

# A study on nighttime–daytime PM<sub>10</sub> concentration and elemental composition in relation to atmospheric dispersion in the urban area of Milan (Italy)

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## Abstract

In this paper, results on a PM<sub>10</sub> daytime–nighttime measurement campaign carried out in Milan to study the evolution of PM<sub>10</sub> concentration and composition in relation to atmospheric dispersion conditions are shown. To account for the evolution of atmospheric dispersion conditions, Radon hourly concentration measurements were performed. The significant correlation between PM<sub>10</sub> and <sup>222</sup>Rn daytime concentrations evidences the dominant role of atmospheric dispersion in determining the temporal variation of PM<sub>10</sub> levels. Whenever <sup>222</sup>Rn concentrations accumulate during the night (indicating the formation of nocturnal atmospheric stability conditions), PM<sub>10</sub> concentrations are higher than those registered during the daytime before, despite a decrease in emissions from active sources. On the contrary, when <sup>222</sup>Rn concentrations do not accumulate during night hours, PM<sub>10</sub> levels are lower than those measured during the daytime before.

As concerns the average elemental concentrations (in ng m<sup>-3</sup>), the nighttime–daytime variations are in the range –17% to +37%; during the night, soil-related elements (Al, Si, Ca, Ti) decrease while anthropogenic elements (Zn, Cu, Fe, Pb) increase.

A case study concerning a ‘green’ Sunday (when traffic was forbidden from 8 a.m. to 8 p.m.) is also discussed. The difference of PM<sub>10</sub> concentration and elemental composition registered during the ‘green’ Sunday daytime and the following nighttime, together with the information on atmospheric dilution power obtained by Radon measurements, allowed the characterisation of the traffic source elemental profile and increased the comprehension of the low effectiveness of some PM<sub>10</sub> reduction strategies.

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*Keywords:* PM<sub>10</sub>; Nighttime/daytime concentration; Traffic source; Atmospheric dispersion

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## 1. Introduction

At present, in the urban area of Milan and in the whole Po valley, airborne particulate matter is a

pollutant of large concern because of its high-concentration levels and its adverse effects on human health. Indeed, several studies suggest an association between fine-particulate air pollution and the increase of the rate of morbidity/mortality cases (Arden Pope and Dockery, 2006, and therein cited literature).

As a consequence of the increasing consciousness about the negative health effects due to the exposure

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to pollutants, the European Community established limit values for PM<sub>10</sub> (atmospheric particles with aerodynamic diameter smaller than 10 µm) with the 99/30/EC Directive. In this Directive, the European Commission encouraged Member States to promote research for the study, physical–chemical characterisation, and measurement of PM<sub>10</sub> and PM<sub>2.5</sub> as well as to prepare action plans and general strategies to abate their concentrations. It should be remembered that, at the moment, in Europe PM<sub>2.5</sub> is not under regulation but it will be soon.

In spite of the actions taken by local authorities of the Lombardy region to limit particulate matter emissions, wintertime PM<sub>10</sub> levels often exceed the EU limit value established for health protection not only in Milan but also at many other urban areas in the Po valley (Marcazzan et al., 2002). It is noteworthy that a strong seasonal effect influences PM<sub>10</sub> values in this area; indeed, wintertime daily concentrations and the number of the days exceeding limit values are much higher than summertime ones. Previous studies carried out by the authors (Vecchi et al., 2004) singled out that, beside the emission loadings, the orography of the Po valley and its typical meteorological conditions play an important role in determining very stable atmospheric conditions and low dispersion of pollutants. Moreover, in Milan fine particles, i.e. PM<sub>2.5</sub> and PM<sub>1</sub> account for a large part of PM<sub>10</sub> mass (Marcazzan et al., 2001; Putaud et al., 2002; Lonati et al., 2005). PM<sub>10</sub> is composed not only of particles with a primary origin (i.e. mineral dust, heavy metals, elemental carbon) but also mainly of secondary components such as nitrates, sulphates and organics; thus, gaseous precursors levels must be also taken into account. Another important parameter is the residence time of atmospheric particles, which depends on their diameter; literature studies (see for example Jaenicke, 1982) report residence times varying from 9 to 120 h for particle sizes in the range 10–1200 nm. In the investigated area, aerosols residence time was estimated to be in the range 18–38 h (Vecchi et al., 2005) as experimentally determined by means of radioactive fine particles measurements, i.e. mainly particles with diameter in the size range 10–1000 nm (Porstendörfer et al., 2000).

The aim of this work is the study of day-time–nighttime patterns of PM<sub>10</sub> concentration and elemental composition in relation to the influence of atmospheric stability conditions. To account for the evolution of atmospheric dispersion

conditions, Radon hourly concentration measurements were performed.

The sampling periods were in winter months typically characterised by high PM<sub>10</sub> concentrations (often exceeding the EC limit). During the campaign, traffic was restricted in the urban area on Sunday, 23 February, from 8 a.m. to 8 p.m. (it was called a ‘green’ Sunday). It was an interesting opportunity to gather information on the traffic source elemental profile in Milan and on the causes of the low effectiveness of some PM<sub>10</sub> reduction strategies. Indeed, the “real-world” traffic emission profile depending on fuels, vehicles type and age, and many other factors, is very complex and often of local character so that on-site measurements can give useful insights.

## 2. Experimental methods

### 2.1. Aerosol sampling and analytical techniques

The monitoring campaign has been performed in Milan, which is located in the centre of the Po valley (Northern Italy), one the most industrialised and populated part of the country. About 2.2 millions of passenger cars circulate daily in the area; in addition, 4000 buses and a very high number of heavy-duty vehicles for goods transport must be also taken into account. According to the available emission inventory (Milan Province, 2000) the main sources contributing to primary PM<sub>10</sub> in Milan are traffic (559 tons yr<sup>-1</sup>), domestic heating (164 tons yr<sup>-1</sup>), incinerators (42 tons yr<sup>-1</sup>) and industrial combustion (12 tons yr<sup>-1</sup>).

PM<sub>10</sub> samplings have been carried out in the University campus on the roof of our Institute, at a height of about 10 m a.g.l., during two winter periods in 2003 (20–30 January and 14–27 February). Particulate matter concentrations registered at this sampling height are not directly influenced by local traffic and can be considered quite representative of the average air pollution in the investigated area (background urban area). PM<sub>10</sub> samplings have been performed during daytime (from 8 a.m. to 8 p.m.) and nighttime (from 8 p.m. to 8 a.m.) using CEN-equivalent samplers operating at a flow rate of 2.3 m<sup>3</sup> h<sup>-1</sup> and particles have been collected on mixed cellulose esters filters (diameter = 47 mm) with a high-retention efficiency (>99%). The gravimetric determination of the PM<sub>10</sub> mass was carried out according to the European norm EN12341.

Energy dispersive X-ray fluorescence analysis was performed obtaining the concentrations of 16 elements (Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb) in all PM<sub>10</sub> aerosol samples. Details on the experimental conditions and set-up can be found elsewhere (Marcazzan et al., 2004).

## 2.2. Radon measurements

As well known, the stability conditions of the lower atmospheric layers on a local scale are very important as influence pollutants concentration on different time scales (although emission rates, chemical transformations and deposition processes play an important role too). In this work, <sup>222</sup>Rn measurements were performed to account for them; literature results (Perrino et al., 2001; Sesana et al., 2003) report that the temporal variation of its concentration can give immediate information on the evolution of the stability conditions and of the mixing layer height in the boundary layer. In Milan, our group measures routinely and continuously Radon hourly concentration at ground level (6 m a.g.l.). Details on the experimental methodology to measure <sup>222</sup>Rn concentration are reported in Marcazzan et al. (2003).

Meteorological parameters and criteria gaseous pollutants data, available from the regional air quality-monitoring network have also been analysed.

## 3. Results and discussion

### 3.1. PM<sub>10</sub> mass concentration and elemental composition

During the measurement periods, high PM<sub>10</sub> mass concentrations were generally registered, a remarkable day-to-day variability was also observed (Fig. 1) and the average PM<sub>10</sub> concentration values for nighttime and daytime are quite similar although slightly higher (+13%) during the night. The daytime and nighttime average concentrations of criteria gaseous pollutants were also high and, like PM<sub>10</sub>, do not show relevant differences during these two time intervals (Table 1). PM<sub>10</sub> concentrations are correlated with NO<sub>x</sub> ( $R^2 = 0.7$ ) during both daytime and nighttime, and NO and NO<sub>2</sub> behave similarly; no significant correlations have been found with other gaseous pollutants.

The nocturnal PM<sub>10</sub> mass concentrations might appear surprising in relation to the nighttime typical

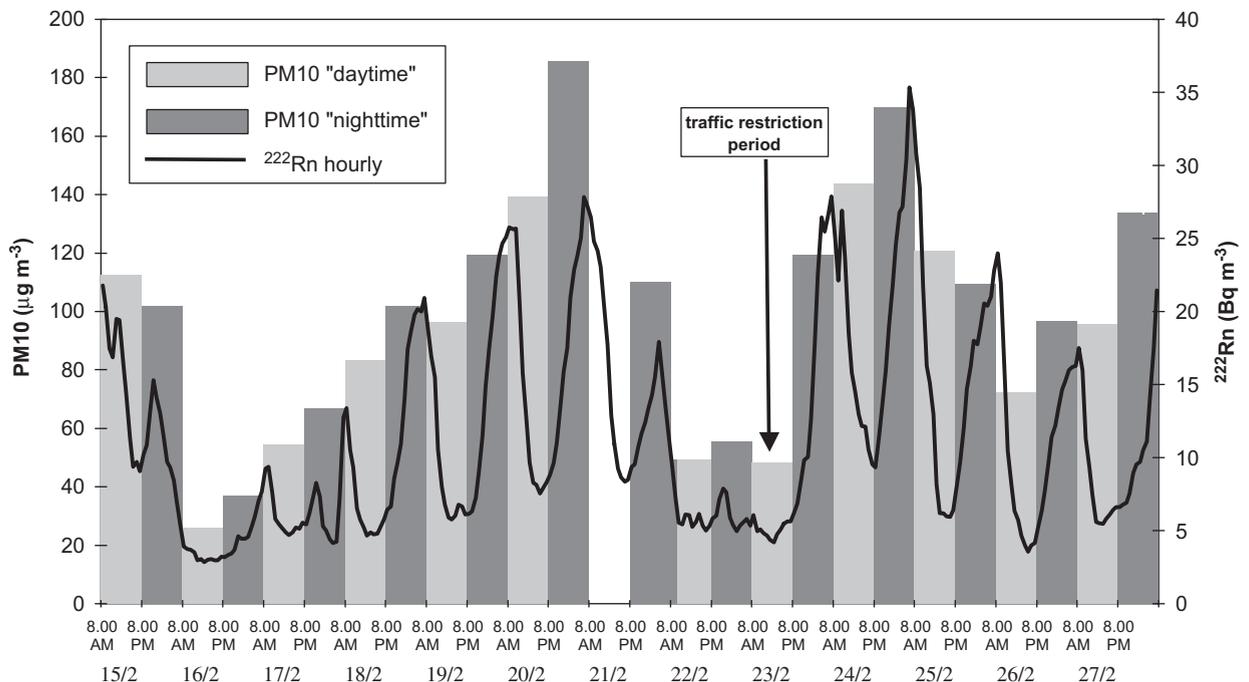


Fig. 1. PM<sub>10</sub> concentrations (light grey, daytime; dark grey, nighttime) together with hourly <sup>222</sup>Rn concentration (solid line) represented for the period 15–27 February 2003.

reduction of major emissions, like those due to traffic (in the night the traffic volume is about 30–40% the daytime one according to measurements performed by the environmental agency at a monitoring station located downtown Milan, see

Table 1

Daytime and nighttime PM10, elements and criteria gaseous pollutants average concentrations for the whole campaign

|                          | Average concentration<br>“daytime” |        | Average concentration<br>“nighttime” |        |
|--------------------------|------------------------------------|--------|--------------------------------------|--------|
|                          | (ng m <sup>-3</sup> )              | (ppm)  | (ng m <sup>-3</sup> )                | (ppm)  |
| PM10                     | 81,400                             |        | 91,900                               |        |
| Al                       | 840                                | 10,840 | 780                                  | 8190   |
| Si                       | 2430                               | 31,300 | 2160                                 | 22,620 |
| S                        | 2360                               | 30,700 | 2540                                 | 30,170 |
| Cl                       | 920                                | 11,980 | 1060                                 | 11,710 |
| K                        | 660                                | 8460   | 770                                  | 8550   |
| Ca                       | 1880                               | 24,890 | 1570                                 | 16,820 |
| Ti                       | 87                                 | 1150   | 83                                   | 905    |
| V                        | 10                                 | 125    | 9                                    | 100    |
| Cr                       | 13                                 | 165    | 16                                   | 165    |
| Mn                       | 45                                 | 575    | 56                                   | 600    |
| Fe                       | 1830                               | 23,130 | 2370                                 | 24,920 |
| Ni                       | 10                                 | 120    | 9                                    | 100    |
| Cu                       | 72                                 | 885    | 89                                   | 940    |
| Zn                       | 180                                | 2255   | 247                                  | 2630   |
| Br                       | 15                                 | 195    | 20                                   | 225    |
| Pb                       | 71                                 | 900    | 93                                   | 1015   |
| NO (ppb)                 | 88                                 |        | 103                                  |        |
| NO <sub>2</sub> (ppb)    | 46                                 |        | 47                                   |        |
| CO (mg m <sup>-3</sup> ) | 2                                  |        | 2                                    |        |
| SO <sub>2</sub> (ppb)    | 13                                 |        | 10                                   |        |

Fig. 2), to domestic heating (in Northern Italy domestic heating can be switched on from 15 October to 15 April during 14h between 5 a.m. and 11 p.m.), to industries and to other human activities. This result can be explained considering that the aerosol fine fraction is characterised by a not negligible residence time (1–2 days), and in Milan during wintertime PM<sub>2.5</sub> to PM<sub>10</sub> ratio is about 0.7–0.8; moreover, frequent temperature inversions (favoured by wind calm) which lead to strong atmospheric stability and low mixing layer heights (see next paragraph) are observed during night hours. Thus, the nocturnal emissions decrease is vanished by the concurrent, strong reduction of atmospheric dilution capability.

The average elemental concentrations (in ng m<sup>-3</sup>, see Table 1) vary in the range from –17% to +37%. A large part of the detected elements increase their concentrations during the night: S, Cl and K values increase similarly to PM<sub>10</sub> mass concentration, while Cr, Mn, Fe, Cu, Zn, Br and Pb increase more (20–35%) than mass concentration. On the contrary, soil-related elements (i.e. Al, Si, Ca, Ti) and the couple (V, Ni) slightly decrease during the night.

Looking at the PM<sub>10</sub> elemental composition given in parts per million (Table 1), three groups of elements come out: the first one with elements whose concentration changes less than 5% during the whole day (i.e. S, Cl, K, Cr, Mn), the second with element concentrations decreasing by 20–30% during the night (i.e. Al, Si, Ca, Ti, V and Ni) and

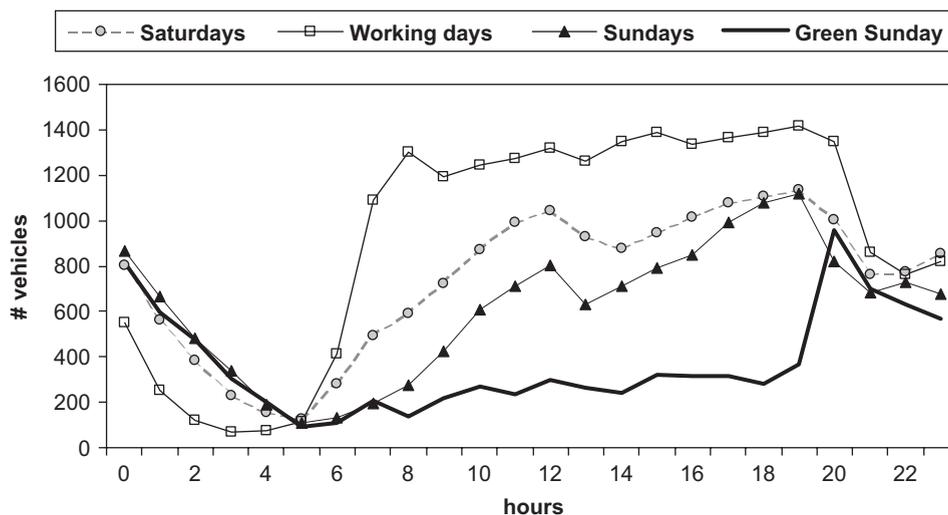


Fig. 2. Traffic volumes in Milan: daily average number of vehicles (length: 0–7 m) in Milan during the sampling period January–February 2003.

the third with elements whose concentrations increase is 8–15% during the night (i.e. Fe, Cu, Zn, Br, Pb).

The soil-related elements decrease is likely due to the fact that they are preferably in the coarse fraction of PM10 (that is composed of particles with aerodynamic diameter between 2.5 and 10  $\mu\text{m}$ ) and are characterised by a higher deposition velocity. In addition, during nighttime, the re-suspension of particles from the soil is less efficient because of the lower intensity of natural and anthropogenic re-suspension processes and the higher humidity of foggy nights frequently occurring during wintertime atmospheric stability conditions.

The concentration increase observed in Fe, Cu, Zn, Br and Pb elements typically found in the traffic source profile (Weckwerth, 2001; Sternbeck et al., 2002; Chellam et al., 2005), is due to the increase of the relative weight of this source emission during the night when emissions from other sources are strongly reduced.

Although characterised by very low values and higher uncertainties, V and Ni concentrations are higher during daytime (both in  $\text{ng m}^{-3}$  and in ppm); this behaviour might be ascribed to the daytime influence of domestic heating and public transportation emissions, which burns combustion oil traced by Ni and V.

### 3.2. PM10 temporal patterns in relation to atmospheric dispersion conditions

In Milan, the typical  $^{222}\text{Rn}$  temporal pattern shows a minimum in concentration during the afternoon and a maximum in the early morning (in Fig. 1 an example is shown for the period 15–27 February). The variation between maximum and minimum Radon concentration in the same day is an index of the maximum height of the mixing layer. The variation of Radon concentration observed between the minimum in the afternoon and the maximum in the following day is a good indicator of the nocturnal mixing layer depth.

The analysis of the temporal sequence of daytime and nighttime PM10 concentrations in relation to  $^{222}\text{Rn}$  concentrations points out clearly that PM10 concentrations in the night are generally higher than those measured during the preceding daylight hours when  $^{222}\text{Rn}$  concentrations increase during nighttime, indicating the formation of a strong atmospheric stability and a low mixing layer height (about a few tens of metres). On the contrary, when

$^{222}\text{Rn}$  does not accumulate, indicating that the atmospheric mixing conditions do not significantly change going from the daylight hours to the night, PM10 nighttime concentrations are similar or lower than daytime ones.

The evaluation of mixing layer heights with hourly resolution has been carried out by means of a box model suitably set up which uses Radon concentration measurements as input data (Pacífico, 2005; Casadei et al., 2006).

PM10 daytime concentrations were well correlated ( $R^2 = 0.85$ ) with the  $^{222}\text{Rn}$  concentrations averaged on the same time interval. From the whole dataset two rainy days were excluded (20–21 January), as the rainfall has either the effect of removing particles from the atmosphere and reducing their re-suspension from the soil. The good correlation evidences the role of atmospheric dispersion conditions as a key parameter in causing remarkable variations in PM10 concentration levels from day to day. PM10 and  $^{222}\text{Rn}$  nighttime concentrations were also correlated ( $R^2 = 0.62$ ). If a multilinear correlation is computed considering also the PM10 values of the preceding night (for the daytime correlation) and of the preceding daylight hours (for the nighttime correlation), a significant increase in the correlation coefficient is observed (as an example, the  $R^2$  goes up from 0.85 to 0.95 and from 0.62 to 0.75 for the daytime and nighttime correlation, respectively). This result shows that the particles residence time in atmosphere is likely not much lower than 12 h, that is a fraction of particles emitted in a time interval (e.g. daytime or nighttime) contributes to the concentration measured in the next 12-h interval, in agreement with the residence time estimations given in the introduction.

### 3.3. A case study: the 'green Sunday'

During our measurement campaign, local authorities restricted traffic from 8 a.m. to 8 p.m. in the urban area during a so-called 'green' Sunday. No private vehicles circulation was allowed during that Sunday (apart from gas-fuelled vehicles and vehicles with special permission) and only public transportation traffic was permitted. This peculiar condition was an opportunity to perform PM10 measurements during a period with very rare traffic conditions for the Milan area (generally heavy trafficked). Moreover, it was an occasion to study the causes of the poor effectiveness of some

reduction strategies (often high daily, PM10 level are registered despite the traffic restrictions).

The 'green' Sunday (23 February) occurred after a prolonged period (17–21 February) of PM10 levels exceeding the EC daily limit value. Nevertheless, starting from the daylight hours of Saturday (22 February), PM10 concentration began to lower due to the presence of a moderate wind speed (average,  $1.8 \text{ m s}^{-1}$ ; ranging from 1 to  $2.8 \text{ m s}^{-1}$ ) and its concentration remained low also during Saturday night.

Daytime PM10 concentration on Sunday, when private traffic was totally restricted in the urban area, decreased to about  $-13\%$  in respect to the night before. Also criteria gaseous pollutants concentrations decreased;  $\text{NO}_2$  and CO concentrations diminished of about  $-35\%$  during the Sunday daytime in respect to the night before.

During the Sunday night when the traffic restriction ended, a huge increase in PM10 ( $+147\%$ ) as well as in gaseous pollutants concentrations ( $+160\%$  for  $\text{NO}_2$  and  $+189\%$  for CO) was measured.

The absence of peaks in the Radon temporal evolution and its low concentrations during the whole Saturday and during Sunday daylight hours indicated good atmospheric dispersion conditions; on the contrary, the sharp increase in Radon concentrations observed during Sunday nighttime highlighted the formation of strong atmospheric stability with low mixing layer heights. However, the lowering of the mixing layer height was not the unique cause for the PM10 levels increase because the reduction of the atmospheric mixing layer can produce, as evaluated during the whole campaign, an average increase of  $10\text{--}20\%$  in PM10 concentrations during the night. This behaviour was also confirmed on Monday (24 February) when PM10 concentrations from a daytime value of  $144 \mu\text{g m}^{-3}$  raised to a nighttime value of  $170 \mu\text{g m}^{-3}$  ( $+18\%$ ) in correspondence with a sharp increase in  $^{222}\text{Rn}$  levels indicating a low mixing layer height.

In conclusion, PM10 levels measured just after the end of the traffic restriction were mainly due to the sudden increase in circulating vehicles (see also Fig. 2) in a period characterised by poor atmospheric dispersion conditions.

During the traffic-limited period, although the decrease in PM10 mass concentration was only  $-13\%$ , in respect to the value measured on Saturday night, the elemental concentrations showed a remarkable decrease for many elements such as Cu ( $-73\%$ ), Mn ( $-61\%$ ), Fe ( $-57\%$ ), Zn ( $-52\%$ ),

Ca ( $-57\%$ ), Si ( $-55\%$ ), Cr ( $-50\%$ ), Al ( $-46\%$ ), K ( $-36\%$ ), Pb ( $-36\%$ ), Ti ( $-24\%$ ) and Cl ( $-22\%$ ). An exception was S whose concentration did not change; on the contrary, the concentrations of Br ( $+50\%$ ), Ni ( $+33\%$ ) and especially V ( $+300\%$ ) increased. A possible explanation for the Vanadium increase might be the enforcement of public transportation (i.e. buses) during the 'green' Sunday; indeed, in the experimental data reported by Samara et al. (2003), the V content in the diesel-fuelled bus emission profile was higher than in diesel-fuelled passenger car (in that work they referred to taxis) profile. The large decrease in Cu concentration and its low absolute value during the 'green' Sunday suggest also that the tram source (i.e. wear and tear of tram cables) was not a significant copper emitter in the Milan urban area, in contrast with the finding of Weckwerth (2001) in the city of Cologne (Germany).

'Green' Sunday peculiarities observed in the particulate matter elemental composition singled out primary (exhaust and wear) emissions together with the road dust re-suspension due to traffic and, on the other hand, indicated the relevance of some heavy metals (i.e. Cr, Mn, Cu, Fe, Zn, Pb) during 'regular traffic' days.

During nighttime (from 8 p.m. to 8 a.m.) the concentration of some elements (Table 2) such as Cr, Cu, Fe, Zn, Pb increased much more than PM10 mass in comparison with daytime, 11 times Cu concentration and 4–7 times Fe, Cr, Zn, Pb levels; this observation points at the primary emission contribution from cars as the most important factor in determining their atmospheric concentrations and, as a matter of fact, Cu is confirmed to be a good marker of traffic emissions. Literature results (Westerlund and Johansson, 2002) show that brakes wear and tear causes not negligible particulate matter emission characterised by high concentrations of Cr, Cu, Zn, Pb and other trace metals. In addition, particulate matter emissions due to wear of brake linings, in the case of gasoline-fuelled cars, are quantitatively comparable with direct emissions from incomplete fuel combustion, although significant difference can be singled out in relation to car type and brand.

Si, Cl and K concentrations increase was slightly larger than PM10 mass, while the Al and Ca concentrations increased similarly to PM10 mass. During the night Al, Si and Ca concentration increased more than Ti, suggesting that the former elements are due to both road dust re-suspension by

traffic and direct emissions from car exhaust. Indeed, many elements are present as impurities in different car fuels; Wang et al. (2003) in diesel soot found all the trace elements typically contained in fuels and, in particular, Si, Ca, Al and Fe. Moreover, Samara et al. (2003) measured high concentrations of Fe, Cl and K in the emission profiles of both gasoline and diesel-fuelled vehicles.

It is also worth noting that S, V, Ni and Br levels did not increase in a significant way, confirming that traffic (in this case mainly due to passenger cars) is a minor source for these elements.

The traffic restriction period during the ‘green’ Sunday can be considered a “blank value” as concerns the traffic emissions, while the strong increase in traffic intensity observed just after the restriction period highlights peculiarities of this

Table 2

Daytime and nighttime PM10 and elemental average concentrations during Saturday (22 February) and the ‘green’ Sunday (23 February). Their ratio is also reported in the last column

|                                 | Saturday |           | Sunday  |           | Ratio nighttime/daytime |
|---------------------------------|----------|-----------|---------|-----------|-------------------------|
|                                 | Daytime  | Nighttime | Daytime | Nighttime |                         |
| PM10 ( $\mu\text{g m}^{-3}$ )   | 49.2     | 55.4      | 48.3    | 119.4     | 2.5                     |
| Elements ( $\text{ng m}^{-3}$ ) |          |           |         |           |                         |
| Al                              | 440      | 455       | 245     | 580       | 2.4                     |
| Si                              | 1230     | 1210      | 535     | 1630      | 3.1                     |
| S                               | 2300     | 2490      | 2480    | 3545      | 1.4                     |
| Cl                              | 570      | 770       | 600     | 1790      | 3.0                     |
| K                               | 410      | 520       | 330     | 965       | 2.9                     |
| Ca                              | 1095     | 1075      | 465     | 1095      | 2.4                     |
| Ti                              | 46       | 42        | 32      | 61        | 1.9                     |
| V                               | 4        | 3         | 12      | 15        | 1.3                     |
| Cr                              | 4        | 4         | 2       | 11        | 5.5                     |
| Mn                              | 36       | 44        | 17      | 42        | 2.5                     |
| Fe                              | 980      | 915       | 390     | 2560      | 6.6                     |
| Ni                              | 2        | 3         | 4       | 8         | 2.0                     |
| Cu                              | 39       | 41        | 11      | 125       | 11.4                    |
| Zn                              | 103      | 131       | 63      | 300       | 4.8                     |
| Br                              | 9        | 12        | 18      | 33        | 1.8                     |
| Pb                              | 35       | 42        | 27      | 105       | 3.9                     |

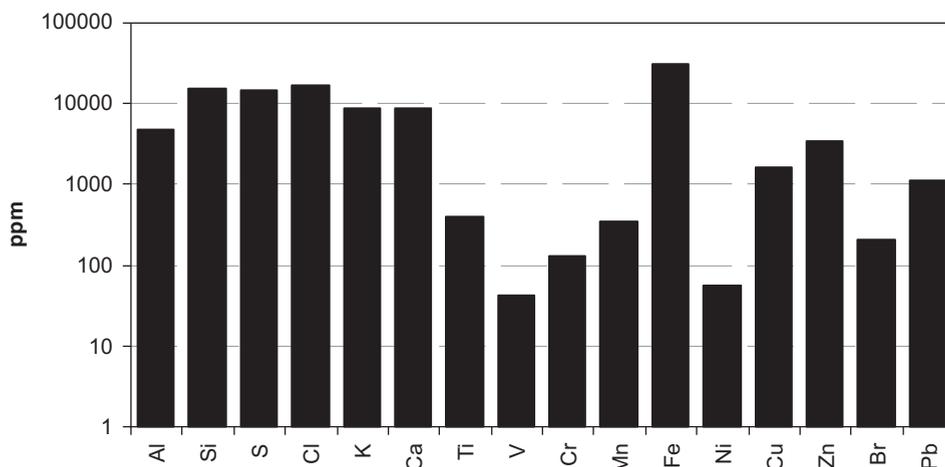


Fig. 3. Relative profile (in ppm) for the traffic source.

emission source. The estimation of the relative traffic profile, although limited to a case characterised by traffic due to mainly passenger cars either diesel and gasoline fuelled has been obtained (Fig. 3) considering the difference between the elemental concentration values measured during Sunday nighttime and those registered during daylight hours.

As represented in Fig. 3 Fe is the most abundant element, followed by Cl, Si, S, K, Ca, Al and, in lower concentrations, by Zn, Cu, Pb, Ti, Mn, Br, Cr, V and Ni. This traffic type in Milan can be a good representation of weekend traffic and traffic in downtown Milan (where heavy vehicles circulation is always restricted). Nevertheless, it should be noted that it does not exactly represent the traffic in the rest of the town during working days and, as a consequence, does not allow a precise quantification of traffic contribution to the different elements in PM10 and in particular to heavy metals emission during working days.

#### 4. Conclusions

The experimental campaign with measurements of PM10, criteria gaseous pollutants and  $^{222}\text{Rn}$  during daytime and nighttime, enhanced the comprehension of the pollution due to airborne particulate matter, a relevant problem in the urban area of Milan especially during wintertime.

This investigation highlights that the dilution power of the atmosphere, with its day-to-day variability, plays a major role in determining pollution levels. The strong stability of the atmosphere occurring frequently from late afternoon to late morning (as indicated by the build-up of  $^{222}\text{Rn}$  concentrations) causes PM10 concentrations higher during nighttime than during the preceding daylight hours even if the source emissions strongly reduce their contribution. Moreover, aiming at the comprehension of the observed values residence times must be also taken into account.

The diurnal temporal evolution of the mixing layer height also explains why some actions (e.g. restriction of private traffic or odd–even plates circulation) taken by local authorities to reduce pollution levels have often little effectiveness. As shown in this work, the limitation of traffic during 12 h from 8 a.m. to 8 p.m. reduces PM10 mass, heavy metals concentrations and criteria gaseous pollutants levels, but it is fully vanished on a 24-h basis if the vehicles circulation starts again during a

period when very poor atmospheric dispersion conditions occur. Moreover, traffic restrictions lasting only a few hours are poorly effective because of the relatively long residence time of fine aerosols.

Although the evaluation of the traffic source contribution has been done on a week end and not on working days with larger traffic volumes, the results here presented show that traffic primary emissions are clearly the major contributor to metals atmospheric levels which have a relevant environmental and health impact even if their concentrations account for a small part of PM10 mass.

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