. Dev. | 70 | 18 | 15 | 28 | 16 |
| Yellow Line | | Duomo-Y | | Crocetta | | Milano-Verziere |
| 19–30 Apr | | Platform | Mezzanine | Platform | Mezzanine | Ambient |
| Daytime | Min | 153 | 39 | 177 | 51 | 21 |
| | Average | 183 | 43 | 209 | 58 | 24 |
| | Max | 205 | 53 | 244 | 67 | 27 |
| | St. Dev. | 22 | 7 | 28 | 7 | 2 |
| Nighttime | Min | 69 | 32 | 65 | 32 | 16 |
| | Average | 254 | 96 | 69 | 36 | 20 |
| | Max | 609 | 189 | 73 | 40 | 25 |
| | St. Dev. | 308 | 74 | 6 | 6 | 7 |

concentrations significantly, with higher PM10 values found in the deeper stations, as shown in Fig. 3, where average PM10 mass concentrations measured on weekdays on the platform levels during train operation hours and during the night are plotted. The trends observed also suggest a variability related to tunnel size and station architecture. Stations with narrow tunnels (e.g. Duomo-Y and Crocetta) show higher PM10 levels, while lower particulate levels are found in larger stations more affected by exchange with outdoor air (e.g. Cadorna).

These results indicate the presence of particulate sources on the platform level, where PM10 is emitted in larger amounts during train operation hours than at night and on weekdays more than on weekends.

Similar daily and weekly trends are observed on the mezzanine levels, but with generally lower concentrations, except for Duomo-Y where average daytime concentrations are 20% lower than nighttime levels, probably because its mezzanine is directly connected with the street level.

### *3.2. Number size distributions*

The number size distributions $\partial C_{num}/\partial \log(d)$ for daytime and nighttime were determined from 1-h average number concentrations. The experimental values obtained were interpolated with the sum of two log-normal curves, and the fitting parameters derived with the least-squares method (Seinfeld and Pandis, 2006; PARFIL Project, 2008). This approach proved adequate for the particulate measured on the mezzanine level, but not for the platform level, especially for the daytime. In this case, for all stations, the interpolating curves underestimated the experimental data in the 0.9–4 μm size range. Therefore, a third log-normal curve was added, thereby obtaining better agreement between measured and estimated values in term of correlation ($R^2 > 0.990$). As an example, the size-segregated number distributions for Piola are shown in Fig. 4. The additional log-normal curve proved necessary to fit a third mode present in the measured distribution that occurs in the 1–5 μm size range and that can be associated with particle production due to train operations (mechanical wear). Therefore, the number size distributions obtained on the platform level for all stations show three modes: one including particles in the ranges of up to 1 μm, one for particles 1–5 μm in diameter, and one for particles with diameter larger than 5 μm. The average number concentrations estimated for these three size ranges and their day/night percentage variations are shown in Table 5. Coarser particle numbers significantly decrease during the night, an effect that can be related to stirred deposition (Hinds, 1999) in the absence of the main emission source (the mechanical wear of metal parts such as wheels, rails, brakes and electric cables) and of the turbulence caused by train passage and, to a lesser extent, by the presence of passengers. The larger the particle size, the greater the effect of deposition. Sub-micrometer aerosol concentrations, on the other hand, do not show a regular behavior and do not appear to be related with the timing of station operations, indicating an origin other than local production.

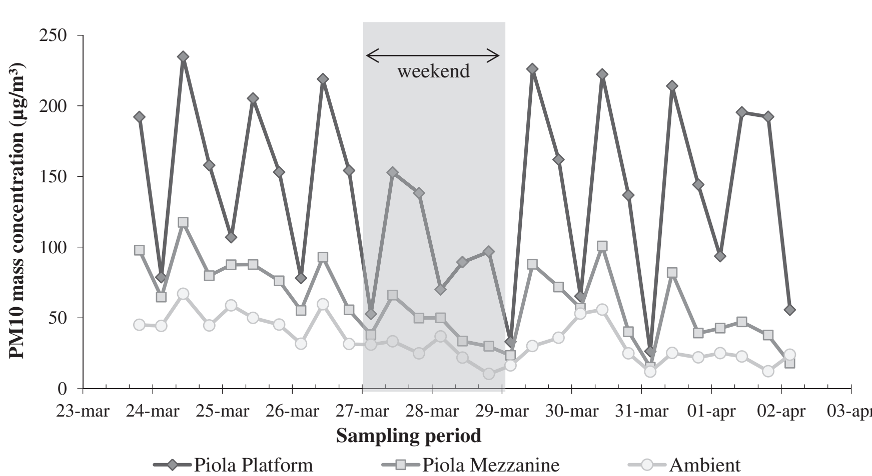



**Fig. 2.** PM10 mass concentrations measured in the Piola station and at the Regional Monitoring Network site of Milano-Verziere.

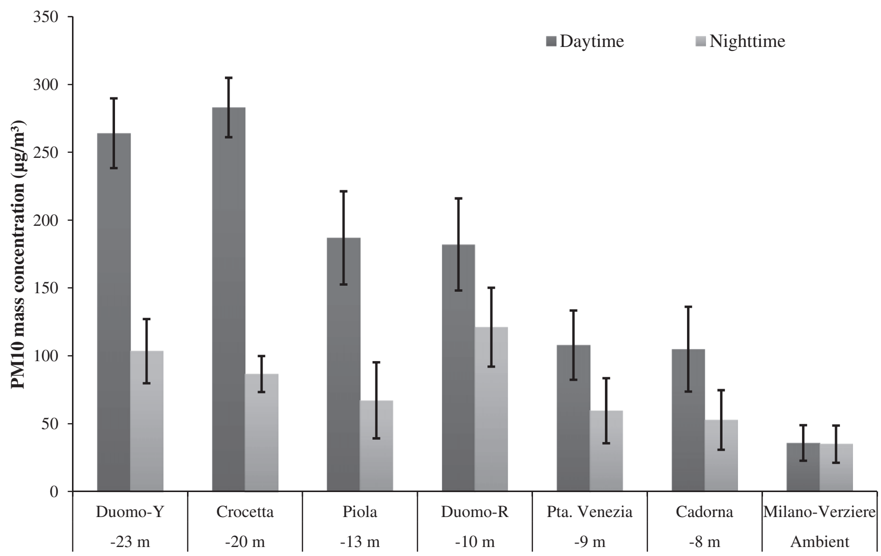



**Fig. 3.** Weekday average PM10 mass concentrations and standard deviations on the platform level for each station.

### 3.3. Correlation with train passages

Average 1-h PM10 concentrations and average number of train passages per hour were correlated separately for weekdays and weekends. The good correlation observed, with $R^2$ coefficients between 0.607 and 0.869, also points to the fact that PM10 levels depend largely on train operation. The daily patterns obtained for Crocetta are shown in Fig. 5. The peak hour, both for number of trains and concentration level, is between 7:00 and 8:00 in the morning.

As examples of two different situations at two different depth, the 1-min number concentrations for the 0.5–0.7 µm size class, representative of the accumulation mode, and for the 2.0–3.0 µm size class, representative of the coarse mode were examined for the morning rush hour at the Crocetta and Cadorna stations. At Crocetta (Fig. 6a) several peaks are observed with concentrations increasing by more than a factor of two over a very short time. Although the time of each train passage was not recorded, the number of trains scheduled during the hour is the same as the number of concentration peaks observed, and their frequency is the same as that of the peaks. The same behavior is observed for the fine and the coarse particles, and it is different from what is typically observed outdoors (Gianelle, 2006). This suggests the passage of trains as the main particulate source in the station, presumably with a two-fold action: particles are directly produced from the wear of metal parts and are also re-suspended by turbulence induced by train passage. For Cadorna (Fig. 6b), where two tracks run in opposite directions in the same larger tunnel, coarse particle concentrations still show recurring peaks, although without the regular behavior observed in Crocetta. Finer particles are less affected by train passage, suggesting an increased contribution from outside air, although a significant impact from local sources is still observed.

### 3.4. Elemental composition

The average concentration of the elements determined through XRF analysis and the standard deviation of the mean over all stations are shown in Table 6. Higher concentrations of Ti, Mn, Ni, Cu, Zn, Br, Rb, Pb, and Fe are observed on the platform level and, to a lesser extent, on the mezzanine floor, than in ambient air. The most enriched element is Fe, with concentrations up to 2 orders of magnitude higher than outdoor levels. A clear diurnal trend is observed, with concentrations decreasing sharply during night hours. Fe levels are also considerably lower on the mezzanine.

Fe, Ba, Mn and Sb are present in the materials used to manufacture rails and wheels (Chan and Stachowiak, 2004; Engberg, 1995; Blau, 2001) and iron and manganese dust accounted for

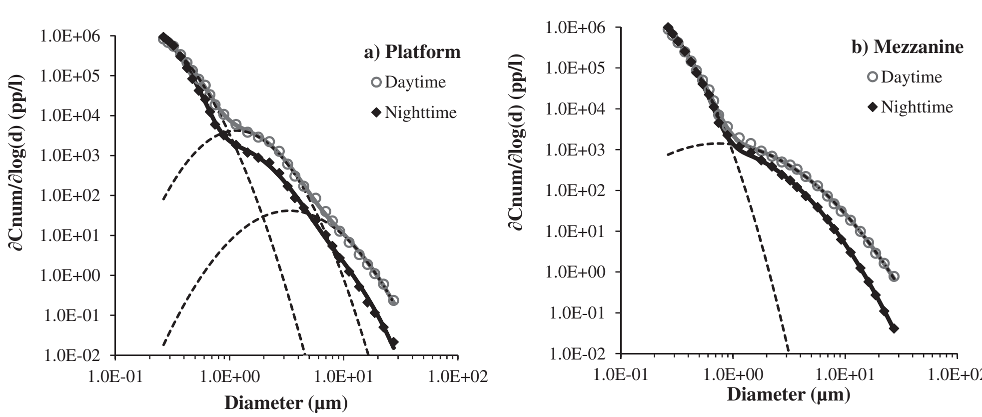



**Fig. 4.** Fit to size-segregated number distributions measured for Piola station (solid line) a) on the platform level and b) on the mezzanine level; the dashed lines represent the single distribution functions used.

**Table 5**
Average number concentrations for the three size classes measured a) on the platform level and b) on the mezzanine level. The percent variations between day and night ($\Delta(N-D)$) are also shown.

| | | 0.3–1 µm | | 1–5 µm | | >5 µm | |
|---|---|---|---|---|---|---|---|
| | | $C_{num}$ (pp l$^{-1}$) | $\Delta(N-D)/D$ (%) | $C_{num}$ (pp l$^{-1}$) | $\Delta(N-D)/D$ (%) | $C_{num}$ (pp l$^{-1}$) | $\Delta(N-D)/D$ (%) |
| *a) Platform* | | | | | | | |
| Piola | Day | 1.80E+05 | −15 | 4.11E+03 | −70 | 3.30E+01 | −74 |
| | Night | 1.53E+05 | | 1.24E+03 | | 8.80E+00 | |
| Cadorna | Day | 1.37E+05 | −1 | 3.71E+03 | −59 | 1.20E+02 | −75 |
| | Night | 1.36E+05 | | 1.51E+03 | | 3.00E+01 | |
| Duomo-R | Day | 1.57E+05 | −22 | 2.55E+03 | −51 | 3.30E+01 | −80 |
| | Night | 1.23E+05 | | 1.25E+03 | | 6.80E+00 | |
| Porta Venezia | Day | 1.59E+05 | −5 | 2.47E+03 | −59 | 5.90E+01 | −62 |
| | Night | 1.51E+05 | | 1.00E+03 | | 2.30E+01 | |
| Duomo-Y | Day | 2.12E+05 | −31 | 3.32E+03 | −56 | 2.20E+01 | −78 |
| | Night | 1.46E+05 | | 1.45E+03 | | 4.90E+00 | |
| Crocetta | Day | 1.99E+05 | −19 | 7.11E+03 | −72 | 1.10E+02 | −77 |
| | Night | 1.61E+05 | | 1.96E+03 | | 2.60E+01 | |
| *b) Mezzanine* | | | | | | | |
| Piola | Day | 1.29E+05 | 0 | 1.42E+03 | −44 | 6.00E+01 | −74 |
| | Night | 1.29E+05 | | 7.96E+02 | | 1.60E+01 | |
| Cadorna | Day | 1.34E+05 | 1 | 2.22E+03 | −41 | 7.20E+01 | −70 |
| | Night | 1.35E+05 | | 1.31E+03 | | 2.10E+01 | |
| Duomo-R | Day | 1.56E+05 | −19 | 1.18E+03 | −27 | 5.70E+01 | −76 |
| | Night | 1.26E+05 | | 8.58E+02 | | 1.40E+01 | |
| Porta Venezia | Day | 1.60E+05 | 0 | 8.98E+02 | 0 | 5.80E+01 | −39 |
| | Night | 1.59E+05 | | 8.99E+02 | | 3.50E+01 | |
| Duomo-Y | Day | 1.66E+05 | −22 | 9.58E+02 | −10 | 3.20E+01 | −83 |
| | Night | 1.30E+05 | | 8.64E+02 | | 5.30E+00 | |
| Crocetta | Day | 1.84E+05 | −23 | 1.49E+03 | −6 | 9.20E+01 | −82 |
| | Night | 1.41E+05 | | 1.41E+03 | | 1.60E+01 | |

the measurable, albeit small, increases in PM concentrations observed in the vicinity of railway lines (Gehrig et al., 2007; Bukowiecki et al., 2007); Cu and Zn can be associated with the wear of electric cables; Ca and Si, typically elements of crustal origin, can also be tracers of occasional construction work in the tunnels.

In order to estimate their contributions to PM10, the concentrations of Fe, Ba, Sb and Mn oxides (henceforth defined as 'Wheel&Brake dust'), of Cu and Zn oxides ('Electric cable dust'), of crustal oxides and of the oxides of the remaining elements ('Other oxides') were calculated using stoichiometric ratios and enrichment factors (EF) estimated as:

$$\mathrm{EF} = \frac{\left[\frac{X_i}{\mathrm{Si}}\right]_{\mathrm{PM10}}}{\left[\frac{X_i}{\mathrm{Si}}\right]_{\mathrm{soildust}}}$$

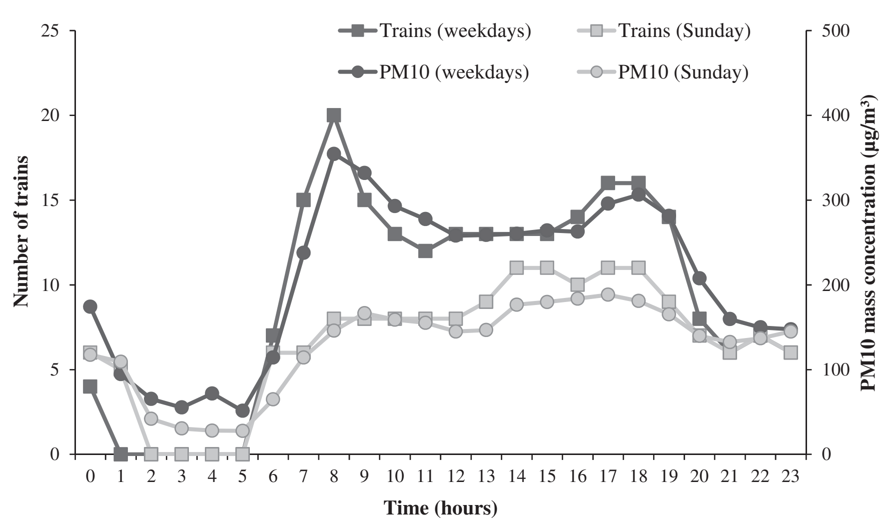



**Fig. 5.** Mean 1-h PM10 concentrations on the platform level and number of trains in transit for the Crocetta station.

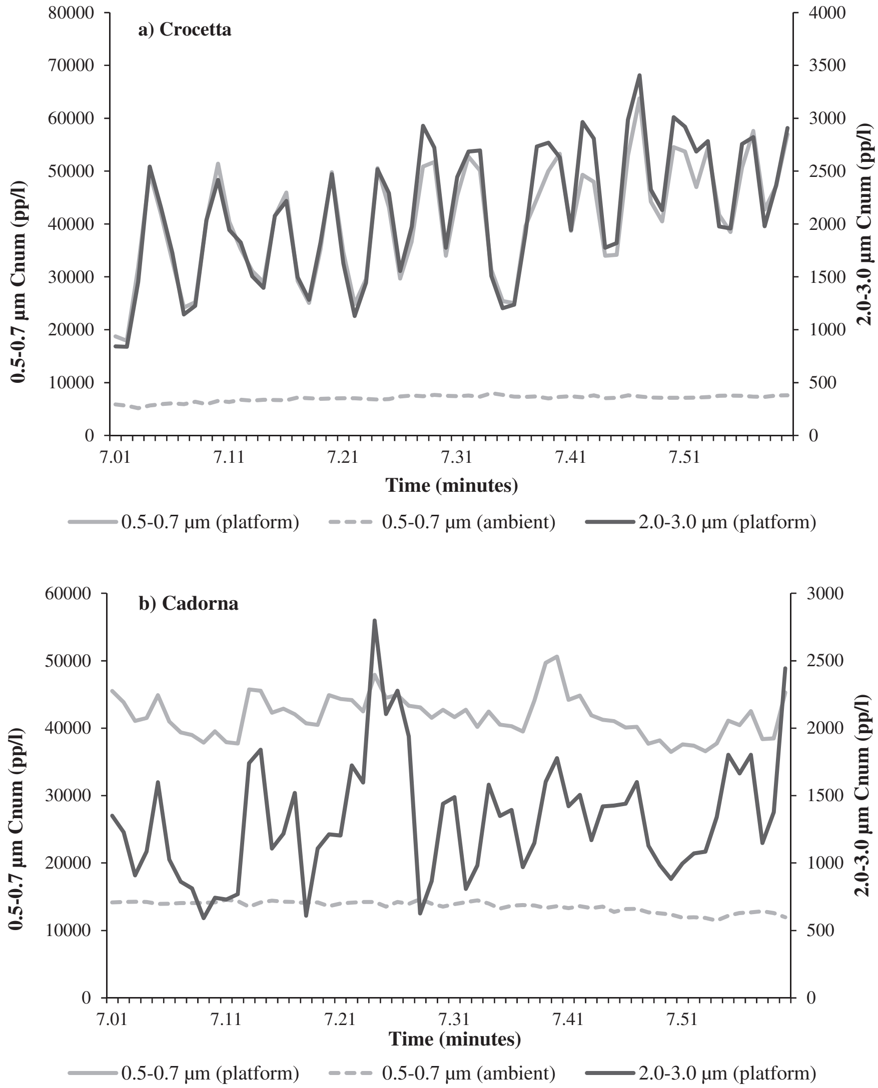



**Fig. 6.** Particle number concentrations for selected size classes measured at the Regional Monitoring Network site of Milano-Pascal and on the platform at a) Crocetta and b) Cadorna.

where $X_i$ is the concentration of the element $i$ and Si is the Silicium concentration. Concentrations in the soil were measured at Milano-Pascal (PARFIL Project, 2008).

The following expressions were used, as described in Eldred et al. (1987):

'Crustal oxides' = (1.890Al + 2.139Si + 1.205(K − K*) + 1.399Ca + 1.668Ti + 1.358(Fe − Fe*))1.15

'Wheel&Brake dust' (as FeO + $Fe_2O_3$ + $Mn_2O_7$ + BaO + $Sb_2O_3$) = 1.358Fe* + 2.019Mn + 1.117Ba + 1.197Sb

'Electric cable dust' (as ZnO + CuO) = 1.245Zn + 1.252Cu

**Table 6**
Average mass concentrations and standard deviations over all stations for PM10 and measured elements. N.D. stands for not determined.

| | PM10 (μg $m^{-3}$) | Al (μg $m^{-3}$) | Si (μg $m^{-3}$) | S (μg $m^{-3}$) | Cl (μg $m^{-3}$) | K (μg $m^{-3}$) | Ca (μg $m^{-3}$) |
|---|---|---|---|---|---|---|---|
| Milano-Pascal | 28 ± 14 | 0.40 ± 0.17 | 1.03 ± 0.52 | 1.29 ± 0.65 | 0.06 ± 0.13 | 0.27 ± 0.09 | 0.87 ± 0.41 |
| Platform | 149 ± 56 | 0.99 ± 0.27 | 3.56 ± 1.07 | 2.67 ± 0.95 | 0.42 ± 0.20 | 0.49 ± 0.11 | 2.35 ± 1.04 |
| Mezzanine | 62 ± 8 | 0.78 ± 0.10 | 3.17 ± 0.77 | 1.54 ± 0.42 | 0.31 ± 0.18 | 0.50 ± 0.05 | 1.96 ± 0.28 |
| | Ti (μg $m^{-3}$) | Cr (μg $m^{-3}$) | Mn (μg $m^{-3}$) | Ni (μg $m^{-3}$) | Cu (μg $m^{-3}$) | Zn (μg $m^{-3}$) | Br (μg $m^{-3}$) |
| Milano-Pascal | 0.048 ± 0.028 | 0.008 ± 0.003 | 0.022 ± 0.010 | 0.003 ± 0.001 | 0.051 ± 0.021 | 0.083 ± 0.042 | 0.005 ± 0.003 |
| Platform | 0.26 ± 0.14 | 0.006 ± 0.007 | 0.48 ± 0.25 | 0.035 ± 0.011 | 1.61 ± 0.51 | 0.84 ± 0.34 | 0.054 ± 0.086 |
| Mezzanine | 0.100 ± 0.018 | 0.008 ± 0.005 | 0.075 ± 0.032 | 0.009 ± 0.004 | 0.25 ± 0.13 | 0.194 ± 0.048 | 0.017 ± 0.017 |
| | Rb (μg $m^{-3}$) | Pb (μg $m^{-3}$) | Sr (μg $m^{-3}$) | Sn (μg $m^{-3}$) | Sb (μg $m^{-3}$) | Ba (μg $m^{-3}$) | Fe (μg $m^{-3}$) |
| Milano-Pascal | <0.001 | 0.023 ± 0.011 | N.D. | N.D. | N.D. | N.D. | 1.28 ± 0.56 |
| Platform | 0.022 ± 0.021 | 0.16 ± 0.10 | 0.072 ± 0.033 | <0.061 | 0.34 ± 0.19 | 3.06 ± 1.72 | 61.3 ± 36.8 |
| Mezzanine | 0.0021 ± 0.0003 | 0.029 ± 0.007 | <0.026 | <0.061 | 0.044 ± 0.018 | 0.34 ± 0.18 | 8.2 ± 3.8 |

'Other oxides' = 2.497S + 2.580Cl + 1.205K* + 1.923Cr + 1.341Ni + 1.701Br + 1.270Sn + 1.183Sr + 1.077Pb + 1.628V with * = total concentration/EF, if EF is greater than 2.

The mass compositions of PM10 thus estimated for each subway site and for the Milano-Pascal monitoring station are summarized in Table 7 and the percentage contributions of each group of metal oxides to PM10 are plotted in Fig. 7. An unaccounted mass of some significance is to be expected, as ions and carbonaceous species were not measured in this work.

In general, the percentage contribution of the 'Wheel&Brake dust' component to PM mass is higher on the platform level than it is on the mezzanine level, and it is higher during the daytime than it is at night. As a consequence, only between 13 and 34% of the total mass is unaccounted for on the platform level during train operation hours, while percentages increase up to 33–68% on the mezzanine level during the night.

As was previously observed for mass concentrations, the Fe + Ba + Sb + Mn oxides component is higher in the stations deeper underground with reduced natural ventilation. It accounts for 70% of total PM10 mass at Duomo-Y and 73% at Crocetta during the day and 50% and 54% at Duomo-Y and Crocetta respectively during the nighttime. In other stations this component is significantly lower during the night, down to only 10% of total PM10 mass at Porta Venezia.

On the mezzanine level, the 'Wheel&Brake dust' component is significantly reduced, both during the day and, especially, during the night, with contributions between 2% (Duomo-Y) and 25% (Duomo-R).

A source enrichment factor (henceforth SEF) for each contributing component was determined, defined as the ratio between the mass contribution of each source to PM10 in the subway environment and the same value estimated for ambient air. The average, standard deviation and maximum values are plotted in Fig. 8, for platform and mezzanine, for daytime and nighttime. While SEF values around 1 are observed for the Crustal oxides, Other oxides and the Undetermined component indicating no significant internal source; significantly enhanced values are found for 'Wheel&Brake dust' (up to 19.5) and for 'Electric cable dust' (up to 6.9). The highest values at the platform level are found at Crocetta and, for the mezzanines, at Duomo.

### 3.5. Cluster analysis

Cluster analysis was applied to daytime and nighttime size-resolved average number concentrations and element concentrations, in order to classify similar time trends. As an example, the resulting dendrograms are shown in Fig. 9 for the platform level at Piola and for the Milano-Pascal site, about 600 m from the Piola station.

The clustering of Zn and Cu further points to their common origin (previously identified as the wear of electric cables), as does the clustering of Fe and Mn, originating from the abrasion of wheels and rails, which are also found to be associated with Ba and Sb, tracers of brake dust. Similar results are found for all stations. Everywhere, particles less that 1 micron stand alone in the tree classification or, at most, form a cluster with S, an element that is not emitted in the subway environment. On the platform level during the daytime on weekdays a second cluster is identified linking particles with diameter between 1 and 3 μm with those elements that have been associated with train operation. At the mezzanine level and during the night particles between 1 and 3 μm are associated with elements of crustal origin, while the elements originating from the wear of metal parts form an independent cluster. Cl can originate from different sources, either external or occasional internal ones such as detergents used in cleaning operations.

These results, and those described in the discussion of the number size distributions, confirm the presence of metal particles of mechanical origin, with size between 1 and 3 μm not observed in

**Table 7**
PM10 mass composition for Milano-Pascal and for the subway stations.

| | | | Crustal oxides ($\mu g\ m^{-3}$) | Other oxides ($\mu g\ m^{-3}$) | Wheel&Brake dust ($\mu g\ m^{-3}$) | Electric cable dust ($\mu g\ m^{-3}$) | Undetermined ($\mu g\ m^{-3}$) |
|---|---|---|---|---|---|---|---|
| Milano-Pascal (23 Mar–30 Apr) | | | 6.1 | 3.4 | 1.0 | 0.2 | 17.3 |
| Piola | Platform | Day | 35.8 | 11.1 | 93.6 | 5.0 | 41.4 |
| | | Night | 15.6 | 6.1 | 8.2 | 0.7 | 36.6 |
| | Mezzanine | Day | 18.8 | 5.3 | 13.4 | 0.9 | 35.8 |
| | | Night | 8.1 | 4.2 | 2.0 | 0.3 | 30.8 |
| Cadorna | Platform | Day | 18.6 | 6.4 | 42.3 | 2.0 | 35.5 |
| | | Night | 9.8 | 3.3 | 7.5 | 0.5 | 31.7 |
| | Mezzanine | Day | 17.8 | 5.5 | 16.6 | 1.0 | 38.8 |
| | | Night | 10.8 | 3.5 | 7.1 | 0.5 | 32.3 |
| Porta Venezia | Platform | Day | 16.4 | 6.4 | 46.4 | 3.4 | 35.4 |
| | | Night | 11.0 | 4.8 | 6.0 | 0.5 | 37.1 |
| | Mezzanine | Day | 18.6 | 3.0 | 3.4 | 0.4 | 35.5 |
| | | Night | 19.1 | 4.0 | 3.2 | 0.4 | 31.6 |
| Duomo-R | Platform | Day | 19.2 | 6.7 | 115.2 | 3.3 | 37.6 |
| | | Night | 20.4 | 11.0 | 30.8 | 1.0 | 58.0 |
| | Mezzanine | Day | 16.6 | 4.0 | 17.8 | 0.7 | 33.5 |
| | | Night | 10.8 | 5.2 | 7.7 | 0.5 | 32.6 |
| Crocetta | Platform | Day | 19.8 | 13.1 | 208.8 | 6.0 | 36.5 |
| | | Night | 9.5 | 7.7 | 47.0 | 1.5 | 20.8 |
| | Mezzanine | Day | 27.5 | 6.0 | 2.6 | 0.4 | 39.8 |
| | | Night | 23.9 | 6.4 | 7.3 | 0.7 | 20.1 |
| Duomo-Y | Platform | Day | 23.2 | 12.0 | 185.8 | 4.9 | 38.1 |
| | | Night | 13.2 | 9.0 | 52.0 | 1.5 | 27.8 |
| | Mezzanine | Day | 17.1 | 5.4 | 1.0 | 0.2 | 26.5 |
| | | Night | 27.0 | 7.1 | 5.8 | 0.8 | 22.3 |

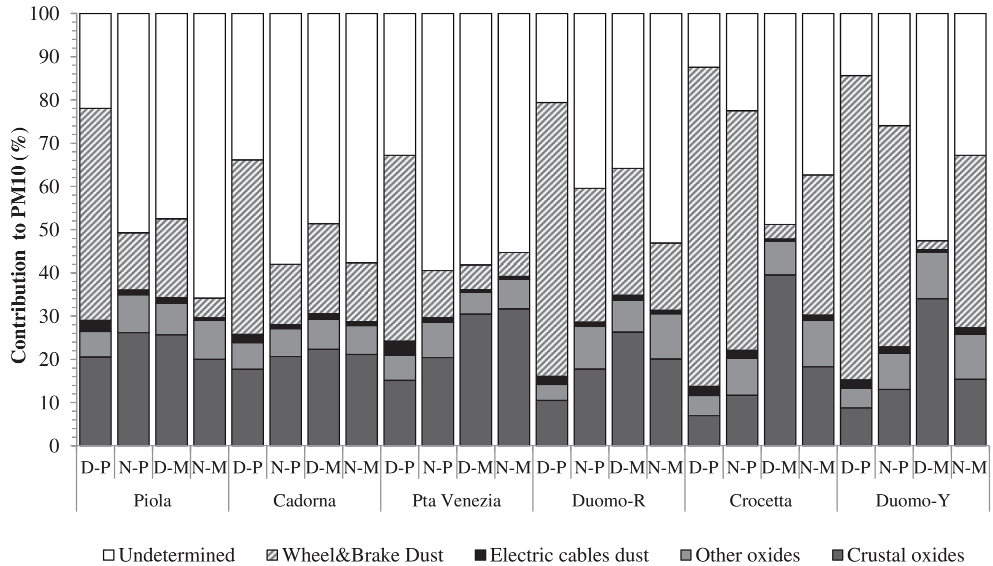



**Fig. 7.** PM10 source apportionment for the daytime (D) and nighttime (N) on the platform (P) and mezzanine (M) levels.

ambient air, where Fe is mostly found in the coarser crustal particulate (Marcazzan et al., 2001).

### 3.6. Discussion

The results described characterize the physical and chemical composition and give indications about the origin of particulate matter found in the two types of subway environments investigated.

On the platform level, in all stations, PM10 and metal concentrations are significantly higher than those found in ambient air, especially during train operation hours, albeit with some differences among stations. In general, a correlation is observed between station depth and PM and metal concentrations. The highest PM levels were measured in the Yellow Line stations (depth $>$ 20 m below ground) where the largest day/night differences were also observed. Number size distributions show that nighttime decreases are mainly caused by the stirred deposition of the coarse fraction occurring when local production of particulate through wear of moving parts and resuspension due to turbulence generated by trains are absent. As for PM elemental composition, Fe compounds represent the most significant fraction of total PM mass in all cases. In the Yellow Line stations they account for almost 70% of the total mass, down to about 50% during the night. The significant enrichment of all metals present in the alloys used in the production of tracks, wheels and brake pads (Fe, Ba, Sb, and Cu), clearly suggests the wear of metal parts as the most important PM source present. External air has little influence on local PM concentrations, and its contribution is mostly observed in the sub-micron size range, as shown by size distribution measurements and cluster analysis, although better air exchanges with the upper level (e.g. Duomo-R) also results in lower concentrations.

On the mezzanine level, during train operation hours, PM10 concentrations are 81% (Duomo-Y) to 24% (Cadorna) lower than they are on the platform level, while at night the two levels tend to become similar wherever there is good air exchange between them.

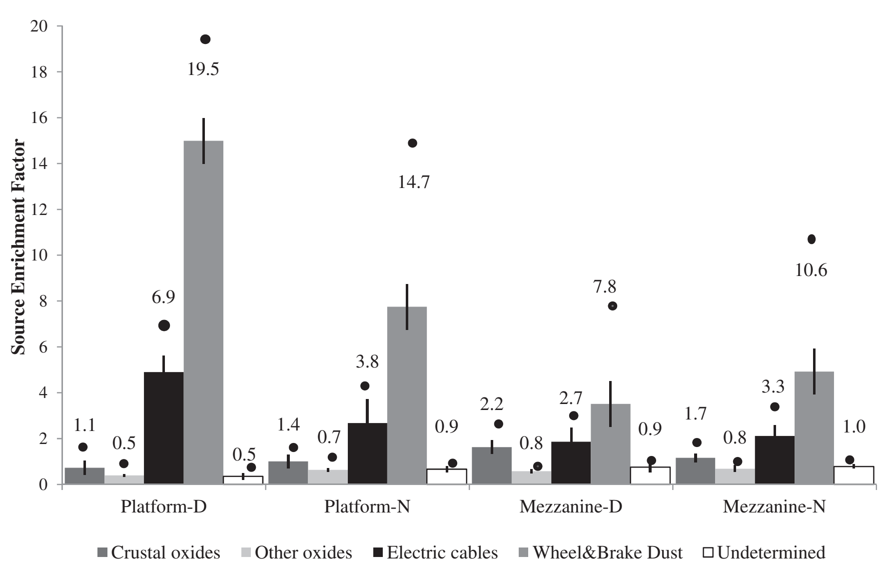



**Fig. 8.** Daytime (D) and nighttime (N) average Source Enrichment Factors for the platform and mezzanine levels. Standard deviations (bars) and maximum values (dots) are also shown.

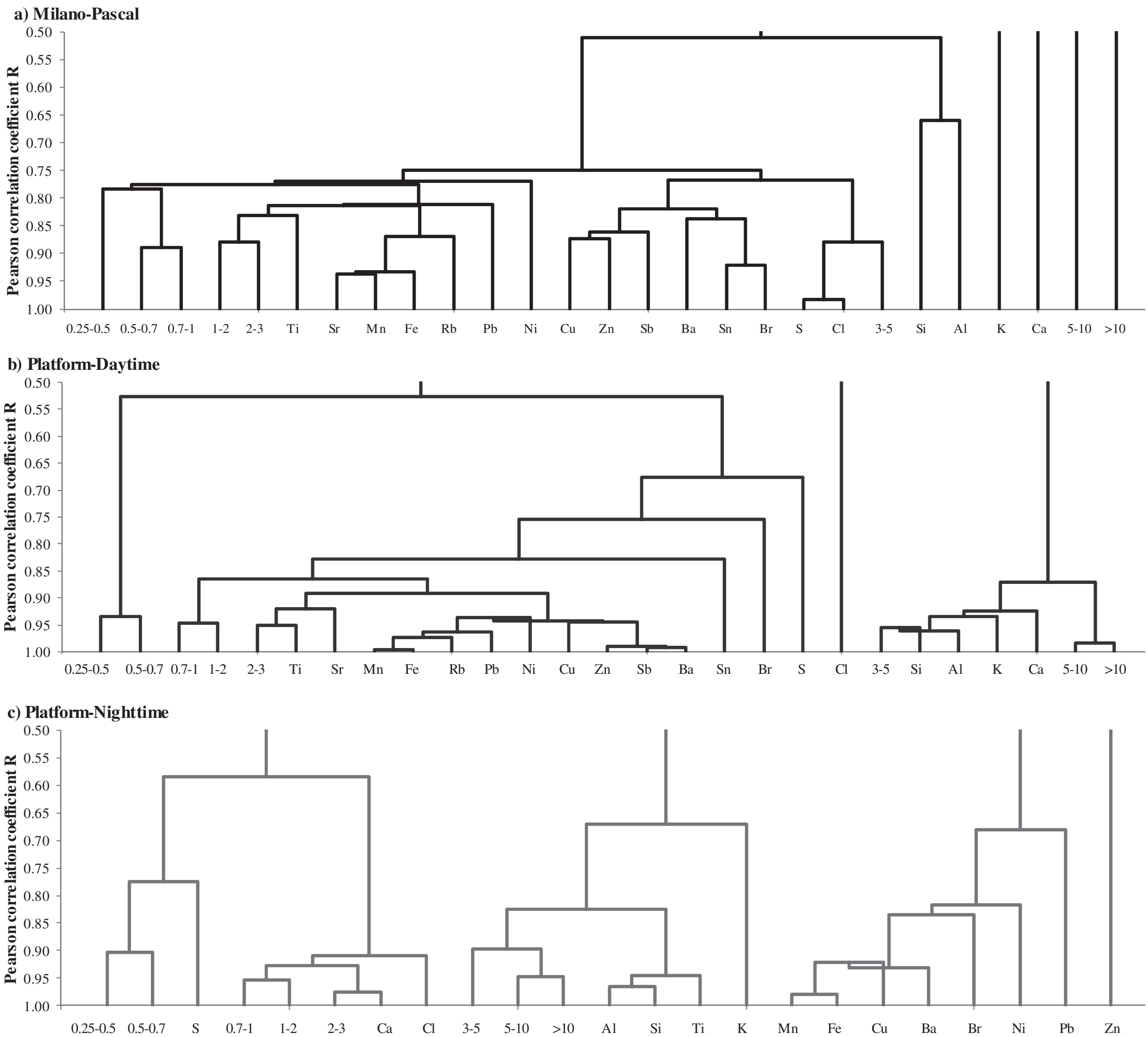



**Fig. 9.** Dendograms obtained for a) Milano-Pascal, b) Piola station on the platform level for the daytime, and c) Piola station on the platform level for the nighttime.

Elemental and cluster analyses show that air quality on the intermediate floor can be explained as the mixing of air masses coming from the outside and from the platform level. Therefore, if the specific contributions could be determined, it would be possible to estimate the effects on mezzanine air quality of particulate abatement measures enacted on the platform level. Under the assumption that no specific PM source exist on the mezzanine levels, the air mixing observed can be described by the following simple expression:

$$C_M = \alpha \cdot C_P + (1 - \alpha) \cdot C_O$$

where $C_M$, $C_P$, and $C_O$ are PM10 concentrations at the mezzanine level, on the platform, and outdoors, respectively, $\alpha$ represents the

**Table 8**
Measured and estimated daytime PM10 concentrations on the mezzanine level for the entire measurement period.

| | PM10 conc. platform (measured) ($\mu g\ m^{-3}$) | PM10 conc. ambient (measured) ($\mu g\ m^{-3}$) | Fraction of air from platform ($\alpha$) | Fraction of air from ambient ($1-\alpha$) | PM10 conc. mezzanine (estimated) ($\mu g\ m^{-3}$) | PM10 conc. mezzanine (measured) ($\mu g\ m^{-3}$) | Correlation coefficient ($R^2$) | PM10 mezzanine (average contribution from platform) (%) | PM10 mezzanine (average contribution from ambient) (%) |
|---|---|---|---|---|---|---|---|---|---|
| Piola | 173 | 35 | 0.24 | 0.76 | 68 | 68 | 0.77 | 64 | 36 |
| Cadorna | 98 | 35 | 0.63 | 0.37 | 75 | 74 | 0.96 | 83 | 17 |
| Duomo-R | 165 | 32 | 0.26 | 0.74 | 67 | 69 | 0.18 | 66 | 34 |
| P. Venezia | 94 | 32 | 0.37 | 0.63 | 55 | 56 | 0.84 | 65 | 35 |
| Duomo-Y | 249 | 33 | 0.09 | 0.91 | 52 | 49 | 0.25 | 39 | 61 |
| Crocetta | 267 | 33 | 0.19 | 0.81 | 77 | 73 | 0.56 | 64 | 36 |

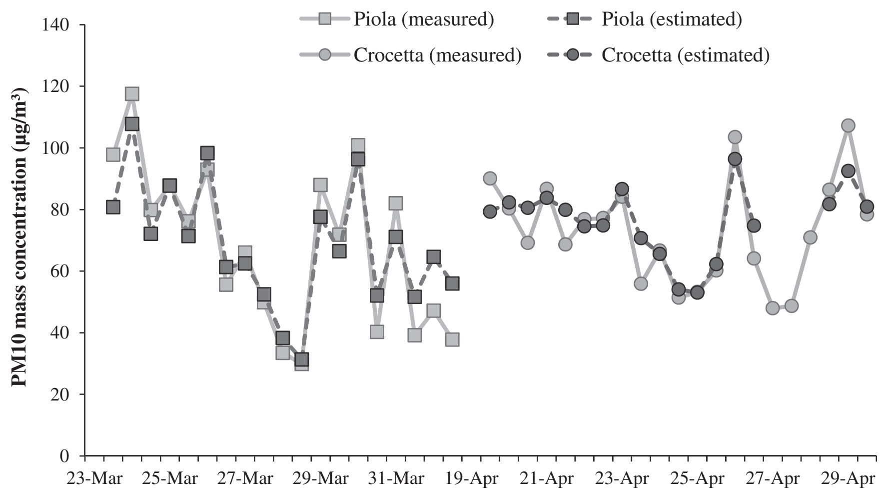



**Fig. 10.** Measured and estimated PM10 mass concentrations on the mezzanine level for the daytime in the Piola (squares) and Crocetta stations (circles).

fraction of air coming from the lower level, and $(1 - \alpha)$ is the contribution from ambient air.

The $\alpha$ coefficients were obtained using a least-squares fit. The percentage contributions of ambient and station air to the air on the mezzanine level were then calculated. PM10 concentrations estimated with this method are well correlated with the measured values. The results, summarized in Table 8, suggest that the volume of air coming from the platform level is less than that coming from the outside, but its high particulate content makes it the dominant contribution to PM10 concentrations on the mezzanine level.

This approach gives reliable results for all cases except that of Duomo, which is a very large station with several connections with the outside. In all other cases, statistically significant estimates of the contributions to PM10 concentrations due to air coming from the platform level are obtained ($R^2$ values between 0.56 and 0.96), ranging from 64% in Piola to 83% in Cadorna. The measured and estimated concentrations are plotted in Fig. 10 for Piola and Crocetta.

## 4. Summary and conclusions

PM10 mass concentration, number and size distribution measurements were conducted in the Milan subway system, both on the platform and on the mezzanine levels, and elemental composition was determined. In all investigated environments concentrations are consistently higher than in ambient air, up to a factor of 8 on the platform and about a factor of 2 on the intermediate floor. The highest concentrations are found on the platform level in smaller stations, stations deeper underground, and those where connections with the outside air are limited. PM10 levels are shown to be well correlated with train traffic, and particulate matter is qualitatively different from that found in typical urban ambient air, both in chemical composition and in size distribution. The characteristic intermediate mode observed in the range from 1 to 5 μm in the particle size distributions measured at the platform level during train operation hours is associated with metals such as Fe, Mn, Sb, Cu, Ba and Zn, which are significantly enriched: Fe, Mn, Sb and Ba oxides, related to wheel, rail and brake wear, account on the average for 40–73% of total PM10 mass, and Cu and Zn oxides, related to electric cable wear, account for 2–3%, whereas total metal oxides in urban ambient air, excluding crustal compounds, represent on the average about 17% of total PM10 mass. The closed environment and the proximity to the emitting source enhance a phenomenon generally observed near railroads, and the extent of the increase is clearly related to tunnel size and depth and station layout.

The different composition of subway particulate matter and typical urban particulate matter makes air quality standards for ambient air not directly applicable to the underground environment, and specific studies concentrate on the additional exposure of transport workers and of the large numbers of subway passengers to metals, mainly Fe, Mn and Cu.

PM10 levels measured on the mezzanine floor are typically intermediate between platform and ambient air concentrations, especially during the daytime. This can be explained as the result of the mixing of external air and air from the station below. The simple least-squares method used to calculate the amount of this mixing can be applied to estimate the effects of particulate reduction measures that are being tested by the Municipal Transport Company (ATM) and investigated as a follow-up of this study.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.01.035.

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