Indoor airborne particle sources and semi-volatile partitioning effect of outdoor fine PM in offices

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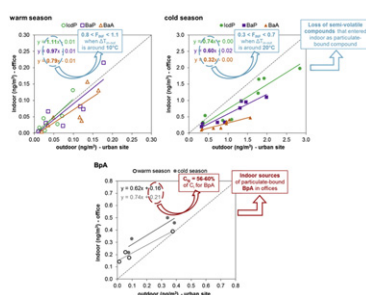[b] Institute for the Dynamics of Environmental Processes — CNR, Dorsoduro 2137, 30123 Venice, Italy
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HIGHLIGHTS

► Indoor-to-outdoor relationship for PM1 and PM2.5 (I/O, F_{INF} and C_{ig}).
► Chemical characterization of inorganic ions, PAHs and BpA in fine PM.
► More than 50% of urban (Milan) fine PM enters the indoor office environments.
► Office indoor sources generate about 60% of indoor particulate-bound BpA.
► Semi-volatile loss from outdoor PM when entering a warmer indoor environment.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

To date, few studies have focused on PM air quality in offices, despite the fact that a lot of people spend many working hours a day in such offices. The aim of the present study is to investigate PM1 and PM2.5 in offices in Milan (Northern Italy) and in the air outside those offices. The PM samples were analyzed to determine the entity of certain compounds with possible direct or indirect adverse effects on human health: PAHs, BpA, and water soluble inorganic ions.

A good correlation between outdoor and indoor PM mass concentrations emerged ($R^2 \sim 0.87$). The maximum I/O concentration ratio was 0.92, suggesting that the indoor PM level was always lower than the outdoor level. The average infiltration factor, F_{INF}, was 0.55, showing that about a half of the outdoor PM had come indoors. The indoor-generated particles, C_{ig}, had values ranging from 0 to 4.4 μg m^{-3} (<25% of the indoor PM), showing that PM indoor sources had only made a limited contribution to total indoor PM.

The results of the indoor-to-outdoor comparisons for the aforementioned chemical compounds demonstrate that the offices were characterized by the absence of effective indoor sources of particulate-bound PAHs and inorganic ions, whereas C_{ig} was around 58% of the indoor concentration for BpA. Our analysis of the F_{INF} data pointed to the presence of a volatilization effect from PM for semi-volatile compounds like ammonium nitrate and 4- or 5-ring PAHs, which affected the measurement of their F_{INF}. We propose the introduction of a new and simple parameter, called volatilization correction, to take account of this effect.

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1. Introduction

Over the last twenty years or so, considerable efforts have been made to clarify the relationship between airborne particulate matter (PM) and human health, and a number of excellent accounts of this relationship are now available (e.g.: Englert, 2004; Lippmann et al., 2003; Valavanidis et al., 2008). Both the short-terms effects (premature mortality, hospital admissions, etc.) and the long-term effects (morbidity, lung cancer, cardiovascular and cardiopulmonary diseases, etc.) of PM have been described.

The toxicity associated with PM is related to both the size and the chemical composition of the particles in question. The smaller (fine and ultra-fine) PM particles have a greater ability to penetrate deeper into the lungs, and as a consequence the majority of studies conclude that they are basically more harmful. Moreover, the presence of specific compounds within the particles seems to increase their potential dangerousness.

Such compounds include several organic species, like Polycyclic Aromatic Hydrocarbons (PAHs) and Bisphenol A (BpA), as well as other inorganic species, such as elements. More specifically, certain PAHs have been classified as proven, probable or potential human carcinogens (International Agency for Research on Cancer). The action mechanisms of PAHs are still being studied, although results so far would seem to suggest that they can directly or indirectly damage DNA (Baird et al., 2005; Farmer et al., 2003). BpA is a suspected endocrine disruptor (Dodds, 1938). Despite the considerable number of studies of the distribution of BpA in different environmental compartments, very few focus on the atmosphere (Fu and Kawamura, 2010; Matsumoto et al., 2005; Wilson et al., 2001).

In addition to the aforementioned compounds, the acidity of the particles has also been associated with negative effects on human health, mainly in terms of lung functions. Many compounds concur to determine particle acidity, although it mainly results from the balance between sulfate and nitrate as acidic compounds, and ammonium as a neutralization species (Seinfeld and Pandis, 2006). Depending on ammonia availability, acidic sulfate and nitrate may be partially or totally neutralized in PM, thus determining particle acidity.

With regard to human health, air quality in indoor environments have been widely studied in recent years, with the focus primarily on schools and residential housing (e.g., Blondeau et al., 2005; Fromme, 2008; Martuzevicius, 2008; Polidori et al., 2009). On the contrary, considerably fewer studies have focused on PM levels in offices (Gemenetzis, 2006; Saraga et al., 2010), despite the fact that they are one of the most common workplaces in a great many countries, where lots of people spend a considerable part of their working day. As a consequence, indoor air quality in offices is of key importance, and is essential, from a health assessment point of view, when drawing up a detailed characterization of the most dangerous compounds present in the PM of offices.

A typical office is generally characterized by a very limited number of PM sources, which only occasionally contribute to indoor PM mass levels, whereas outdoor air quality can strongly affect the indoor environment. Office PM sources are represented by electronic equipment, such as: printers, photocopiers, multi-function office machines and computers (He et al., 2007; Koivisto et al., 2010; Ren et al., 2006; Wensing et al., 2008). Air conditioners (Fisk et al., 2000), together with human activity (Luoma and Batterman, 2001), can also generate PM.

The aim of the present study is to investigate PM pollution and its chemical characterization in offices in Milan and in the air outside those offices. Milan is the most densely populated, heavily polluted city in Northern Italy (Fig. 1). The service sector is the city's most important from the employment point of view, and many people spend a large part of their working day in such offices. Thus, the air quality in Milan's offices is very important for the health of a large number of workers. Moreover, the outdoor is a very strong particle source for indoor environments. The target of the study is fine PM (PM2.5 and PM1), which has been identified as the most dangerous fraction from a human health point of view. Moreover, the degree of infiltration of particles into buildings depends on particle size, and is lowest for the coarse fraction, PM2.5–10 (Hussein et al., 2005; McAuley et al., 2010). The PM samples were analyzed to determine some of the compounds with possible adverse effects on humans, i.e., PAHs, BpA, and water soluble inorganic ions.
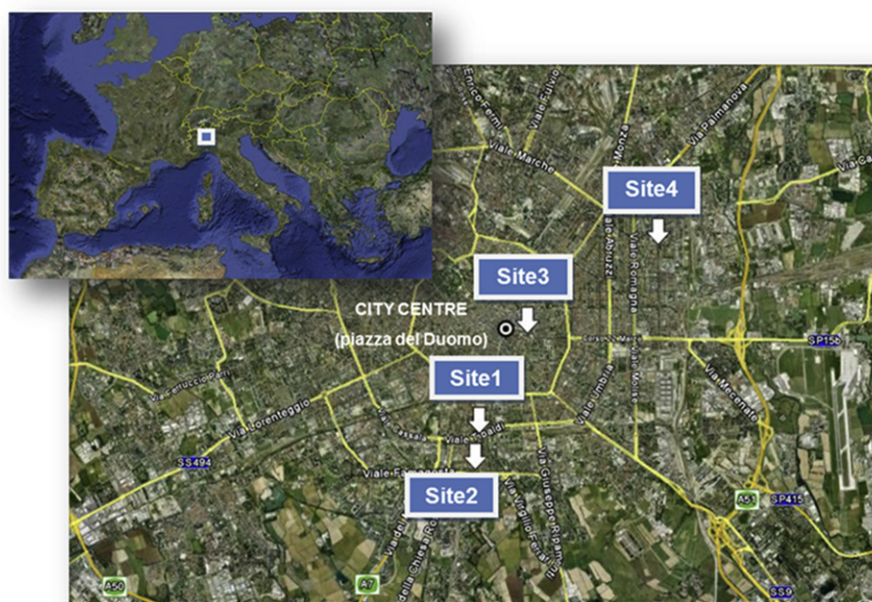

Fig. 1. Location of the four sampling sites distributed across the city of Milan, North Italy.

2. Methods

2.1. The sampling sites

The study focused on the city of Milan in Northern Italy (Fig. 1). The high level of air pollution in the city has already been well documented (see Baltensperger et al., 2002; Vecchi et al., 2004), and it derives from both anthropogenic activities (mainly traffic and heating; Perrone et al., 2012) and weak atmospheric dispersal conditions (i.e., a short mixing layer), especially during the wintertime (Ferrero et al., 2011a, 2011b, 2010; Sangiorgi et al., 2011). The result is the presence of high emissions of air pollutants in a troposphere characterized by low dispersive movements.

Four sites were selected for the sampling of PM, all of them located within or immediately outside the inner city (Fig. 1). The sampling sites were chosen in order to have four distinct sampling positions with similar population densities, human activities and local pollutant sources. All of the four sites were located in areas characterized by considerable human activity and intense traffic. Four offices, one for each sampling site, were selected as our indoor environments. The buildings were representative of many of the inner Milan city's blocks. They were all built between the 1950s and the 1970s and none of them were renewed during the last 15 years. The perimeter walls were made of solid bricks and covered in plaster. The windows were made of wooden frames and single glass and were characterized by a low insulation. The general structure and preservation conditions of the buildings favored the penetration of the outdoor air. All the offices were at ground floor. They were characterized by the presence of a limited number of indoor PM sources. Smoking was forbidden, air supply systems were absent and the movement of people through the office was limited and occasional. The only possible indoor sources were the standard items of electronic equipment (computers, printers and photocopying machines) and the occasional movement of people. The characteristics of the sampling area (high pollution level) and indoor environment (no effective indoor sources) made it possible to highlight the impact of outdoor pollution on the indoor air.

2.2. The sampling strategy

Two sampling campaigns were conducted (Table 1): the first in summer and autumn (warm season; 22 Aug − 14 Oct 2007), the second in the winter (cold season; 15 Jan − 09 Mar 2008). Each site was sampled once during each campaign, for a period of 12 consecutive days. The samplings were not simultaneously performed at the four sites, in order to collect PM samples which were more representative of the variable seasonal conditions. No air conditioning systems were present in the offices. However, it should be noted that the environmental temperatures during the warm season were not so high, and that people in offices tended to keep the windows closed almost all the time to a similar extent during the two campaigns.

The sampling was performed at the same time both inside and outside the office building, using two identical low-volume samplers (38.3 l min^{-1}, HYDRA dual channel, FAI Instruments, Rome, Italy). Both indoors and outdoors, 24-h samples of PM1 and PM2.5 were collected simultaneously on Teflon filters. In order to guarantee the quality of the PM measurements and chemical analyses, a number of field blank filters were used at each site during each campaign (28 field blank filters in all). The description of the sample handling and quality control of gravimetric data is presented in Supplementary Material (Section A).

2.3. PM chemical characterization

The collected filters were cut into multiple sections; one section of each daily filter was dedicated, individually or together with other sections from the same season, site and environment (indoor or outdoor), to determine the content of water-soluble inorganic ions, PAHs and BpA (BpA was only analyzed in PM2.5 samples). The composited samples were intended to raise the analytical signals.

As regards the sample filters, the field blank filters were cut into sections and analyzed, either individually or pooled in composited samples, to determine water-soluble inorganic ions, PAHs and BpA. The procedure was followed in order to determine any potential contamination of the samples from field and laboratory manipulation of the filters. The detection limit (dl) was computed as the average plus three times the standard deviation (inorganic ions and PAHs) or three times the standard deviation (BpA) of the field blank concentration (Tab. SM1). Only those figures above dl were admitted as valid. The following is a brief description of the analytical procedures (details are in Perrone et al., 2010, 2012). For sample processing and analysis to determine BpA, see the Supplementary Material (Section B).

2.3.1. Water-soluble inorganic ions

The water-soluble inorganic ions were determined by extracting the composited samples in 3 ml of ultra-pure water (18.2 MΩ cm^{-1}, Milli-Q water system, Millipore, Billerica, MA, USA) for 20 min in an ultrasonic bath (SONICA$^{®}$, Soltec, Milan, Italy). The extract was filtered (0.45 μm pore size PTFE filter) and analyzed by two ion chromatographic systems (ICS-90 and ICS-2000, Dionex, Sunnyvale, CA, USA) coupled with an autosampler (AS, Dionex). An isocratic elution (0.5 ml min^{-1}) and a chemical suppression mode were used. The method was used for the separation and quantification of the anions F^{-}, Cl^{-}, NO$_3^{-}$, PO$_4^{2-}$, SO$_4^{2-}$ and the cations Na^{+}, NH$_4^{+}$, K^{+}, Mg^{2+}, Ca^{2+}. Since the concentration of F^{-}, Cl^{-} and PO$_4^{3-}$ was always very low and close to dl, they will not be taken into account.

2.3.2. Polycyclic Aromatic Hydrocarbons

The PAHs were analyzed after extracting the composited samples using 2 ml of acetonitrile (HPLC analyzed, Mallinckrodt Baker, Deventer, Holland) for 20 min in an ultrasonic bath. The extract was filtered (0.45 μm pore size PTFE filter) and analyzed by means of high-pressure liquid chromatography with a fluorimetric detector (HPLC-FD, Shimadzu, Kyoto, Japan). The separation was performed on a C18 column (Vydac PAH column, Alltech,

Table 1
Dates of the indoor and outdoor sampling campaigns and average daily temperatures measured at the four sites (Milan, Italy).

	Warm season				Cold season			
	Sampling		T (°C)		Sampling		T (°C)	
	Start	End	Outdoor	Indoor	Start	End	Outdoor	Indoor
Site 1	22/08/2007	02/09/2007	19–28	24–28	26/02/2008	09/03/2008	6–16	21–26
Site 2	04/09/2007	16/09/2007	18–23	23–26	29/01/2008	07/02/2008	4–10	20–24
Site 3	18/09/2007	30/09/2007	11–21	21–25	12/02/2008	24/02/2008	3–12	20–25
Site 4	02/10/2007	14/10/2007	15–21	20–25	15/01/2008	27/01/2008	5–14	22–25

Nicholasville, KY, USA) with a guard cartridge (Prosphere HPC18, Alltech). Acetonitrile and ultra-pure water were used in a gradient elution program (1 ml min^{-1}). Ten PAHs were quantified: pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBahA), indeno [1,2,3-cd]pyrene (IcdP), and benzo[ghi]perylene (BghiP). All the PAH concentrations were above dl, with the exception of DBahA, the level of which was often below it; as such, it will not be taken into consideration.

2.3.3. Bisphenol A

BpA was determined after extracting the composited samples in 0.5 ml of methanol (LC-MS ChromaSolv$^®$ grade, 99.9% purity, Fluka, Sigma—Aldrich, Milan, Italy) for 10 min in an ultrasonic bath. The extract was filtered (0.45 μm pore size PTFE filter) and analyzed by HPLC/(−)ESI—MS/MS (Agilent, Waldbronn, Germany) and a mobile phase constituted by ultra-pure water and methanol. Data were collected in negative ion mode by multiple reaction monitoring. Details of the method are set out in the Supplementary Material (Section B.1). All BpA concentrations in the samples were above dl.

2.4. Indoor—outdoor relationship

I/O is the ratio between the indoor and outdoor concentration of PM or of a compound. It is a very simple, useful parameter, since it can be easily calculated and it enables to quickly establish whether the indoor environment is enriched with PM or compounds compared with the outdoor (e.g., Chen and Zhao, 2011; Hussein et al., 2005).

However, the indoor concentrations of PM and its chemical compounds are typically a mix of those from outside that come indoors, and those generated indoors, and the I/O ratio does not enable to separate the two. Several studies have discussed this topic, showing that the indoor and outdoor concentrations can be linearly related in order to roughly separate the contributions made by the two sources. A simple linear equation is offered by many authors (e.g., Hänninen et al., 2004; Ho et al., 2004; Hoek et al., 2008):

$$C_{in} = F_{INF} \times C_{out} + C_{ig} \tag{1}$$

where C_{in} and C_{out} are the PM or compound concentrations measured in the indoor and outdoor environments, respectively, F_{INF} is the fraction of outdoor PM or compound that comes indoors and remain airborne, and C_{ig} is an estimate of the PM or compound concentration measured indoors and generated by indoor sources. F_{INF} is called the infiltration factor, C_{ig} is the indoor-generated particle concentration. Eq. (1) is derived from a more complex mass-balance model including parameters taking into account the indoor—outdoor air exchange rate, penetration efficiency, and particle deposition rate (Chen and Zhao, 2011; Hänninen et al., 2004). However, it should be pointed out here that there is no parameter that takes account of the potential loss of semi-volatile compounds from PM due to the shifting of its gas-particle partitioning equilibrium (e.g., resulting from a rise in temperature). The two approaches to the indoor—outdoor relationship will be presented in the following section. An ordinary least squares algorithm was used for the linear regression of Eq. (1).

3. Results and discussion

The concentration and chemical composition of PM are affected both by the sources of the area surrounding the sampling site, and by the meteorological conditions during the sampling campaign. In order to best represent the impact of the average meteorological conditions during a season (warm and cold), and of the PM sources within the urban Milan area, the sampling campaigns were conducted at four different sites throughout the city during different periods (Sections 2.1 and 2.2). As a consequence, we will not compare the results site by site, but we will focus on the relationship between outdoor and indoor PM features (Section 2.4.).

3.1. PM mass concentration

Fig. 2 and Table SM2 show the daily PM concentrations during the sampling campaigns; Table 2 summarizes the average values. The typical seasonal trend of ambient PM level for Milan emerges (Ferrero et al., 2011a, 2011b, 2010; Perrone et al., 2010): concentrations were lower during the summer and generally higher during the winter. It should also be noted that the sampling campaign from late September to October (Sites 3 and 4) revealed a "transition" period between the summer and winter levels of PM. Despite the variability of PM levels between sites and seasons, a good correlation between outdoor and indoor concentrations can be seen: R^2 was 0.86—0.88 for PM1 and PM2.5 during both the seasons. Typically, PM1 represented about 70% of PM2.5.

3.1.1. Indoor—outdoor relationship of PM mass concentration

The average I/O was 0.64 ± 0.13, with a maximum of 0.92, suggesting that the indoor level of PM concentration was always lower than the outdoor level. A slightly higher I/O characterized PM1 (0.66 ± 0.12 as average over the two campaigns) compared with PM2.5 (0.62 ± 0.14), as foreseen by previous studies (Hussein et al., 2005; McAuley et al., 2010).

Fig. 3 shows Eq. (1) for PM1 and PM2.5 during the warm and cold seasons. F_{INF} (i.e., the infiltration factor, the slope of the linear regression line) settled at about 0.55 and varied very little between PM sizes and campaigns. Thus, about a half of outdoor PM had come indoors, regardless of the season or the particle size (PM1 or PM2.5). It should be pointed out here that the windows of the offices were kept closed for most of the time during both sampling campaigns, given the likely autumnal temperatures measured outdoors during the warm season (Table 1), thus limiting the exchange of air between outdoors and indoors. This may explain the lack of a clear seasonal trend for F_{INF}.

During the warm season, the C_{ig} (i.e., the indoor-generated particles, the intercept of the linear regression line) was positive, suggesting that few μg m^{-3} of the indoor PM (3.2 ± 0.6 μg m^{-3} for PM1; 4.4 ± 0.9 μg m^{-3} for PM2.5) were generated by indoor sources, corresponding to about 25% of indoor PM concentrations. On the contrary, during the cold season, indoor-generated particles were absent (C_{ig} <0: −0.1 ± 1.2 μg m^{-3} for PM1; −1.8 ± 1.9 μg m^{-3} for PM2.5). The C_{ig} reveals the very limited contribution of indoor sources to fine PM mass concentration, which indeed fell to zero during the cold season.

3.2. PM chemical composition

The PM samples were analyzed to quantify the concentration of several compounds (Section 2.3): water-soluble inorganic ions, PAHs, and BpA. These chemical species include molecules that can have direct or indirect negative effects on human health (section 1). The results of the chemical characterization of fine PM will be presented and discussed below (Fig. 4, Tables SM3 and SM4). As regards PM mass concentration, we are not going to compare the data site by site, but to discuss the average value for each sampling site and season, with the focus on indoor—outdoor ratios (Section 2.4.).
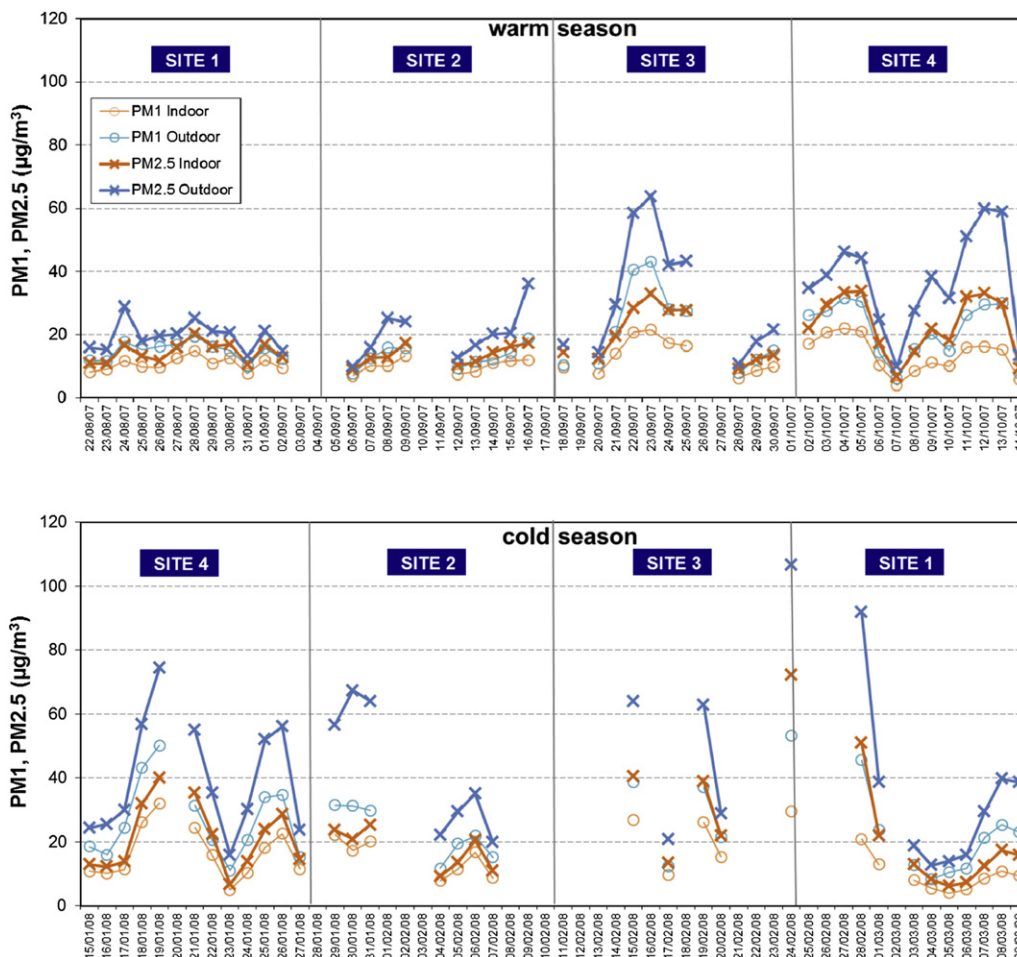
Fig. 2. Fine PM indoor (office) and outdoor (urban site) concentrations, measured during two sampling campaigns conducted at four sites in Milan (Italy).

A general seasonal trend is clear for all species, with site average concentrations higher during the cold season than during the warm season (for the PAHs, winter concentrations were of a greater magnitude).

The average concentration of the sum of the 7 inorganic ions (NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) during the entire campaign was within the 4–27 μg m^{-3} range. A major fraction of PM was composed by inorganic ions, as their total mass accounted for 28% and 49% of indoor and outdoor PM respectively. NO_3^-, SO_4^{2-} and NH_4^+ were the three main inorganic ions, each one accounting for about 30% of all ions. The average concentration of the sum of the 9 PAHs during the entire campaign was in the 0.5–13.0 ng m^{-3} range. The PAHs only made a very limited contribution to PM mass, which was about 6 times higher during the cold (0.028 ± 0.004%) than during the warm season (0.005 ± 0.001%). The average concentration of BpA during the

entire campaign was 0.24 ± 0.16 ng m^{-3} (min–max 0.01–0.79 ng m^{-3}) in PM2.5 (BpA was only analyzed in PM2.5 samples). The BpA concentration range in outdoor, from 0.01 to 0.73 ng m^{-3}, is similar to that reported by Fu and Kawamura (2010) in PM2.5 samples collected along several outdoor urban sites of China (0.02–2.34 ng m^{-3}). A higher range of concentration is showed for an urban-traffic site in Thessaloniki (Greece) by Salapasidou et al. (2011; 0.06–18.6 ng m^{-3}). The indoor concentration range, from 0.13 to 0.79 ng m^{-3}, was lower than presented for similar indoor environments (houses and offices) by Inoue et al. (2006; up to 3.6 ng m^{-3}). For a detailed description of the BpA field measurements, see the Supplementary Material (Section B.2).

3.2.1. Indoor–outdoor relationships of PM chemical compounds

The indoor-to-outdoor ratios of the compounds detected in PM samples will be described in the present section using I/O and Eq.

Table 2
Mean, standard deviation, minimum and maximum fine PM concentrations measured during the warm season and cold season campaigns conducted in indoor (office) and outdoor (urban site) environments (Milan, Italy).

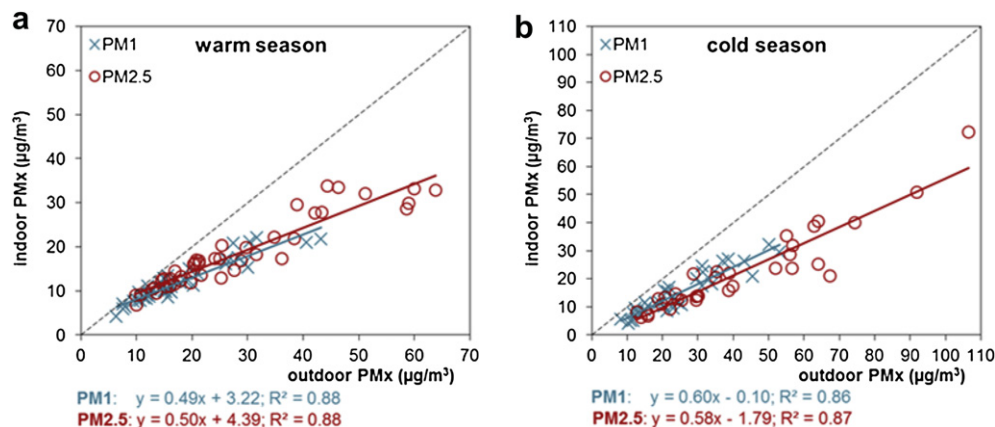|	Warm season				Cold season			
	Indoor		Outdoor		Indoor		Outdoor	
	PM1 (μg m^{-3})	PM2.5 (μg m^{-3})	PM1 (μg m^{-3})	PM2.5 (μg m^{-3})	PM1 (μg m^{-3})	PM2.5 (μg m^{-3})	PM1 (μg m^{-3})	PM2.5 (μg m^{-3})
Mean	12.1	18.1	18.1	27.6	15.0	21.9	25.0	41.1
Dev. St.	4.5	7.8	8.7	14.8	7.8	14.3	12.0	23.3
Min	4.1	6.9	6.4	9.9	4.1	6.2	8.4	12.8
Max	22.1	33.8	43.2	63.8	32.1	72.3	53.1	106.5

Fig. 3. Linear regression of outdoor (urban site) vs. indoor (office) fine PM concentrations at four sites of Milan (Italy) during a) warm and b) cold season campaigns.

(1) (Section 2.4). The slope and intercept of Eq. (1) were calculated for each analyte by means of linear regression (ordinary least squares). As a general rule, a good correspondence of the I/O was found between PM1 and PM2.5 (Tables SM3 and SM4). As a consequence, we will refer to the I/O ratio of each compound as the average of PM1 and PM2.5 taken together, sub-divided according to the two campaign seasons. Similarly, Eq. (1) was applied to the chemical composition data without separating the PM1 and PM2.5 samples, in order to extend the data set. The results are shown in Table SM5 and in Fig. 5.

3.2.1.1. Indoor-to-outdoor concentration ratios (I/O). Almost all of the I/O were below or slightly above one, with the sole exception of BpA, which revealed values of 2.42 ± 1.51 and 2.22 ± 1.05 during the warm season and the cold season, respectively (Table SM5). Of

the other compounds, PAHs were characterized by a slightly narrower set of I/O values than were the inorganic ions (the difference between the maximum and minimum I/O was 1.0 and 0.3 during the warm season, and 0.7 and 0.5 during the cold season, for the inorganic ions and the PAHs respectively). Moreover, it appears that the I/O values were always higher during the warm season than during the cold season, and the seasonal difference was more pronounced for PAHs than it was for inorganic ions or BpA.

3.2.1.2. Indoor-generated particles (C_{ig}). By applying Eq. (1), a good correlation emerges between the indoor and outdoor concentrations of almost all the compounds: R^2 was above 0.6, with very few exceptions (Ca^{2+} and PYR). In general, the C_{ig} showed negative, or close to zero, values during the two sampling campaigns. Comparing it with the average indoor concentrations, it was always
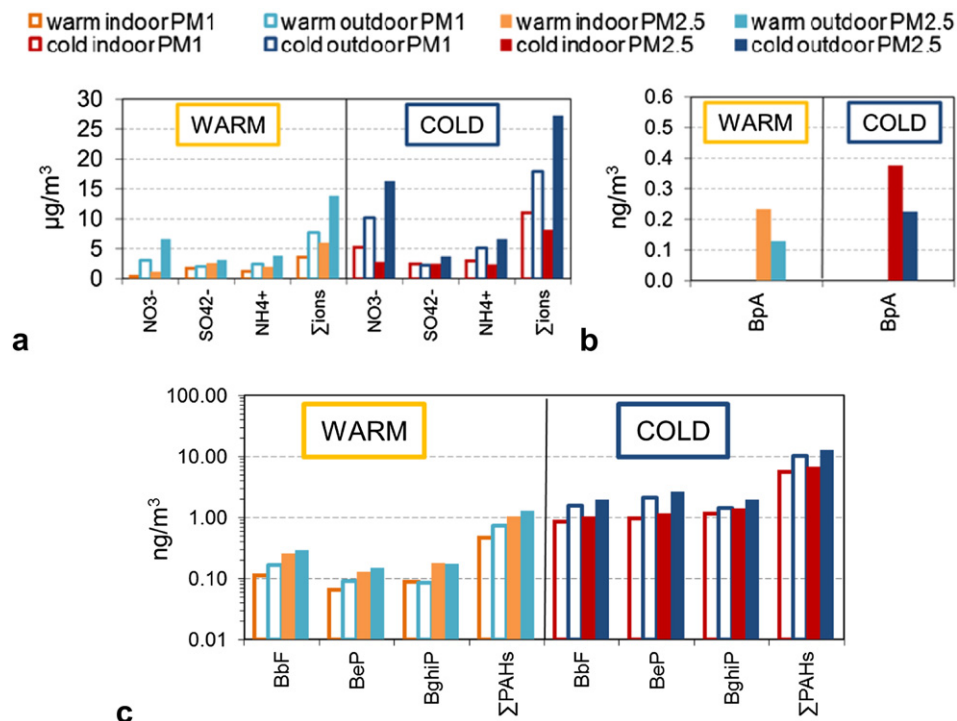

Fig. 4. Average concentrations of the compound species measured indoors (office) and outdoors (urban site) during two sampling campaigns conducted at four sites in Milan; a) water-soluble inorganic ions, b) BpA, and c) PAHs.
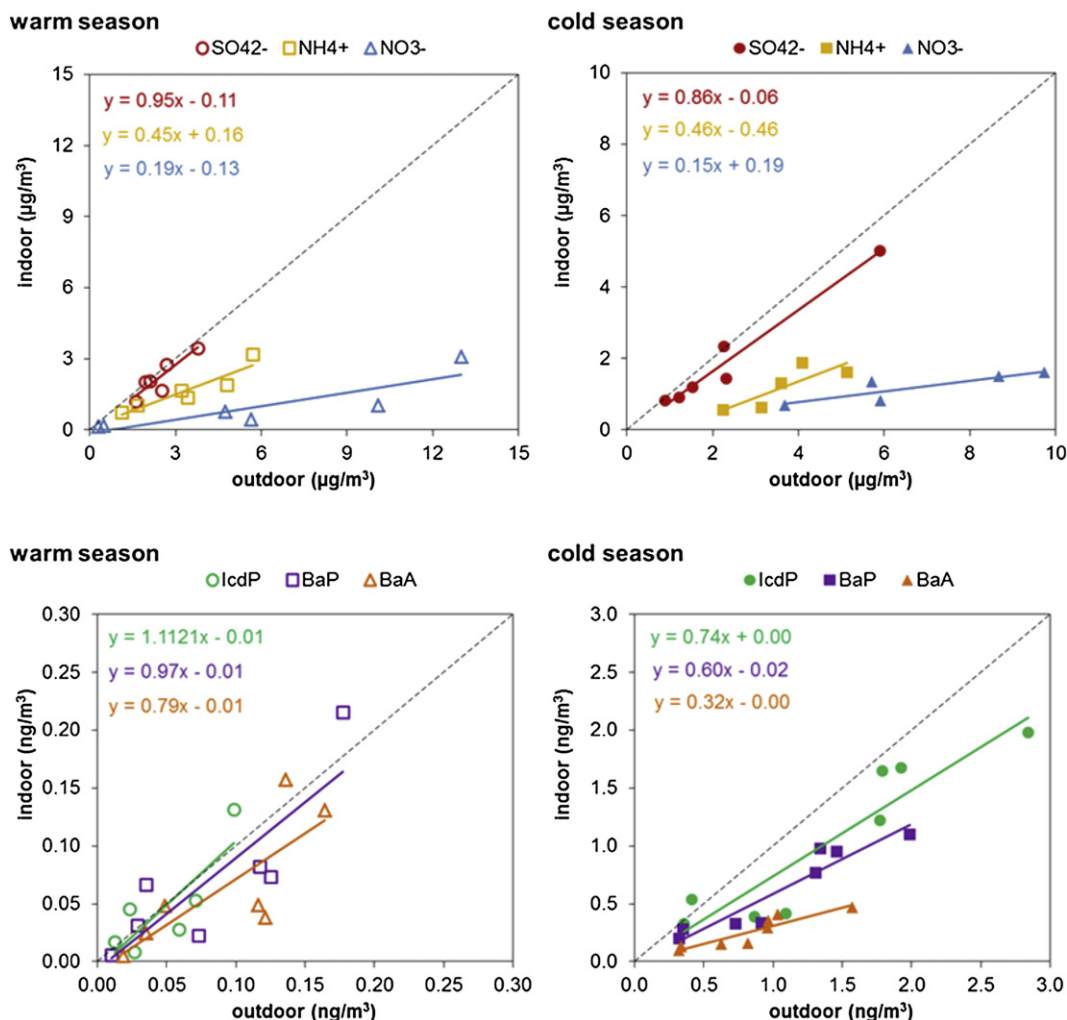
Fig. 5. Linear regression of outdoor (urban site) and indoor (office) concentration of inorganic ions (up) and PAHs (down) in fine PM; the slope of the linear regression lines is F_{INF}, the intercept is C_{ig}.

$\leq 20\%$ (the less abundant inorganic ions K^+, Mg^{2+} and Ca^{2+} displayed a C_{ig} only slightly higher than 20%). The main exception was BpA, for which it was 60% and 56% during the warm and cold seasons, respectively. The results suggest that, as would be expected given the characteristics of the selected offices, there were no relevant indoor sources of the selected compounds. Only BpA had an actual indoor source that acted constantly during the two sampling periods. One possible indoor source of BpA is office equipment, such as computers and printers (Owens et al., 2007; Salapasidou et al., 2011).

3.2.1.3. Infiltration factor (F_{INF}). As with I/O, F_{INF} constantly displayed higher values during the warm season, when it generally stood above 0.7, than during the winter, when it stood under 0.7. However, it should be said that the highlighted seasonal trend was clear for the PAHs, for which F_{INF} fell from 0.8–1.2 during the warm season to 0.3–0.7 during the cold season, whereas BpA and the inorganic ions in general tended to display very similar F_{INF} values during the two periods.

The analyzed species feature certain semi-volatile compounds, the transfer of which from the particulate to the gaseous phase could affect their F_{INF}. When transferred indoors from outdoors, the particle-bound compounds are subjected to a change in environmental conditions: as a rule, the temperature increases and the

relative humidity decreases, particularly during winter. The gas-particulate partitioning is a process depending on both of the aforesaid parameters, especially temperature (Lohmann and Lammel, 2004; Ohura et al., 2004). When entering the warmer indoors, a semi-volatile molecule will tend to partition more in the gaseous phase, thus reducing its particulate concentration. This process is also facilitated by the adsorption of the gaseous compounds onto the indoor surfaces, which promotes a further movement of particulate semi-volatile molecules to the gaseous phase (Weschler and Nazaroff, 2008). Studies have shown that the new gas-particulate equilibrium for semi-volatile PAHs and ammonium nitrate entering buildings can be rapidly reached (Lunden et al., 2003; Naumova et al., 2003).

To demonstrate the semi-volatile loss for the volatilization effect on PM collected during the Milan campaigns, we divide the analyzed species into: a) non-volatile compounds (e.g., $(NH_4)_2SO_4$ and Na^+), and b) semi-volatile compounds (e.g., 4–5 ring PAHs and NH_4NO_3).

As non-volatile molecules in PM, SO_4^{2-} (present as ammonium sulfate) and Na^+ are taken as a model. They were characterized by a high F_{INF} during the two campaigns, which settled at about 0.9. As expected for non-volatile species, the infiltration factor was not affected by the temperature differences between outdoors and indoors, or between warm and cold periods.

Of the analyzed semi-volatile compounds, particulate ammonium nitrate exists in equilibrium with ammonia and nitric acid in the gas phase. The 4-ring PAHs partition themselves between the gas and particulate phases; the PAHs with 5 aromatic rings are more distributed in the particulate phase; PAHs with 6 or more rings are to be found almost exclusively in the particulate phase. Ammonium and nitrate displayed a fairly constant F_{INF} during the sampling campaigns, at around 0.17 and 0.45 for NO_3^- and NH_4^+, respectively. Of the PAHs, the 4-rings displayed the lowest values (PYR, BaA and CHR; average: 0.92 and 0.44 during the warm season and the cold season, respectively); the 5-rings displayed intermediate values (BbF, BeP, BaP, BkF, DBahA; 0.88 and 0.46); the 6-rings displayed the highest values (IcdP and BghiP; 1.17 and 0.72), with a decreasing F_{INF} going from the warm to the cold season.

As regards the PAHs' behavior, the F_{INF} trend reflected the compound's volatility: higher values were measured for the less volatile compounds. However, it is likely that the *real* F_{INF} was very similar for all PAHs, although the more volatile compounds tended to be redistributed in the gaseous phase when coming indoors, leading to a reduction in their particulate concentration. The volatilization effect could also be the reason for the seasonal differences in the F_{INF} measured for the PAHs. In fact, the PM mass and non-volatile compound F_{INF} suggest the constant infiltration of particles during the two sampling campaigns. However, during the cold period the semi-volatile PAHs were subjected to a higher change in temperature when going from outdoors to indoors, and this probably favored a stronger transfer of them from the particulate to the gaseous phase. As a result, the F_{INF} decreased more, as the volatilization effect was stronger.

The seasonal trend described for the F_{INF} of PAH did not emerge in the case of ammonium nitrate. It is likely that ammonium nitrate and ammonium sulfate had the same F_{INF}, but once indoors only ammonium nitrate − as a semi-volatile compound − tended to move toward the gaseous phase. Thereby, NO_3^- displayed a very low F_{INF} because of the high volatility of ammonium nitrate, whereas NH_4^+ displayed a F_{INF} value somewhere between that of NO_3^- and SO_4^{2-} because only the ammonium of ammonium nitrate − and not that of ammonium sulfate − was semi-volatile. The lack of a seasonal trend for the F_{INF} of ammonium nitrate is a consequence of its very high vapor pressure (3×10^{-3} mmHg): even a very small increase in temperature can affect the ammonium nitrate equilibrium in favor of the gaseous phase.

Several studies have reported indoor concentrations of ammonium nitrate or PAHs that are lower than would be expected due to solely penetration and deposition loss effects (e.g., John et al., 2007; Kliucininkas et al., 2011; Lunden et al., 2003; Naumova et al., 2003), thus supporting the volatilization effect of semi-volatile compounds in different situations. A detailed study of the gas-particulate distribution of PAHs both outdoor and indoor can be found in Naumova et al. (2003), that demonstrates a net decrease of PAHs concentration in the particulate phase. They attributed the described effect mainly to the temperature change (and, to a lesser extent, to the particulate content of elemental and organic carbon). The same was showed by Lunden et al. (2003) for ammonium nitrate, which measured indoor concentrations are significant lower than would be expected by penetration and deposition losses. They claimed that the dramatic reduction of particulate ammonium nitrate indoor should be attributed to the transfer in gaseous phase (as ammonia and nitric acid) as effect of the increase of their evaporation rate with the temperature increase.

3.2.2. The volatilization effect of semi-volatile compounds

Starting from the volatilization effect of semi-volatile compounds presented in the previous section, we propose the modification of Eq. (1) with the introduction of a new factor:

$$C_{in} = F_{exp} \times C_{out} + C_{ig} \qquad (2)$$

where F_{exp} is the experimental infiltration factor, that is, the apparent infiltration factor of a compound calculated from the measured indoor and outdoor concentrations. It is equal to the real F_{INF} for a non-volatile compound, but is affected by the volatilization effect for a semi-volatile compound. Thus, we propose the introduction of a corrective parameter, v_c, called the *volatilization correction*, designed to take account of the loss of a semi-volatile compound that is partially redistributed to the gaseous phase when entering a warmer environment. It is calculated as follows:

$$v_c = F_{exp}/F_{INF-nv} \qquad (3)$$

where the F_{INF-nv} is the real infiltration factor, corresponding to the experimental infiltration factor of a non-volatile compound (e.g., $(NH_4)_2SO_4$). The F_{INF-nv} depends on the penetration efficiency of PM, the air exchange rate and the deposition rate of the particles. Eq. (2) can be re-written as follows:

$$C_{in} = F_{INF-nv} \times v_c \times C_{out} + C_{ig} \qquad (4)$$

The new correction parameter, v_c, may range from 0 to 1. It is 0 for a particle phase compound which, when entering a warmer indoor environment, will be redistributed completely in the gaseous phase. It is 1 for a non-volatile compound or a semi-volatile compound that enters an indoor environment in which its gas-particle equilibrium does not change. An intermediate value of v_c would be associated to a semi-volatile compound (e.g., PAHs and NH_4NO_3) that experiences a gas-particle equilibrium change when entering a warmer environment. Clearly, v_c is mainly a function of compound volatility and temperature change. We are assuming here that the indoor sources emit compounds that very quickly achieve their gas-particle partitioning. In this way, v_c is not affected by C_{ig} (i.e., the gas-particle equilibrium of a semi-volatile compound is not affected by the indoor-generated particles).

The correction parameter v_c can be roughly estimated for NH_4NO_3 and PAHs (Table 3) in relation to the described sampling campaign conditions, taking $(NH_4)_2SO_4$ as a non-volatile compound and setting its F_{exp} equal to F_{INF-nv}. The v_c kept the same value, during both seasons, for NH_4NO_3 (average: 0.19). On the contrary, all the PAHs displayed a v_c close to one during the warm season, while during the cold period it was lower and varied according to the volatility of the compounds. The 4-ring PAHs displayed the lowest value (0.44 on average), followed by the 5-ring PAHs (0.59) and the 6-ring PAHs (0.84).

Table 3
Initial estimations of the volatilization correction parameter, v_c, for the semi-volatile ammonium nitrate and PAHs.

V_c	Season	
	Warm	Cold
NH_4NO_3	0.20	0.17
PYR	/	0.60
BaA	0.84	0.37
CHR	0.86	0.36
BbF	1.00[a]	0.58
BkF	0.81	0.59
BeP	1.00[a]	0.50
BaP	1.00[a]	0.70
IcdP	1.00[a]	0.86
BghiP	1.00[a]	0.81

[a] Values >1 are set at 1.

4. Conclusions

The research focused on the study of outdoor PM influence on indoor PM levels, and on the change in its chemical composition when coming indoors. The study was conducted in Milan, both outside and inside four typical office buildings, during the summer–autumn and the winter, and the target was fine PM (PM1 and PM2.5).

The results show the considerable influence of the outdoor environment on indoor PM, as confirmed by the strict correlation between indoor and outdoor PM concentrations ($R^2 = 0.86-0.88$), and by the infiltration factor, which settled at about 0.55 regardless of PM size or the sampling period. However, the indoor concentrations were always lower than those measured outdoors (the maximum I/O was 0.92), while any effective indoor source was highlighted ($C_{ig} \leq 4$ μg m^{-3}).

No significant indoor sources were found for the analyzed chemical compounds ($C_{ig} \leq 20\%$ of the indoor concentrations of water-soluble inorganic ions and PAHs), with the exception of BpA, the I/O (~2.3) and C_{ig} (~58%) of which demonstrated the clear presence of indoor sources (e.g., printers and photocopiers). This is an important finding, as it proves the presence of indoor sources which did not contribute toward a high PM mass emission, but which significantly affected human health through the apportionment of particles enriched by dangerous compounds such as BpA.

A second important finding from the present study is the demonstration of the loss of semi-volatile compounds through volatilization from the particulate phase when outdoor PM comes indoors, mainly because of the increase in temperature. Clearly, this effect is greater for the more volatile compounds, such as ammonium nitrate, but lower in the case of less volatile compounds, such as 4- and 5-ring PAHs. This is an important process that affects the composition of indoor PM, and it should be taken into consideration when analyzing the infiltration factor F_{INF}. Thus, we have proposed the introduction of a new parameter − the volatilization correction v_c − in order to include this process in the indoor-to-outdoor linear regression.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2012.10.050.

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