Vertical Variation of PM2.5 Mass and Chemical Composition, Particle Size Distribution, NO2, and BTEX at a High Rise Building

Zauli Sajani, Stefano; Marchesi, Stefano; Trentini, Arianna; Bacco, Dimitri; Zigola, Claudia; Rovelli, Sabrina; Ricciardelli, Isabella; Maccone, Claudio; Lauriola, Paolo; Cavallo, Domenico Maria; Poluzzi, Vanes; Cattaneo, Andrea; Harrison, Roy

DOI:
10.1016/j.envpol.2017.12.090

Document Version
Peer reviewed version

Citation for published version (Harvard):
Zauli Sajani, S, Marchesi, S, Trentini, A, Bacco, D, Zigola, C, Rovelli, S, Ricciardelli, I, Maccone, C, Lauriola, P, Cavallo, DM, Poluzzi, V, Cattaneo, A & Harrison, R 2018, 'Vertical Variation of PM2.5 Mass and Chemical Composition, Particle Size Distribution, NO2, and BTEX at a High Rise Building' Environmental Pollution, vol. 235, pp. 339-349. https://doi.org/10.1016/j.envpol.2017.12.090

Vertical variation of $PM_{2.5}$ mass and chemical composition, particle size distribution, NO_2, and BTEX at a high rise building

Stefano Zauli Sajani[1*], Stefano Marchesi[1], Arianna Trentini[2], Dimitri Bacco[2] , Claudia Zigola[3], Sabrina Rovelli[4], Isabella Ricciardelli[2], Claudio Maccone[2], Paolo Lauriola[1], Domenico Maria Cavallo[4], Vanes Poluzzi[2], Andrea Cattaneo[4] and Roy M. Harrison[5†]

[1] Regional Centre for Environment and Health
ARPAE Emilia-Romagna, Via Begarelli, 13
41121 Modena, Italy

[2] Regional Centre for Urban Areas
ARPAE Emilia-Romagna, Via Rocchi, 19
40138 Bologna, Italy

[3] Provincial District of Ravenna
ARPAE Emilia-Romagna, Via Giulio Alberoni, 17,
48121 Ravenna, Italy

[4] Department of Science and HighTechnology
Università degli Studi dell'Insubria
Via Valleggio 11
22100 Como, Italy

[5] Division of Environmental Health and Risk Management
School of Geography, Earth & Environmental Sciences
University of Birmingham
Edgbaston, Birmingham, B15 2TT
United Kingdom

[*] Corresponding Author: Stefano Zauli Sajani, Email: szauli@arpae.it, Via Begarelli 13, 41121 Modena (Italy), Tel: +39 (059) 433626

[†] Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia

ABSTRACT

Substantial efforts have been made in recent years to investigate the horizontal variability of air pollutants at regional and urban scales and epidemiological studies have taken advantage of resulting improvements in exposure assessment. On the contrary, only a few studies have investigated the vertical variability and their results are not consistent. In this study, a field experiment has been conducted to evaluate the variation of concentrations of different particle metrics and gaseous pollutants on the basis of floor height at a high rise building. Two 15-day monitoring campaigns were conducted in the urban area of Bologna, Northern Italy, one of the most polluted areas in Europe. Measurements sites were operated simultaneously at 2, 15, 26, 44 and 65 m a.g.l. Several particulate matter metrics including $PM_{2.5}$ mass and chemical composition, particle number concentration and size distribution were measured. Time integrated measurement of NO_2 and BTEX were also included in the monitoring campaigns. Measurements showed relevant vertical gradients for most traffic related pollutants. A monotonic gradient of $PM_{2.5}$ was found with ground-to-top differences of 4% during the warm period and 11% during the cold period. Larger gradients were found for UFP (~30% during both seasons) with a substantial loss of particles from ground to top in the sub-50 nm size range. The largest drops in concentrations for chemical components were found for Elemental Carbon (-27%), iron (-11%) and tin (-36%) during winter. The ground-to-top decline of concentrations for NO_2 and benzene during winter was equal to 74% and 35%, respectively. In conclusion, our findings emphasize the need to include vertical variations of urban air pollutants when evaluating population exposure and associated health effects, especially in relation to some traffic related pollutants and particle metrics.

Capsule abstract: Need to include vertical variations of air pollutants when evaluating population exposure

Keywords: $PM_{2.5}$; Size distribution; Chemical composition; Exposure; Vertical variability.

1. INTRODUCTION

Throughout the last 30 years, an increasing body of research has consistently shown statistically significant positive associations between ambient $PM_{2.5}$ and mortality and various indices of morbidity (REVIHAAP, 2013). However it is still not clear which physical and/or chemical characteristics of particulate matter (PM) are most closely linked to health effects (REVIHAAP, 2013, Brunekreef and Holgate, 2002, Harrison and Yin, 2000) as well as the mechanisms of action. Recently, research has focused on ultrafine particles (UFP, particles with aerodynamic diameter <100 nm), because of their ability to affect deep airways (Peters et al., 2011; Hoek et al., 2010; von Klot et al., 2005), and to the specific chemical components of particles (Samoli et al., 2016; Basagana et al., 2015).

Moreover, while research is generally more focused on various metrics of PM, some gaseous pollutants such as nitrogen dioxide (NO_2), benzene, toluene, ethylbenzene, xylenes (BTEX) are not only responsible for relevant health effects (Andersen et al., 2011; Gauderman et al., 2005) but are also used as air quality indicators, and markers of traffic-related pollution (Spinazzè et al., 2013; Janssen et al., 2001).

Substantial efforts have recently been made to investigate the horizontal variability of air pollutants at regional and urban scales (Eeftens et al., 2012). In this field, significant improvements have been made in the estimation of ambient air pollutant concentrations within urban areas by a mix of fixed site monitoring station data with satellite data, dispersion models and Land Use Regression models (LUR) which combine measured air pollution concentrations together with predictor variables such as various traffic-related variables, land use, and population density (Hoek et al., 2008a). These studies have shown a limited spatial variability for $PM_{2.5}$ mass while more substantial differences at a suburban scale were found with respect to UFP concentrations (van Nunen et al., 2017), some gaseous pollutants such as NO_2 and BTEX (Wang et al., 2013) and some traffic-related chemical components such as iron and elemental carbon (de Hoog et al., 2013). Marked spatial variability of

some pollutants was also observed at the micro-scale near highways (He and Dhaniyala, 2012) or crossroads (Goel and Kumar, 2016) and at buildings which fronted onto a trafficked street (Zauli Sajani et al., 2016).

Therefore, in the last decade the horizontal variability of air pollutants on a regional and urban scale has been deeply investigated and their findings recently included in the most important epidemiological studies (Beelen et al., 2014; Raaschou-Nielsen et al., 2013). On the contrary, only a few studies have assessed the vertical variability of air pollutant concentrations within urban areas.

During the 90s some studies investigated the vertical variation of gaseous pollutants within street canyons, i.e. streets flanked by buildings on both sides creating a canyon-like environment. Several studies were published on CO and NO_2 (Qin, 1993; Zoumakis, 1995; Vakeva, 1999) and showed a marked decrease of concentration with increasing height.

Studies assessing the vertical profile of different particle metrics such as $PM_{2.5}$ mass and chemical composition, particle number concentration (PNC) and size distribution are more recent. As with gaseous pollutants, the studies were most frequently focused on street canyon configurations (Kumar et al., 2008; Weber at al., 2006; Li et al., 2007). To our knowledge only very few papers have assessed the vertical variation of air pollutants on isolated buildings or in non-canyon configurations. Table 1 gives an overview of these studies for the air pollutants and particle metrics considered in this study. It is clear from the table that very few studies are available in literature on this topic and most of them are from Asian countries. With regards to particle metrics only one study was carried out in Europe but not within an urban area (Kholer, 2005; Imhof, 2005). To author's knowledge no studies are available on vertical profiles of metals and ions.

In this paper we present the results of an experimental study aimed at assessing the vertical variation of air pollution at an isolated tall building located in a highly polluted urban area in Northern Italy. $PM_{2.5}$ mass and chemical composition, particle size distribution, NO_2 and BTEX

concentrations were simultaneously measured at different heights during the warm and the cold season.

2. METHODS

2.1 Study design and study area

The study area is the city of Bologna, Italy. This is an urban area of about 400,000 inhabitants located in the Po plain, a region surrounded by mountains and affected by high levels of air pollution. In the period 2013-2016 the city-average $PM_{2.5}$ annual mean concentration (derived from two fixed-site monitoring stations) was 17.9 µg m^{-3} (EU limit 25 µg $m^{-3}$and WHO guideline value 10 µg m^{-3}) and the annual mean number of exceedances of the WHO $PM_{2.5}$ daily guideline value (25 µg m^{-3}) was 72. All parameters monitored in the study have traffic as the main source or one of the major ones (https://webbook.arpae.it/shared/documenti/ARIA/Emissioni/Ar_Emissioni_Rer_2010.xls). For some pollutants traffic is a primary source (BTEX) or is a major contributor (NO_2), while for $PM_{2.5}$ the contribution of traffic emissions to secondary formation is more relevant (Larsen et al., 2012).

The monitoring site is a tall (~ 70 m high) building located at 2km from the historical centre very close to a trafficked street (daily traffic volume of about 41000 vehicles per day with 3–4% heavy duty vehicles). Figure 1 shows an overview of the monitoring sites and area. The building has a very regular shape and instruments were placed on balconies which fronted the busy street. Instruments were placed at the ground floor (at 2 m above ground, from now on Level 0), at the 2nd floor (15 m above ground – Level 1), at the 5th floor (26 m above ground – Level 2), at the 10th floor (44 m above ground – Level 3) , at the 16th floor (65 m above ground – Level 4). $PM_{2.5}$, NO_2 and BTEX were measured at each level while chemical composition was analyzed only at level 0, 2 and

4 due to funding contraints. The availability of two spectrometers allowed the monitoring of particle size distribution at the ground and at the 16th floor.

Two monitoring campaigns were conducted in the period February-June 2015. Each monitoring campaign lasted for 15 days: 1st campaign from 20 February to 6 March and 2nd campaign from 28 May to 11 June. Supplemental campaigns were performed from 15 to 26 February 2016 for BTEX and from 22 September to 9 October 2016 for particle size distribution due to instrumental problems in the first and second campaign, respectively.
All the above mentioned parameters were measured simultaneously at the different floors.

2.2 Instrumentation and monitoring procedure

$PM_{2.5}$ concentrations were measured by means of five identical gravimetric samplers (Skypost PM, TCR TECORA Instruments, Corsico, Milan, Italy) operating at a flow rate of 2.3 $m^3 h^{-1}$. The instruments were placed on balconies at Level 0,1,2,3,4 (see figure 1). Samples were weighed following the procedure defined in European Standard EN 12341:2014. $PM_{2.5}$ samples were collected on quartz fiber filters (Whatman, 47 mm diameter) and analyzed for various chemical species. Filters were changed daily at each measurement site, and chemical speciation was performed sequentially every three days for metals, ions, and carbon (Elemental Carbon - EC - and Organic Carbon - OC). During the first two campaigns EC and OC were measured on an 8 hour basis in order to avoid an overload of the filters (Ricciardelli et al., 2017). In this paper we present the data of the chemical species having more than 50% of contemporary data above the limit of quantification (LOQ). LOQs for chemical components as well as methods and procedure for chemical speciation are reported in the Supplementary Material (Table 1_S).

Two Fast Mobility Particle Sizers (FMPS model 3091; TSI, Shoreview, MN, USA) were used to measure particle size distributions and to estimate UltraFine Particle (UFP) concentrations. The FMPS spectrometer measured the size and number concentration of particles from 5.6 nm to 560 nm with 32 size bins every one second (Tammet et al. 2002). Size bins below 8 nm were not included in the analysis because of the amount of data below the detection limit and also because of artifacts in the size distribution observed in other studies (Kaminski et al., 2013; Jeong et al., 2009). Intercomparison tests between the two FMPS were carried out before and after each monitoring campaign in order to guarantee comparability between the two spectrometers. The two instruments were operated in parallel for some days (2-3 days) measuring ambient air. Then linear regression coefficients were calculated for each season and size bin taking always the same instrument as reference. Finally, size specific corrections were applied to the channels below 100 nm based on the paper by Jeong et al. (2009). The number of particles detected in the channels between 8 and 100 nm was considered as UFP concentration. Data were recorded every minute. Hourly and daily averages were calculated from 1-minute data after QA/QC analyses (see the next section).

NO_2 and BTEX samples were collected by means of radial symmetry diffusive samplers (Radiello®; Sigma-Aldrich Inc., Milano, Italy). Diffusive samplers were exposed in duplicate at each study floor over the entire summer and winter campaigns. From each batch of samples, two laboratory blanks were always retained and analyzed following the same analytical procedure applied on real samples, to check for any possible blank contributions.

For NO_2 analysis, 5 mL of ultrapure water were poured into the plastic tube containing the cartridge. The solution was stirred well for 2 min to allow the complete dissolution of nitrite ions into the water. Appropriate reagents (sulfanilamide and NEDA) were subsequently added to the aqueous solution and NO_2 concentrations were determined colorimetrically via UV/visible spectrophotometry at the wavelength corresponding to the maximum absorbance value (537 nm) (Vardoulakis et al., 2009). The precision of final results, expressed as the coefficient of variation

(CV%) of duplicate measurements, was always quite good (0.1-11.1%; in two cases, CV% was > 15%). The limit quantification (LOQ), calculated as ten-fold the standard deviation of laboratory blanks divided by the nominal sampling volume, was 3.6 µg m^{-3}. All NO_2 measurements were above the LOQ.

BTEX were analyzed by solvent desorption (Cocheo et al., 2009). Briefly, the extraction was accomplished by introducing 2 mL of CS_2 and 100 µL of internal standard solution (2-fluorotoluene; final concentration: 5 ppm) directly into the radiello® storage tube without removing the cartridge. After 30 min, a volume of 5 µL of the CS_2 solution was injected into the gas chromatograph (GC). The GC system (HRGC MEGA 2 series, MFC 800, Fisons Instruments) was equipped with a capillary column (Supelcowax-10, 60 m x 0.53 mm, film thickness 1 µm) and a Flame Ionization Detector (FID, EL-980, Fisons Instruments) set at 250°C. The following temperature program was used: a first isotherm at 50°C for 5 min, followed by a run from 50 to 100°C at 2°C min^{-1}, a further run from 100 to 200°C at 10°C min^{-1} and a final isotherm at 200°C for 10 min with helium as the carrier gas (1 mL min^{-1}) and nitrogen as the auxiliary gas (30 mL min^{-1}). Also for BTEX, the precision was in a satisfactory range (0.1-14.4%). LOQs calculated as ten-fold the standard deviation of the lowest standard solution used for calibration (0.1 ppm for benzene, ethylbenzene and xylenes; 0.2 ppm for toluene) were equal to 0.02, 0.05, 0.005, 0.006, 0.006 and 0.007 ppm for benzene, toluene, ethylbenzene, p-, m- and o-xylenes, respectively. All BTEX measurements were above the respective LOQs.

Meteorological data were obtained from the “Bologna Urbana” station (http://www.arpa.emr.it/sim/?osservazioni_e_dati/dati_stazioni_regionali) belonging to the urban meteorological network of ARPAE Emilia-Romagna. The station is located at an horizontal distance of 3.0 km from the building and is on the top of a 25-metres building. The station measures hourly temperature, relative humidity, and wind speed and direction.

2.3 QA/QC and statistical analysis

Agreements among gravimetric $PM_{2.5}$ measurements were checked in several intercomparison campaigns (Zauli Sajani et al., 2016). The differences for slope (from identity) and intercepts (from zero) were never significant and no corrections were applied to $PM_{2.5}$ data. 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 using an orthogonal regression approach (Fuller, 1987), which is the most appropriate when variables are affected by errors and are not causally related. Data with residuals larger than three times the standard deviation were identified as anomalous.

The procedure adopted for quality control of FMPS data was already presented in a previous paper (Zauli Sajani et al., 2016). In brief, UFP minute data stratified in time slots of three hours classified as anomalous if they were higher than the mean plus three times the standard deviation calculated for each campaign and time slot. Non-anomalous data were then averaged on an hourly and daily basis.

Due to the lack of normality of the statistical distributions of several parameters, we decided to adopt a non-parametric approach for summary statistics and tests. Statistical significance of the differences between the ground floor and 16^{th} floor was evaluated by applying the paired Wilcoxon test with a significance level of 95%, i.e. differences were considered significant with p-value less than 0.05 and highly significant with p-value less than 0.01.

Multiple linear regression with standardized coefficients were applied to analyze the relationship between ground-top differences in concentrations of $PM_{2.5}$ and UFP and some meteorological parameters (mixing height, temperature, relative humidity and wind speed). Collinearity was verified using the variance inflationary factor (VIF) test.

Statistical analyses were performed using the R package (Version 3.0.1).

3. RESULTS AND DISCUSSION

Weather conditions during the monitoring campaigns were quite representative of the typical climatic characteristics of the area. In particular, wind roses derived from both the cold and the warm measurement periods were very similar to the wind roses obtained from cold (Jan-Apr and Oct-Dec) and warm (May-Sep) months in the years 2015-2016 (Figure 1_S and Table 4_S in Supplementary Material). Both campaigns were characterized by low wind speed (2.1 and 1.8 m s^{-1} during the cold and the warm period, respectively), very similar to the normal for the area (1.8 m s^{-1} for the cold months and 1.9 m s^{-1} for the warm months). Hourly temperature ranged from 1.8 to 14.1 °C during the cold period (data from the meteorological station) and from 13.3 to 31.8ºC during the warm period (Table 2). Precipitation was scarse during both measurement periods. Traffic flows in the street fronted by the monitoring site were almost constant during all measurement periods (Figure 2_S in Supplementary Material).

No anomalous data were identified by the QC procedure outlined in the methods section.

3.1 $PM_{2.5}$ and chemical components

Summary statistics of $PM_{2.5}$ levels during the two monitoring campaigns is reported in Table 3. We found a small monotonic vertical gradient for $PM_{2.5}$ with ground – top differences equal to 4% in the warm period and 11% in the cold period (Figure 2) with only the latter difference being statistically significant. The comparison between seasons of the ground-top differences was found to be highly significant. In a one-week measurement period during the Australian warm season, Quang et al. (2012) found a larger decrease (about 50%) of $PM_{2.5}$ concentrations between the ground and the top of the building named B (78.5 m). High vertical gradients were also found in Building A (14.5 m) and C (21.5 m) during the Australian cold period with marked drops of concentrations above 5-6 m from the ground. A 16% decrease in concentrations between 8 and 100

m was found in Beijing (Chan et al., 2005) during summer. A 62% decrease from ground to 79 m was observed by Wu at al. (2002) in a winter 1-day measurement campaign in Macao, China. All the above mentioned studies used portable photometers to measure $PM_{2.5}$ concentrations.
Different vertical profiles were found by Kalaiarasan et al. (2009) in a study carried out in Singapore. The experimental results showed that mean $PM_{2.5}$ particle mass concentrations were markedly higher at the midfloors (10^{th}) of two high rise buildings (20-storey and 16-storey) when compared to those measured at upper and lower floors (17^{th}/14^{th} and 4^{th}, respectively). The particulate samples were collected using portable, battery operated low volume samplers.
No well defined relationship between floor and $PM_{2.5}$ concentration was found by Jung at al. (2011) in monitoring campaigns lasting from October 2005 to July 2010 in 339 residences in New York City. The somewhat inconsistent picture of literature findings is probably due to the rather short monitoring periods of the studies, to the climatic differences of the measurement sites, and to the frequent use of portable instruments. We also found some other studies in literature focusing on canyon configurations (Weber et al., 2006; Kumar et al., 2008; Li et al, 2007) that were considered less comparable with the present study.

The analyses carried out on the vertical variation of chemical components (see Table 2_S and Table 3_S in Supplementary Material for descriptive statistics of data) gave different results with respect to the various chemical components. Figures 3 and 4 show the mean differences in concentrations for the selected ions, carbonaceous species and metals at Level 0, Level 2 and Level 4. Much larger vertical gradients were found for EC compared to OC in both seasons with EC concentrations 27-28% lower at Level 4 compared to the ground and OC concentrations at the highest level less than 3% lower than at the ground. This can be easily explained considering that EC is commonly used as a good tracer of local traffic (Cao et al., 2005) while OC can also originate from chemical reactions in the atmosphere (Saarikoski et al., 2008). As a consequence the OC/EC ratio increased with height from 3.11 to 4.10 during the cold period and from 3.36 to 4.46 during the warm period. No

statistically significant differences were found for the ground-top differences.

Different vertical profiles were found among the metal chemical components. Almost constant concentrations or a slight decrease with height at the three levels in both seasons were found for non-traffic related elements such as K, As, V and La. K is regarded as a tracer for biomass burning (Calvo et al., 2013; Saarikoski et al., 2007; Reid et al., 2005) while As and V as tracers of industrial emissions, coal and unrefined fossil fuel combustion (Calvo et al., 2013; Gugamsetty et al., 2012). Marked decreases in both season were found for Fe and Sn, as these are typical traffic-related trace elements emitted from brake and tire wear (Thorpe and Harrison, 2008). Seasonally dependent profiles were observed for Mn, Ni, Zn, Sb which showed concentrations decreasing with height during the cold season and the opposite during the warm season. Most notable was the 90% increase in concentrations from the ground to the top of the building for Ni during the warm season. Only for Cd was a coherent but slight increase in concentrations with height found during the warm and the cold season. Statistically significant ground-top differences between seasons were found only for Ni and Mn.

Scarce information is available in literature on PM chemical composition at different heights and focused only on carbonaceous species. Chan et al. (2005) reported data in good qualitative agreement with our findings, with larger vertical gradients of EC concentrations compared to OC. The authors observed a 12% decrease from 0 to 100 m for OC and a 19% decrease for EC during the summer season. Slightly lower values were found in their work for OC/EC ratios. Kalaiarasan et al. (2009) found a vertical summer profile for both EC and OC similar to the already mentioned non-monotonic profile found for $PM_{2.5}$ mass. In fact, the data showed an increase from the 4^{th} to 10^{th} floor and then a decrease from 10^{th} to the upper floor which showed concentrations lower than the 4^{th} floor. The authors hypothesized an influence of trees around the two monitored buildings as

a cause of the non-monotonic vertical trend. Both EC and OC concentrations were much higher than those found in our study and OC/EC ratios much lower.

In conclusion, we found low vertical gradients for $PM_{2.5}$ mass and for the chemical components more related to secondary particulates (OC, NO_3, SO_4, NH_4). More pronounced vertical gradients were associated with primary emissions from road traffic such as EC, Fe and Sn.

The drop of concentrations with height are considered to be associated with those pollutants with a predominant ground-level source, such as EC (diesel exhaust) (Suvendrini Lena et al., 2002) and Fe, Sb and Sn (brake wear and resuspension) (Thorpe and Harrison, 2008). Secondary constituents are likely to be well mixed and show only minor gradients, as observed for sulphate, nitrate and ammonium. OC has both primary and secondary sources, and therefore shows intermediate behaviour. Constituents such as Ni, Mn and Zn which show a marked increase with height in the warm period are likely to have a predominant elevated source, such as an oil-fired combustion plant emitting through a high stack.

This qualitative data interpretation was not supported by an accurate analysis aimed at identifying the potential emission sources and quantifying their contribution in the study area mainly because of the limited number of samples (only 5 samples per each campaign per species), which did not actually allow the application of robust receptor modeling (e.g., Positive Matrix Factorization). Moreover, also the use of other source analysis tools (such as Principal Component Analysis or other type of source identification) was limited by the absence of detailed and accurate information about the local emission profiles.

3.2 Size distribution and UFP

Similarly to $PM_{2.5}$ mass we found higher concentrations of UFP during the cold period compared to the warm (Table 3). UFP concentrations measured at level 4 were 33-34% lower than at ground

level during both measurement campaigns. PSD showed similar shapes at the two measurement levels, with modes in the distribution at about 15 nm during both measurement periods. Marked decreases in concentrations with height were evident for all size bins but with higher gradients for smaller particles (Figure 5). This effect, most clearly seen in the winter data, is likely to be the result of traffic emissions, which reduce with height, dominating the sub-100 nm particles, while the larger secondary pollutant particles show little vertical gradient (Figure 5, upper panel). Highly statistically significant ground-top differences were found within both seasons; the Wilcoxon test showed no significant differences between seasons.

Similar results were obtained by Imhof et al. (2005) who performed one-day measurements in a rural area near Heidelberg (Germany) in May 2001 at 3, 18 and 33m investigating the influence of a motorway on the vertical distribution of aerosol particles. They found no vertical differences in size distribution and PNC in upwind conditions but strong vertical gradients in downwind conditions. No coherent vertical trends were observed by Quang et al. (2012) who carried out 1-day monitoring campaigns at three buildings (building A and C in summer and building B in winter) in Brisbane (Australia) with only a clear impact of nucleation events which caused an increase of PN with height. He and Dhaniyala (2012) performed 3-day measurements at two sites near a highway in Liverpool (NY - US) and found an increase in PNC from 0.55 m to 3.4 m and nearly uniform or slightly decreasing concentrations up to 9.1 m above ground. A decrease in PN concentration from 3 to 17.7 m was also found in California by Zhu and Hinds while no significant correlation between particle concentration and height was observed by Morawska et al. (1999).

3.3 NO_2 and BTEX

The average concentration levels monitored for NO_2 and BTEX during the monitoring campaigns are reported in Table 4. A marked decrease of concentrations with height was found for all gaseous

pollutant measured in the study (Figure 2). The highest decay rate was found for NO_2 in the cold season (ground-top difference -74%) while NO_2 concentrations during the warm season and BTEX levels in both seasons showed top-to-ground vertical variations ranging from 35 to 50%. Larger ground-to-top differences were generally found during the cold season but with less regular profiles.

Almost all the studies we found in literature investigating vertical profiles of BTEX and NO_2 in urban areas were from Asian countries and most of them with monsoon climate (Korea, Singapore). Only data from Italy (Rubino et al., 1998) and the BAB II project in Germany (Kohler et al. 2005) are available from Europe. Our results are in good qualitative agreement with previous studies which generally found lower traffic related gaseous concentrations at higher floors compared to ground level.

A marked decrease in BTEX concentrations with height was found by Rubino et al. (1998) at a tall tower (30-storey, 130 m) in Milano. Kohler et al. (2005) observed a drop in NO_2 concentrations from 8 to 50 m at about 60 m downwind of a highway in a rural area near Heidelberg, Germany. However, different NO_2 profiles were observed in some other studies. Cheong et al. (2012) in some monitoring campaigns during the monsoon season at two tall buildings (53 and 42 m) in Singapore observed a slight increase of NO_2 concentrations from ground to 15/20 m and a subsequent slight decrease up to the top of the buildings. Complex vertical profiles were found by Meng et al. (2008) in two measurements campaigns carried out at a 325 m height meteorological tower in Beijing, China in March 2001 and August 2003. The authors found very different and non monotonic vertical profiles during the monitoring campaigns. Such complex profiles probably result from the mixing of NO-rich traffic emissions from ground-level with ozone-rich air from aloft, leading to formation of NO_2 at intermediate heights.

We found only a few studies on BTEX vertical profiles. Petrea et al., (2005) found a decrease in BTEX concentrations in the first 20 m especially in downwind conditions. All the other studies were carried out in Asian countries. Jo and Kim (2002) investigated thirty apartment buildings in

Korea with 10 or more storeys in both winter and summer. They found lower concentrations of BTEX (about 20%-30%) at higher floors compared to lower floors with no marked differences between seasons. Similar results were found in an analogous monitoring campaign carried out in the same city from March to May 2001 (Jo et al., 2003). Even higher vertical differences in BTEX concentrations were found by Wang and Zhao (2008) in Nanjing, China. In 12-h diurnal monitoring at 11 different elevations from 1.5 to 50 m at an urban site near a major road the authors found about two times higher concentrations of benzene, toluene and ethylbenzene at the lowest level compared to 50 m sampling height.

3.4 Vertical profiles and meteorological variables

Figure 3_S in Supplementary Material shows some simple bivariate regressions between down-top differences of daily $PM_{2.5}$ and hourly UFP concentrations and some meteorological variables (mixing height, temperature, relative humidity and wind speed). A marked and significant negative trend (solid lines in the figure) was observed for the relationships between down-top differences of $PM_{2.5}$ and both mixing height and temperature. A less pronounced vertical trend was found for UFP with significant coefficients for mixing height, temperature and wind speed.

The application of linear multiple regression models provided the joined influence of all the above mentioned meteorological variables on $PM_{2.5}$ and UFP ground-top difference in concentrations. The VIF test showed low levels of collinearity among variables. The standardized coefficients showed the primary role of mixing height and, as opposite to bivariate regressions, a relevant role of relative humidity in relation to both $PM_{2.5}$ and UFP ground-top difference. Standardized regression coefficients are reported at the end of the Supplementary Material.

A further analysis was carried out to investigate the effect of wind direction. The underlying goal was to assess the influence of wind coming from the street next to the monitoring site on the vertical

profiles of UFP. A similar analysis was not possible for the other air pollutants and particle metrics due to the low number of available observations. The orientation of the street axis was about 235°N. We compared the vertical profiles obtained with wind coming from the directions 205-265°N (downwind conditions) and 25-85°N (upwind conditions). Figure 4_S in Supplementary Material shows the increased vertical gradients for UFP when the monitoring site is downwind. While ground UFP concentrations resulted much higher when wind flew from the street, top concentrations were not affected by wind direction. Similar results were obtained by Imhof et al. (2005) during their 1-day measurement campaign near a motorway.

4. CONCLUSIONS

A field experiment has been conducted to evaluate the variation of concentrations of different particle metrics and gaseous pollutants on the basis of floor height at a high rise building in one of most polluted area of Europe. Measurements were conducted in different seasons and showed clear vertical gradients for most of traffic related pollutants such as NO_2 and BTEX, and some particle metrics and chemical components such as UFP, EC, Fe and Sn. A relevant impact of mixing height and wind direction vertical gradients was found. In conclusion, our findings emphasize the need to include vertical variation of urban air pollutants when evaluating population exposure and associated health effects, especially in relation to some traffic-related pollutants and particle metrics.

ACKNOWLEDGEMENTS

This research was conducted as part of the Supersito Project, which was supported and financed by the Emilia-Romagna Region (Deliberation of the Regional Government n. 1971/13) and the Regional

Agency for Prevention, Environment and Energy of Emilia-Romagna, Italy (Arpae Emilia-Romagna).

REFERENCES

Andersen, Z. J., Hvidberg, M., Jensen, S. S., Ketzel, M., Loft, S., Sørensen, M., Tjønneland, A., Overvad, K., Raaschou-Nielsen, O., 2011. Chronic obstructive pulmonary disease and long-term exposure to traffic-related air pollution: a cohort study. Am. J. Respir. Crit. Care Med. 183, 455-461.

Basagaña, X., Jacquemin, B., Karanasiou, A., Ostro, B., Querol, X., Agis, D., Alessandrini, E., Alguacil, J., Artiñano, B., Catrambone, M., de la Rosa, J.D., Díaz, J., Faustini, A., Ferrari, S., Forastiere, F., Katsouyanni, K., Linares, C., Perrino, C., Ranzi, A., Ricciardelli, I., Samoli, E., Zauli-Sajani, S., Sunyer, J., Stafoggia, M.; MED-PARTICLES Study group., 2015. Short-term effects of particulate matter constituents on daily hospitalizations and mortality in five South-European cities: results from the MED-PARTICLES project. Environ. Int. 75, 151-158.

Beelen, R., Raaschou-Nielsen, O., Stafoggia, M., Andersen, Z.J., Weinmayr, G., Hoffmann, B., Wolf, K., Samoli, E., Fischer, P., Nieuwenhuijsen, M., Vineis, P., Xun, W.W., Katsouyanni, K., Dimakopoulou, K., Oudin, A., Forsberg, B., Modig, L., Havulinna, A.S., Lanki, T., Turunen, A., Oftedal, B., Nystad, W., Nafstad, P., De Faire, U., Pedersen, N.L., Östenson, C.-G., Fratiglioni, L., Penell, J., Korek, M., Pershagen, G., Eriksen, K.T., Overvad, K., Ellermann, T., Eeftens, M., Peeters, P.H., Meliefste, K., Wang, M., Bueno-de-Mesquita, B., Sugiri, D., Krämer, U., Heinrich, J., de Hoogh, K., Key, T., Peters, A., Hampel, R., Concin, H., Nagel, G., Ineichen, A., Schaffner, E., Probst-Hensch, N., Künzli, N., Schindler, C., Schikowski, T., Adam, M., Phuleria, H., Vilier, A., Clavel-Chapelon, F., Declercq, C., Grioni, S., Krogh, V., Tsai, M.-Y., Ricceri, F., Sacerdote, C., Galassi, C., Migliore, E., Ranzi, A., Cesaroni, G., Badaloni, C., Forastiere, F., Tamayo, I., Amiano, P., Dorronsoro, M., Katsoulis, M., Trichopoulou, A., Brunekreef, B., Hoek, G., 2014. Effects of long-term exposure to air pollution on natural-cause mortality: an analysis of 22 European cohorts within the multicentre ESCAPE project. Lancet. 383, 785-795.

Brunekreef, B., Holgate, S.T., 2002. Air pollution and health. Lancet 360, 1233-1242.

Calvo, A.I., Alves, C., Castro, A., Pont, V., Vicente, A.M., Fraile, R., 2013. Research on aerosol sources and chemical composition: past, current and emerging issues. Atmos. Res. 120-121, 1-28.

Cao, J.J., Wu, F., Chow, J.C., Lee, S.C., Li, Y., Chen, S.W., An, Z.S., Fung, K.K., Watson J.G., Zhu, C.S., Liu, S.X., 2005 Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter 2003 in Xi'an, China. Atmos. Chem. Phys. 5, 3127-3137.

Chan, CY, Xu, XD, Li, YS, Wong, KH, Ding, GA, Chan, LY, Cheng, XH., 2005. Characteristics of vertical profiles and sources of $PM_{2.5}$, PM_{10} and carbonaceous species in Beijing. Atmos. Environ. 39, 5113-5124.

Chan, L. Y., Kwok, W.S., 2000. Vertical dispersion of suspended particulates in urban area of Hong Kong. Atmos. Environ. 34(26), 4403-4412.

Cheong KWD, Tham KW, Balasubramanian R and Kalaiarasan M. 2012. Vertical Distribution of NO_2 in an Urban Area: Exposure Risk Assessment in Children. J. Civil. Environ. Eng. 2, 115.

Cocheo, C., Boaretto, C., Pagani, D., Quaglio, F., Sacco, P., Zaratin, L. and Cottica, D. (2009). Field evaluation of thermal and chemical desorption BTEX radial diffusive sampler radiello®

compared with active (pumped) samplers for ambient air measurements. J. Environ. Monitor. 11, 297-306.

de Hoogh, K., Wang, M., Adam, M., Badaloni, C., Beelen, R., Birk, M., Cesaroni, G., Cirach, M., Declercq, C., Dėdelė, A., Dons, E., de Nazelle, A., Eeftens, M., Eriksen, K., Eriksson, C., Fischer, P., Gražulevičienė, R., Gryparis, A., Hoffmann, B., Jerrett, M., Katsouyanni, K., Iakovides, M., Lanki, T., Lindley, S., Madsen, C., Mölter, A., Mosler, G., Nádor, G., Nieuwenhuijsen, M., Pershagen, G., Peters, A., Phuleria, H., Probst-Hensch, N., Raaschou-Nielsen, O., Quass, U., Ranzi, A., Stephanou, E., Sugiri, D., Schwarze, P., Tsai, M.Y., Yli-Tuomi, T., Varró, M.J., Vienneau, D., Weinmayr, G., Brunekreef, B., Hoek, G. 2013. Development of land use regression models for particle composition in twenty study areas in Europe. Environ. Sci. Technol. 47, 5778-5786.

EC, 2010. Guide to the demonstration of equivalence of ambient air monitoring methods. Report by an EC Working Group on Guidance for the Demonstration of Equivalence, EN 15267, n 3). URL: http://europa.eu.int/comm/environment/air/pdf/equivalence_report3.pdf

Eeftens, M., Tsai, M.-Y., Ampe, C., Anwander, B., Beelen, R., Bellander, T., Cesaroni, G., Cirach, M., Cyrys, J., de Hoogh, K., De Nazelle, A., de Vocht, F., Declercq, C., Dedele, A., Eriksen, K., Galassi, C., Grazuleviciene, R., Grivas, G., Heinrich, J., Hoffmann, B., Iakovides, M., Ineichen, A., Katsouyanni, K., Korek, M., Krämer, U., Kuhlbusch, T., Lanki, T., Madsen, C., Meliefste, K., Mölter, A., Mosler, G., Nieuwenhuijsen, M., Oldenwening, M., Pennanen, A., Probst-Hensch, N., Quass, U., Raaschou-Nielsen, O., Ranzi, A., Stephanou, E., Sugiri, D., Udvardy, O., Vaskövi, É., Weinmayr, G., Brunekreef, B., Hoek, G., 2012. Spatial variation of $PM_{2.5}$, PM_{10}, $PM_{2.5}$ absorbance and PM coarse concentrations between and within 20 European study areas and the relationship with NO_2 - results of the ESCAPE project. Atmos. Environ. 62, 303-317.

Fuller, W.A., 1987. Measurement Error Models. Wiley, New York.

Gauderman, W. J., Avol, E., Lurmann, F., Kuenzli, N., Gilliland, F., Peters, J., & McConnell, R. 2005. Childhood asthma and exposure to traffic and nitrogen dioxide. Epidemiology. 16, 737-743.

Goel A, Kumar P., 2016. Vertical and horizontal variability in airborne nanoparticles and their exposure around signalised traffic intersections. Environ. Pollut. Jul;214:54-69

Gugamsetty, B., Wei, H., Liu, C.-N., Awasthi, A., Hsu, S.-C., Tsai, C.-J., Roam, G.-D., Wu, Y.-C., Chen, C.-F., 2012. Source characterization and apportionment of PM_{10}, $PM_{2.5}$ and PM_1 by using positive matrix factorization. Aerosol Air Qual. Res. 12, 476-491.

Harrison, R.M., Yin J., 2000. Particulate matter in the atmosphere: Which particle properties are important for its effects on health? Sci. Total Environ. 249, 85-101.

He, M., Dhaniyala, S., 2012. Vertical and horizontal concentration distributions of ultrafine particles near a highway. Atmos. Environ. 46, 225-236.

Hoek, G., Boogaard, H., Knol, A., de Hartog, J., Slottje, P., Ayres, J.G., Borm, P., Brunekreef, B., Donaldson, K., Forastiere, F., Holgate, S., Kreyling, W.G., Nemery, B., Pekkanen, J., Stone, V., Wichmann, H.E., van der Sluijs, J., 2010. Concentration response functions for ultrafine particles and all-cause mortality and hospital admissions: results of a European expert panel elicitation. Environ. Sci. Technol. 44, 476-482.

Hoek, G., Beelen, R., de Hoog, K., Viennau, D., Gulliver, J., Fisher, P., Briggs, D.A., 2008a. Review of land-use regression models to asses spatial variation of outdoor air pollution. Atmos. Environ 42, 7561-7578.

Imhof, D.; Weingartner, E.; Vogt, U.; Dreiseidler, A.; Rosenbohm, E.; Scheer, V.; Vogt, R.; Nielsen, Ole John; Kurtenbach, R.; Corsmeier, U.; Kohler, M.; Baltensperger, U., 2005. Vertical distribution of aerosol particles and NO_x close to a motorway. Atmos. Environ. 39, 5710-5721.

Janssen, N. A., van Vliet, P. H., Aarts, F., Harssema, H., & Brunekreef, B. 2001. Assessment of exposure to traffic related air pollution of children attending schools near motorways. Atmos. Environ., 35, 3875-3884.

Jeong, C.H., Evans, G., 2009. Inter-Comparison of a fast mobility particle sizer and a scanning mobility particle sizer intercorporating an ultrafine water-based condensation particle counter. Aerosol Sci. Technol. 43, 364-373.

Jo, W. K., Kim, K. Y., Park, K. H., Kim, Y. K., Lee, H. W., Park, J. K., 2003. Comparison of outdoor and indoor mobile source-related volatile organic compounds between low-and high-floor apartments. Environ. Res. 92(2), 166-171.

Jo W-K, Kim K-Y., 2002. Vertical variability of volatile organic compound (VOC) levels in ambient air of highrise apartment buildings with and without occurrence of surface inversion. Atmos. Environ. 36, 5645-5652.

Jung, K. H., Bernabé, K., Moors, K., Yan, B., Chillrud, S. N., Whyatt, R., Camann, D., Kinney, P.L., Perera, F.P., Miller, R. L., 2011. Effects of floor level and building type on residential levels of outdoor and indoor polycyclic aromatic hydrocarbons, black carbon, and particulate matter in New York City. Atmosphere. 2, 96-109.

Kalaiarasan, M., Balasubramanian, R., Cheong, K. W. D., and Tham, K. W., 2009. Traffic-generated airborne particles in naturally ventilated multi-storey residential buildings of Singapore: Vertical distribution and potential health risks. Build. Environ. 44, 1493–1500.

Kaminski, H., Kuhlbusch, T.A.J., Rath, S., Gotz, U., Sprenger, M., Wels, D., Polloczek, J., Bachmann, V., Dziurowitz, N., Kiesling, H.-J., Schwiegelshohn, A., Monz, C., Dahmann, D., Asbach, C., 2013. Comparability of mobility particle sizers and diffusion chargers. J. Aerosol Sci. 57, 156-178.

Kohler, M., Corsmeier, U., Vogt, U., Vogel, B., 2005. Estimation of gaseous real world traffic emissions downstream a motorway. Atmos. Environ. 39, 5665-5684.

Kumar, P., Fennell, P., Britter, R.E., 2008. Pseudo-simultaneous measurements for the vertical variation of coarse, fine and ultra-fine particles in an urban street canyon. Atmos. Environ. 42, 4304-4319.

Larsen, B.R., Gilardoni S., Stenström K., Niedzialek J., Jimenez J., Belis C.A., 2012. Sources for PM air pollution in the Po Plain, Italy: II. Probabilistic uncertainty characterization and sensitivity analysis of secondary and primary sources. Atmos. Environ. 50, 203-213.

Li X.L., Wang, J.S., Tu, X.D., Liu, W., Huang, Z., 2007. Vertical variations of particle number concentration and size distribution in a street canyon in Shanghai, China. Sci. Total Environ. 378, 306-316.

Meng, Z.Y., Ding, G.A., Xu, X.B., Xu, X.D., Yu, H.Q., Wang, S.F., 2008. Vertical distributions of SO_2 and NO_2 in the lower atmosphere in Beijing urban areas, China. Sci. Total Environ. 390, 456-465.

Morawska, L., Thomas, S., Gilbert, D., Greenaway, C., Rijnders, E., 1999. A study of the horizontal and vertical profile of submicrometer particles in relation to a busy road. Atmos. Environ. 33(8), 1261-1274.

Peters, A., Ruckerl, R., Cyrys, J., 2011. Lessons from air pollution epidemiology fro studies of engineered nanomaterials. J. Occup. Environ. Med. 53, S8-S13.

Petrea, M., Kurtenbach, R., Wiesen, P., Vogt, U., Baumbach, G., 2005. NMHC measurements of motorway emissions during the BAB II field campaign. Atmos. Environ. 39(31), 5685-5695.

Quang, T., He, C., Morawska, L., Knibbs, L., Falk, M., 2012. Vertical particle concentration profiles around urban office buildings. Atmos. Chem. Phys. 12, 5017-5030.

Qin, Y., Kot, S.C., 1993. Dispersion of vehicular emission in street canyons, Guangzhou City, South China (P.R.C.). Atmos. Environ. Part B, Urban Atmosphere, 27, 283-291.

Raaschou-Nielsen, O., Andersen, Z.J., Beelen, R., Samoli, E., Stafoggia, M., Weinmayr, G., Hoffmann, B., Fischer, P., Nieuwenhuijsen, M.J., Brunekreef, B., Xun, W.W., Katsouyanni, K., Dimakopoulou, K., Sommar, J., Forsberg, B., Modig, L., Oudin, A., Oftedal, B., Schwarze, P.E., Nafstad, P., De Faire, U., Pedersen, N.L., Östenson, C.-G., Fratiglioni, L., Penell, J., Korek, M., Pershagen, G., Eriksen, K.T., Sørensen, M., Tjønneland, A., Ellermann, T., Eeftens, M., Peeters, P.H., Meliefste, K., Wang, M., Bueno-de-Mesquita, B., Key, T.J., de Hoogh, K., Concin, H., Nagel, G., Vilier, A., Grioni, S., Krogh, V., Tsai, M.-Y., Ricceri, F., Sacerdote, C., Galassi, C., Migliore, E., Ranzi, A., Cesaroni, G., Badaloni, C., Forastiere, F., Tamayo, I., Amiano, P., Dorronsoro, M., Trichopoulou, A., Bamia, C., Vineis, P., Hoek, G., 2013. Air pollution and lung cancer incidence in 17 European cohorts: prospective analyses from the European Study of Cohorts for Air Pollution Effects (ESCAPE). Lancet Oncol. 14, 813-822.

Reid, J. S., Koppmann, R., Eck, T. F., Eleuterio, D.P., 2005. A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. Atmos. Chem. Phys. 5, 799-825.

REVIHAAP, 2013. Review of evidence on health aspects of air polluiton - REVIHAAP Project. Technical Report, World Health Organization, Regional Office for Europe, Copenhagen.

Ricciardelli, I., Bacco, D., Rinaldi, M., Bonafè, G., Scotto, F., Trentini, A., Bertacci, G., Ugolini, P., Zigola, C., Rovere, F., Maccone, C., Pironi C., Poluzzi, V., 2017. A three-year investigation of daily $PM_{2.5}$ main chemical components in four sites: the routine measurement program of the Supersito Project (Po Valley, Italy). Atmos. Environ. 152, 418-430.

Samoli, E., Atkinson, R.W., Analitis, A., Fuller, G.W., Beddows, D., Green, D.C., Mudway, I.S., Harrison, R.M., Anderson, H.R., Kelly, F.J., 2016. Differential health effects of short-term exposure to source-specific particles in London, U.K. Environ. Int. 97, 246-253.

Saarikoski, S., Timonen, H., Saarnio, K., Aurela, M., Järvi, L., Keronen, P., Kerminen, V.-M., Hillamo, R., 2008. Sources of organic carbon in fine particulate matter in northern European urban air. Atmos.Chem. Phys. 8, 6281-6295.

Saarikoski, S., Sillanpää, M., Sofiev, M., Timonen, H., Saarnio, K., Teinilä, K., Karppinen, A., Kukkonen, J., Hillamo, R., 2007. Chemical composition of aerosols during a major biomass burning episode over northern Europe in spring 2006: Experimental and modelling assessments. Atmos. Environ. 41, 3577-3589.

Spinazzè, A., Cattaneo, A., Garramone, G., and Cavallo, D. M. 2013. Temporal variation of size-fractionated particulate matter and carbon monoxide in selected microenvironments of the Milan urban area. J. Occup. Environ. Hyg. 10, 652-662.

Suvendrini Lena, T., Ochieng, V., Carter, M., Holguin-Veras, J., Kinney, P.L., 2002. Elemental carbon and $PM_{2.5}$ levels in a urban community heavily impacted by truck traffic. Environ. Health Persp. 110, 1009-1015.

Tammet, H., Mirme, A., Tamm, E., 2002. Electrical aerosol spectrometer of Tartu University. Atmos. Res. 62, 315-324.

Thorpe, A., Harrison, R. M. 2008. Sources and properties of non-exhaust particulate matter from road traffic: a review. Sci. Total Environ. 400, 270-282.

Vakeva, M., Hameri, K., Kulmala, M., Lahdes, R., Ruuskanen, J., Laitinen, T., 1999. Street level versus rooftop concentrations of submicron aerosol particles and gaseous pollutants in an urban street canyon. Atmos. Environ. 33, 1385-1397.

Vardoulakis, S., Lumbreras, J. and Solazzo, E. (2009). Comparative evaluation of nitrogen oxides and ozone passive diffusion tubes for exposure studies. Atmos. Environ. 43, 2509-2517.

van Nunen. E., Vermeulen, R., Tsai, M.Y., Probst-Hensch, N., Ineichen, A., Davey, M., Imboden, M., Ducret-Stich, R., Naccarati, A., Raffaele, D., Ranzi, A., Ivaldi, C., Galassi, C., Nieuwenhuijsen, M., Curto, A., Donaire-Gonzalez, D., Cirach, M., Chatzi, L., Kampouri, M., Vlaanderen, J., Meliefste, K., Buijtenhuijs, D., Brunekreef, B., Morley, D., Vineis, P., Gulliver, J., Hoek, G. 2017. Land Use Regression Models for Ultrafine Particles in Six European Areas. Environ. Sci. Technol. 51, 3336-3345.

von Klot, S., Peters, A., Aalto, P., Bellander, T., Berglind, N., D'Ippoliti, D., Elosua, R., Hörmann, A., Kulmala, M., Lanki, T., Löwel, H., Pekkanen, J., Picciotto, S., Sunyer, J., Forastiere, F., 2005. Ambient air pollution is associated with increased risk of hospital cardiac readmissions of myocardial infarction survivors in five European cities. Circulation 112, 3073-3079.

Wang, M., Beelen, R., Basagana, X., Becker, T., Cesaroni, G., de Hoogh, K., Dedele, A., Declercq, C., Dimakopoulou, K., Eeftens, M., Forastiere, F., Galassi, C., Gražulevičienė, R., Hoffmann, B., Heinrich, J., Iakovides, M., Künzli, N., Korek, M., Lindley, S., Mölter, A., Mosler, G., Madsen, C., Nieuwenhuijsen, M., Phuleria, H., Pedeli, X., Raaschou-Nielsen, O., Ranzi, A., Stephanou, E., Sugiri, D., Stempfelet, M., Tsai, M.Y., Lanki, T., Udvardy, O., Varró, M.J., Wolf, K., Weinmayr,

G., Yli-Tuomi, T., Hoek, G., Brunekreef, B. 2013. Evaluation of land use regression models for NO2 and particulate matter in 20 European study areas: the ESCAPE project. Environ. Sci. Technol. 47, 4357-4364.

Wang, P., Zhao, W., 2008. Assessment of ambient volatile organic compounds (VOCs) near major roads in urban Nanjing, China. Atmos. Res. 89, 289–297.

Weber, S., Kuttler, W.,Weber, K., 2006. Flow characteristics and particle mass and number concentration variability within a busy urban street canyon, Atmos. Environ. 40, 7565-7578.

Wu, Y., Hao, J., Fu, L., Wang, Z., Tang, U., 2002. Vertical and Horizontal Profiles of Airborne Particulate Matter near Major Roads in Macao, China. Atmos. Environ. 36, 4907-4918.

Zauli Sajani, S., Trentini, A., Rovelli, S., Ricciardelli, I., Marchesi, S., Maccone, C., Bacco, D., Ferrari, S., Scotto, F., Zigola, C., Cattaneo, A., Cavallo, D.M., Lauriola, P., Poluzzi, V., Harrison, R.M.. 2016. Is particulate air pollution at the front door a good proxy of residential exposure? Environ. Poll. 213, 347-358.

Zhu, Y, Hinds W.C., 2005. Predicting particle number concentrations near a highway based on vertical concentration profile. Atmos. Environ. 39.8, 1557-1566.

Zoumakis, N.M., 1995. A note on average vertical profiles of vehicular pollutant concentrations in urban street canyons. Atmos. Environ. 29, 3719-3725.

List of tables

Table 1. Overview of the available studies on vertical profiles of $PM_{2.5}$, Particle Size Distribution (PSD), Particle Number Concentrations (PNC), BTEX and NO_2. Studies dealing with data from street canyon configuration are not included.

Author(s) - Year	Country	Pollutants	Measurement site	Measurement period	Main findings
$PM_{2.5}$ and chemical composition					
Quang et al. (2012)	Brisbane, Australia	$PM_{2.5}$	Three buildings (15, 77, 22 m)	22 Jul - 16 Aug 2009; 14 - 30 Jan 2010; 24 Jun - 16 Jul 2010	$PM_{2.5}$ highest at groundfloor
Jung et al. (2011)	New York City (US)	$PM_{2.5}$	256 homes in multi-storey buildings (0-2nd, 3rd-5th and 6th-32nd floor)	Oct 2005 - Jul 2010 (two week for each home)	$PM_{2.5}$ slightly higher at midfloors
Kalaiarasan et al. (2009)	Singapore	$PM_{2.5}$, EC, OC	Two buildings (20 and 16 stories)	2-27 July 2007	$PM_{2.5}$, EC and OC highest at midfloors
Chan et al. (2005)	Beijing, China	$PM_{2.5}$, EC, OC	Meteorological tower (325 m)	10 - 25 Aug 2003	Complex vertical profiles for $PM_{2.5}$, EC and OC
Wu et al. (2002)	Macao	$PM_{2.5}$	High rise building (79 m)	3 - 12 Dec 2001	$PM_{2.5}$ highest at groundfloor
Chan and Kwok (2000)	Hong Kong	$PM_{2.5}$	Two buildings (18 and 25 m)	Nov 1998 - Jan 1999	No coherent results between the two buildings
PSD and PNC					
He and Dhaniyala (2012)	Liverpool, US	PNC	Mobile tower (10 m)	13-16 Sep and 16-18 Sep 2009	No well defined vertical profiles
Quang et al. (2012)	Brisbane, Australia	PSD	Three buildings (15, 77, 22 m)	22 Jul - 16 Aug 2009; 14 - 30 Jan 2010; 24 Jun - 16 Jul 2010	Building dependent profile of PN concentration
Imhof et al. (2005)	Heidelberg, Germany	PSD	Two towers (52 m)	13-14 May 2001	Particles <300 nm e > 1 um highest at ground floor
Zhu and Hinds (2005)	Los Angeles (US)	PNC	Tower (20 m)	17-18 July 2001	PN concentration highest at 3 m in downwind conditions
Morawska et al. (1999)	Brisbane, Australia	PSD	Three buildings (8, 25, 11 m)	26 Nov - 13 Dec 1996	No well defined vertical profiles
BTEX					
Wang and Zhao (2008)	Nanjing, China	BTEX	High rise building (50 m)	40 days in Apr 2006 - Jan 2007	BTEX highest at groundfloor
Petrea et al. (2005)	Heidelberg, Germany	BTEX	Two towers (52 m)	4 weeks in April - May 2001	BTEX highest at groundfloor
Jo et al. (2003)	Daegu, Korea	BTEX	120 homes in 56 high rise buildings (>10 stories)	March - May 2001	BTEX highest at groundfloor
Jo and Kim (2002)	Daegu, Korea	BTEX	252 homes in 65 high rise buildings (>10 stories)	20 Dec 2000 - 28 Feb 2001 and 28 Jun - 30 Aug 2001	Marked decrease of BTEX in inversion conditions
Rubino et al. (1998)	Milano (Italy)	BTEX	Tall building (30 stories, 130 m)	22 days during winter 1994-95	BTEX highest at groundfloor
NO_2					
Cheong et al. (2012)	Singapore	NO_2	Two buildings (42 and 53 m)	2005 - 2008 (5 weeks for each building)	NO_2 highest at midfloors
Meng et al. (2008)	Beijing, China	NO_2	Meteorological tower (325 m)	Few weeks from Feb 2001 to Aug 2003	Complex vertical NO_2 profiles
Kohler et al. (2005)	Heidelberg, Germany	NO_2	Two towers (52 m)	1 -25 May 2001	NO_2 highest at ground

Table 2. Summary statistics of the hourly values of some meteorological parameters during the two monitoring campaigns: temperature (Temp), relative humidity (RH), precipitation (Prec), wind speed (Ws), and mixing height (Hmix). Mean, median, min, max and interquartile range (IQR) values are based on daily measurements (for Hmix) whereas for all other parameters data was registered on hourly basis.

	Cold period					Warm period				
	Mean	Median	Min	Max	IQR	Mean	Median	Min	Max	IQR
Temp (°C)	8.5	8.2	1.8	14.1	3.5	23.6	23.1	13.3	31.8	7.0
RH (%)	68.1	68	29	100	28.5	49.2	49	22	90	21.5
Prec (mm h^{-1})	0.2	0.0	0.0	4.4	0.0	0.0	0.0	0.0	2.2	0.0
Ws (m sec^{-1})	2.1	1.8	0.0	8.4	1.7	1.8	1.7	0.0	4.9	1.3
Hmix (m)	310	220	140	1950	220	730	260	140	2500	1190

Table 3. Summary statistics of $PM_{2.5}$ and UFP during the two monitoring campaigns. Number of samples (N), mean, median, min, max and interquartile range (IQR) values are referred to daily observations for $PM_{2.5}$ and hourly observations for UFP.

	Cold period						Warm period					
	N	Mean	Median	Min	Max	IQR	N	Mean	Median	Min	Max	IQR
$PM_{2.5}$ (*)												
Level 0	15	27	26	1	54	20	15	15	15	7	24	3
Level 1	15	26	22	5	53	23	15	15	14	7	22	6
Level 2	15	26	22	7	51	21	15	15	15	6	24	7
Level 3	15	25	22	5	52	21	15	14	14	6	22	4
Level 4	15	24	22	1	50	20	15	14	14	5	22	4
UFP (**)												
Level 0	318	144	121	20	710	105	359	99	84	19	382	73
Level 4	318	97	88	12	274	73	359	65	58	9	213	53

(*) $PM_{2.5}$ data are expressed in $\mu g\ m^{-3}$

(**) UFP data are expressed in hundred of particles

Table 4. Summary statistics of some gaseous pollutant during the two monitoring campaigns. Mean, min and max value are referred to the data provided by the replicates of passive samplers located at each building level (two duplicate passive samplers at each floor - only for BTEX during the cold period there were three passive samplers at each floor).

NO_2							
	Level 0	70.5	68.8	72.2	41.2	41.1	41.3
	Level 1	63.6	59.6	67.5	34.4	34.4	34.4
	Level 2	62.9	62.1	63.7	32.1	29.6	34.6
	Level 3	38.7	28.4	49.0	30.0	28.9	31.0
	Level 4	18.1	14.7	21.4	25.3	24.5	26.1
Benzene							
	Level 0	1.91	1.90	1.94	0.48	0.46	0.49
	Level 1	2.06	2.06	2.06	0.43	0.41	0.45
	Level 2	1.43	1.39	1.45	0.37	0.35	0.39
	Level 3	1.59	1.49	1.64	0.34	0.32	0.36
	Level 4	1.24	1.14	1.34	0.31	0.30	0.32
Toluene							
	Level 0	3.67	3.45	3.79	3.58	3.55	3.60
	Level 1	3.70	3.67	3.72	3.51	3.47	3.54
	Level 2	2.24	2.16	2.31	3.04	2.81	3.26
	Level 3	2.49	2.44	2.52	2.89	2.75	3.03
	Level 4	1.91	1.63	2.29	2.34	2.23	2.44
Ethylbenzene							
	Level 0	0.76	0.74	0.80	0.40	0.39	0.40
	Level 1	0.82	0.79	0.85	0.38	0.38	0.38
	Level 2	0.50	0.49	0.51	0.31	0.28	0.34
	Level 3	0.58	0.54	0.63	0.28	0.27	0.28
	Level 4	0.42	0.38	0.47	0.25	0.22	0.27
Xylenes							
	Level 0	3.21	3.10	3.28	2.01	2.00	2.02
	Level 1	3.33	3.28	3.37	1.86	1.83	1.88
	Level 2	2.01	1.99	2.05	1.59	1.48	1.69
	Level 3	2.22	2.09	2.29	1.48	1.40	1.56
	Level 4	1.62	1.56	1.72	1.21	1.14	1.27

All data are reported in $\mu g\ m^{-3}$

List of figures

Figure 1: Overview of the monitoring sites and area

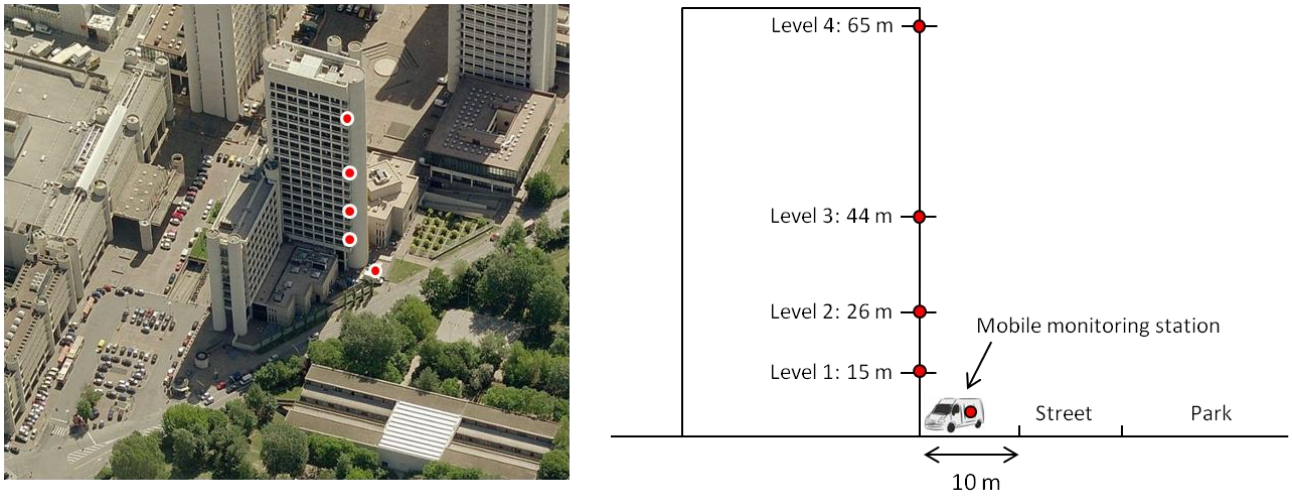


Figure 2: Vertical profiles of $PM_{2.5}$, NO_2, benzene, toluene, ethylbenzene and xylenes during the summer (open squares) and winter (full circles) campaign. (*) means statistically significant ground-top differences at least at 95% probability.

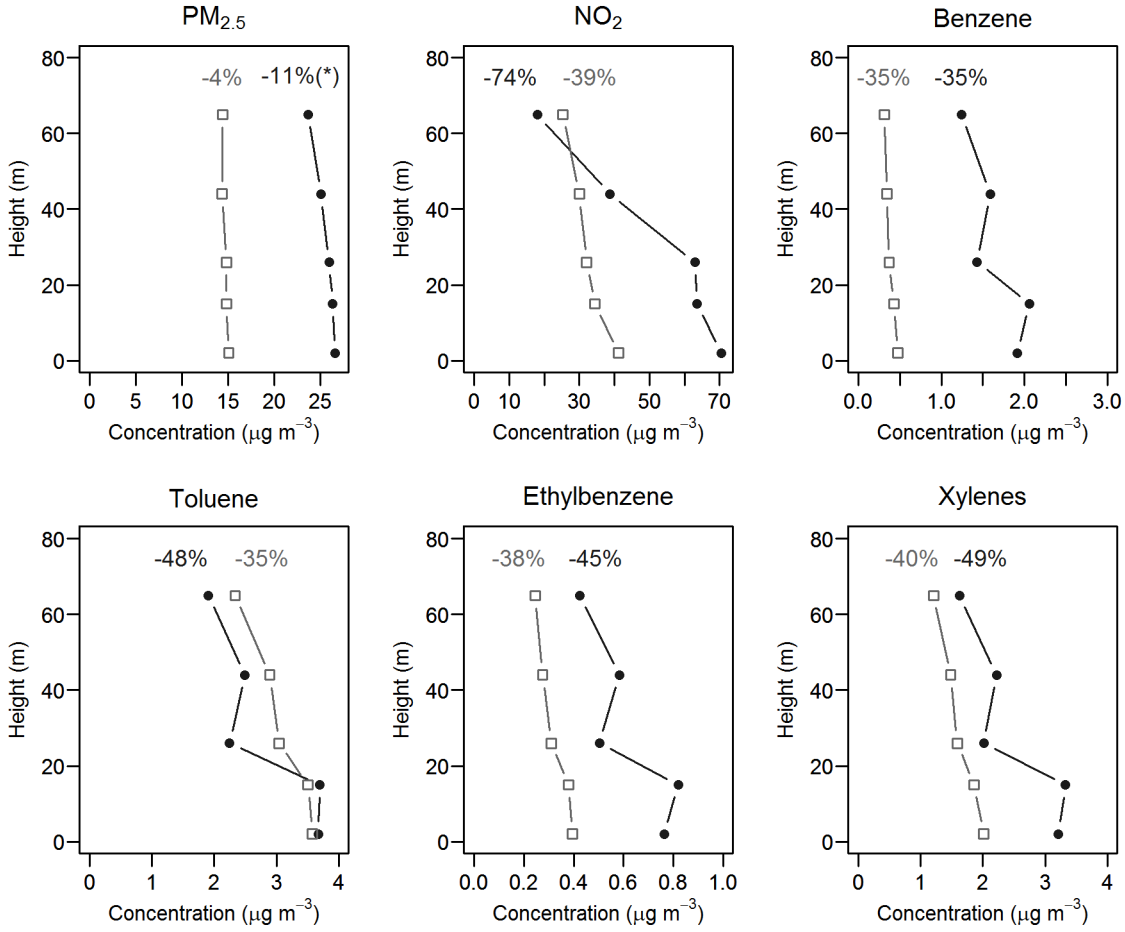


Figure 3: Vertical profiles of EC, OC, TC, NO_3, SO_4 and NH_4 components of $PM_{2.5}$ during the summer (open squares) and winter (full circles) campaign.

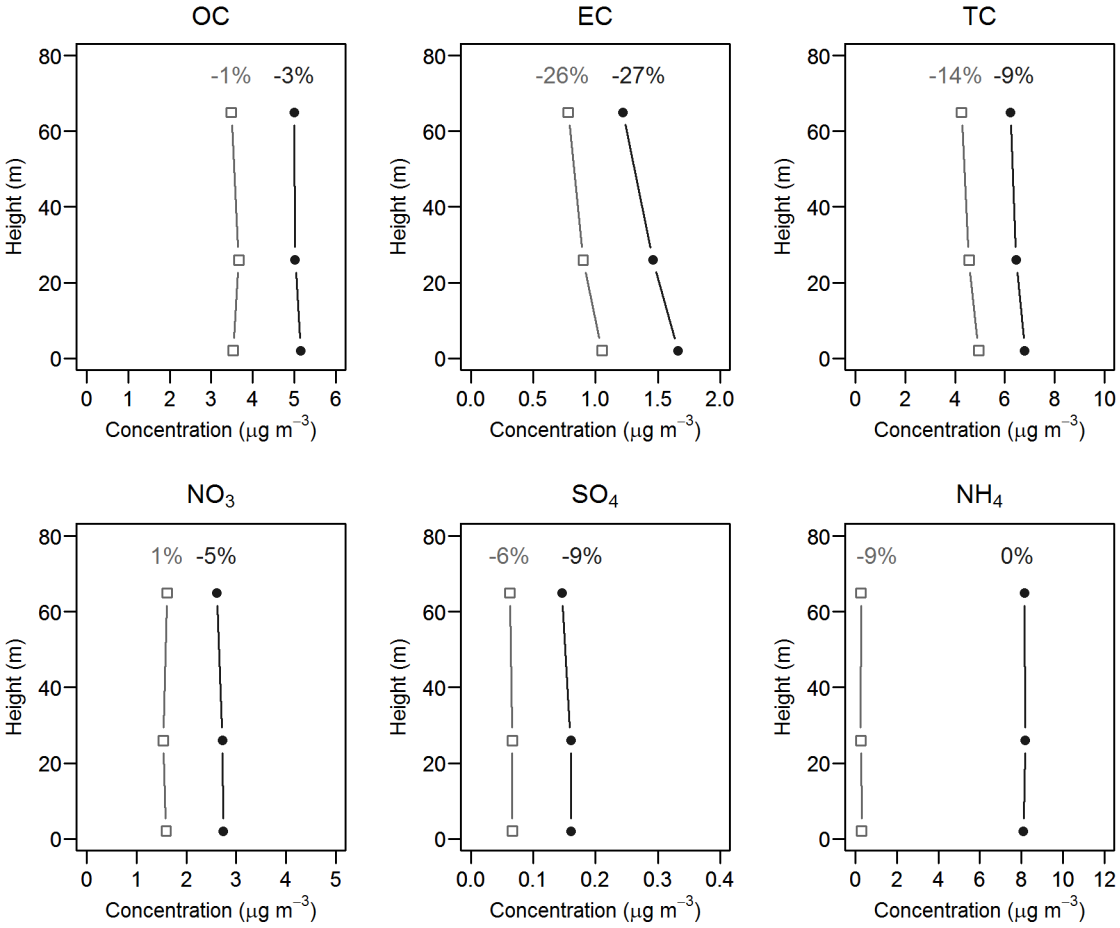


Figure 4: Vertical profiles of some metal components of $PM_{2.5}$ during the summer (open squares) and winter (full circles) campaign.

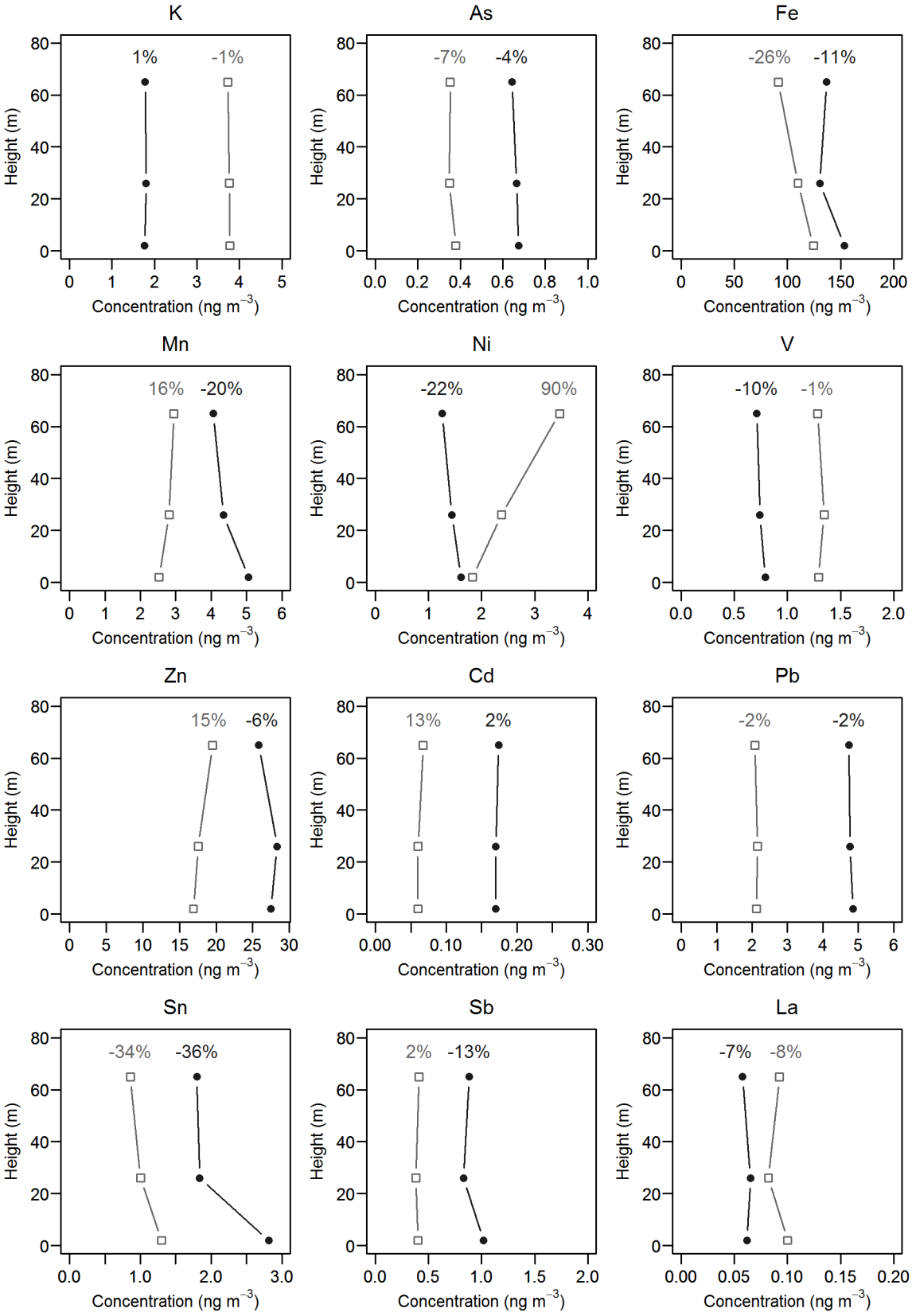
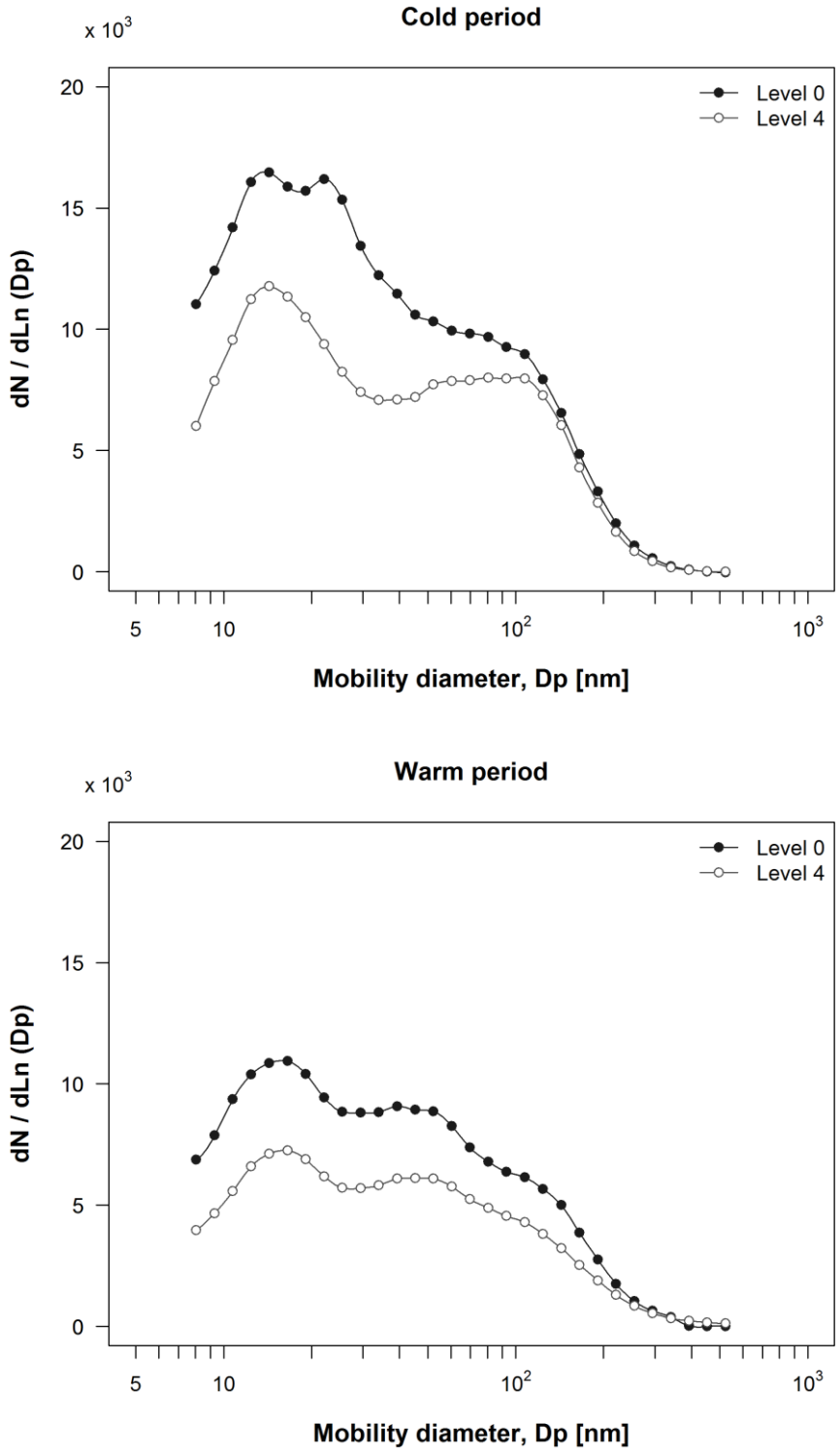


Figure 5: Particle size distribution during the winter (upper panel) and summer (lower panel) campaign.



SUPPLEMENTARY MATERIAL

Methods and procedure for chemical speciation

Organic Carbon (OC) and Elemental Carbon (EC) were quantified by means of themal-optical trasmittance (Lab OC-EC Aerosol Analyzer, Sunset Laboratory Inc., Tigard, Oregon, USA) using the EUSAAR_2 protocol (Cavalli et al., 2010*). OC and EC values were subsequently summed to obtain the Total Carbon (TC). Inorganic ions were determined by extracting species in 10 mL of ultrapure water. The extracts were analyzed by Ion Chromatography (Dionex ICS-1000 for anions and ICS-1100 for cations, Thermo Fischer Scientific Inc., USA) and metals by Inductively Coupled Plasma – Mass Spectrometry (8800 ICP-MS, Agilent Technologies Inc., USA). Sample digestion with nitric acid and hydrogen peroxide in a microwave digestion apparatus and analysis were made according to European Standard EN 14902:2005, with a recovery efficiency over 85%. Due to the availability of a unique filter for each day and measuring site, the chemical speciation was performed sequentially every three days for metals, ions, and carbon (Elemental Carbon and Organic Carbon).

(*) Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J.-P., 2010. Toward a standardised thermaloptical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech. 3, 79–89.

Table 1_S: Limits of quantification for chemical species

LOQs	Chemical species
0.03 ng m^{-3}	Arsenic (As),
0.03 ng m^{-3}	Vanadium (V),
0.01 ng m^{-3}	Cadmium (Cd),
0.18 ng m^{-3}	Lead (Pb),
0.04 ng m^{-3}	Tin (Sn),
0.14 ng m^{-3}	Antimonium (Sb),
0.7 ng m^{-3}	Chromium (Cr),
0.5 ng m^{-3}	Manganese (Mn),
36 ng m^{-3}	Iron (Fe),
12.2 ng m^{-3}	Zinc (Zn),
0.04 μg m^{-3}	Ammonium (NH_4^+),
0.04 μg m^{-3}	Potassium (K^+),
0.05 μg m^{-3}	Nitrate (NO_3^-),
0.09 μg m^{-3}	Sulfate (SO_4^{2-}),
2.1 μg m^{-3}	Organic Carbon (OC),
0.3 μg m^{-3}	Elemental Carbon (EC).

Table 2_S. Summary statistics of the concentrations of the main chemical components of $PM_{2.5}$ during the two monitoring campaigns. All data are reported in μg m^{-3}.

		Cold period				Warm period			
		Mean	Min	Max	n	Mean	Min	Max	n
OC									
	Level 0	5.2	2.3	8.0	5	3.5	2.6	4.5	4
	Level 2	5.0	2.5	8.0	5	3.7	2.7	4.4	5
	Level 4	5.0	2.5	7.9	5	3.5	2.6	4.2	5
EC									
	Level 0	1.7	0.9	2.5	5	1.1	0.7	1.4	4
	Level 2	1.5	0.8	2.3	5	0.9	0.5	1.3	5
	Level 4	1.2	0.7	2.1	5	0.8	0.5	1.2	5
TC									
	Level 0	6.8	3.3	10.4	5	4.9	3.3	6.3	5
	Level 2	6.5	3.3	10.2	5	4.6	3.3	5.5	5
	Level 4	6.2	3.2	10.0	5	4.3	3.1	5.2	5
NO_3									
	Level 0	2.7	0.1	4.5	5	1.6	0.9	2.2	5
	Level 2	2.7	0.1	4.5	5	1.5	0.9	2.2	5
	Level 4	2.6	0.2	4.5	5	1.6	0.9	2.3	5
SO_4									
	Level 0	0.2	0.1	0.2	5	0.1	0.1	0.1	5
	Level 2	0.2	0.1	0.2	5	0.1	0.1	0.1	5
	Level 4	0.1	0.1	0.2	5	0.1	0.1	0.1	5
NH_4									
	Level 0	8.1	0.9	14.0	5	0.3	0.2	0.4	5
	Level 2	8.2	0.9	14.1	5	0.3	0.2	0.3	5
	Level 4	8.1	0.9	14.3	5	0.3	0.2	0.4	5

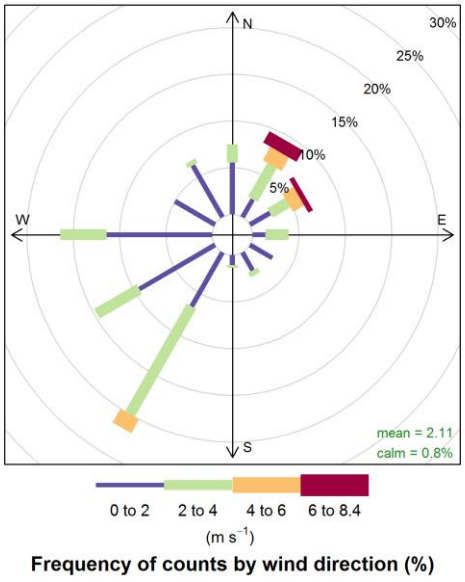
Table 3_S. Summary statistics of the concentrations of some metal components of $PM_{2.5}$ during the two monitoring campaigns. All data are reported in ng m^{-3}.

		Cold period				Warm period			
		Mean	Min	Max	n	Mean	Min	Max	n
K									
	Level 0	1.8	0.7	2.5	5	3.8	1.9	5.8	5
	Level 2	1.8	0.7	2.6	5	3.8	1.8	5.6	5
	Level 4	1.8	0.7	2.5	5	3.7	1.8	5.7	5
As									
	Level 0	0.7	0.4	0.9	5	0.4	0.1	0.7	5
	Level 2	0.7	0.4	0.8	5	0.3	0.1	0.6	5
	Level 4	0.6	0.4	0.8	5	0.4	0.1	0.6	5
Fe									
	Level 0	154	65	310	5	124	82	189	5
	Level 2	130	48	245	5	110	75	152	5
	Level 4	137	104	196	5	91	64	123	5
Mn									
	Level 0	5.1	3.0	6.9	5	2.5	1.9	3.3	5
	Level 2	4.3	2.5	5.9	5	2.8	2.2	3.1	5
	Level 4	4.1	2.2	5.4	5	2.9	2.0	3.6	4
Ni									
	Level 0	1.6	1.0	2.1	5	1.8	0.8	3.2	5
	Level 2	1.4	1.0	2.1	5	2.4	1.1	4.6	5
	Level 4	1.3	0.8	1.7	5	3.5	2.5	5.1	5
V									
	Level 0	0.8	0.3	1.4	5	1.3	0.2	3.4	5
	Level 2	0.7	0.3	1.3	5	1.3	0.2	3.6	5
	Level 4	0.7	0.3	1.3	5	1.3	0.2	3.6	5
Zn									
	Level 0	27.5	16.0	35.6	5	16.9	12.1	20.8	4
	Level 2	28.3	20.3	37.6	5	17.6	16.0	19.5	5
	Level 4	25.8	19.5	29.5	5	19.5	13.2	23.0	5
Cd									
	Level 0	0.17	0.06	0.23	5	0.06	0.04	0.09	5
	Level 2	0.17	0.07	0.24	5	0.06	0.04	0.08	5
	Level 4	0.17	0.06	0.24	5	0.07	0.05	0.08	4
Pb									
	Level 0	4.9	3.2	5.8	5	2.1	1.1	3.4	5
	Level 2	4.8	3.4	6.3	5	2.2	1.2	3.2	5
	Level 4	4.7	3.2	6.0	5	2.1	0.9	3.2	5
Sn									
	Level 0	2.8	2.3	3.6	5	1.3	0.6	2.2	5
	Level 2	1.8	1.5	2.2	5	1.0	0.4	1.6	5
	Level 4	1.8	1.4	2.2	5	0.9	0.5	1.2	5
Sb									
	Level 0	1.0	0.7	1.6	5	0.4	0.1	0.6	5
	Level 2	0.8	0.5	1.5	5	0.4	0.2	0.6	5
	Level 4	0.9	0.4	1.5	5	0.4	0.2	0.6	5
La									
	Level 0	0.06	0.03	0.10	5	0.10	0.04	0.22	4
	Level 2	0.07	0.03	0.09	4	0.08	0.04	0.22	5
	Level 4	0.06	0.04	0.07	4	0.09	0.05	0.22	4

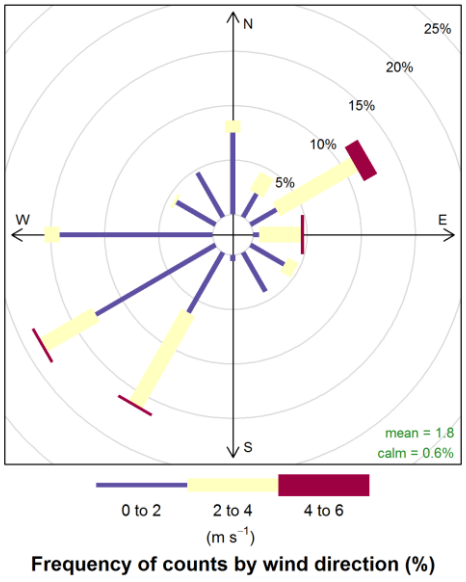
Table 4_S. Summary statistics for some meteorological parameters comparing the monitoring campaigns with the "typical" cold (Jan-April and Oct Dec 2015-2016) and warm (May-Sep) period. Measurement units: Wind speed (m sec^{-1}), RH (%), Temp (°C), Prec (mm), Mixing height (m)

	Wind speed	**RH**	**Temp**	**Prec**	**Mixing height**
Cold period 2015-2016	1.8	73	9.7	0.11	315
Cold period - Campaign	2.1	68	8.5	0.2	312
Warm period 2015-2016	1.9	52	23.1	0.06	691
Warm period - Campaign	1.8	49	23.6	0.01	733

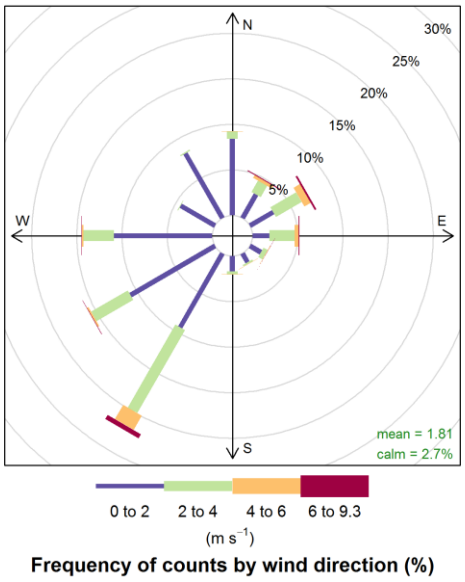
Wind rose cold period



Wind rose warm period



Wind rose cold months 2015-2016



Wind rose warm months 2015-2016

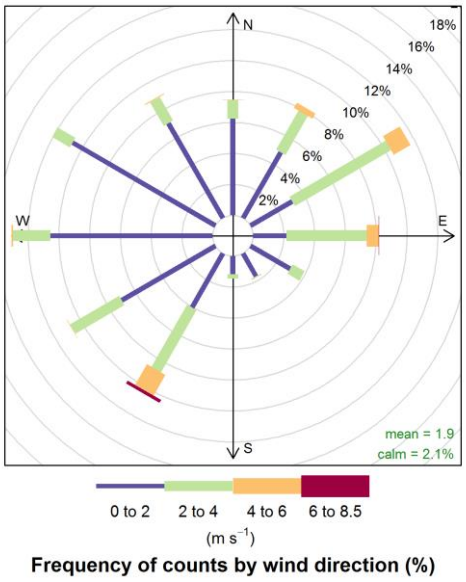


Figure 1_S: Wind roses for the monitoring campaigns and for the years 2015-2016

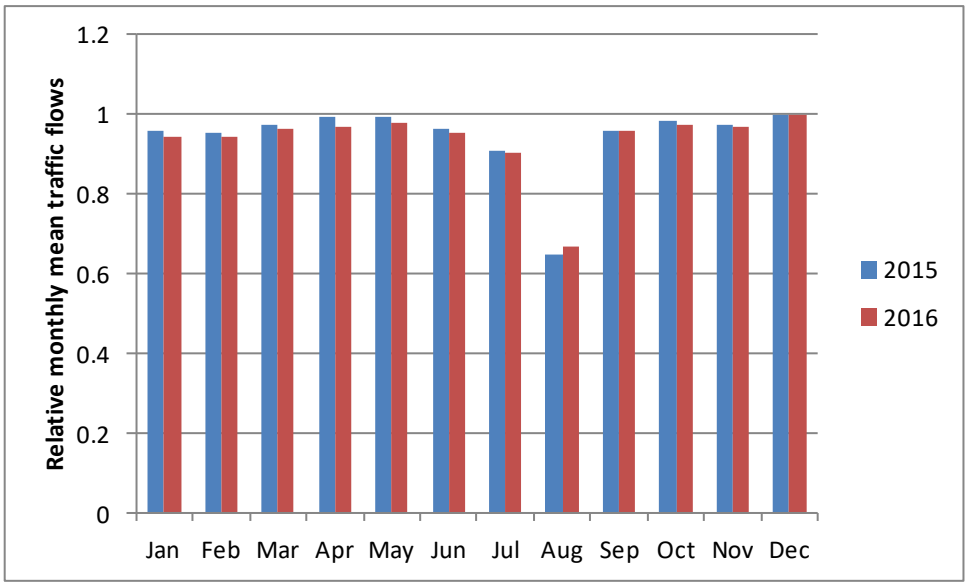


Figure 2_S: Mean monthly traffic flows for 2015 and 2016 at the monitoring site. Data are normalized based on December data.

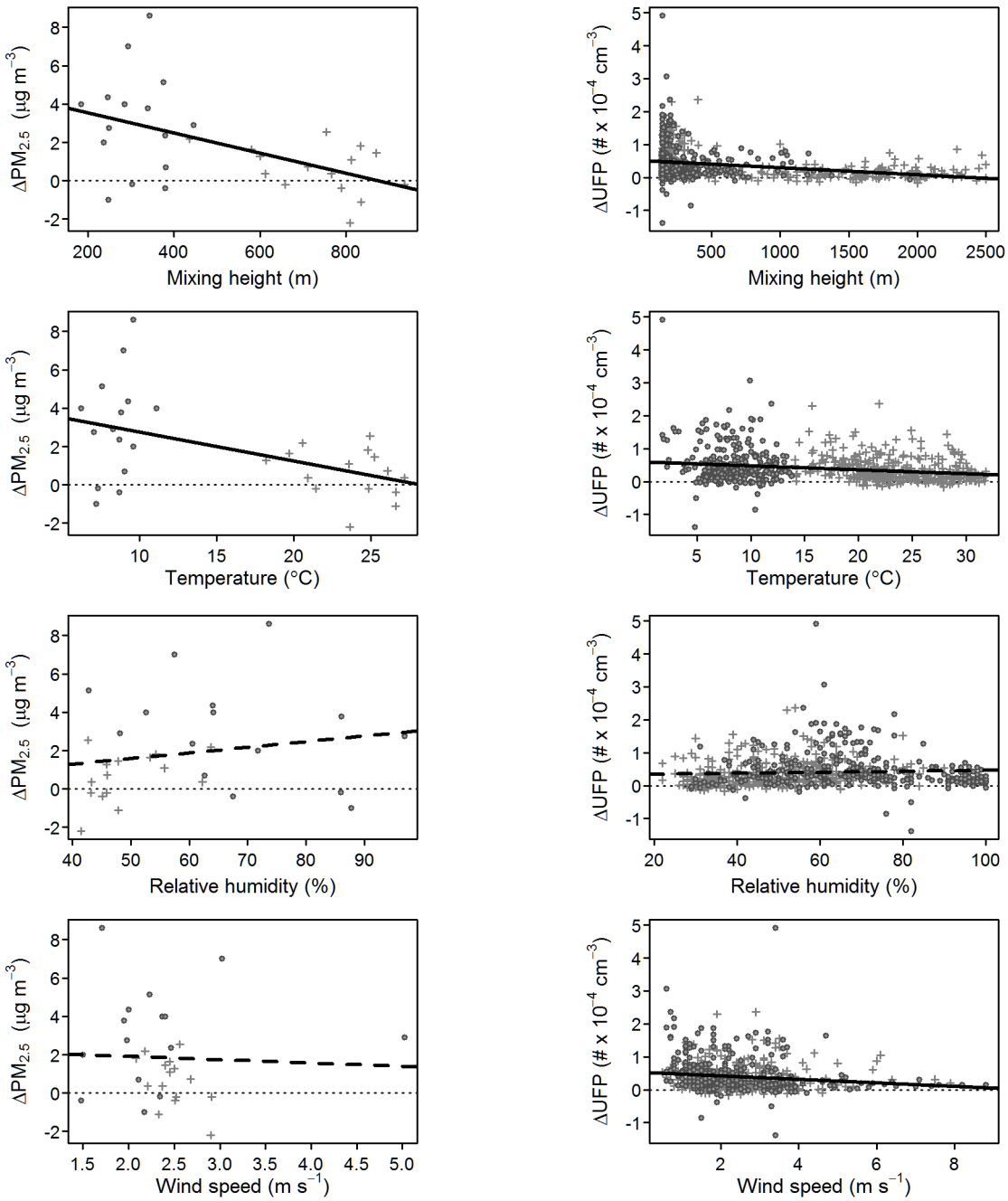


Figure 3_S: Scatter plot and regression lines between down-top differences of PM2.5 and UFP concentrations and mixing height, temperature, relative humidity and wind speed. Solid and dotted lines show regressions with significant and not significant slopes, respectively. Circles are referred to cold period data while crosses to warm period data.

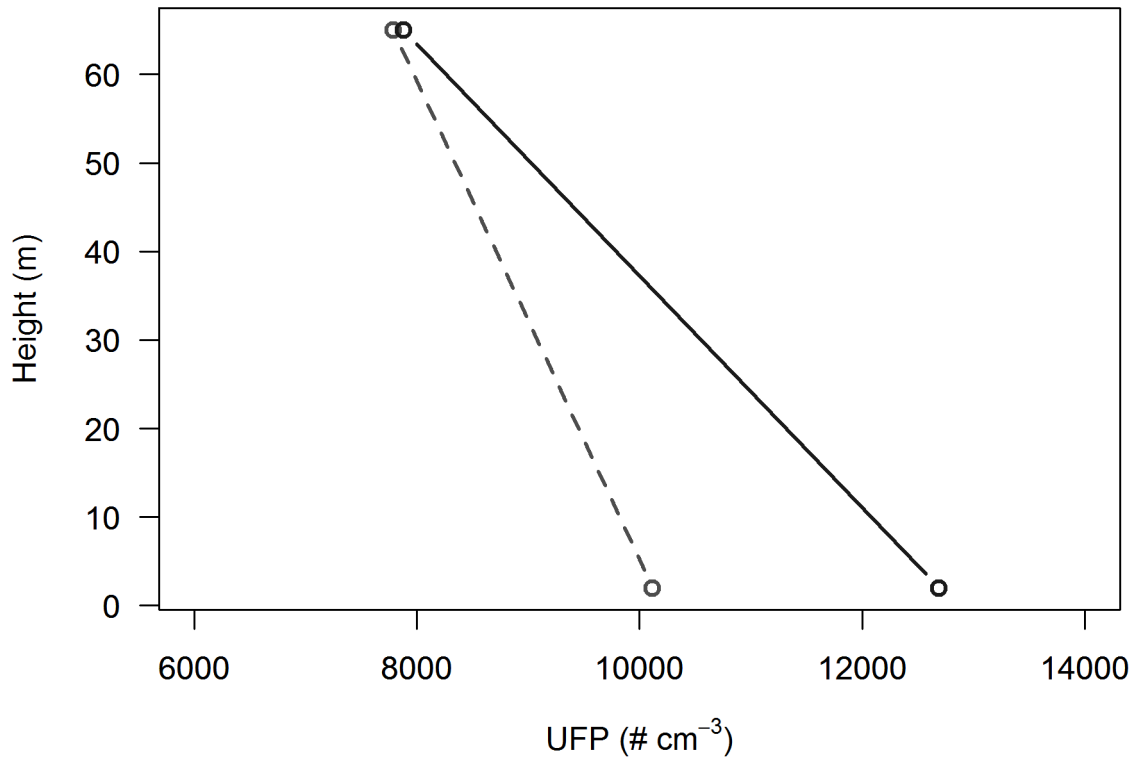


Figure 4_S: Ground-top differences in UFP concentrations when monitoring site is downwind (solid line) and upwind (dashed line) to the nearby street.

Multiple Regression output for $PM_{2.5}$ - Standardized Coefficients:

	Estimate	Std. Error	t value	Pr(>|t|)	
(Intercept)	1.8467	0.3888	4.749	7.13e-05	***
scale(Hmix)	-1.5092	1.2382	-1.219	0.234	
scale(Temp)	-0.3074	1.2245	-0.251	0.804	
scale(RH)	-0.8332	0.6039	-1.380	0.180	
scale(Wind_S)	-0.1243	0.4700	-0.265	0.794	

Residual standard error: 2.13 on 25 degrees of freedom

Multiple R-squared: 0.3281, Adjusted R-squared: 0.2206

F-statistic: 3.052 on 4 and 25 DF, p-value: 0.03538

Multiple Regression output for UFP - Standardized Coefficients:

	Estimate	Std. Error	t value	Pr(>|t|)	
(Intercept)	0.40437	0.01704	23.729	< 2e-16	***
scale(Hmix)	-0.13819	0.02110	-6.551	1.14e-10	***
scale(Temp)	-0.09841	0.02371	-4.151	3.73e-05	***
scale(RH)	-0.12520	0.02373	-5.277	1.77e-07	***
scale(Wind_S)	-0.07626	0.01715	-4.447	1.02e-05	***

Residual standard error: 0.4427 on 672 degrees of freedom

(43 observations deleted due to missingness)

Multiple R-squared: 0.134, Adjusted R-squared: 0.1288

F-statistic: 25.99 on 4 and 672 DF, p-value: < 2.2e-16