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Spatial and Indoor/Outdoor Gradients in Urban Concentrations of Ultrafine Particles and $PM_{2.5}$ Mass and Chemical Components

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ABSTRACT

In order to investigate relationships between outdoor air pollution and concentrations indoors, a novel design of experiment has been conducted at two sites, one heavily trafficked and the other residential. The novel design aspect involves the introduction of air directly to the centre of an unoccupied room by use of a fan and duct giving a controlled air exchange rate and allowing an evaluation of particle losses purely due to uptake on indoor surfaces without the losses during penetration of the building envelope which affect most measurement programmes. The rooms were unoccupied and free of indoor sources, and consequently reductions in particle concentration were due to deposition processes within the room alone. Measurements were made of indoor and outdoor concentrations of $PM_{2.5}$, major chemical components and particle number size distributions. Despite the absence of penetration losses, indoor to outdoor ratios were very similar to those in other studies showing that deposition to indoor surfaces is likely to be the major loss process for indoor air. The results demonstrated a dramatic loss of nitrate in the indoor atmosphere as well as a selective loss of particles in the size range below 50 nm, in comparison to coarser particles. Depletion of indoor particles was greater during a period of cold weather with higher outdoor concentrations probably due to an enhancement of semi-volatile materials in the outdoor particulate matter. Indoor/outdoor ratios for $PM_{2.5}$ were generally higher at the trafficked site than the residential site, but for particle number were generally lower, reflecting the different chemical composition and size distributions of particles at the two sites.

Keywords: Indoor-outdoor air; deposition; $PM_{2.5}$; nanoparticles

1. INTRODUCTION

Atmospheric aerosol has been documented to cause increased mortality, morbidity, decreased lung function and other adverse effects upon health (Beelen et al., 2014; Raaschou-Nielsen et al., 2013), although there is considerable uncertainty about which physical and/or chemical characteristics of particulate matter (PM) are most important as determinants of health effects (Brunekreef and Holgate, 2002, REVIHAAP, 2013). Recently, toxicological and epidemiological studies have focused on health effects from exposure to ultrafine particles (UFP, particles with diameter <100 nm) due to their toxicity and ability to penetrate deeply in the human lung (Peters et al., 2011; Hoek et al., 2010; von Klot et al., 2005)

Traffic is the main source of fine and ultrafine particles and a principal determinant of the spatial pattern of air pollution within urban areas. While exposure to PM from vehicular emissions has been demonstrated to have detrimental impacts on human health (HEI, 2010) epidemiological evidence of adverse health effects associated with residential proximity to traffic is still limited. Some studies have shown a higher prevalence of respiratory symptoms (e.g. Delfino et al., 2014), especially in children (Gasana et al, 2012) but others did not find any effects (Badaloni et al., 2013; Macintyre et al., 2014).

A key issue in studies on residential proximity to traffic is exposure assessment. Substantial efforts have been made in this field and a significant improvement has been reached with Land Use Regression Models (LUR) which make use of a spatially dense network of measured air pollution concentrations together with predictor variables such as population density, land use, and various traffic related variables to estimate outdoor air pollution concentrations within urban areas (Hoek et al., 2008a). However, exposure to pollutants takes place mainly indoors (Monn, 2001) and assessment of both indoor and outdoor variability of concentrations and characteristics of particles

are of primary importance to better understand the way residential proximity to traffic sources could affect human health.

The relationships between indoor levels due to outdoor and indoor sources vary between cities, regions and countries due to differences in factors that can influence the indoor levels, e.g. climate, building characteristics, human activity, ventilation and heating systems (Monn, 2001; Nazaroff, 2004; Ashmore and Dimitroulopoulou, 2009). However, it is reasonable that indoor sources could be considered a relevant, sometimes dominant, white noise superimposed upon spatial variation of exposure due to outdoor air that infiltrates indoors. Thus, it is particularly important to assess the penetration characteristics of particles into indoor environments, and the differences in physical and chemical properties of particles of outdoor origin.

There are two possibilities to assess the mean differences in exposure due to proximity to traffic. The first is to measure a large number of indoor environments filtering out the effects of indoor sources and personal habits (Fuller et al., 2013; Spinazzè et al., 2013) . This type of study has the drawback of a strong limitation of the number of indoor environments which can be studied, and of the measurement duration of air pollutants, personal habits and air exchange rates. The other is to compare uninhabited indoor environments with characteristics and air exchange rates typical of residential settings. Very few studies have been conducted using this second approach (Schneider et al., 2004).

In this paper we present the results of an experimental study carried out in a highly polluted city in Northern Italy following this second approach. Indoor and outdoor $PM_{2.5}$ mass and chemical composition as well as the size distribution of ultrafine particle have been contemporaneously measured at two sites with very different characteristics in relation to proximity to traffic sources. The objectives of the study were to compare indoor/outdoor (I/O) ratios of particulate pollutants in two similar unoccupied buildings with very different proximity to traffic, and to quantify I/O ratios

when air exchange ratios were well defined and penetration losses were eliminated by experiment design.

2. METHODS

2.1 Study Design

The study area is the city of Bologna, Italy. This is a highly polluted urban area of about 400,000 inhabitants in northern Italy. In the period 2010-2012 the city-average annual mean number of exceedances of the daily PM_{10} limit value (50 $\mu g/m^3$) was 52.

The main objective of the study was to compare exposure conditions of people living in residential settings with those in high traffic areas. The measurements at the two sites were conducted simultaneously indoors and outdoors at a residential as well as a traffic site. We selected indoor environments with the following characteristics: uninhabited, very similar in terms of volumes and building materials, and with very similar air exchange rates. The main goal was to assess the differences of population exposure to particles in relation to traffic without considering specific indoor characteristics and personal behaviours. We controlled the air exchange rates by installing in each indoor environment a mechanical system to force air to be exchanged between indoors and outdoors. The system consisted of an external fan connected to an air pipe (length = 1.2 m) carrying the air to the centre of the room (at a height of 2 m). Increased indoor air pressure caused the flow to exit the room through a grid. The fan in each room was set at a specific value related to the volume of the room in order to obtain an estimated 0.5 h^{-1} air exchange rate in each room, a typical level for residential environments (Cattaneo et al., 2011). The air inflow was measured with a TESTO 417 Anemometer. There was concern that this experimental arrangement for providing a forced input of aerosol might lead to depletion due to passage through the fan and pipe. This possibility was tested by experiments in which the particle number size distribution was measured at the inlet to the fan and outlet to the pipe by an FMPS system with rapid switching between the

two sampling locations (upstream and downstream). The air inflow system was found to cause a minor loss of particles (additional information can be found in the Supplemental Information). This was considered a negligible source of error. The heating systems in the two indoor monitoring sites were kept always off.

The traffic site was located in a busy street which surrounds the historical centre of Bologna. This is one of the busiest streets of the entire municipal area with a traffic load of 31,000 vehicles (4–5% heavy duty vehicles) each working day. The building is located in a broad (20 m) two-way street canyon. The indoor monitoring site was on the ground floor in a two-storey building. The volume of the room was 55 m^3 with a ceiling height of 3.7 m. The floor was covered with marble. The ceilings and the walls were painted with acrylic paint.

The residential site was located in a low traffic area about 2 km from the historical centre of Bologna. The nearest street has a traffic volume of 6,000 vehicles per day. The measuring room was on the ground floor in a four-storey building. The volume of the room was 63 m^3 with a 3.7m ceiling height. The floor was covered with marble. The ceilings and the walls were painted with acrylic paint.

The outdoor $PM_{2.5}$ monitoring sites were located at 2 m above ground and for practical reasons at a distance of about 50 m from the indoor sites along the same streets. It is possible that the specific location of the outdoor $PM_{2,5}$ monitoring site could have produced a small reduction of the indoor/outdoor ratio for $PM_{2,5}$ and for some chemical components associated with primary emissions from traffic.

Three monitoring campaigns were conducted in the period February-June 2012. Each monitoring campaign lasted 15 days: 1st campaign from 22 February to 7 March, 2nd campaign from 16 to 30

April, and 3rd campaign from 28 May to 12 June. Filters were changed daily at each measurement site, and chemical speciation was performed sequentially every three days for metals, ions, and carbon (EC and OC). During the first two campaigns elemental and organic carbon were measured on an 8 hour basis in order to avoid an overload of the filters.

2.2 Instrumentation and Monitoring Procedure

Four identical low volume samplers (Skypost, TCR TECORA, Corsico – Mi) were operated to measure indoor and outdoor daily $PM_{2.5}$ concentrations at the two sites (flow rate 2.3 m^3h^{-1}). The samplers provide automatic filter changing after each 24-h period and are designed according to CEN standards. Each of these samplers consists of a $PM_{2.5}$ sampling inlet that is directly connected to a filter substrate and a regulated flow controller. Following completion of the sampling period, the $PM_{2.5}$ mass collected on the filter was determined gravimetrically. The filters were conditioned at 20°C and 50% relative humidity prior to weighing. Samples were collected on quartz fiber filters (Whatman, 47 mm diameter) and weighed following the procedure outlined in UNI EN 12341.

Agreements among the four instruments used in this study and some other identical instruments were checked in several intercomparison campaigns carried out in the years 2008-2012. Both correlation levels and test for differences for slope and intercept (1 ± 2 standard error (s.e.), 0 ± 2 s.e., respectively) of orthogonal regressions between co-located instruments were used as statistical indicators (EC, 2010). Determination coefficients were always higher than 0.972 (mean correlation 0.985). Typical errors (standard deviation of the differences between samplers) were about 2 $\mu g/m^3$ and were quite similar among the various intercomparisons. The differences for slope (from unity) and intercepts (from zero) were usually not significant and not related to specific instruments. Consequently, no corrections were applied to $PM_{2.5}$ data.

183 $PM_{2.5}$ samples were analyzed for a various chemical species. In this paper we present the findings
184 of the chemical species having more than 50% of contemporary data above the limit of
185 quantification (LOQ) for indoor and outdoor samples at both sites. LOQs for chemical components
186 were 0.028 μg/m^3 for iron (Fe), 0.04 μg/m^3 for ammonium (NH_4^+), 0.04 μg/m^3 for potassium (K^+),
187 0.05 μg/m^3 for nitrates (NO_3^-), 0.09 μg/m^3 for sulfates (SO_4^{2-}), 2.1 μg/m^3 for daily Organic Carbon
188 (OC), 0.3 μg/m^3 for daily Elemental Carbon (EC). OC and TC were quantified by means of
189 thermal-optical transmittance (Sunset Laboratory Inc., USA) using the EUSAAR_2 protocol.
190 Inorganic ions were determined by extracting species in 10mL of ultrapure water. The extracts were
191 filtered and analyzed by Ion Chromatography (Dionex ICS-1000 for anions and ICS-1100 for
192 cations, Thermo Fischer Scientific Inc., USA). Iron was analyzed by Inductively Coupled Plasma –
193 Mass Spectrometry (8800 ICP-MS, Agilent Technologies Inc., USA). Sample digestion was made
194 with nitric acid and hydrogen peroxide in a microwave digestion apparatus, according to
195 UNI14902:2005, with a recovery efficiency over 85%
196
197 Two Fast Mobility Particle Sizers (FMPS model 3091; TSI, Shoreview, MN, USA) were used to
198 measure particle size distributions and to estimate UltraFine Particle (UFP) concentrations. The
199 FMPS was developed based on electrical aerosol spectrometer technology from Tartu University
200 (Tammet et al. 2002). The instrument consists of a particle charger column, a classification column,
201 and a series of detection electrometers. After passing through the cyclone, the aerosol flow passes
202 through a negative charger to prevent overcharging, and then a positive charger which applies a
203 predictable charge on the sample using a corona unipolar diffusion charger. Small particles with
204 high electrical mobility are repelled to the electrometers near the top of the column, and large
205 particles with low electrical mobility are deflected further downstream. The particles transfer their
206 charges to the electrometers generating currents that are inverted to produce a particle size
207 distribution. The FMPS spectrometer measured the size and number concentration of particles from
208 5.6 nm to 560 nm with 32 size bins every one second. Size bins below 13 nm were not included in

209 the analysis because of the amount of data below the detection limit and also because of
210 questionable peaks in the size distribution observed in other studies. (Kaminski et al., 2013) (Jeong
211 et al., 2009). UFP concentrations were obtained summing the number of particles detected in the
212 channels below 100 nm. Hourly and daily data were calculated and used in the analyses.
213 In the preliminary phase of the monitoring campaign we carried out a 1-week intercomparison
214 between the two spectrometers using the same methodology applied for $PM_{2.5}$ samplers. We applied
215 orthogonal linear regressions between data of each bin of the two instruments. Table 1S
216 (Supplementary Information) shows the regression coefficients for each size bin. We found
217 significant but small differences in the slopes and intercepts for the majority of size bins. Based on
218 these findings we decided to apply bin-specific correction factors calculated during the
219 intercomparison campaign to the data collected from one spectrometer during the field monitoring
220 campaigns. The aim of this correction was to obtain an improvement of the comparability between
221 the two FMPS. UFP number concentrations were calculated after the correction. Typical errors
222 (standard deviation of the differences between UFP hourly data from the intercomparison campaign
223 after the correction) were 320 part./cm^3, and the determination coefficient was 0.989.
224
225 Nearly simultaneous indoor and outdoor size distributions were obtained with a switching system
226 (Mod 11sc200, Pneumoidraulica Engineering S.r.l., Vicenza, Italy) which allowed for sampling
227 from indoor and outdoor air, switching from one to the other within a time frame set by the user. A
228 valve installed in the system could switch between sampling from the outdoor air, or from the
229 indoor air. After the valve switched, there was a short time delay before the air from the sampled
230 environment reached the instruments, which was the time the air travelled from the valve to the
231 instruments. The system switched every 10 min between the indoor and outdoor measurements. In
232 order to avoid the possibility of mixing of the outdoor and indoor air streams, the 2 min samples
233 taken at the beginning of each 10 min period were deleted from the database.
234

Two digital thermo-hygrometers (Testo 175 H2, Testo AG, Lenzkirch, Deutschland) were used to measure temperature and relative humidity in the two indoor environments. Data were collected every 30 minutes.

2.3 Analysis

Summary statistics and paired t-test results have been calculated to investigate differences between series of measurements. Pearson correlation coefficients and regression analysis has been used to address linear relationships between data . We adopted an orthogonal regression approach (Fuller, 1987) which is the most suitable when both dependent and independent variable are affected by errors and are not related by a causal relationship.

Quality control of $PM_{2.5}$ mass and chemical composition data was carried out based on residuals calculated by regression analysis between indoor and outdoor data. We identified as anomalous (not necessarily not valid) the data with residuals larger then three times the standard deviation of residuals.

For FMPS data quality control we used the following procedure: a) applying a log10 function on the UFP minute data; b) stratifying data in time slots of three hours (0-3, 3-6 etc) and calculating the summary statistics for each slot and campaign; c) classifying data as anomalous if they were higher than the mean plus three times the standard deviation for the corresponding campaign and time slot. Then we averaged non-anomalous data on an hourly and daily basis.

Statistical data analysis was carried out using the R package (Version 3.0.1).

3. RESULTS AND DISCUSSION

3.1 Measurement Campaigns and Meteorological Conditions

The meteorological conditions during the study periods are summarized in Table 2S (Supplementary Information). The sampling periods were quite representative of the typical annual variations in the area. The first campaign took place after an heavy snow event and was characterized by minimum temperatures similar to the typical values of the period but maximum temperature significantly higher than the climatological average values. In particular, in the second part of the first monitoring period maximum temperature reached 21.7ºC, i.e. 4.2ºC higher than the typical maximum temperature of the period. The second campaign was characterized by varying weather conditions with rainy and sunny days, and the third campaign was a typical early summer period. The area is characterized by low wind intensities and this was a common characteristic of the three monitoring campaigns (mean wind intensities from 1.9 m/s during the third campaign to 2.6 m/s during the first campaign). Reasonably constant was also relative humidity which showed very similar mean values (55.2, 53.8, 50.4% for the three campaigns) but large day to day variations. Precipitation events were rare and small for all the sampling periods. In particular during the first campaign we had only three rainy days with 2 mm mean precipitation.

The temperatures measured at the two indoor monitoring sites showed very similar values and temporal patterns. Seasonal differences were clearly reduced compared to the outdoor values especially due to higher minimum temperatures. On the contrary, we found larger seasonal variations in indoor compared to outdoor RH values although RH indoor values were always below 50%.

3.2 Measurements of Indoor and Outdoor Particles

It is important to recognise that the design of this experiment is different from most earlier work on indoor and outdoor particle measurements. Most earlier studies have depended upon natural ventilation processes involving exchange of air through cracks around doors and windows or through open windows which lead to air exchange. In these experiments, air exchange was forced by a fan driving air into the room and consequently the processes of particle loss will be subject to some differences. In the absence of indoor sources, indoor particle concentrations are generally found to be lower than those outdoors due to particle loss on surfaces during the infiltration of air and due to loss on internal surfaces within the building. In these experiments, the first loss mechanism is insignificant as the air introduction method caused only very small changes to particle concentrations and hence the reductions in airborne concentrations are due almost solely to deposition to surfaces. The removal of air by the FMPS and filtration of particles by the $PM_{2.5}$ sampler are at a rate far smaller than the air exchange for the room and consequently have only a modest influence upon the measured indoor concentrations.

In their review article, Chen and Zhao (2011) define both an Infiltration Factor which represents the equilibrium fraction of particles which penetrates indoors and remains suspended, and a Penetration Factor which describes the penetration efficiency of particles through the building envelope. In our study design, the Penetration Factor is 1.0 (100%), and we measure an Infiltration Factor.

3.2.1 Comparison of the sites

3.2.1.1 Indoor and outdoor $PM_{2.5}$ mass

Indoor and outdoor $PM_{2.5}$ concentrations during the three monitoring campaigns are shown in Figure 1 (upper panel) and Table 1. No $PM_{2.5}$ data was identified as anomalous and removed from the database. Outdoor concentrations in the first campaign were about three times higher compared

311 to the other two monitoring periods. Very small variations (less than 10%) were found between the
312 second and third campaign. Much higher concentrations during the winter season are typical of the
313 area (Bigi et al., 2012).
314
315 We found very small and non-significant differences in $PM_{2.5}$ outdoor concentrations between the
316 sites (see Figure 2). Average $PM_{2.5}$ concentrations at the traffic site were about 6% higher than at
317 the residential site. The highest values for daily mean $PM_{2.5}$ concentrations were 72 $\mu g/m^3$ for the
318 traffic site and 70 $\mu g/m^3$ for the residential site. The $PM_{2.5}$ spatial variability found in our study was
319 a little lower than the mean within-city variability reported in the ESCAPE study, a very large
320 epidemiological study in Europe which included monitoring campaigns on air pollution spatial
321 variability in urban areas (Eefftens et al., 2012). In that study the mean ratio between traffic sites
322 and urban background sites was 1.14, with a quite broad range of values (0.96 – 1.30). However, it
323 should be taken into account that we compared a traffic with a residential site in a low traffic area,
324 whilst background sites in many other studies have been placed in parks. In fact, our aim was to
325 assess the variability of $PM_{2.5}$ concentrations between areas where people live. In addition, a
326 reduced relative spatial variability of $PM_{2.5}$ could be explained also by the higher background
327 contribution of secondary particulate matter to the total $PM_{2.5}$ mass in this area (Perrino et al.,
328 2013).
329
330 Indoor/outdoor (I/O) ratios of $PM_{2.5}$ were close to 0.4 during the first campaign at both monitoring
331 sites. The I/O ratio increased in the subsequent campaigns with mean values equal to 0.9 at the
332 traffic site and 0.7 at the residential site for the second and third campaign. This range of I/O ratios
333 was in good agreement with previous studies on indoor settings (Chen and Zhao, 2011). Inter-
334 campaign variations of $PM_{2.5}$ in the indoor sites were lower than outdoors. The ratios between mean
335 indoor concentrations during the first campaign and the other two were 1.6 and 1.3 for the traffic
336 site and 2.3 and 1.8 for the residential site. The major difference in I/O ratio between the first

campaign and the latter two seems most likely related to the aerosol composition. The outdoor nitrate content was much higher in the cooler first campaign, leading to a much reduced I/O ratios (Figure 3). The higher I/O ratios observed at the traffic site in the second and third campaign seems most likely related to the higher I/O ratio for elemental and organic carbon and iron (Figure 3) which were the (traffic-related) constituents showing the largest difference between the sites.

Values of Infiltration Factor for $PM_{2.5}$ reviewed by Chen and Zhao (2011) range from around 0.35 to 0.82. Penetration factors in the size range of 0.1-2.5 µm, in which most $PM_{2.5}$ mass resides are typically in the range of 0.75-1.0, with many measured values close to 1.0. Chen and Zhao (2011) highlight the anomalous behaviour of reactive particles such as nitrates. If a Penetration Factor of 0.9 is applied to the above range of Infiltration Factors (0.35 to 0.82), it yields adjusted values of 0.39 to 0.91 which should be, and are broadly equivalent to the I/O values determined in our study. The only divergences appear to be due to semi-volatile nitrates which lead to lower values of I/O ratio. The more recent review of Diapouli et al. (2013) also summaries results for the penetration efficiency and infiltration factor for $PM_{2.5}$. The former ranges from 0.54-1.0, with the majority of data in the 0.8-1.0 range. The infiltration factor lies between 0.4-0.85 in the various studies reviewed, which is very consistent with that reported above, no doubt because both reviews include many studies in common.

Figure 2 shows the scatter plots and the correlation coefficients calculated among the measurement sites. We found a very high level of correlation between outdoor $PM_{2.5}$ concentrations at the two sites. Indoor $PM_{2.5}$ concentrations were highly correlated as well. Pearson coefficients were equal to 0.97 for the outdoor correlations and 0.88 for the indoor correlations. Somewhat lower correlations were found between indoor and outdoor concentrations. I/O correlation coefficients at the traffic and the residential site were equal to 0.75 and 0.82, respectively. The latter coefficients are similar

to the highest values found in other studies (e.g. Hanninen et al., 2004) and this is probably related to the absence of indoor sources.

3.2.1.2 Indoor and outdoor UFP number concentrations

Based on the procedure outlined in the methods section, 0.83% and 1.33% of minute data in the residential and traffic site, respectively were classified as outliers and removed from the database. The completeness of hourly data at the outdoor traffic site, indoor traffic site, outdoor residential site, indoor residential site was 100%, 98%. 86% and 73%, respectively. Completeness of data at the residential site was lower because the switching unit had problems during the first campaign and nighttime indoor data at the residential site were not available.

Figure 1 (lower panel) and Table 1 give an overview of the ultrafine particle concentrations during the monitoring campaigns. Outdoor concentrations at the traffic site were much higher than at the residential site. Mean outdoor UFP concentrations measured at the traffic site during the three campaigns were 3.4, 3.2 and 1.7 times higher than at the residential site. The highest hourly value at the traffic site was 129,400/cm^3 while the highest value in the residential site was 37,790/cm^3. These findings were in good agreement with the findings of studies carried out in Los Angeles (Moore et al., 2009) and in Spain (Rivera et al., 2012). Similar results were also found in another study in Athens (Diapouli et al., 2011) showing a spatial variability ranging from ratios of 1.8 to 2.6 depending on the season. Significantly lower gradients were found in a study of four major European cities (Puustinen et al., 2007), but indoor sources were present.

The indoor concentrations of UFP at the residential site varied over a relatively small range compared to the larger day to day variations evident at the traffic site (Figure 2 and Figure 4). The ratio between indoor UFP concentrations at the two sites varied between the three campaigns (Table 1) with UFP levels at the traffic site approximately 2-4 times those of the residential site.

As with $PM_{2.5}$, the I/O ratio for UFP increased at the traffic site from 0.38 in the first campaign to 0.69 in the third campaign. On the contrary, the I/O ratio at the residential site remained more constant at around 0.5. Diapouli et al. (2011) found an I/O ratio for particles in the 10-400 nm size range equal to 0.6 in the 0.5-1 range of AER while I/O ratios between 0.3-0.4 were found in Erfurt (Germany) (Cyrys et al., 2004) and in other major European urban areas (Hoek et al., 2008b)

Ultrafine particles show marked increases between 7-9 a.m. and 7-8 p.m. (Figure 5) in correspondence with the rush hours. These peaks were significantly higher at the traffic site. The maximum concentrations in the morning were reached at 8 a.m. at the residential site and at 9 a.m.. at the traffic site. During the afternoon the maximum was reached at 9 p.m. at the residential site and at 7 p.m. at the traffic site during the first campaign. In the second campaign the afternoon peaks were shifted one hour later. Morning peaks were typically higher than the late afternoon peaks. The differences in UFP concentrations between indoor levels at the two sites were quite constant during the day for all campaigns. The differences in concentrations between indoor levels decreased slowly during the night leading to almost identical indoor concentrations at the two sites at around 5 a.m.. These results were in good agreement to those reported by Lianou et al. (2011).

The Pearson correlation coefficient between daily outdoor UFP concentrations at the two sites was equal to 0.89, significantly higher than those reported in other studies of particle number concentrations (Puustinen et al., 2007). Correlations between indoor UFP concentrations were much lower (R=0.42). Very similar correlation coefficients were found between indoor and outdoor UFP concentrations at the traffic and residential sites (R= 0.57 and 0.63 respectively). A broad range of correlations between I/O daily data was found by Hoek et al. (2008b) with values ranging from 0.41 in Helsinki to 0.80 in Athens. The correlation coefficient between hourly outdoor concentrations was equal to 0.71. Slightly higher correlations between indoor hourly data were found than for the daily data, with I/O hourly correlation coefficients almost equal to 0.60 for both sites.

With the exception of the third campaign, I/O ratios were markedly higher at the residential site than the traffic site (Table 1). This seems most probably related to more efficient loss of the traffic-generated ultrafine particles which predominate at the traffic site, as seen in Figure 6. The higher temperatures in the third campaign probably minimised the contribution of this aerosol component due to its semi-volatile nature (Fujitani et al., 2012) as reflected in the lower outdoor particle number counts in this campaign (Table 1).

3.2.1.3 Indoor and outdoor size distribution

Figure 6 shows the mean indoor and outdoor size distributions at the two sites. Multimodal distributions with sharp peaks at about 30 nm in the outdoor concentrations were found at the traffic site. The same peak was present also at the other indoor and outdoor monitoring sites though much less pronounced. A second peak was present at about 80-100 nm. This is typical of heavily trafficked sites, with the modes arising from the semi-volatile nucleation particles and solid graphitic particles respectively (Harrison et al., 2011). The plateau in the indoor distribution of the traffic site may be the joint effect of the coexistence of two modes, an Aitken mode peak at about 40-50 nm and an accumulation mode peak at 100-200 nm. The two principal peaks were evident for all hours during the day and all monitoring campaigns although their relative weight was highly variable, especially during the day. Figure 7 shows the huge increase of the 30 nm peak during the rush hours. The highest particle number concentrations were found at 9 a.m. (i.e. between 8 a.m. and 9 a.m). The subsequent hours showed a decrease of this peak with a further increase in the late afternoon (5 p.m. to 8 p.m.). The differences between morning and late-afternoon of particle number concentration in the 30 nm size range were more evident during the first campaign and decreased in the following campaigns. Similar patterns were seen at the residential site with a much less pronounced peak in the 30 nm size range. Indoor particle concentrations were lower compared to outdoor concentrations for both sites and all size bins. Very similar particle size distributions

were found after midnight at both indoor and outdoor sites. Indoor size distributions were similar to the findings of Hussein et al. (2004) with an increase of the nucleation mode associated with rush hours. Minor intra-day variations were found for particles in the accumulation mode. Much lower relative weight of the nucleation mode compared to the accumulation mode was found indoors compared to the outdoor size distributions, as reported in previous studies (Hussein et al., 2004; Diapouli et al., 2011). The comparison of the indoor size distributions between sites showed similar trends but relevant absolute differences. Differences in the nucleation mode were much reduced compared to outdoor distributions. This was probably due to the importance of size-dependent removal mechanisms that show a maximum in the lower and upper part of the spectrum. (Riley et al., 2002)

Diapouli et al. (2013) review data for ultrafine particles from three studies for penetration efficiency, showing values from 0.47-0.80. For infiltration factor, two studies give values close to 0.60 (Diapouli et al., 2013). While caution is needed in making comparisons of studies due to the high size-dependence of ultrafine particle losses, these values imply I/O ratios similar to the I/O ratios in Table 1 for UFP, which range from 0.38-0.69. The application of the highest penetration efficiency of 0.80 to an infiltration factor of 0.60 (both figures from Diapouli et al., 2013) suggests an I/O ratio equivalent to that in our experiment of 0.75.

The presence of a bi (or tri)-modal distribution was also shown in previous studies (Morawska et al., 2008; Hussein et al., 2005) and is in line with knowledge of particle emissions and transformation. The 30 nm mode is due to the combination of freshly nucleated particles formed as the exhaust gases are diluted with ambient air and particles directly emitted by vehicles (Charron et al., 2003). Particles emitted from diesel engines are in the size range 20–130 nm and from petrol engines in the range 20–60 nm (Ristovski et al., 2006). Emission factors for petrol (gasoline) cars are much lower than for diesel (Beddows and Harrison, 2008), although petrol vehicles during

acceleration show particle number emissions close to those observed from diesel vehicles (Graskow et al., 1998). Nucleation mode particles are associated with the hot exhaust gases expelled from the tailpipe of a vehicle. These gases cool and condense to form large numbers of very small particles in the air (Shi and Harrison, 1999). On-road dilution of the exhaust plume is very important in the generation of particles in the exhaust plume. These nucleation processes are favoured by low ambient temperatures and high relative humidity (Charron et al., 2003). In addition, the gaseous precursors condense or adsorb on to the surface of carbon particles in the accumulation mode. If the concentration of carbon particles is low, the gases will nucleate homogeneously, giving rise to large concentrations of semi-volatile nanoparticles.

The differing meteorological conditions between the first campaign and the other campaigns can explain the differing indoor/outdoor ratios. The cooler atmospheric conditions of the first campaign would tend to increase the semi-volatile nucleation mode particles relative to the coarser graphitic mode particles in the traffic aerosol. Upon entry into the building, not only would the nucleation mode fraction show a higher deposition velocity than the coarser graphitic mode (Riley et al., 2002), it would be subject to evaporation at the higher indoor temperatures (Dall'Osto et al., 2011) and the hydrocarbon vapours released would tend to adsorb to indoor surfaces (Weschler and Nazaroff (2008) and settled indoor dusts (Weschler and Nazaroff, 2010). Such processes would contribute to a relatively rapid loss of the nucleation mode of particles hence explaining both the changes in size distribution seen in Figure 5 and the far higher outdoor/indoor ratios seen at the trafficked site in the first campaign (Table 1). Semi-volatile components of the $PM_{2.5}$ might also show lower I/O ratios in cold weather due to enhanced volatilisation in the warmer indoor environment.

It is clear from Figures 6 and 7 that a large proportion of the sub-200 nm particles have been lost between the traffic and residential sites, as a result of dispersion processes, and of evaporation for

491 the smaller sized particles. However, as these particles are also lost with high efficiency in the
492 indoor environment, the mean indoor size distributions differ little between the sites, although a
493 concentration difference remains (Figure 6).

494

495 **3.2.1.4 Indoor and outdoor chemical composition of $PM_{2.5}$**

496 All concentrations of chemical components had more than 75% of values above LOQ with the
497 exceptions of residential indoor iron (73% of data above LOQ), traffic indoor potassium (60%),
498 residential indoor potassium (53%). No data on chemical composition of $PM_{2.5}$ was identified as
499 anomalous and removed from the database. OC was found to be the largest contributor to outdoor
500 PM2.5 mass at both sites followed by nitrates, elemental carbon and sulfates. The contribution of
501 OC to indoor $PM_{2.5}$ was even larger followed by elemental carbon and sulfates. Mean
502 concentrations appear in Figure 3.

503

504 Significant differences (paired t-test, significance level = 0.05) between traffic outdoor and
505 residential outdoor data were found for iron, elemental carbon and total carbon: 222 vs 135 ng/m^3
506 for iron, 2.9 vs 1.8 $\mu g/m^3$ for elemental carbon. Minor and non-significant differences were found
507 for the other chemical components. Very similar spatial gradients were found for indoor data. A
508 large impact of traffic proximity on iron and carbonaceous species has been reported in several
509 studies. Iron has been found an elemental marker for both exhaust and non-exhaust emissions (Pant
510 and Harrison, 2013) while carbonaceous particles have been related mainly to exhaust emissions.

511

512 Indoor concentrations were lower than outdoor for all chemical species and both sites with the only
513 exceptions of elemental carbon at the traffic site. The higher concentrations of elemental carbon
514 found indoors at the traffic site may have been caused by the specific location of the outdoor
515 measurement site. As already mentioned in Section 2.1, the outdoor monitoring site was some 50 m
516 away from the indoor site in a location which was less influenced by the canyon effect. Very large

differences were found especially for nitrates, ammonium, potassium and sulfates. The lowest I/O ratio was observed for nitrates. Average nitrate concentrations at the two outdoor measurements sites were 4.6 and 4.7 μg/m^3 while indoor concentrations were equal to 0.3 μg/m^3. I/O ratios for ammonium and sulfates were 0.3 and 0.6, respectively. The outdoor and indoor EC/TC ratios were respectively 0.35 and 0.4 at the traffic site and 0.24 and 0.13 in the residential site. These values are similar to those reported for outdoor urban air data by Naser et al. (2008).

Table 2 shows the Pearson correlation coefficients calculated among the chemical components data. Outdoor data at the two sampling sites were highly correlated (correlation coefficients always greater than 0.9). High correlation levels between within-city outdoor concentrations of organic carbon, elemental carbon, ammonium, nitrates and sulfates was found by Bell et al. (2011). Similar results were found for organic carbon and elemental carbon by Naser et al. (2008). High correlations were found also between indoor data with the exception of iron (R=0.33). Correlation levels were also generally very high in respect of I/O data. Low values were found only for ammonium (R=0.24) and iron (R=0.38) at the traffic site and ammonium (R=0.45) at the residential site. High correlations between indoor and outdoor concentrations of organic carbon and elemental carbon were also found by Sawant at al. (2004) in several schools in California . The I/O correlations for ammonium found by Sawant et al. (2004) showed large variability in the different schools. Particles of outdoor origin can undergo substantial changes and may be lost to building walls during indoor penetration. A study investigating the transformation of ambient ammonium nitrate aerosols in indoor environments has shown that measured indoor concentrations were considerably lower than the values predicted based only on penetration and deposition losses (Lunden et al., 2003). This is due to the semi-volatility of ammonium nitrate, leading to loss as nitric acid vapour and ammonia which attach to indoor surfaces. Varying ratios of volatile ammonium nitrate to involatile ammonium sulphate will lead to varying indoor-outdoor ratios of ammonium and hence the weaker correlation.

543 The only major inter-site differences in behaviour appearing in Figure 3 are for iron and elemental
544 carbon. Both are primary emissions from road traffic and the apparent behaviour at the traffic site
545 is probably anomalous because of the spatial separation of the indoor and outdoor samplers referred
546 to above.
547
548 **3.3 Strengths and Weaknesses of the Study**
549 A major strength of the study was the contemporary measurements of a number of particle metrics
550 and characteristics in indoor and outdoor environments with very different characteristics in relation
551 to traffic sources. The absence of indoor sources and the attention devoted to make air exchange
552 rates as similar as possible should reduce to a minimum the noise due to personal behavior and
553 specific indoor characteristics. Thus concentration gradients between sites should be almost solely
554 due to proximity to traffic sources.
555
556 A weakness was related to the use of a very simple system to impose an air exchange rate in the two
557 environments. Direct measurements of the air exchange rates were not made. However, it should be
558 taken into account that air exchange rates are almost always measured at only one or a few points in
559 time during a monitoring campaign. Therefore this is a general weakness of this type of study
560 because air exchange rates vary significantly in time in relation to outdoor conditions and several
561 other factors. Even if AER had been measured directly we would not have had much greater
562 guarantee on the exact level of AER in the two indoor environment during the 45 day measurement
563 period. Moreover, the main goal was to have similar AER in the two indoor environments and this
564 goal should have been achieved using two identical systems for ventilation. Our experimental
565 system should facilitate measurements under different controlled ventilation conditions.
566 Additionally, it has the benefit of allowing evaluation of indoor deposition processes independently
567 of losses during infiltration through the building shell.
568

4. SUMMARY AND CONCLUSIONS

This study addressed the issue of the difference in exposure to particles in relation to proximity to traffic within an urban area. In particular, we analysed indoor and outdoor $PM_{2.5}$ mass and chemical composition, size distribution and particle number concentrations in a heavy traffic site compared to a residential area.

Large spatial variability in the concentrations of UFP, iron and elemental carbon was found both indoors and outdoors. Concentrations of UFP were much higher at the traffic site. Mean indoor concentrations at the traffic site were higher than outdoor concentrations at the residential site. Indoor variability was higher than outdoors for iron and elemental carbon. Significant differences were also found for the shape of particle size distributions for outdoor particles while indoor particles showed very similar distributions. Indoor concentrations were much lower than outdoor for $PM_{2.5}$ mass and UFP, especially when outdoor concentrations were high and air temperatures low. Taking into account the chemical components, deposition to the building surfaces was protective especially for nitrates, ammonium, potassium, and sulfates. Both indoor and outdoor $PM_{2.5}$ concentrations were highly correlated while indoor UFP correlations were much lower than outdoor. The temporal trends of all chemical species at the two indoor sites were highly correlated with the exception of iron.

Our findings represent a contribution to understanding the appropriate particle metrics and data to be collected in epidemiological studies of the health effects of air pollution. In particular, our analyses showed that fixed site monitoring stations represent quite well the temporal trend of population exposure for $PM_{2.5}$ together with its chemical components. Although indoor exposure could be significantly lower than outdoor, they are spatially very well correlated considering both indoor and outdoor concentrations. Some caution should be adopted for iron which showed high correlation between outdoor data but low correlation between indoor data. UFP concentrations

showed lower correlations compared to $PM_{2.5}$, in particular between indoor concentrations. Therefore fixed site stations could be less representative of the temporal trends of population exposure. With regards to size distribution, an important decrease of the relative concentration of the nucleation mode relative to the accumulation mode in the indoor air compared to the outdoor was found at the traffic site.

With regards to the epidemiological studies aiming at assessing the health impact of proximity to traffic, we observed that largest gradients in exposure were found for UFP, iron and elemental carbon. Tiny and insignificant differences were found for $PM_{2.5}$ and the other chemical components. Indoor spatial gradients generally reflected outdoor gradients quite closely.

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TABLE LEGENDS

Table 1 Summary statistics of $PM_{2.5}$ mass (μg m^{-3}) and UFP number (cm^{-3}) during the monitoring campaigns.

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Table 1. Summary statistics of $PM_{2.5}$ mass (μg m^{-3}) and UFP number (cm^{-3}) during the monitoring campaigns.

	Traffic					**Residential**				
	Number of valid data	Outdoor mean (min - max)	Number of valid data	Indoor mean (min - max)	I/O mean	Number of valid data	Outdoor mean (min - max)	Number of valid data	Indoor mean (min - max)	I/O mean
PM2.5 (24-hour data)										
All data	45	22.5 (5.1 - 72.0)	45	13.0 (5.3 - 27.0)	0.74	45	21.3 (3.9 - 70.0)	45	10.0 (3.1 - 31.0)	0.59
1st campaign	15	40.7 (20.0 - 72.0)	15	16.3 (11.0 - 27.0)	0.42	15	38.4 (18.0 - 70.0)	15	15.1 (8.0 - 31.0)	0.40
2nd campaign	15	12.9 (5.1 - 27.6)	15	10.2 (5.3 - 15.2)	0.88	15	13.0 (3.9 - 28.7)	15	6.6 (3.1 - 10.8)	0.70
3nd campaign	15	14.0 (7.7 - 18.5)	15	12.6 (8.4 - 18.1)	0.92	15	12.5 (6.4 - 16.1)	15	8.4 (6.0 - 13.7)	0.69
UFP (1-hour data)										
All data	1,075	24,006 (2,193 - 129,386)	1,063	8,641 (1,418 - 21,933)	0.48	934	6,810 (1,446 - 37,790)	785	2,836 (396 - 13,375)	0.52
1st campaign	360	31,042 (3,973 - 129,386)	360	9,117 (2,568 - 21,933)	0.38	292	10,148 (3,642 - 37,790)	146	4,885 (2,969 - 13,375)	0.54
2nd campaign	357	25,752 (2,193 - 108,588)	353	7,939 (1,418 - 20,407)	0.38	282	6,024 (2,156 - 22,191)	283	2,439 (1,315 - 6,088)	0.47
3nd campaign	358	15,189 (2,552 - 60,773)	350	8,859 (2,363 - 20,952)	0.69	360	4,718 (1,446 - 13,988)	356	2,311 (396 - 8,287)	0.54

Sampling periods: 1st campaign from 22 February 2012 to 7 March 2012; 2nd campaign from 16 to 30 April 2012; 3rd campaign from 28 May to 12 June

Table 2. Pearson correlation coefficients for different chemical species.

	Traffic indoor vs traffic outdoor			Residential indoor vs residential outdoor			Traffic outdoor vs residential outdoor			Traffic indoor vs residential indoor		
	R	Slope	Intercept ($\mu g/m^3$)	R	Slope	Intercept ($\mu g/m^3$)	R	Slope	Intercept ($\mu g/m^3$)	R	Slope	Intercept ($\mu g/m^3$)
Iron (Fe)	0.38	0.64	0.066	0.87	0.29	0.014	0.9	1.62	0.003	0.33	11.61	-0.397
Ammonium (NH_4)	0.23	0.08	0.48	0.42	0.12	0.35	0.99	0.97	0.06	0.95	1.09	-0.01
Nitrates (NO_3)	0.86	0.03	0.17	0.81	0.04	0.16	1	0.97	0.04	0.93	0.69	0.07
Sulfates (SO_4)	0.99	0.72	-0.22	0.94	0.69	-0.33	0.97	1.12	-0.35	0.96	1.15	-0.07
Organic carbon (OC)	0.91	0.52	2.42	0.88	0.58	2.21	0.99	0.9	0.65	0.97	0.8	1.02
Elemental carbon (EC)	0.77	0.74	1.2	0.94	0.48	0.05	0.98	0.83	1.48	0.68	1.51	2.03
Total carbon (TC)	0.93	0.55	3.91	0.92	0.55	2.27	0.99	0.89	2.11	0.91	0.88	3.12

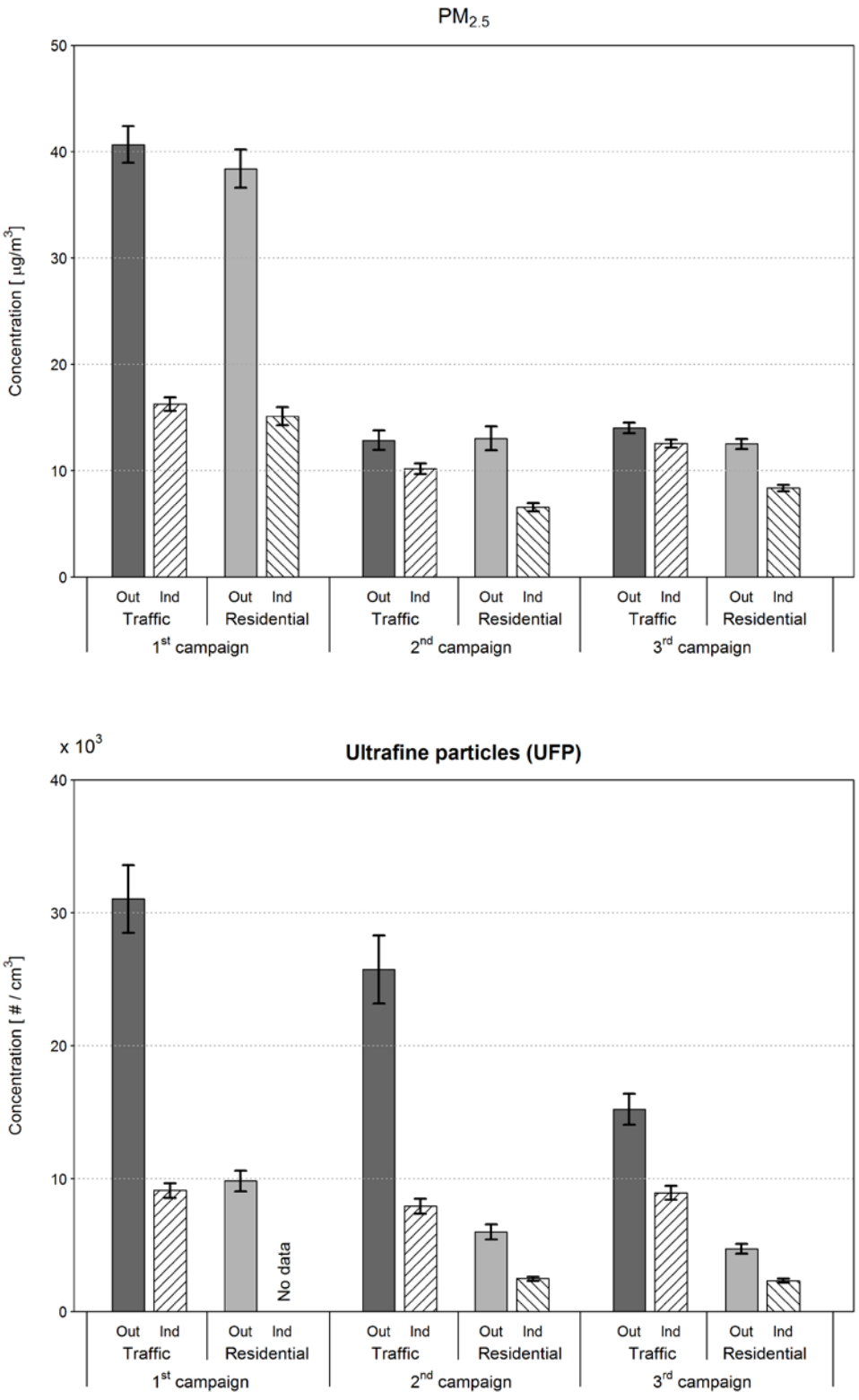

Figure 1. Average value and standard error of $PM_{2.5}$ (upper panel) and UFP (lower panel) during the three monitoring campaign.

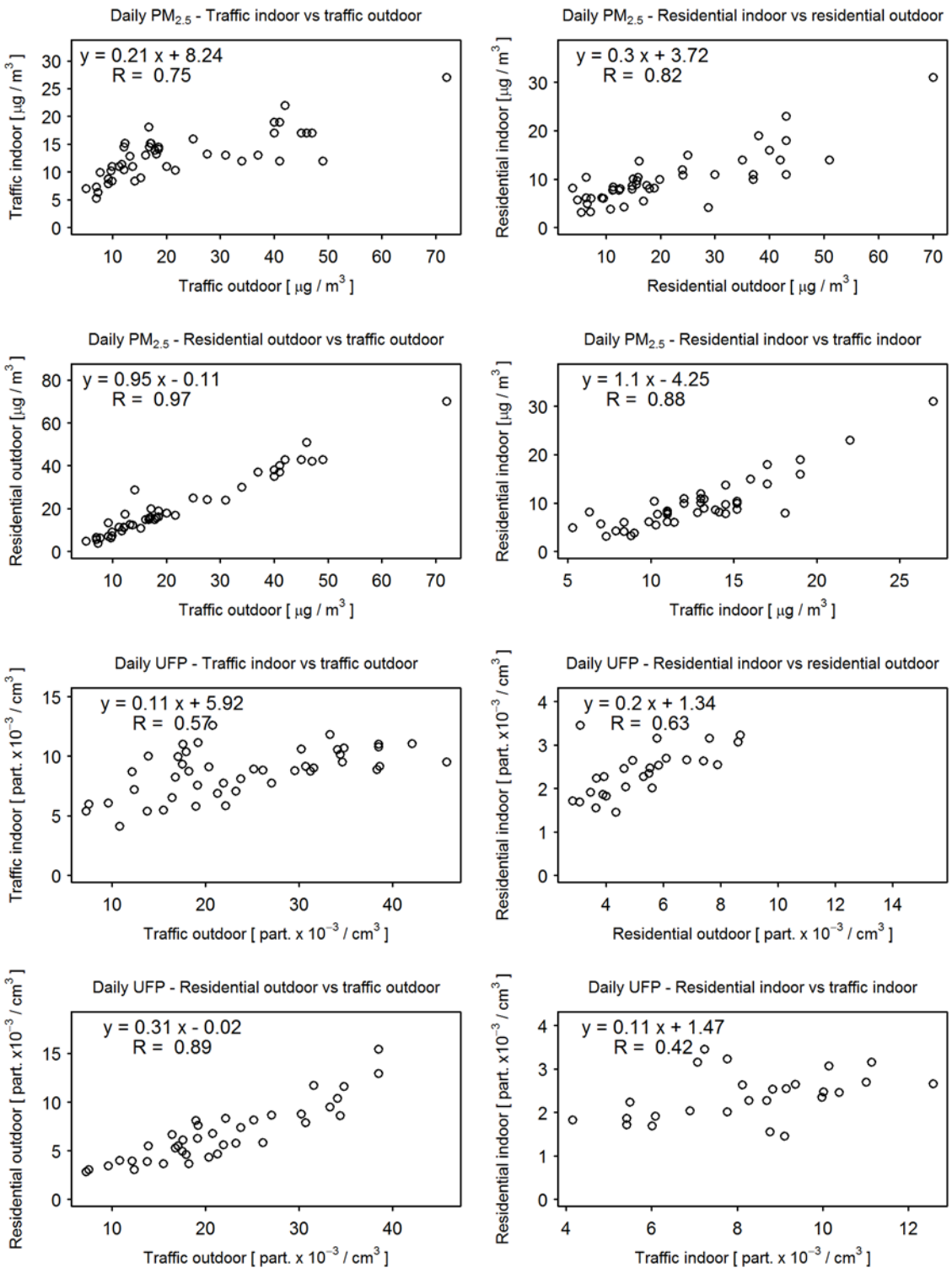

Figure 2. Scatter plot for daily $PM_{2.5}$ mass and UFP number.

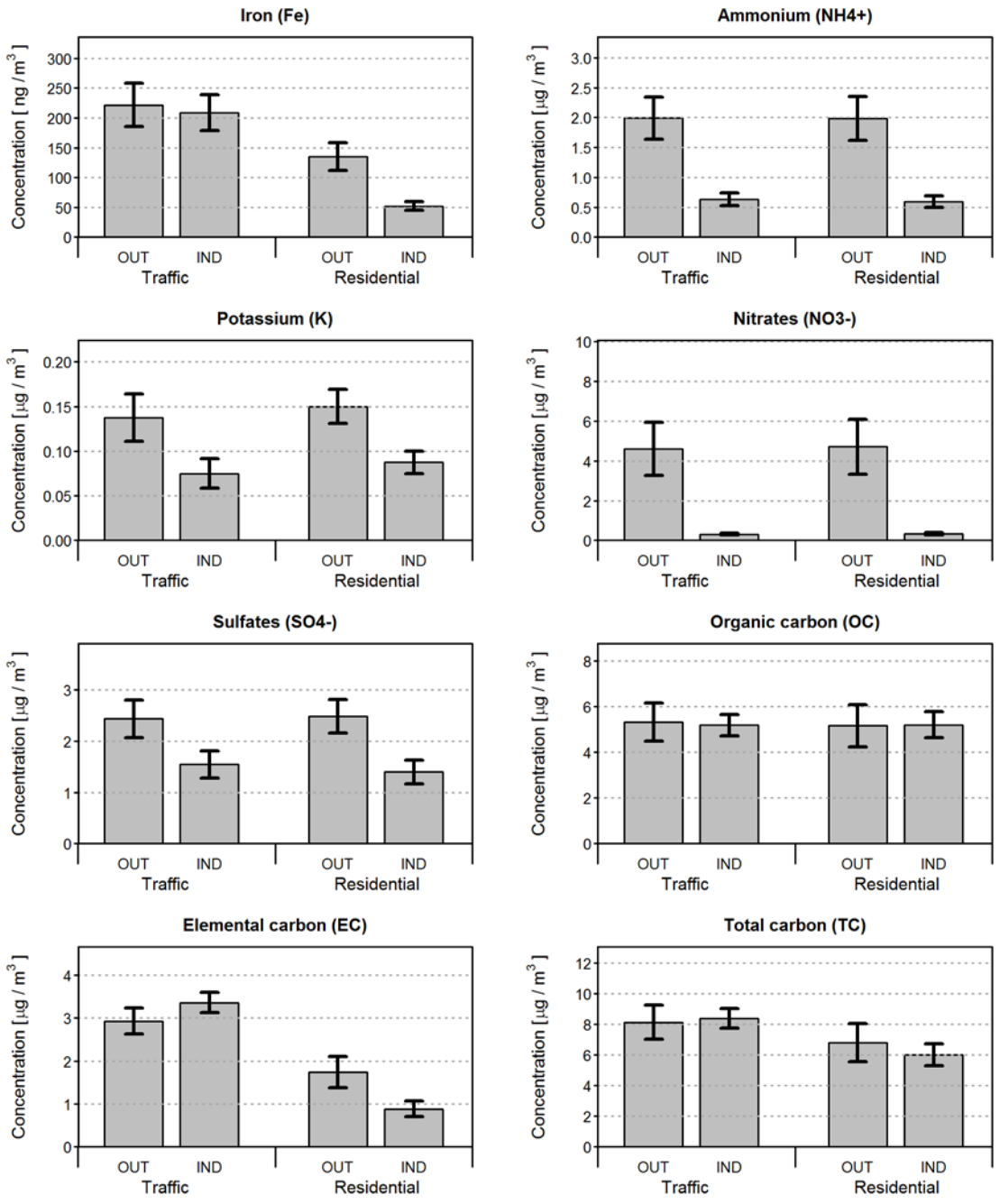

Figure 3. Average value and standard errors of the chemical species.

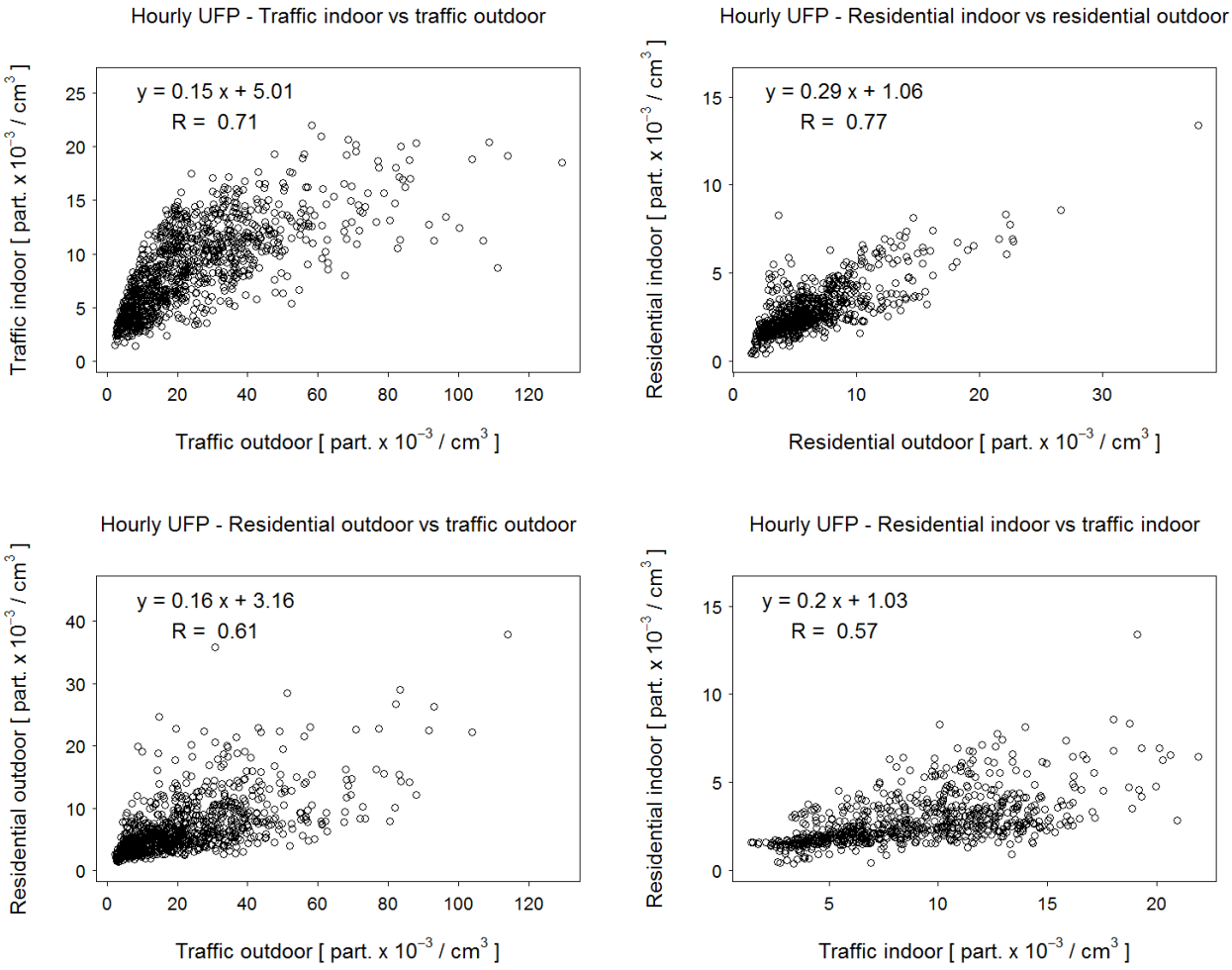

Figure 4. Scatter plot for hourly UFP number.

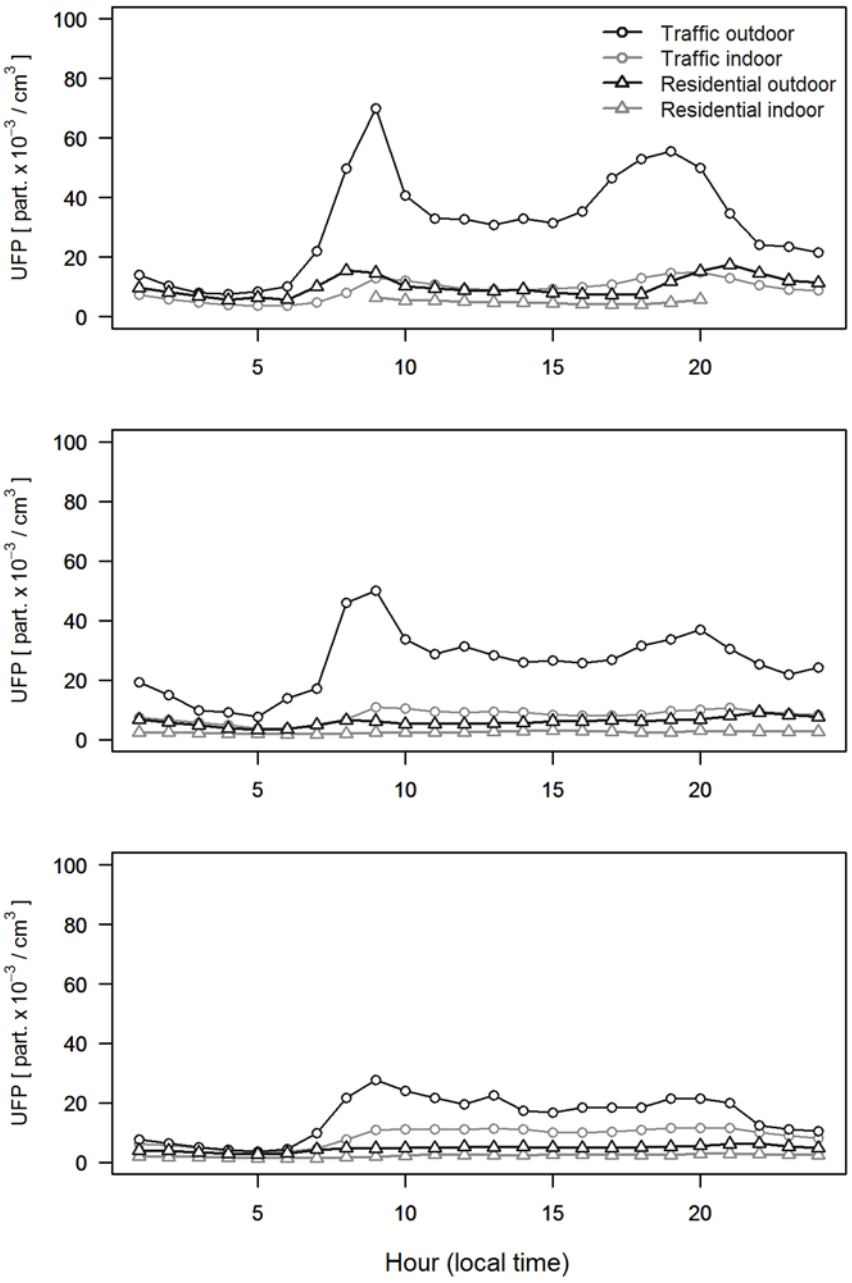

Figure 5. Daily temporal trend of UFP number during the three monitoring campaigns.

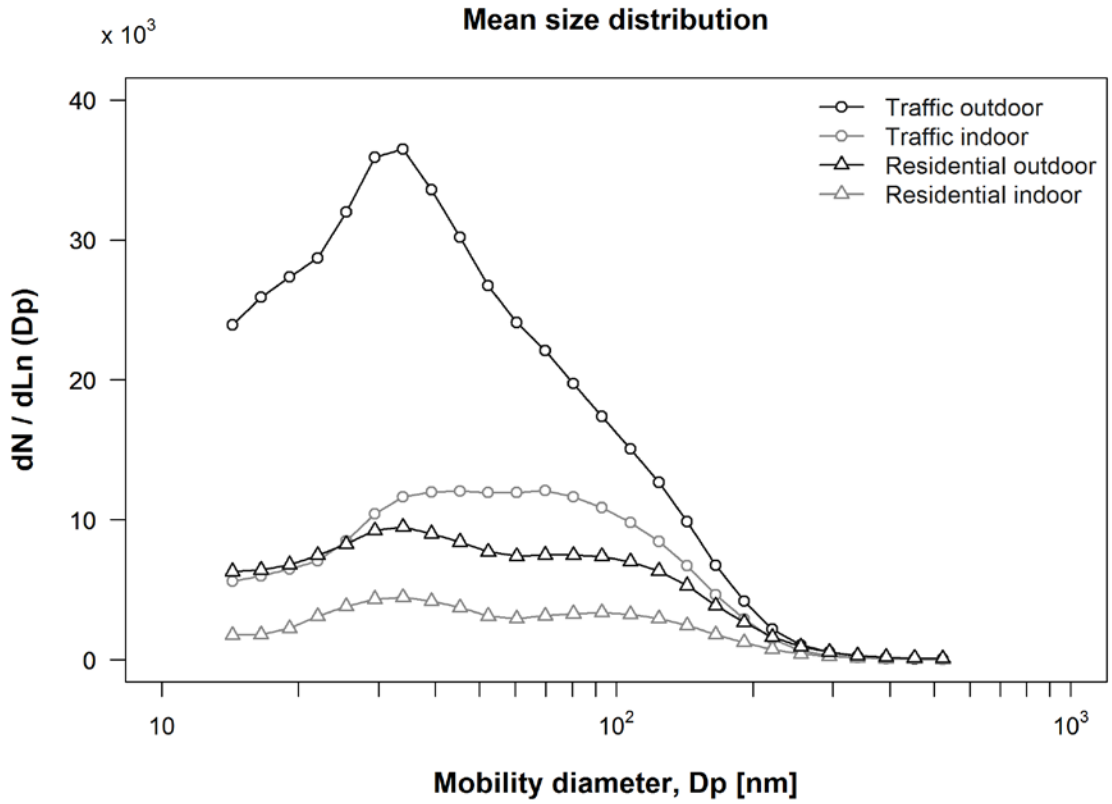

Figure 6. Mean particle size distribution of hourly data.

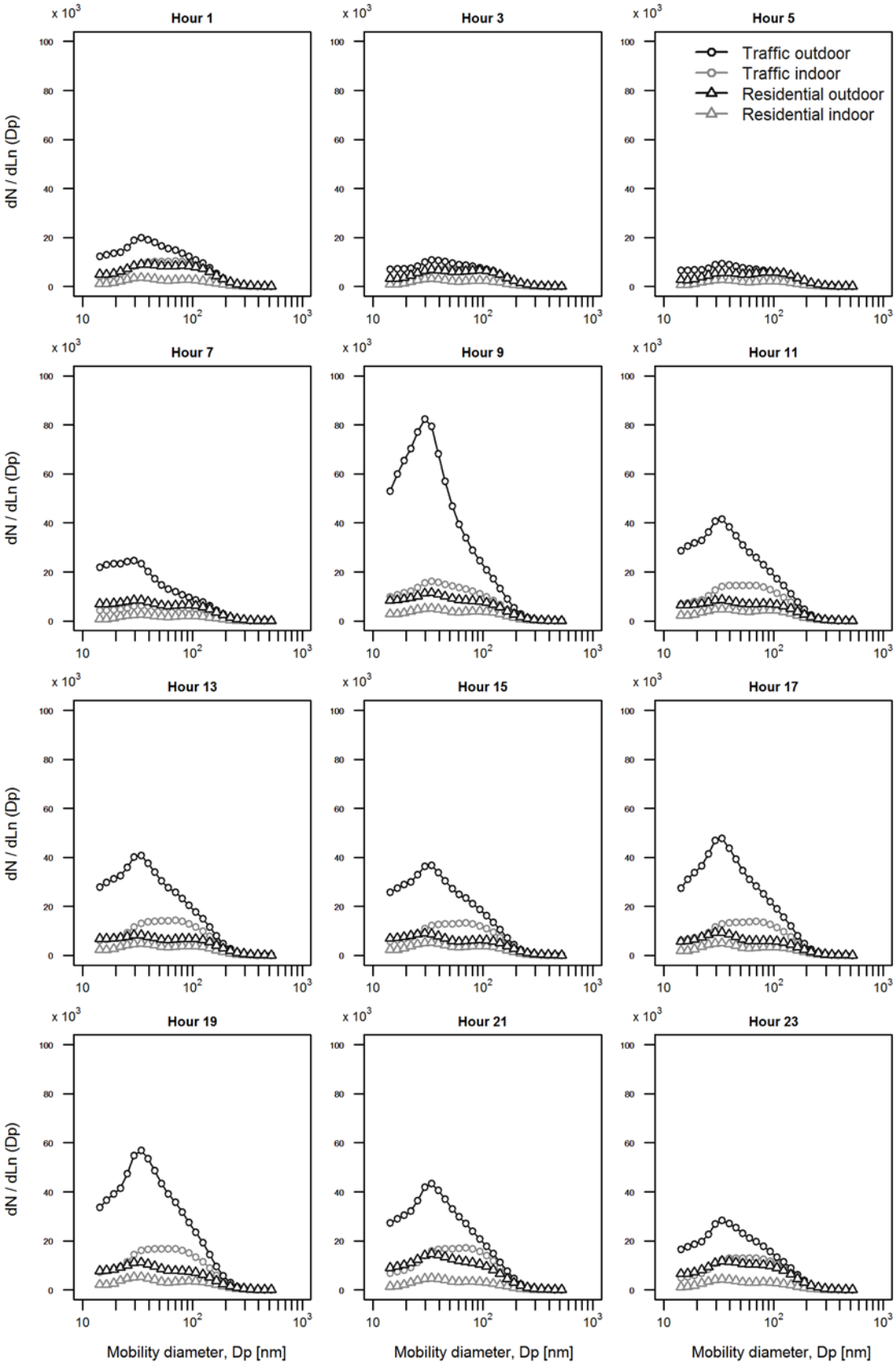

Figure 7. Mean particle size distribution of hourly data at specific time of the day.