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Exposure concentration levels to ultrafine particles and black carbon along a pedestrian route in Milan

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1 Introduction

In the last years more and more researches were published in literature about mobile monitoring of air pollutants for exposure assessment. There is some evidence that for some kind of air pollutants, like ultrafine particle (UFP) and black carbon (BC), the assessment of the personal exposure provided by personal monitoring data is higher in comparison to the exposure estimated from fixed measurement stations (Peters et al., 2014). In particular, in order to properly assess the personal exposure to traffic related pollutants it is not enough to rely on fixed air quality measurements only but it is necessary, if not mandatory, to enforce researches with mobile pollutant monitoring too.

In literature, mainly two kind of studies were described: in the first kind, portable instruments were carried around by study subjects in order to measure the concentration levels to which they are exposed during daily activities or in micro-environments during travel; in the second kind of study mobile monitoring instruments are used to create air pollutant maps at high spatial and temporal resolution; exposure to pollutant is read from those maps. However, it should be noted that for the construction of high resolution maps, a large quantity of data is required.

Motorized traffic, especially diesel engine exhaust, is recognised as the main contributor to UFP and BC pollution in urban areas (Nikolova et al., 2011). Therefore, during daily trips along urban roads, people is directly exposed to elevated average concentration levels but also to high peaks of BC, fine and ultrafine particles. Exploiting portable instrumentation, it becomes possible to perform direct measurements of exposure concentration levels at high time resolution.

It is proved that at ambient concentration below 1 µg/m3 BC is responsible for health problems like cardiovascular effects or respiratory effects. Though currently not regulated by any air quality standard, BC is a suitable indicator of traffic related air pollution. Also for his impact on global warming, BC is included in several high level policy documents (UNECE 2010; UNEP 2011; WHO 2012). Currently UFP concentrations is not regulated at European level.

Predictive dispersion models for UFP and BC concentrations in urban environment can't be easily applied. Many factors affect the concentration of UFP, notably fluctuations in the wind flow and direct emissions in atmosphere. Often, for example in cities, the areas show both a complex geometry and canopy, leading to complex air flows and turbulence patterns that can have a great impact on UFP concentration levels that are therefore hardly predictable.

Epidemiological and toxicological studies indicate particle toxicity to be dependent on particle size. Due to the high number and high surface area per given mass, deposition probability in deep lung regions is higher and causing disease. For this reason, increased knowledge in this area is fundamental.

1.1 Ultrafine Particles and particle number concentration

UFPs are characterized by a particle diameter smaller than 100 nm and account for the majority of atmospheric aerosols in terms of number, yet they have a low contribution to the overall particulate mass. Due to the high concentration typical of urban environments, cities are considered hotspots for health risks associated to UFP exposure.

Many studies in several urban environments related elevated UFP concentration levels near roadways to motorized traffic to adverse human health effects. Depending also from other causes like occupation and life style, UFP exposure during travelling on urban roads could account for 17-50% of the daily UFP exposure. Several transportation modes have been taken in account, but UFP concentrations were compared across separate routes, on different times of the day and without comparison of meteorological conditions, in particular mixing height. The roadway design influences as well pollutant concentrations, and time spent in transport microenvironments contributes significantly to the personal daily exposure to UFP. Despite the awareness for air pollution in hot-spot areas like Milan, knowledge about the relation between UFP sources and concentration levels is still incomplete.

Literature studies shows UFP number concentration (PNC) levels in the 102 – 105 pt cm^{-3} range (particles per cubic centimetre) in urban environments, and contribution up to 70 – 90% of the total particle number concentration. As far as traffic emissions are concerned, two different origins are recognizable based on the particle number size distribution: particles with a diameter lower than 30 nm are originated from nucleation of vehicle exhaust gases immediately after release in atmosphere (within 0.5 seconds after release); particles in the 50–200 nm size range are directly emitted as combustion by-product, mainly as soot particles composed by carbonaceous agglomerates and adsorbed materials. Type and sulphur content of lubricant oil in diesel vehicles can also affect UFP emissions. High humidity promote nucleation too.

In addition to traffic, other primary sources in urban environments are combustion process for domestic heating and industrial processes. However, also secondary UFP can significantly contribute to total PNC. Main precursors of new particle formation are sulphate, inorganic ions like ammonia, nitrate and organic compounds. The required energy for those new formation processes is provided by solar radiation which allows photochemical reactions of precursors to form oxidized low volatile compounds.

Several studies reported seasonal, weekly and daily patterns due to variation in source strength and meteorological conditions. In literature, increasing PNC values were usually reported during the winter season due to the higher emission sources (domestic heating) and unfavourable atmospheric conditions (lower mixing height and atmospheric stability).

In urban areas the UFP weekly trend is generally characterized by lower PNC levels during weekends compared to working days. Daily PNC patterns are linked to traffic intensity, frequently pointing out higher concentrations during morning rush hours than afternoon's, due to the lower mixing height during the morning hours. Diurnal variations are more marked for traffic exposed sites than for urban background sites. Hussein et al. 2005, reported UFP concentrations to decrease exponentially with ambient temperature while larger particles (d_p>100nm) concentrations were proportional to temperature. Wind speed affects dispersion, dilution and re-suspension of particles influencing in different ways ultrafine and larger particles. UFP concentration have been observed to decrease exponentially with increasing wind speeds due to enhanced dilution, while re-suspension at high wind speed tends to increase larger particles concentration. Due to the washout effect, lower PNC were reported during precipitation events.

Good correlation between PNC and traffic related pollutants (CO, NOx, BC) have been observed in different studies both at roadside and urban background sites confirming traffic as a main source of urban particles. In general, stronger correlations were observed during winter indicating the increased effect of the combination of primary emission and unfavourable meteorological conditions, like the shallow atmospheric mixing height.

Due to the short lifetime of UFP and the strong influence of traffic sources, in urban areas PNC levels show rather high spatial variability both in terms of concentrations and size distribution. A rapid decrease of PNC with increasing distance to traffic was observed (Quiros, Lee, Wang, & Zhu, 2013). UFP concentration gradients near roadways have been reported to follow exponential laws. Roadside studies agree in the indication of increasing spatial gradient with decreasing particle size.

1.2 Black Carbon

Black Carbon (BC) is one of the most light absorbing components in atmospheric aerosols. By changing earth's radiative balance, BC plays an important role in climate change (Jacobson, 2011). Compared to other particulate matter, BC has very different optical and radiative proprieties, being the dominant light-absorbing aerosol component in atmosphere. The direct radiative forcing of BC aerosol has been estimated to be around 0.9 W m-2, suggesting that BC is the second strongest contributor to current climate warming after carbon dioxide. (Zha et al., 2014) The World Health Organization classified BC as a Category I Carcinogen and associated it with health problems like cardiovascular dysfunction, increasing thrombus formation, and cancer (WHO, 2012).. The major sources of atmospheric BC are fossil fuel combustion and biomass burning. Fossil fuel combustion leads to nitrogen oxides, carbon monoxide and particulate matter made up by an high amount of BC and organic compounds. Incomplete combustions due to low temperature, low turbulence or low fuel residence time are the main parameters that influence the formation of carbonaceous particulate matter. The size of the carbonaceous particles depends on which source issued. BC is therefore an excellent marker for organic fuel combustions sources (Sandradewi et al., 2007; Schneider et al., 2008) Concurrent measurements of PNC and BC performed in different European cities showed how in Northern and central Europe PNC and BC vary simultaneously through the whole day.

Dons et al (2012) showed that exposure during transport (even if short in duration) can be important in integrated daily exposure to BC. Concentration in micro-environment during transport can be from 2 up to 5 times higher than average concentration at home. Dons demonstrate that even if people spend on average only 6% of their time in transport, this leads to over 20% of their inhaled daily dose. (Dons et al., 2013)

According to Kaur et al. (2007), BC levels during transport are connected to the following four factors:

- personal factors (time activity, timing of trips and breathing rate),
- mode of transport factors (active or motorized travellers),
- meteorological factors (mixing height, wind speed, temperature, humidity),
- traffic factors (rush hours)

1.3 Scope of the work

Aim of this thesis is the investigation of the seasonal, weekly and daily concentration levels of PNC and BC variation in order to quantify and assess pedestrian exposure to such pollutants in the urban area of Milan. It is well known that Lombardy, Italy's most industrialized region and the city of Milan in particular, is an European hot spot for atmospheric pollution with the air quality standards for criteria pollutant frequently not attained, also due to the unfavourable geographical location characterized by low average wind speeds preventing frequent air masses changes.

Currently PNC is not measured by the air quality network and BC monitoring was implemented only recently in few stations. Furthermore, as already mentioned, air quality monitoring at stationary sites may not provide comprehensive information on PNC and BC levels over the whole urban area, therefore not provide an accurate assessment of the actual human exposure of the population. In order to collect information on the spatial pattern of PNC and BC monitoring campaigns were simultaneously performed at a fixed monitoring site and along a 17 km-long pedestrian route through the city. The fixed site was set up far from primary emission sources in the University campus in order to quantify urban pollution background levels. Concentration levels along the pedestrian route were measured by walking through six different urban zones, each characterized by different traffic regulation, in order to assess the spatial and temporal variation of PNC and BC.

Other purpose of present work is to investigate the relationship between black carbon aerosols and particle number concentration at the traffic and at the background site and verify the effectiveness of mitigation policies adopted by the city of Milan (in particular congestion charge Area C).

2 Materials and methods

Monitoring campaigns were performed from December 2013 to July 2014. The resulting data set was split into a cold period subset (from December to March) characterized by stronger emissions and atmospheric stability, and a warm period subset (from April to July) in order to describe seasonal PNC and BC variability. Each month, measurements were carried out during morning and afternoon rush hours (8 – 11 am and 15 – 18 pm) in order to describe diurnal and weekly pollutants variability. The mobile monitoring route consist in a 17 km long pedestrian city track, passing through suburban areas, traffic limited areas and pedestrian zones. During the cold season, 30 individual runs were performed covering approximately a distance of 510 km. Warm season consists of 42 individual runs, walking approximately for 714 Km. Overall monitoring campaign consists therefore of 72 individual runs and approximately more than 1200 Km through Milan, collecting more than 130000 concentration data. Collected data were corrected and averaged over a 10-secon time resolution in order to preserve high time and spatial resolution. Beside seasonal comparisons, also differences between working days, Saturdays and public transport strike days were performed.

A detailed calendar of the samplings is reported in Table 0.1 (Annex I) For the real-time measurement of particle number concentration and black carbon exposure concentration, two portable condensation particle counter and two portable Aethalomters were used.

Characterization of the spatial variability of BC and PNC, permits the construction of pollution maps in urban environments, an important tool to better understand the phenomenon and respond with appropriate regulatory policies. A large number of mobile concentration data is therefore necessary.

2.1 Sampling instrumentation

2.1.1 AethLabs Aethalometer AE 51

A portable Aethalometer Model AE51 was used to measure the optically-absorbing component of aerosol particles Black Carbon ('BC'). The small size (117 mm L x 66 mm W x 38 mm D) and light weight (280 g) of the MicroAeth allow it to be used to gather data in a wide range of operational scenarios. The instrument is based on Aethalometer technology that is widely used for studying indoor or outdoor air quality, and for the mobile mapping of the air quality impacts of localized sources. Real-time analysis are made by measuring the rate of change in absorption of transmitted light due to continuous collection of aerosol deposit on a PTFE-coated borosilicate glass fiber filter. The manufacturer recommends to use it in an operating range between 0 and 40 °C.

Figure 2:1 Micro-Aethalometer AE51

The MicroAeth draws the air flow through a 3 mm diameter portion of filter media. Optical transmission through the 'Sensing' spot is measured by a stabilized 880 nm LED light source and photo diode detector. The absorbance ('Attenuation, ATN') of the spot is measured relative to an adjacent 'Reference' portion of the filter once per time-base period. The gradual accumulation of optically-absorbing particles leads to a gradual increase in ATN from one period to the next. The electronics and microprocessor measure and store the data each period to determine the increment during each time-base. This is then converted to a mass concentration of BC expressed in nanograms per cubic meter (ng/ m^3) using the known optical absorbance per unit mass of Black Carbon material. The MicroAeth derives its power from an internal rechargeable battery.

The instrument will operate for 6 to 24 hours on a single charge, depending on operational settings.

The filter strip consists in a small section of filter material held between and supported by a filter holder, in order to create the filter strip assembly. As the aerosol sample is drawn through the filter media by the instrument's integrated, internal sample pump, the aerosol sample collects gradually on the filter medium to create a grey spot 3 mm in diameter. The MicroAeth determines the attenuation of the source light as the accumulated black carbon increases the optical density of the filter spot. After the optical density reaches a certain level, the filter strip must be replaced to maintain measurement integrity. The MicroAeth start-up sequence automatically begins when the power is turned on. It is very important to confirm the date and time of the PC prior to synchronizing to the MicroAeth. Once confirmed, it is good operating practice to always synchronize the date and time when configuring the MicroAeth before starting a new sample session. It is recommend to use lower flows in areas with high BC concentrations, and higher flow rates when maximum sensitivity is required in areas of low BC concentration. A lower flow rate should also be selected for longer run times and extended battery life. Secure mode will allow the MicroAeth to be shut down by pressing and releasing the power button three times in succession. The data files are plain text with the extension .dat or .csv.

Different Black Carbon measurement scenarios require different operational settings for optimum performance. The value of BC mass concentration, measured at 880 nm wavelength, is based on the assumption that the attenuation of light beam is linearly proportional to the mass of BC deposited on the filter strip through a constant called specific absorption cross section (m^2 g^{-1}). The value of the constant we applied was suggested by the manufacturer.

The choice of these parameters affects the operation and data as follows:

	Longest ←	——— Filter Life ———		→ Shortest
	50 ml/min	100 ml/min	150 ml/min	200 ml/min
1 s	'Data Acquisition Mode' for immediate emissions and impacts at high concentrations.	'Data Acquisition Mode' for emissions and impacts in typical urban and traffic environments.	'Data Acquisition Mode' for higher time resolution at lower BC concentrations.	'Data Acquisition Mode' for higher time resolution at lower BC concentrations or shorter sampling durations.
10 s	Traffic and transporation impacts in high BC concentrations.	Traffic and transporation impacts.	Traffic and transporation impacts at lower BC concentrations.	Traffic and transporation impacts at lower BC concentrations.
30 s	Personal Exposure Monitoring in high BC concentrations. Occupational Exposure.	Recommended Setting for General Applications. Personal Exposure Monitoring. Traffic impact. High time resolution ambient monitoring.	Personal Exposure Monitoring. Traffic impact. High time resolution ambient monitoring.	Personal Exposure Monitoring. Traffic impact. Ambient monitoring. Higher sensitivity for low BC concentrations.
60 s	Personal Exposure Monitoring. Occupational Exposure. High BC concentrations.	Personal Exposure Monitoring. Indoor Air Quality.	Personal Exposure Monitoring. Indoor Air Quality. Low BC concentration.	Personal Exposure Monitoring. Higher sensitivity for low BC concentrations.
300 s	Epidemiology. Area monitoring. Indoor air quality. High BC concentration.	Epidemiology. Area monitoring. Indoor air quality.	Epidemiology. Area monitoring. Indoor air quality. Low BC concentration.	Epidemiology. Area monitoring. Indoor air quality. Lowest BC concentration. Lowest data noise.

Table 2:1 Suggested operational settings for AE 51

Both instruments were therefore set on a 10 second sampling interval and a air flow of 100 ml min^{-1}, typical for investigation on traffic and transportation impacts.

2.1.1.1 BC data processing

Filter based optical BC measurements are based on the relationship between the light attenuation value ATN and the BC particles sampled on the surface of the filter. ATN values should constantly increase, but when the AE51 is sampling at high time resolutions in order from seconds to minutes, or when in the sampled air stream the BC concentrations are low, electrical and optical noise can lead to an erroneous ATN value. The calculation of BC concentrations is based on successive differences. An erroneous BC data due to noise at one time point is followed by an subsequent erroneous high or low BC data at the next time point. The instrument can also report negative data when the real BC concentrations are low compared to the magnitude of the noise. Given that negative data are impossible to explain, those data need to be corrected. The simple removal of negative data would amplify the noise of the positive fluctuations. Another alternative could be averaging the data over an longer time period. This will certainly lead to a reduction of noise in the signal, but this would compromise the spatial resolution of the data and the ability to detect real variations and trends in the data will be lost.

Numerous post-processing methods are described in literature (Hagler, Yelverton, Vedantham, Hansen, & Turner, 2011). The need to keep the highest time resolution possible leads to the use of the Optimized Noise-reduction Averaging method (ONA).

A view of the original 10-second AE51 data set reveal irregular and high amplitude fluctuations. The aethalmeter calculates the average BC concentration for time interval i as:

$$BCi = (A * \Delta ATNi)/(Q * Eatn * \Delta ti)$$

Where A is the deposit filter area [L2], Q is the sampled volumetric flow rate [L3/ t], Eatn is the effective mass absorption efficiency of the deposited particles [L2/M], ΔATN is the difference between ATN at time point ti+1 and ATN value at time ti. Both AE51 models were set to operating at a time base of 10 seconds. At high time resolutions, the change in ATN value can be sufficiently small to be significantly influenced by measurement noise even with high deposition rates. The ONA smoothing algorithm has been set by the user on a minimum change in attenuation (ΔATNmin) which for a given BC concentration results in an adjusted time base Δt'.

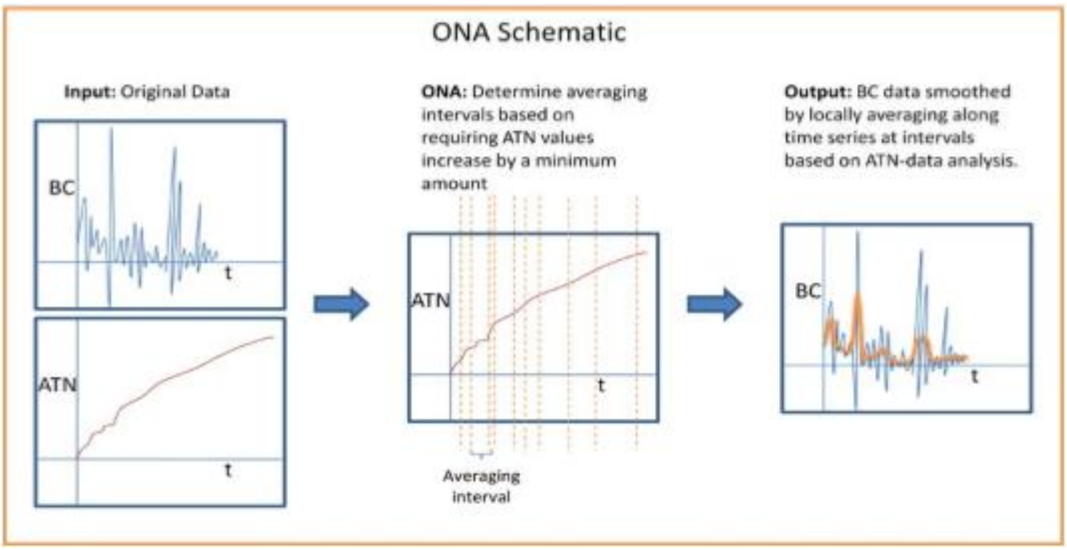

Figure 2:2 Operating principle of the noise reduction program ONA

For high BC concentrations ΔATNi will be greater than ΔATNmin and the spatio-temporal resolution will be preserved. For lower BC concentrations, ΔATNi will be less than ΔATNmin and the data will be smoothed over a time interval Δt'> Δti needed to reach ΔATNmin. The ATN value at the end of time interval Δt' must be the last occurrence in the rest of the data collection. This extend Δt' up to that ATN value. This constraint causes a data smoothing even if ΔATNmin is set to zero. EPA has developed a version of the ONA algorithm, which is publically available on their website.

Halger et al. (2011) have evaluated the relationship between the minimum ΔATN value applied in the ONA algorithm and the reduction of instrumental noise. The original noise level in the data set was estimated to be 12,500 ng/m3. Applying ONA by changing the minimum ΔATN in the range from 0.00 to 0.10, a sostanzial reduction of the noise level has highlighted, from 2,185 to 11 ng/m3 . Even with ΔATNmin set to zero, a six fold reduction in noise level occurred. Noise vas estimated as the average absolute value of the instantaneous change in BC in the data set:

$$Noise = \frac{1}{n}\sum |BCi + 1 - BCi|$$

An increasing of the ΔATNmin cause a reduction of noise level until an asymptote is reached at ΔATN = 0.05. For this reason, for the post processing data ONA algorithm an ΔATNmin=0.05 was applied. In the case study treated by Halger et al. the BC levels are maintained constant, while in our case the conditions are more variable and data are more subjected to instrumental noise. In the post processed data set, the occurrence of negative data is dropped to zero.

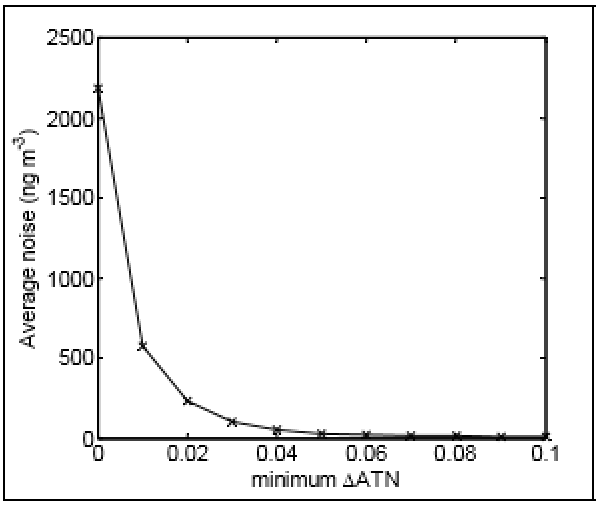

Figure 2:3 Comparison of estimated noise in the post-processed BC signal versus the input minimum change in ATN required by the post-processing program

2.1.2 TSI P-Trak 8525

The P-trak model 5825 is a portable condensation particle counter able to measure PNC in the 20-1000 nm size range ($PNC_{20\text{-}1000}$) at various time resolutions, detecting particle concentration up to 5 x 10^5 cm^{-3}. The ambient air drawn into the instrument is first saturated with isopropyl alcohol vapour that then condenses onto the particles causing them to grow into larger droplets detectable by means of a photo-detector when flashed by a focused laser beam. The Data Log mode is used to record particle concentration readings over a period of time, and store these readings in the instrument memory.

The P-trak particle counter contains liquid isopropyl alcohol, which is absorbed into a porous wick. Under most operating conditions, the alcohol remains absorbed in the wick. However, if the instrument is tilted for a period of time, the alcohol will slowly seep out of the wick. This liquid alcohol may be drawn into the optical chamber, causing false particle counts and possibly flooding the optics causing a temporary loss of performance.

Figure 2:4 TSI P-trak modes 5852

Before beginning to sample with the P-trak particle counter, it is important to verify that the instrument is operating normally. A daily zero check should be performed at least once a day. Each day, before starting the monitoring, a supplied zero filter was fixed to the inlet screen. The particle concentration should go to zero in approximately 5 to 10 seconds. Leave the zero filter attached to the instrument for 30 seconds, to make sure the zero reading is stable. The P-trak particle counter displays the measured particle concentration in units of particles per cubic centimetre. The display updates once per second. The instrument range is from 0 to 500,000 pt/cm^3.

2.1.3 Instrumental comparison

Before starting the monitoring campaign, an instrumental comparison was needed to ensure the proper functioning of sampling instrumentation. Available particle condensation counters have different ages and it is therefore necessary to make some tests in order to verify instrumentations good agreement.

During December 2013 and January 2014 over 13 hours tests in all whether conditions were performed to this purpose. Comparison of the two particle counter were firstly performed. From 2th to 4th December, both P-trak (model 8525) were positioned side-by-side at the fixed monitoring station assembled at Politecnico's garden for an overall time period of 13 hours, collecting 46438 PNC data at a 1-second time resolution. Original sampled data were downloaded and plotted on a scatterplot, given in Fig 3.5

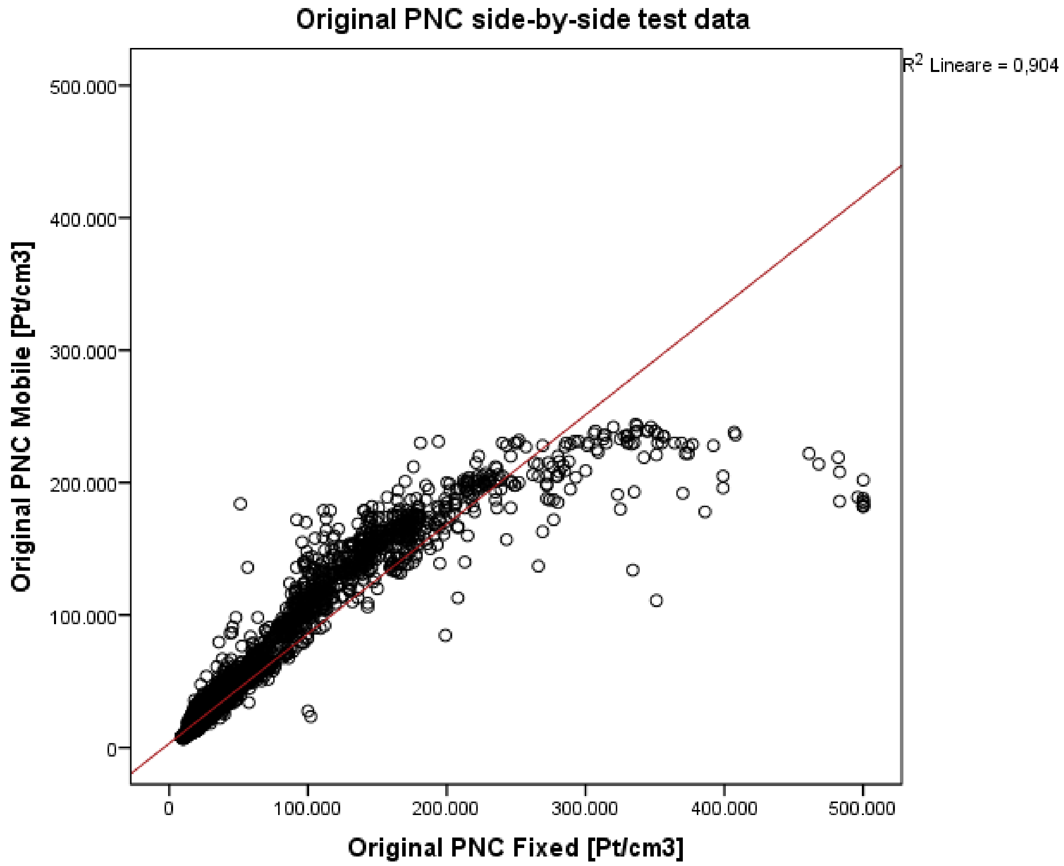

Figure 2:5 Linear correlation of original 1- second fixed and mobile PNC data. R^2=0.904

The high value of the computed coefficient of correlation, R^2 = 0.904 , indicates a good agreement between the two instruments. However, a discordant trend was noted at high particle concentrations. Up to approximately 3 x 10^5 Pt/cm3 concentration levels, data of the two P-traks follow the same pattern. After this critical limit value, the elder instruments reaches full scale values (5 x 105 Pt/cm3), while the other particle condensation counter remains at lower values. It was therefore decided to leave the elder P-trak at the fixed monitoring station during the monitoring campaign, as it was supposed that full scale values were reached less frequently at the background site than at the mobile monitoring site. A 10-second averaging algorithm was applied at the resulting raw PNC dataset. In Fig 3.6, the relationship between the 10-second averaged data is given. The resulting higher coefficient of correlation, $R^2 = 0.924$ indicate a better agreement between the two instruments.

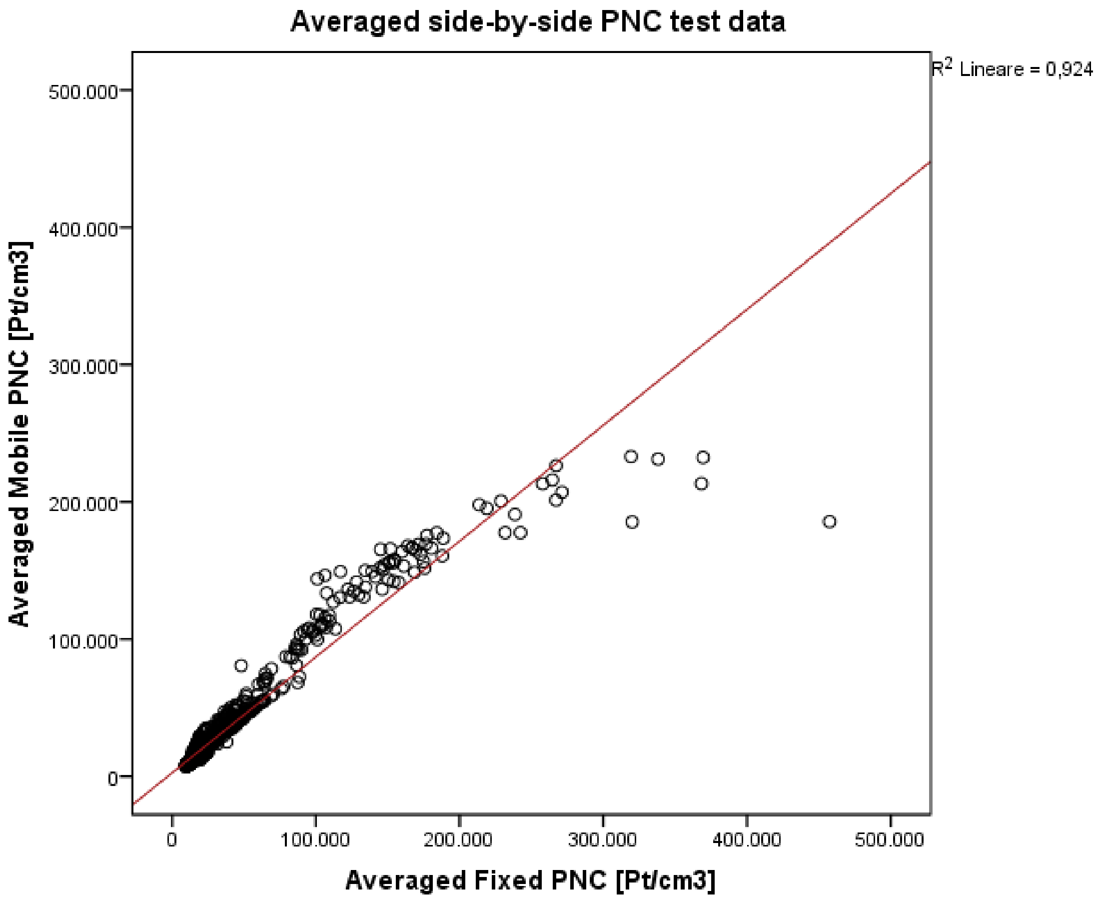

Figure 2:6 Linear correlation of 10-second averaged fixed and mobile PNC data. R^2=0.924

Same procedure as previously described was applied at both aethalometers (model AE51). Fig 3.7 present the relationship between the unprocessed black carbon data. Also in this case a high correlation was observed ($R^2 = 0.966$). Observing the raw BC concentration data, the presence of negative concentration data highlights. Given that negative concentration data are impossible to be explained, those data are due to an erroneous instrument functioning. Data needed therefore to be treated. The only cancelling of negative data would lead to an overestimation of average concentration levels, as described in section 3.7.

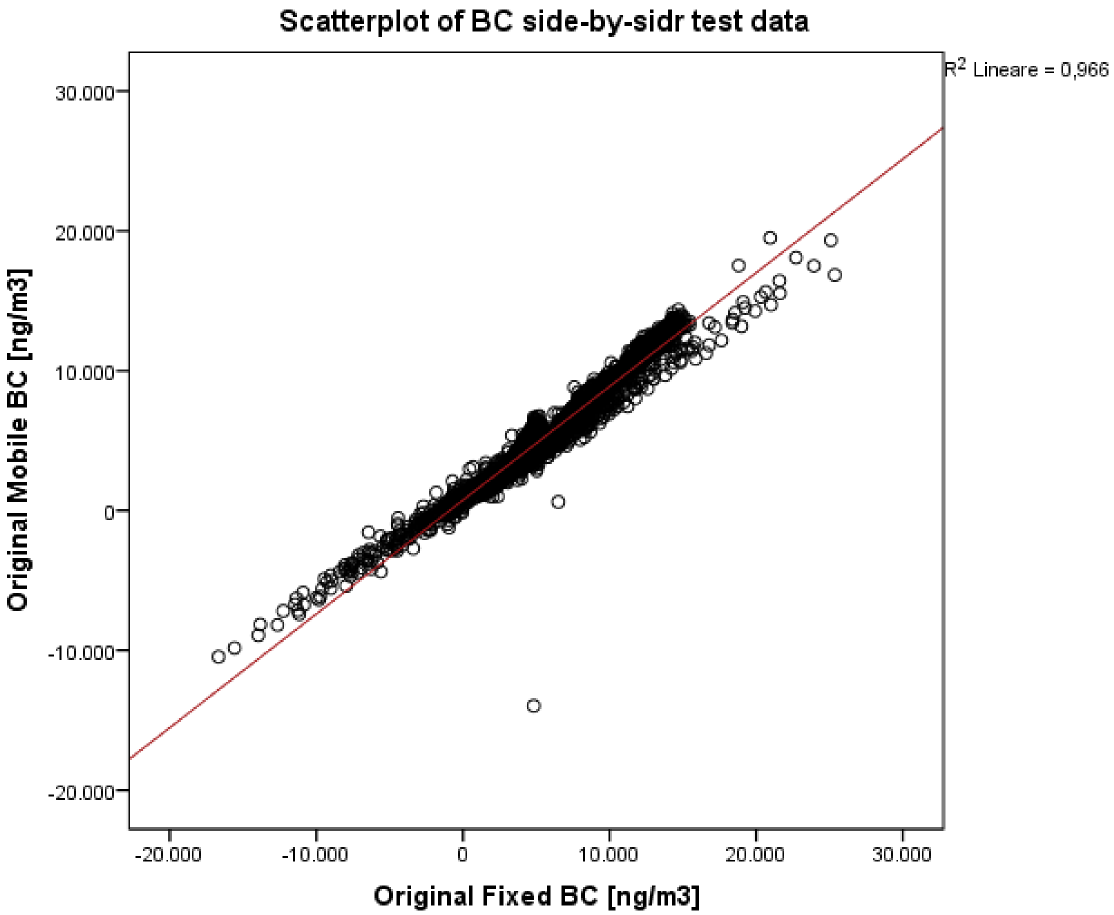

Figure 2:7 Linear correlation of original 10-second fixed and mobile BC data. R^2=0.966

Fig 4.4 present the relationships between the 10 second BC concentration levels measured over the whole sampling period, obtained from the original data treated by the ONA noise reduction algorithm. Negative BC levels may be present using AE51 at low actual BC levels or at a high time-resolution. The negative values can be eliminated very effectively by the ONA method as given in Fig 4.4, showing an extremely high correlation value: R^2 = 0.993.

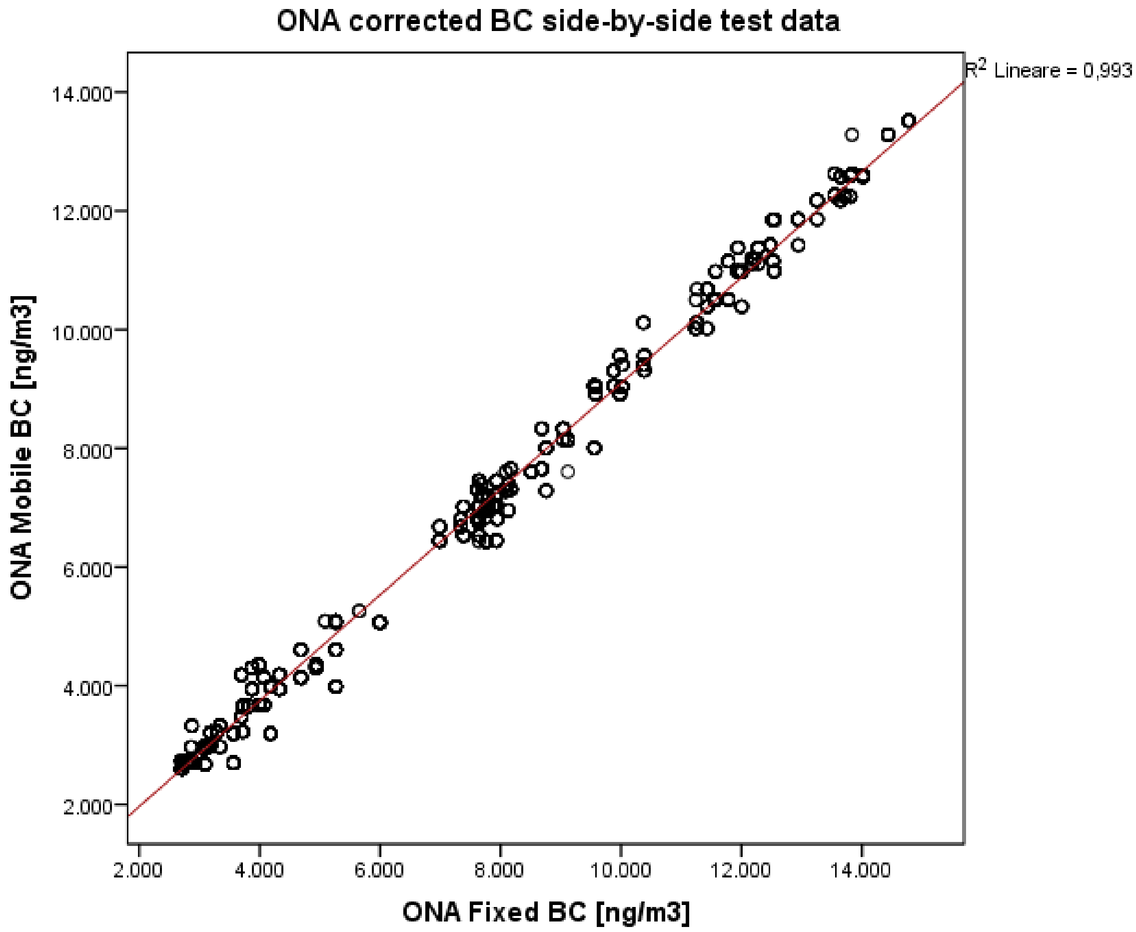

Figure 2:8 Linear correlation of ONA treated fixed and mobile BC data. R^2=0.993

2.2 Meteorological data

Meteorological data were obtained from a weather station of the regional environmental protection agency (ARPA Lombardia) monitoring networks. All meteorological data can be free downloaded from the website of ARPA Lombardia.

Following variables are aviable:

- Temperature [°C]
- Precipitation [mm]
- Relative humidity [%]
- Global radiation [W m^{-2}]

- Atmospheric pressure [hPa]

Meteorological data were obtained as hourly averages, except those referred to precipitation for which the data correspond to the hourly cumulative. It must be noted that wind direction and wind speed wasn't taken into account. The so-called "canyoning effect" in urban areas makes less significant the use of data obtained from a fixed measurement station to simulate wind characteristics along the monitoring route. All data are referred to the Central European Time (UTC+1).

2.3 Monitoring sites

Measurements of ultra-fine particle number and black carbon concentration were performed in two different monitoring sites. The first one is a 17 km long mobile urban traffic site located in the city of Milan which leads through several urban areas, from the suburbs to the centre. The second is situated close to via Bassini and via Ponzio in the garden of Politecnico di Milano in Città Studi district. This site represents the urban background due to the absence of relevant primary traffic sources.

Milan is the largest city in Northern Italy and the capital of Lombardy with a population of 1.3 million. The urban area of Milan is the fifth largest in the EU and with the highest population (about 8.3 million) and industry density of Italy. Milan is located in the north-western section of the Po Valley. The municipal territory is entirely flat, the highest point being at 122 m above sea level. The administrative commune covers an area of about 181 square kilometres, with a population, in 2013, of 1,324,169 and a population density of 7,315 inhabitants per square kilometre. Around the city lies a vast urbanized valley that expands mainly to the north, engulfing many communes in a continuous urban landscape. The contiguous built-up area trespass by far the city limits, forming a vast urban agglomeration that stretches North-East and North-West to reach Varese, Como, Lecco and Bergamo. In the north, Po valley is bordered by the Alps while the south is bordered by the Appennines. These particular orographic structure leads to typical stagnant meteorological conditions. In consequence of the high activity density and the related high density of air pollutant sources, Po valley is one of the main air pollution hot-spots in Europe. Regulatory air quality standards are not attended in the last years.

2.3.1 Monitoring route

A monitoring campaign conducted on foot through Milan was carried out during the months of December 2013, January, March, April, May and July 2014. A fixed route was defined before starting the campaign. Covering all areas of the city and developing along two main streets conducting in and out the city. On these streets the presence of many shops and other commercial activity involves a high turnout of pedestrians on the kerbside.

Following the hypothetical journey made by a tourist, the monitoring route starts in Piazza Argentina close to the underground station of Piazzale Loreto where the metro lines M1 and M2 intersect. The route continues following up on Corso Buenos Aires, a straight 1.4 km long road to Porta Venezia. Traffic proceeds on two asphalted lanes in each direction. At both sides of the road there is an approximately five meter large kerbside. In the morning rush hours (8.00-10.00) traffic is very intensive and often idling due to traffic lights and the high traffic intensity. This road is one of the main arteries to get into the city from the north-east direction. Many clothing stores and bars are located on both sides, this implies the presence of many pedestrians on sidewalks. Corso Buenos Aires crosses three busy streets. The first one near the M1 station of Lima, Via Plinio on the left and Via Vitruvio on the right are crossed. After 500 meters Viale Tunisia is crossed. The last major intersection of Corso Buenos Aires is in Porta Venezia, where the area is enclosed by the ancient city walls and the related traffic limitation zone begins (Area C). At each of those intersections, time was written down on the trip diary. The route continues straight to take Corso Venezia, a 1.0 km long asphalted street which brings into Piazza San Babila where the pedestrian zone begins. The first 300 meters, since the Palestro M1 station, are flanked on the right by the city-park Giardini Pubblici di Indro Montanelli and a large kerbside. After other 400 meters Corso Venezia intersects Via Senato, a busy road which is part of the inner ring road. In the last stretch of the road the kerbside becomes narrower, only 1-2 meters and also traffic intensity decreases.

Once reached the Piazza San Babila the pedestrian zone begins. A more or less 1.0 km long cobbled street brings to Piazza del Duomo along Corso Vittorio Emanuele. Access to this road is allowed only for cyclist an pedestrians. The only motorized vehicles that can access are police cars, road cleaning vehicles and armoured vans to carry money to shops and banks of the city centre. After passing the monument dedicated to Vittorio Emanuele II at the end of Piazza del Duomo, the route turns left in Via Giuseppe Mazzini. This street is not very long, approximately 350 meters but characterized by cobblestones and traffic limitations. The access for motorized vehicles is only allowed to trams and cabs. Kerbside is only few meters large, and high surrounding buildings form a typical urban canyon effect. Once reached Piazza Missori the route turns left in Corso di Porta Romana, a 1.4 Km long straight street developing in South-East direction along the route of underground line M3. The first 550 meters, up to the intersection with Via Sforza (inner ring road), are characterized by a tight kerbside, cobblestones on the ground and low traffic conditions. Proceeding along the street, vehicular traffic increase. After passing M3 Crocetta station, the monitoring campaign route reaches Porta Romana where the traffic limitation zone Area C ends. Crossing the square, the route proceeds straight along Corso Lodi, a 2.3 km long road. The first 850 meters of Corso Lodi until reaching Piazzale Lodi are characterised by the presence of access roads on both sides. The consequence is the increase of the street width. In this way the sidewalks are more distant from the most busy zone of the road. Being out of Area C, traffic intensity increases significantly. In Piazzale Lodi the monitoring route intersects Viale Isonzo on the right and Viale Umbria on the left. Those two avenues are part of the external city ring road and always crowded at each time of the day. A further significant traffic flow is added, especially heavy diesel vehicles. Corso Lodi is one of the most important access roads to the city. After Piazzale Lodi, the street overpasses the railway station of Porta Romana. Proceeding on the cycle lane between the two roadways, the route arrives at Piazzale Corvetto. After having covered the full perimeter of the square, the route turns back to follow exactly the route described above (on the same street side) until reaching again Piazza Argentina where the monitoring route ends after 17 km. Sketches of each street section are reported in Annex I.

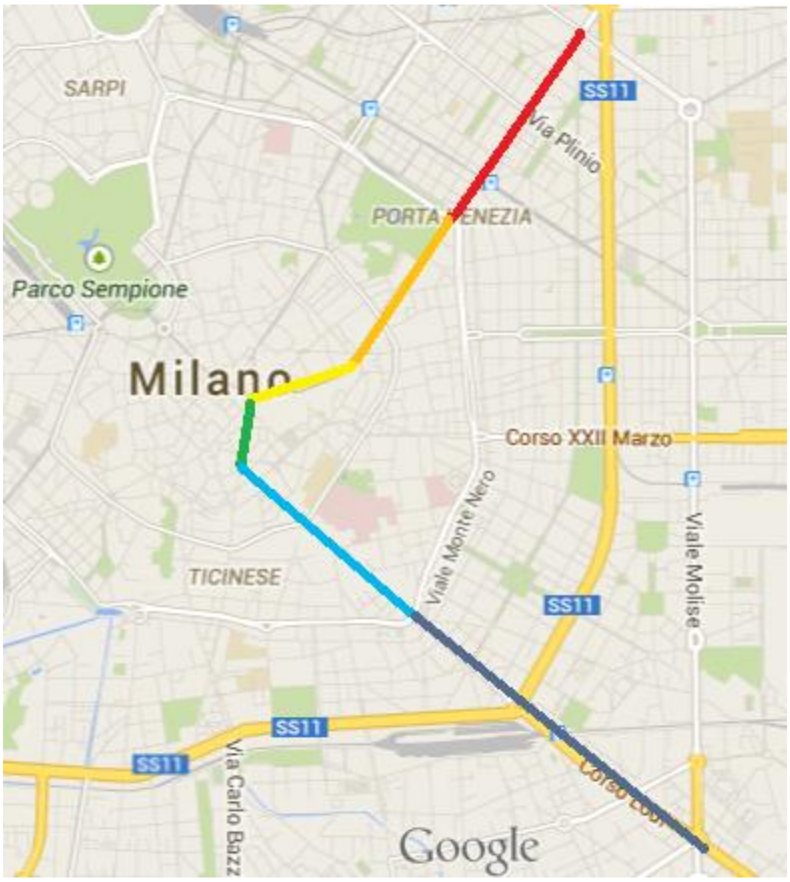

Figure 2:9 Monitoring route through Milan

Route	Tag	Length	Characteristics
Piazza Argentina - Porta Venezia	AV	1.6 km	Heavy traffic, No Area C
Porta Venezia - San Babila	VB	1.2 km	Heavy traffic, Area C
San Babila - Duomo	BD	0.8 km	Pedestrian zone
Duomo - Missori	DM	0.4 km	Only public transport
Missori - Porta Romana	MR	1.8 km	Modestly crowded, Area C
Porta Romana - Corvetto	RC	2.7 km	Heavy traffic, No Area C

Table 2:2 Street characteristics of each urban section

Walking along the monitoring route, several city areas are passed. Suburbs without traffic limitations, the area enclosed by the ancient city walls, which is subject to traffic limitations and finally the pedestrian zone in the city-centre. Several characteristics like traffic intensity, road type, road speed and road width change along the monitoring route.

2.3.2 Background measurement station

The fixed measurement station located in Politecnico's garden close to Via Bassini and Via Ponzio and is not directly exposed to primary pollution sources and serves as a background monitoring site. The main UFP end BC primary source is due to the heating of the surrounding university buildings.

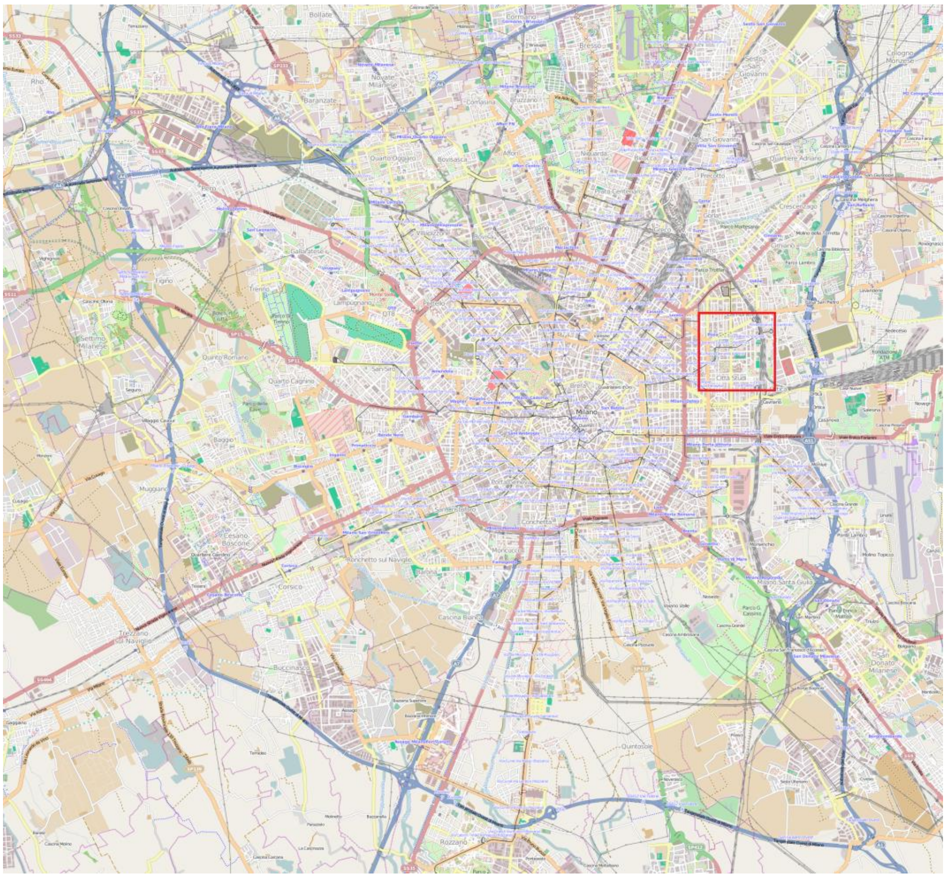

Figure 2:10 Geogrephical localization of the urban background area

Figure 2:11 Geogrephical localization of the urban background fixed AQ station

3 Results and discussion

Before starting statistical analysis, data were manually analysed in order to detect erroneous data containing codes of instruments malfunctioning. Those data were not considered in statistical analysis. However, only few unreliable PNC and none BC data were found in the entire dataset.

For each sampling site, data were analysed separately for each season. BC data were acquired at a 10-second time resolution, while particle number concentration at 1-second time resolution. In order to allow a correct comparison between BC and PNC data, PNC data were averaged over a 10 second period. All statistical analysis were performed on the 10 second averaged database. For each month, data were analysed separately. A further distinction between workdays, Saturday (including holidays) and days of public transport strike were made.

As described in section 2, measuring campaigns were performed during different periods from December 2013 to July 2014. The resulting PNC and BC dataset was divided into a cold period (December-March) and warm period (April-July) in order to investigate and compare seasonal, inter- and intra-site observed pollutants concentration levels. Summary statistics of the sampled PNC and BC concentration data are shown through whiskers box-plots, representing median value, interquartile range and extreme cases of each single variable. Each box-plot is associated to a chart which display the 95% confidence interval for the average value of each considered variable (shown in Annex II and Annex III). Main descriptive statistics are summarized in tables. A detailed calendar of samplings at each measuring site is shown in Table 0:1 in Annex I.

3.1 Cold period

During the cold period monitoring campaign, and after a manual data screening, for each aethalometer, 16564 Black Carbon (BC) data were collected at a 10-second time resolution. Particle number concentration in the 20-1000 nm range ($PNC_{20-1000}$) data are more numerous due to the higher time resolution of the instrument (1-second) and to the fact that during the month of December only P-traks were available. After applying a 10-secon averaging algorithm, 25433 data for the fixed P-trak and 26280 data for the mobile P-trak were available. Therefore, the entire cold period dataset consists of 84841 data at a 10-second time resolution. Cold seasons characteristics differs in several aspects from the warm period. Strong differences in primary source intensity can be noted. Due to the lower average temperature during the cold period, emissions from domestic heating are relevant and must be added together with traffic emissions and urban background concentration levels. While BC is emitted directly from primary sources, fine and ultrafine particles are also formed by secondary processes, strictly dependent from precursors, temperature and humidity. This will be reflected in different seasonal variations for BC and PNC data. Low temperatures lead to a reduced use of active travel modes (cyclists and pedestrians) and to a consequent increase of motorized traffic on urban roads. Other consideration should be made about weather conditions. Situation of atmospheric stability characterize the typical winter weather conditions in northern Italy, leading to low atmospheric mixing conditions. All these considerations suggest higher concentration values for both pollutants during the cold period compared to the warm season.

3.1.1 Black Carbon data results

The original recorded datasets were first processed with the ONA correcting algorithm (as explained in section 2.1) and then for statistical analyses and potential outlier detection. The main statistical parameters of the cold period BC data distributions for the overall datasets and for the morning and afternoon datasets separately are reported in Table 3.1: data from the stationary instrument at the urban background site are reported as “BC fixed” whereas those recorded along the pedestrian route as “BC mobile”. The box-plots of Figure 3.1 summarize the morning and afternoon datasets for the fixed and mobile instrument in terms of the median values, interquartile ranges, extreme values and outliers; morning and afternoon average values, together with 95% confidence intervals are plotted in Figure 9.1 (Annex II)

Instrument and route		N	Minimum	Maximum	Mean	Std. Deviation
BC Fixed	Overall	16564	393	17638	5162	3481
	Morning	10912	393	17638	5599	4117
	Afternoon	5652	1978	7395	4319	1311
BC Mobile	Overall	16564	2121	26994	6578	3159
	Morning	10912	2121	26994	7040	3563
	Afternoon	5652	2653	13966	5686	1877

Table 3:1 Main descriptive statistics for Fixed and Mobile BC concentrations

Overall, BC fixed data are in the 393-17638 ng/m^3 range, with an average of 5162 ng/m^3 and a standard deviation of 3481 ng/m^3: corresponding figures for BC mobile data are 2121-26994 ng/m^3, 6577 ng/m^3, and 3158 ng/m^3. Compared to fixed data, mobile data are shifted towards higher values, as highlighted by both the min-max range and by the significantly (α = 0.05) higher mean (about 1.3 times higher than that measured at the fixed sampling site); however, the two datasets show similar values for the standard deviations. Therefore, despite their restricted range, fixed data are characterized by a larger variability, as stated by the comparison of the values computed for the coefficient of variations (CV = 0.67 for BC fixed vs. 0.48 for BC mobile).

BC mobile data are significantly higher than fixed data also when separately considering the morning and the afternoon route: the mean values for the BC mobile datasets are 1.2 and 1.3 times higher than those of the BC fixed on morning and afternoon subsets, respectively. Higher average mobile concentrations are due to the proximity to primary emission sources.

Data variability is always larger in the morning, and at the urban background site in particular (CV = 0.74 for BC fixed vs. CV = 0.51 for BC mobile), then in the afternoon when, conversely is larger for the BC mobile dataset (CV = 0.30 for BC fixed vs. CV = 0.33 for BC mobile).

For both the fixed and mobile dataset the highest and lowest values were recorded in the morning.

3.1.1.1 Daily variability

The comparison between morning and afternoon values shows that during the morning hours concentration levels are significantly higher for both the fixed and mobile instrument: on the average, morning concentration are 1.3 times higher than in the afternoon for BC fixed and 1.24 times higher for BC mobile

Potential outlier detection showed that these values are mostly present in the morning hours dataset for the mobile instrument: in particular, data label analysis highlights that the morning outliers shown in Figure 3.1 were all recorded on January 23th whereas the few afternoon outliers of the mobile instrument were all recorded on January 31th. In the fixed instrument dataset only a couple of potential outliers were recognized for the morning hours and none for the afternoon hours.

However, it must be considered that outlier detection is a merely statistical procedure intend to recognize those values that are inconsistent (i.e.: anomalous) with the whole dataset. Nevertheless, such anomalous values may be the result of very peculiar environmental conditions that, even though very infrequent and rarely occurring, are at the same time likely to happen. It is not surprising that the recognized potential outliers were mainly detected in the BC mobile dataset: indeed, the closer exposition to traffic exhaust emissions and peculiar environmental conditions from the emission standpoints (i.e.: queue of idling vehicles, busy crossroads, emission plume for fast accelerating vehicles) can determine short-time concentration peaks. On both instruments (fixed and mobile), higher average BC concentrations were recorded during morning hours compared to the afternoon. This is probably due to the lower mixing height which limits the diffusion of pollutants in the lower atmosphere. Another factor to consider is that morning traffic rush flow is more concentrated compared to the afternoon which is spread over more hours. During the morning, the majority of traffic is due to business reasons and the large majority of vehicles is driven by a single person. Differently during the afternoon and evening, commuting is due to personal reasons and car sharing with other passengers is more diffuse. This lead to reduced traffic flow during afternoon hours. Specially for the cold period, during the morning hours a larger portion of cold stated vehicles were observed compared to the afternoon. All this reasons may explain higher concentration levels during morning hours.

Highest values were observed on the mobile instrument which is directly exposed to traffic related pollutants and the lowest value was sampled at the fixed station, both values were recorded in the morning hours. Afternoon's average mobile BC concentration is therefore comparable to morning's average fixed BC value (Fig. 9.2 Annex II).

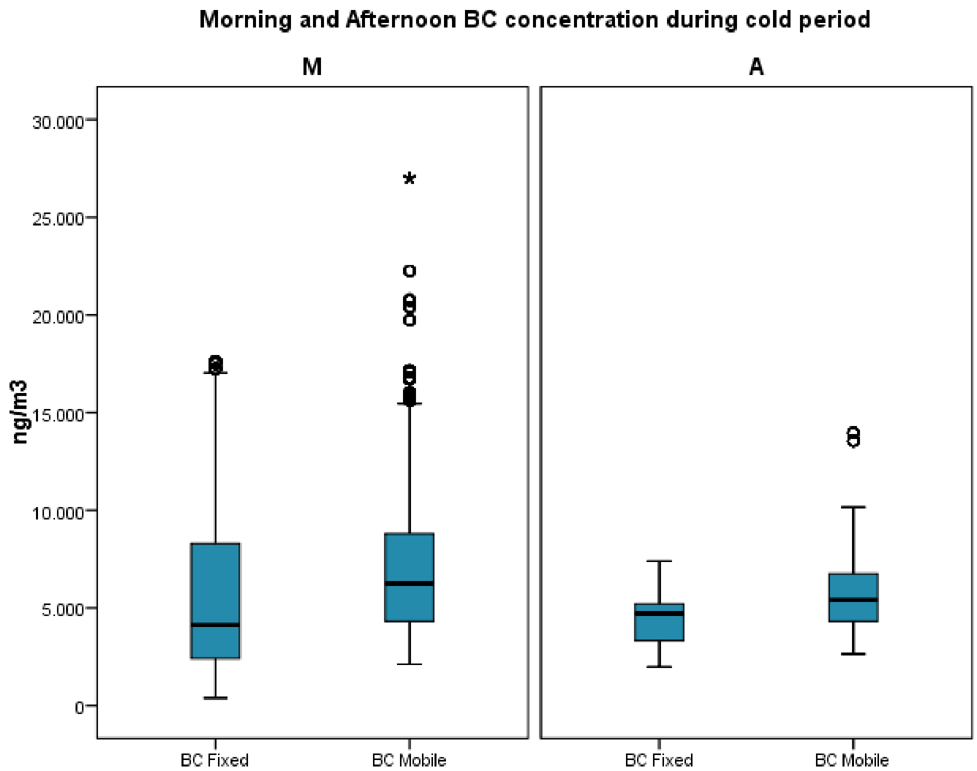

Figure 3:1 Box-plot of morning and afternoon fixed and mobile BC. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.1.1.2 Weekly variability

BC datasets were further stratified by kind of the day, namely separately analysing data collected on working days and on Saturdays; additionally, data from one working day (Wednesday 5th March) when a public transport service strike occurred were extracted from the working days subset. Corresponding distributions of the BC concentration levels are plotted in Figure 3.3 and 9.4 (Annex II).

In all cases average mobile BC data along the monitoring route are significantly higher than those at the fixed monitoring station, namely by a 1.2 factor on working days by a 1.3 factor on Saturdays and by a 1.7 factor on the strike day. Background BC working days data are in the 390 -17638 ng/m^3 range with an average of 5461 ng/m^3 and a standard deviation of 3662 ng/m^3. Mobile BC corresponding values are 2121 – 26994 ng/m^3, 6838 ng/m^3 and 3278 ng/m^3. Working days fixed BC data turn out to be characterized by a larger variability than mobile BC data (CV_{fixed} = 0.67 vs CV_{mobile} = 0.48).

Saturday's fixed BC data are in the 1989 – 6403 ng/m^3 range, with an average of 3684 ng/m^3 and a standard deviation of 1418 ng/m^3. Saturday's average background levels result to be 0.7 times lower than during work days. Mobile BC data on Saturdays are characterized by a larger range (2827 – 10170 ng/m^3) and a higher average value and standard deviation (4828 ng/m^{3}and 1856 ng/m^3): compared to the fixed values, 1.3 and 1.3 times fixed values. On Saturdays BC data variability turn out to be the same for fixed and mobile BC datasets ($CV_{fixed} = CV_{mobile} = 0.38$).
Local public transport strike occurred on a normal working day: Wednesday 5th March from 8:45 am until 18:00 pm. Consequences of the strike are: suspension of the traffic limitation zone (Area C), an increase of private traffic on roads, but also a backward shifting of commuters rush hours. During this day, samplings were performed on a cloudy and foggy morning with an average air temperature of 10 °C. Fixed BC range (1192 – 7522 ng/m^3) is clearly lower than during normally working days, while mobile BC values are in the 3706 - 12915 ng/m^3 range. BC average values on strike day are 3291 ng/m^3, and 5769 ng/m^3 for fixed and mobile BC respectively. As observed for morning' BC data, despite their restricted range, strike day data variability is higher for the fixed BC than the mobile BC ($CV_{fixed} = 0.42$ vs. $CV_{mobile} = 0.30$).
Average BC background concentration on working days is therefore 1.5 times higher than on Saturdays and 1.7 than on the strike day. This trend is also observable on the mobile instrument where the ratio between working days and Saturdays BC concentration is 1.4. Less marked is the ratio between work days and strike days fixed BC average concentration which result to be 1.2.
As shown in Fig. 9.3 (Annex II), outliers are mostly referred to working days and in particular to the 23th January for both instruments. On Saturdays no outliers were shown, while those on strike days, for both instruments are attributable to the same time interval, around 10:30 am.
Lower average concentrations of both instruments during Saturdays compared to those from normally working days, clearly indicate the lower traffic related contribution to mean BC levels. Contribution to average mobile BC concentration is higher during the strike day than during the other week days. Despite the public transport strike, average mobile BC is lower than during working days, probably due

to the backward shifted commute rush hours The difference between mobile and fixed average BC values is higher during the strike day compared to the other days.

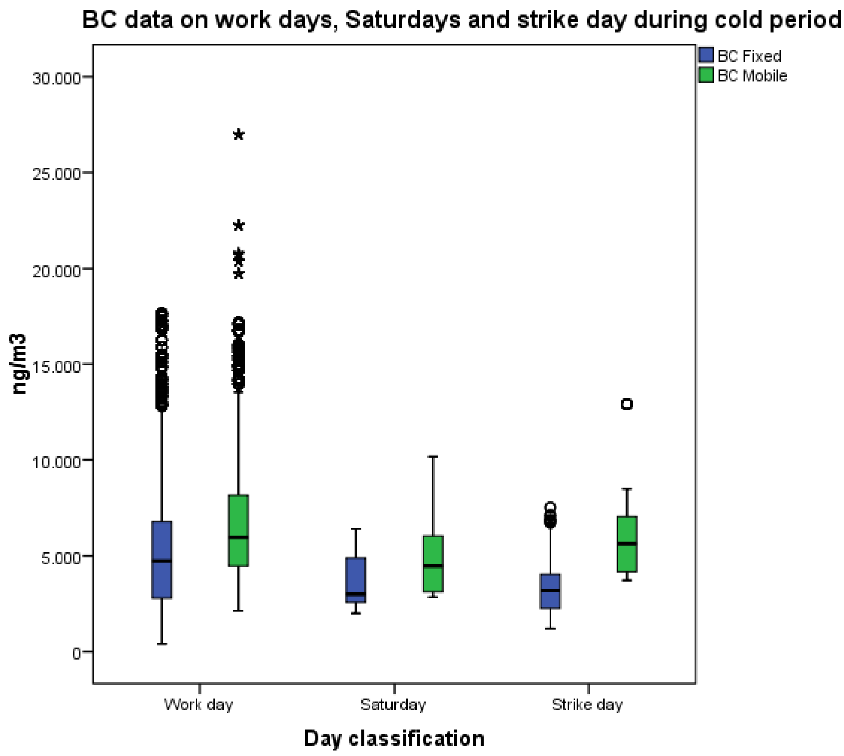

Figure 3:2 Box-plot of fixed and mobile BC classified by day type. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Day tipe and instrument		N	Minimum	Maximum	Mean	Std. Deviation
Work day	**BC Fixed**	13983	393	17638	5461	3662
	BC Mobile	13983	2121	26994	6838	3278
Saturday	**BC Fixed**	1645	1989	6403	3684	1418
	BC Mobile	1645	2827	10170	4828	1856
Strike day	**BC Fixed**	936	1192	7522	3291	1395
	BC Mobile	936	3706	12915	5769	1731

Table 3:2 Main descriptive statisctics of fixed and mobile BC clasified by day type.

3.1.1.3 Spatial variability

Subdivision of the monitoring route into different areas, as described in Section 2.3.1, shows off differences between urban areas. The box-plots of Figure 3.5 summarize for each urban zone datasets for the fixed and mobile instrument in terms of the median values, interquartile ranges, extreme values and outliers; 95% confidence intervals for mean values are plotted in Figure 9.6 (Annex II). Highest BC concentrations were recorded in the areas without traffic limitation (out of Area C, sections AV and RC). In Corso Buenos Aires (AV), mobile BC concentration data vary in the range of 2121 – 20829 ng/m^3, with an average BC concentration of 7365 ng/m^3, which is 1.3 times higher than the urban background levels at the same time period (average 5596 ng/m^3; 393 – 17638 ng/m^3 range). Comparable high BC concentrations were observed in Corso Lodi (RC), where values vary in the range of 2827 – 26994 ng/m^3 with an average value of 7522 ng/m^3 (1.5 times background BC concentrations) and a standard deviation of 3631 ng/m^3. It must be noticed that the adopted methodology imply that traffic peaks has been always verify in Corso Buenos Aires, whereas in Corso Lodi traffic was less intense. Data variability result to be larger for mobile BC data in RC site than mobile BC data in AV sites stated by the comparison of the values computed for the coefficient of variations (CV_{AV} = 0.44 vs. CV_{RC} = 0.48). Entering in areas subjected to Area C traffic limitations (sections VB, BD, DM and MR), average mobile BC concentrations becomes lower. The mean value for the BC mobile datasets in Corso Venezia (VB) is 5977 ng/m^3 (1.1 times mean fixed BC value) and data vary in the 2878 – 14129 range, with a standard deviation of 2459 ng/m^3 , comparable with other areas subjected to traffic limitations. BC mobile data are significantly higher than fixed data also in Corso Porta Romana (MR) where average BC mobile data is 5735 ng/m^3 (1.1 time higher than average fixed BC) and vary in the 2422 – 14898 ng/m^3 with a standard deviation of 2530 ng/m^3. Highest minimum BC mobile value was recorded in MR site. Observing CV values, as for VB, also considering MR, fixed data results to have a larger variability (CV_{fixed} = 0.70 vs. CV_{mobile} = 0.41).

Lowest average concentration was observed in the pedestrian zone (BD): mean value result to be 4922 ng/m^3 ; 0.9 times fixed BC average value. Mobile BC data vary in the 2422 – 13111 ng/m^3 range and a standard deviation of 1887 ng/m^3. However, absolute lowest mobile BC data of the entire monitoring route was sampled in the pedestrian zone, but more than two times higher than lowest fixed BC data sampled at the same time lapse. Analysis of coefficient of variance shows a major data variability on the fixed BC (CV_{fixed} = 0.68 vs. CV_{mobile} = 0.38). Comparable values are obtained also in Via Mazzini (DM) where mean mobile BC concentration data is 5060 ng/m^3 , comparable to the average background level. Mobile BC data vary in the 2422 – 13111 ng/m^3 as BD zone; while standard deviation is 2275 ng/m^3. As for BD, also for DM zone, Fixed BC results to be characterized by a greater data variability (CV_{fixed} = 0.67 vs. CV_{mobile} = 0.45). Potential outlier detection on the mobile BC dataset showed that these values are mostly present in most crowded urban zones: in particular, high outliers were recorded on the most traffic exposed road sections during the morning rush hours of January 23th (AV and RC). Other high values were observed on traffic limited areas (VB and MR) respectively on January 22th and 23th . Outliers on the pedestrian zone (BD) and Via Mazzini were observed on March 6th. It is not surprising that recognized potential outliers were mainly detected on the most traffic congested roads where exposure to traffic related pollutants can determine short-time concentration peaks. Major traffic contribution on mobile BC values is shown by the significantly (α = 0.05) higher means of crowded zones compared to traffic limited areas (Fig 0.6 Annex II).

Section and instrument		N	Minimum	Maximum	Mean	Std. Deviation
AV	BC Fixed	3614	393	17638	5596	3717
	BC Mobile	3614	2121	20829	7365	3208
VB	BC Fixed	2307	725	17638	5351	3751
	BC Mobile	2307	2878	14129	5977	2459
BD	BC Fixed	1519	1042	17007	5213	3570
	BC Mobile	1519	2422	13111	4922	1886
DM	BC Fixed	856	862	16940	5066	3404
	BC Mobile	856	2422	13111	5060	2275
MR	BC Fixed	3049	591	16250	4952	3261
	BC Mobile	3049	2422	14898	5735	2530
RC	BC Fixed	5219	591	15330	4902	3261
	BC Mobile	5219	2827	26994	7522	3631

Table 3:3 Overall main statistics of fixed and mobile BC clasified by city zone.

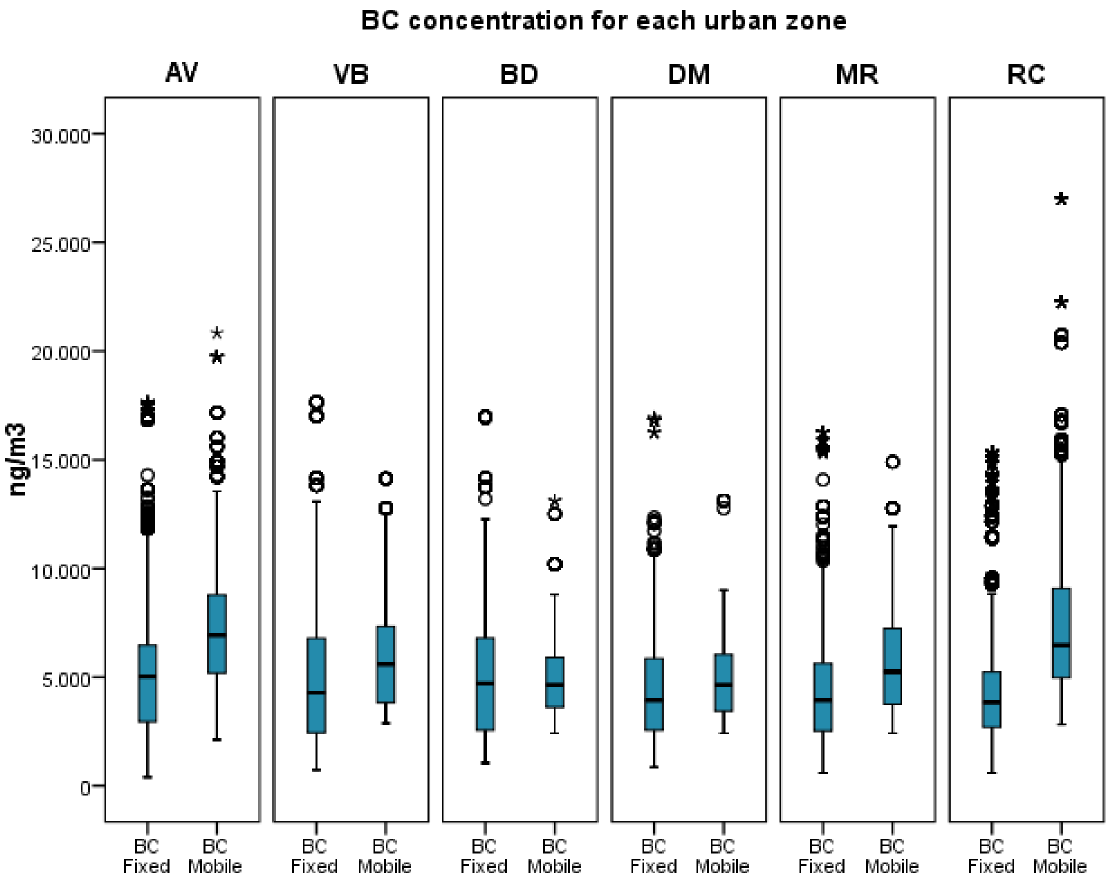

Figure 3:3 Box-plot of fixed and mobile BC classified by city zone. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Same daily trends previously described are observable for each analysed section, as reported in Table 0.4 (Annex I).

Comparing only morning's mobile BC values along the monitoring route with those measured at the fixed station, except for the pedestrian zone, mobile average data are always higher than urban background data. Along the first stretch of road (AV), BC concentrations vary in the 2121 – 20829 ng/m^3 range, with an average concentrations of 7709 ng/m^3 ; 1.3 times higher than the background levels and 1.4 higher than in the pedestrian zone (BD). Compared to BC afternoon's values (3593 – 13551 ng/m^3 range; average 6735 ng/m^3), morning's average value is 1.1 times higher. Observing CV values, mornings mobile BC values are always characterized by an higher variability for each urban zone, compared to afternoon values. Morning's mobile BC CV values vary in the 0.39 – 0.52 range, while afternoon's CV values vary in the 0.22 – 0.29 range.

Proceeding on Corso Porta Venezia (VB), morning's mobile BC average level is 7709 ng/m^3, 0.8 times lower than in Corso Buenos Aires (AV) but 1.1 higher than average urban background levels. Mobile morning's BC data vary in the 2878 – 14129 ng/m^3 while afternoon's levels in the 3434 – 7632 ng/m^3 with an average value of 5179 ng/m^3.

Lowest morning's average BC levels were sampled along the pedestrian zone (5427 ng/m^3) were the ratio with background levels is 0.9. Mobile BC morning data vary in the 2422 – 13111 ng/m^3 as in DM zone. Afternoon's BC levels vary in the 2653 – 5417 ng/m^3 range with an average of 3995 ng/m^3; 0.7 times lower than morning's average values and 0.9 times background levels. Instantaneous peaks are mainly due to cigarette smoke and soot coming from street food shops, especially during the Christmas period and in morning hours. BC concentrations in Via Mazzini (DM) are comparable with background levels. Due to the low travel speed of public transport vehicles along this road, no relevant increasing of average concentrations is observed (morning average 5623 ng/m^3 and afternoon average 3987 ng/m^3) compared to pedestrian zone. Compared to DM, an 1.1 times increasing of average exposure concentration is observed during the morning in Corso Porta Romana, probably linked to the increasing traffic intensity and higher traffic speed. Average mobile BC value is 6303 ng/m^3 in the morning and 3987 ng/m^3 in the afternoon. Morning values vary in the 2422 – 14898 ng/m^3 range, while afternoon's values vary in the 2653 – 6710 ng/m^3 range. Comparing mobile CV values in MR zone, data variability result higher during morning hours than in the afternoon ($CV_{morning}$ = 0.45 $CV_{afternoon}$ = 0.24). Concentration peaks were sampled in proximity to main road intersections, particularly intersection with Via Sforza. Highest average BC concentrations have been measured in Corso Lodi (RC). On this street, during morning hours, mobile BC average concentration is 8025 ng/m^3; 1.5 and 1.4 times higher than background's and pedestrian's zone average BC levels. BC dataset vary in the 2827 – 26994 ng/m^3 range in the morning and in the 3693 – 13966 ng/m^3. High peaks were observed mainly close to Piazzale Corvetto and mostly during morning hours, but also in correspondence of stop-and-go traffic caused by traffic lights along Corso Lodi.

Decreasing average BC concentrations in the afternoon hours are probably explainable by the lower traffic volume which causes a reduction of idling traffic. It should be also noted that atmospheric turbulence increases usually in the afternoon hours and an increasing of the mixing layer height causes a reducing of pollution concentration levels. However, daily BC concentration differences are less marked in heavily trafficked areas (AV, VB and RC) compared to the less crowded streets (BD, DM and MR). This differences are due to the high traffic contribution to pollutants concentration levels.

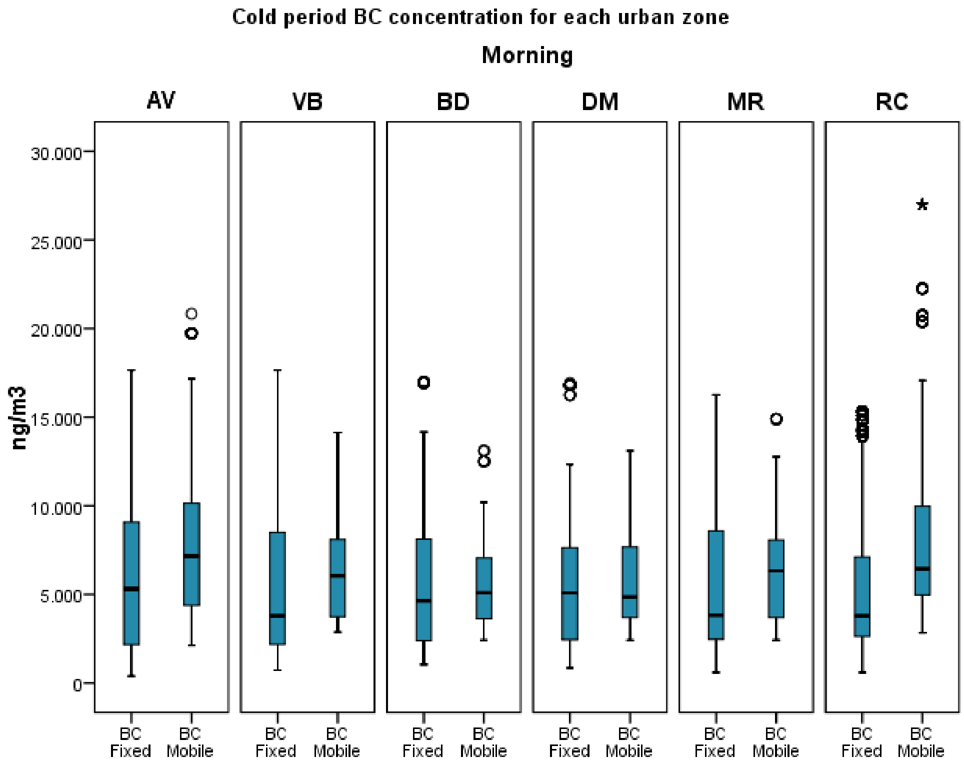

Figure 3:4 Box-plot of morning's fixed and mobile BC classified by city zone. Boxes represent the median values, interquartile ranges, extreme values and outliers.

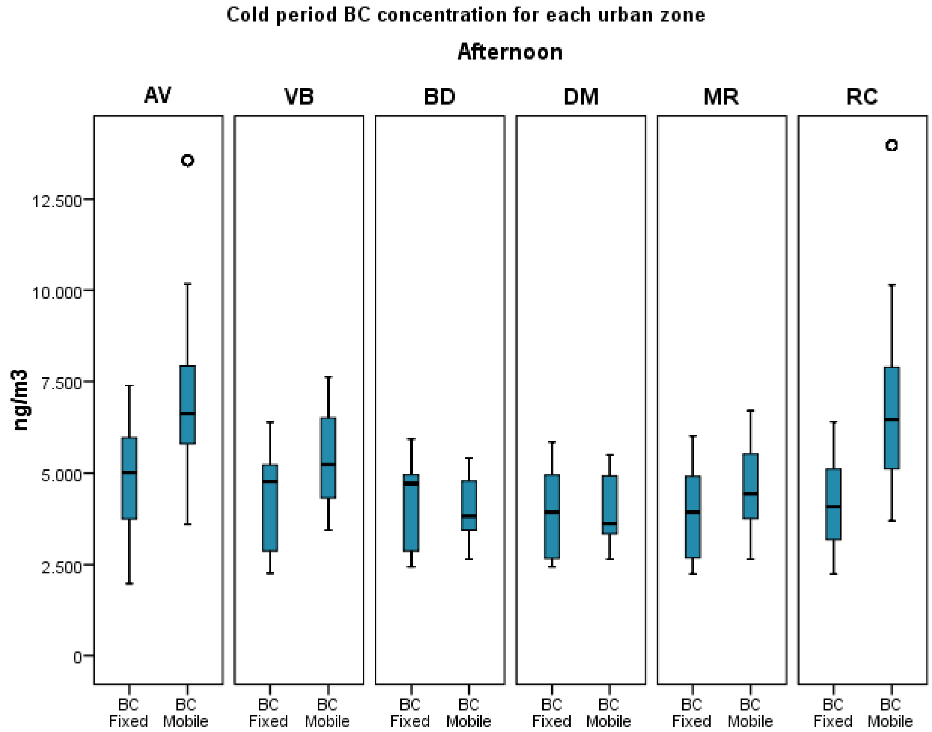

Figure 3:5 Comparison of estimated noise in the post-processed BC signal versus the input minimum change in ATN required by the post-processing program

Subdividing each section in subclasses it is possible to better ivestigate relevant internal differences in terms of pollutants concentrations for each urban zone.

Corso Buenos Aires (AV) was divided into three parts (1A, 1B and 1C) as described in section 2.3.1.

In the first section (1A) average mobile BC concentration value is 7565 ng/m^3 and the dataset vary in the 2121 – 20829 ng/m^3 range. Analogous values were observed in section 1B (average 7393; range 2121 – 17167 ng/m^3) and in section 1C (average 6952 ng/m^3; range 2121 – 14943 ng/m^3). Lower average values at the end of Corso Buenos Aires (close to Porta Venezia) are probably due to the fact that the street reach a large square, getting out of the street canyon. However, no relevant statistical differences were found between average mobile BC concentrations in the three subclasses (Fig 9.6, Annex II). Observing CV values, data variability is comparable in each section (CV_{1A} = 0.44, CV_{1B} = 0.43, CV_{1C} = 0.44). Highest peaks were observed in the first street section.

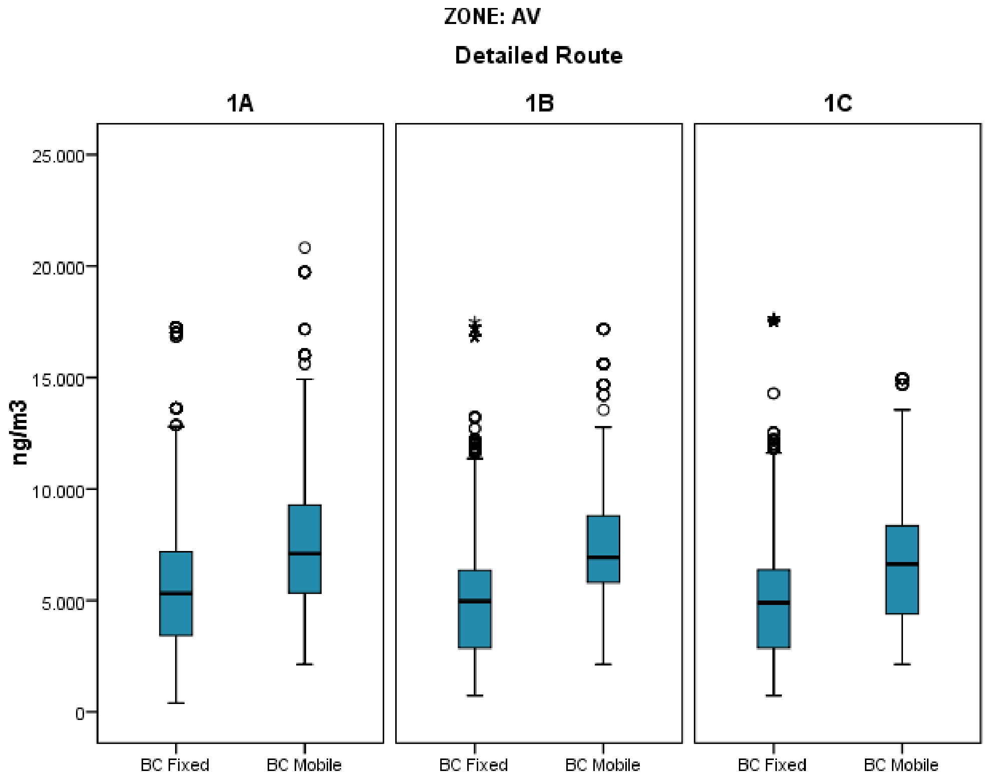

Figure 3:6 Box-plot of fixed and mobile BC in city zone AV. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Corso Porta Venezia was divided into two sections. Boundary of the two section is the intersection with Via Senato, an important main road of the inner city circle. Despite the proximity to a city park (Giardini Indro Montanelli) and the larger street, section 2D have an average BC value of 6306 ng/m^3 and results to have an average value 1.2 times higher than the less crowded but narrower street section 2E (average 5291 ng/m^3), as given in Figure 9.7 (Annex II). Mobile BC vary in the 2878 – 14129 ng/m^3 in section 2D, while data in section 2E vary in the 2910 – 12510 ng/m^3 range. Comparing CV values, data variability is similar in both sections (CV_{2D} = 0.44 and CV_{2E} = 0.43).

Pedestrian zone (BD) and the traffic limited Via Mazzini (DM) were not further divided due to the absence of significant discontinuity along the monitoring route and formerly described (Fig 9.8 to 9.11, Annex II).

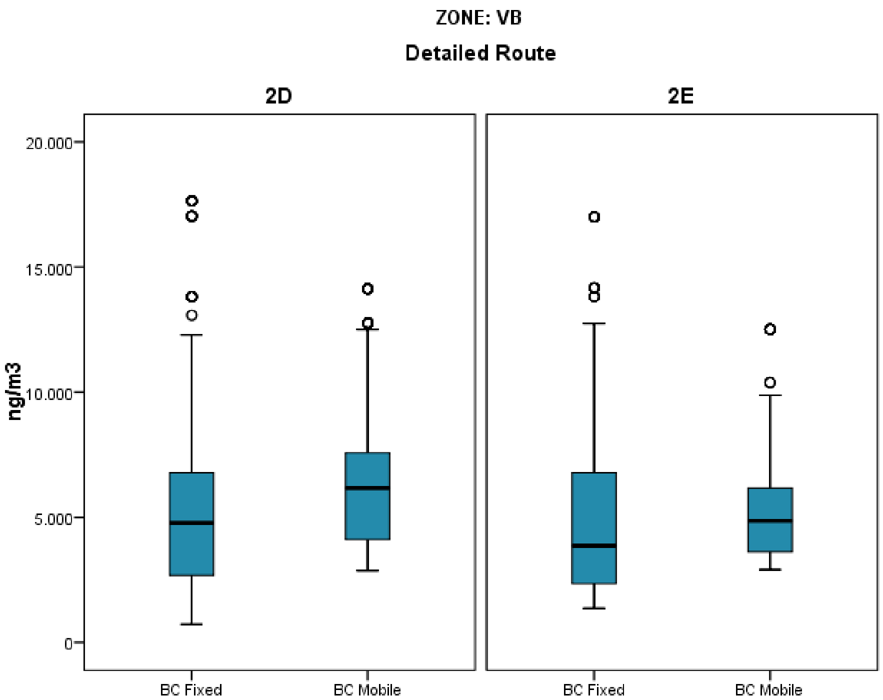

Figure 3:7 Box-plot of fixed and mobile BC in city zone VB. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Until reaching the intersection whit Via Sforza (5H), Corso di Porta Romana is less crowded then the second section (5I). Both sections are covered by public surface transport lines, and are made by cobblestones. However also in this case differences between average BC values not suggest significant statistical differences, as highlighted in graph 9.12. In section 5I mobile BC data vary in the 2422 - 12765 ng/m^3 , while average BC concentration result to be 5931 ng/m^3, 1.1 times higher than in section 5H (average value: 5444 ng/m^3; range: 2422 - 14898 ng/m^3).

Traffic contribution seems to be quite higher in section 5I, consistently with the traffic volume increase. CV values suggest an higher data variability on the first section (CV_{5H} = 0.45 vs. CV_{5I} = 0.43). High BC concentration peaks were observed close to the intersection with Via Sforza.

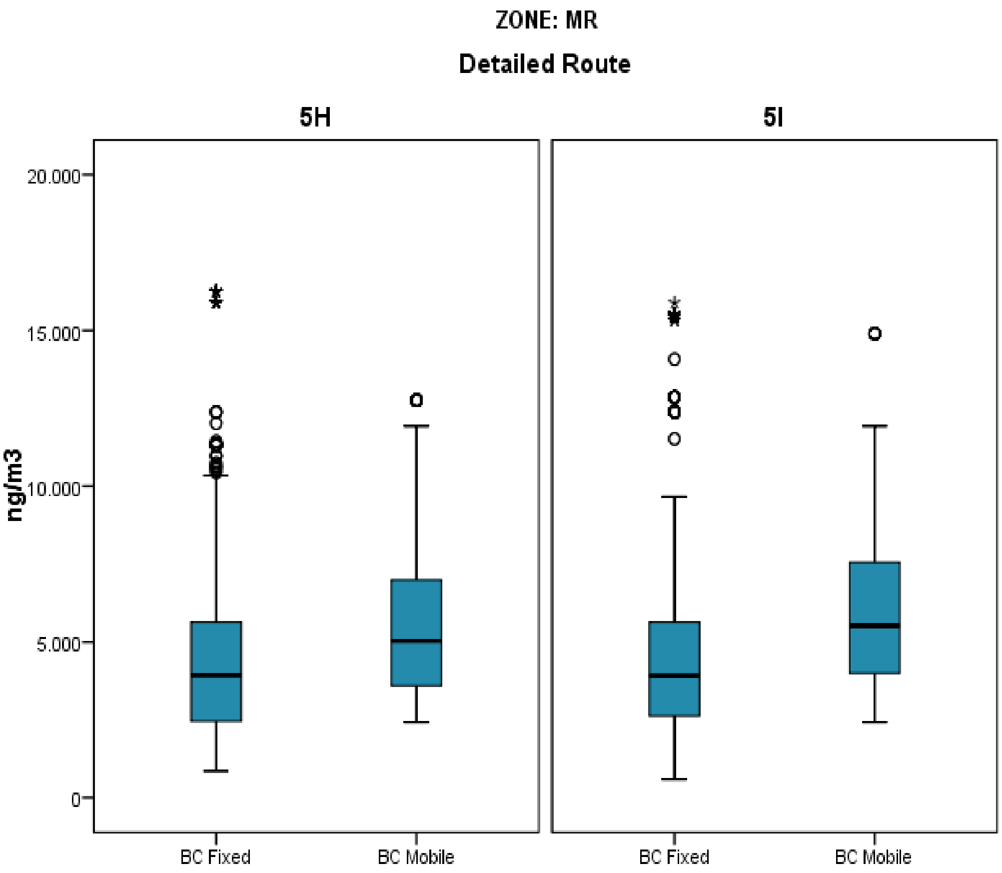

Figure 3:8 Box-plot of fixed and mobile BC in city zone MR. Boxes represent the median values, interquartile ranges, extreme values and outliers.

The longest section (RC) was divided into four parts (6L, 6M, 6N and 6O). Highest average concentrations were observed in Piazzale Corvetto (6O), an important junction with the south-east suburbs. The first part of Corso Lodi (6L) is characterized by the presence of access roads, implying a greater distance between kerbside and motorized traffic. This results in lower average concentrations (average: 6752 ng/m^3; range: 2827 – 20738 ng/m^3) which are 0,7 times those measured in Piazza Corvetto (average: 8944 ng/m^3; range: 4472 - 26994 ng/m^3). Significant statistical differences on the average BC concentration were not found between section 6M (average: 7884 ng/m^3; range: 3205 – 22248 ng/m^3) and 6N (average: 7893 ng/m^3; range: 4472 – 20386 ng/m^3), both characterized by idling traffic, as shown in Fig 3.9 and 9.12 (Annex II).

A detailed summary of the main descriptive statistics for each street section is given in Table 0.5 (Annex I).

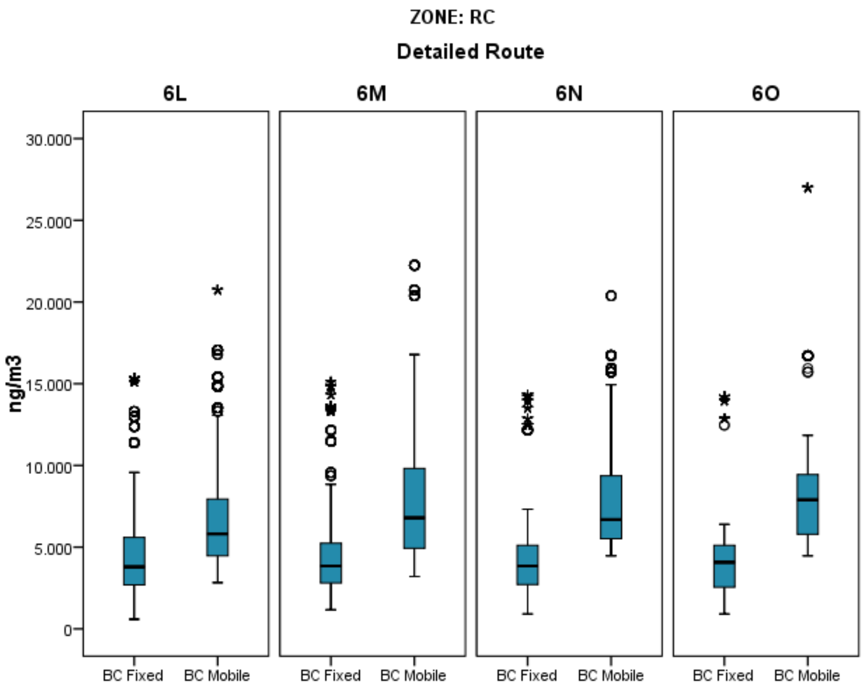

Figure 3:9 Box-plot of fixed and mobile BC in city zone RC. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.1.1.4 Congestion charge area effects

Comparing morning's mobile BC data inside traffic limitation zone Area C with those outside Area C, average concentration values are significantly higher in non-traffic limited urban areas, as shown in graph 9.13 ($\alpha = 0.05$, Annex II). Out of Area C, mobile BC morning average concentration is 7897 ng/m^3 (1.4 times average fixed BC concentration and 1.3 times higher than average BC concentration in Area C zone) and data vary in the 2121 – 26994 ng/m^3. Area C average mobile BC concentration is 6074 ng/m^3 (only 8% higher than average background concentration) and vary in the 2422 – 14898 ng/m^3 range. Computing coefficient of variation for each dataset, mobile BC data outside Area C are characterized by a larger variability than inside Area C data ($CV_{Area\ C} = 0.44$ vs. $CV_{No\ Area\ C} = 0.51$).

Considering afternoon's average mobile BC values, inside Area C, BC concentrations are 1.1 times background levels (average mobile BC: 4582 ng/m^3; range: 2653 – 7632 ng/m^3). More marked is the difference between afternoon's average BC level Out of Area C and average fixed BC concentration, where the ratio with the fixed measurement station is 1.5 (average mobile BC: 6625 ng/m^3; range: 3593 – 13966 ng/m^3). Afternoon's average mobile BC results to be 1.4 times higher than in the inner city circle. Also in this case, Area C data are less variable than No Area C data ($CV_{Area\ C} = 0.25$ vs. $CV_{No\ Area\ C} = 0.28$).

Therefore, excluding heavy traffic (especially diesel vehicles) from the inner city circle, leads to a BC concentration reduction of 0.7 and 0.8 times those measured outside Area C (in the morning and in the afternoon respectively), but always about 10% higher than background concentration levels.

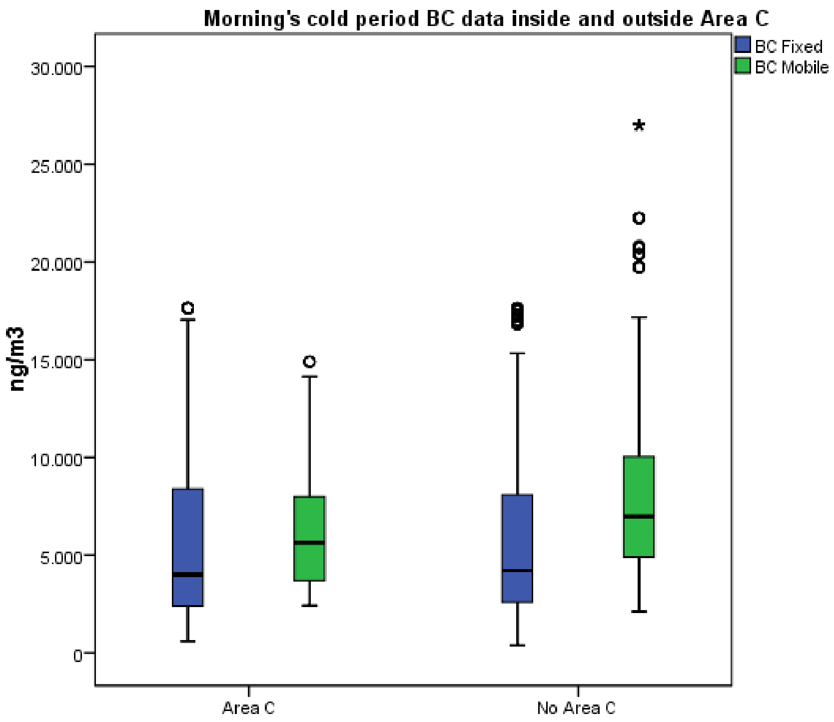

Figure 3:10 Box-plot of morning's fixed and mobile BC inside and outside Area C. Boxes represent the median values, interquartile ranges, extreme values and outliers.

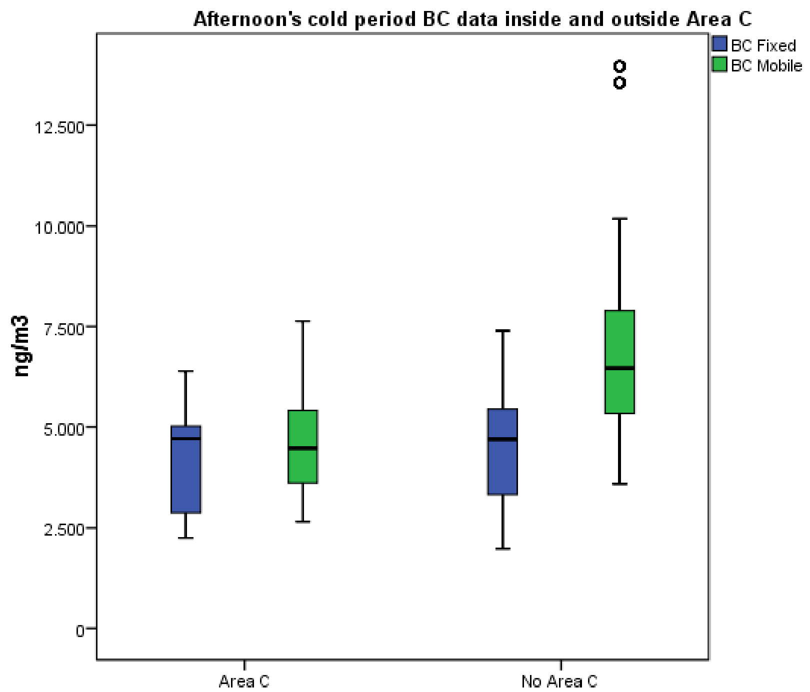

Figure 3:11 Box-plot of afternoon's fixed and mobile BC inside and outside Area C. Boxes represent the median values, interquartile ranges, extreme values and outliers.

			N	Minimum	Maximum	Mean	Std. Deviation
Morning	**Area C**	**BC Fixed**	5133	591	17638	5614	4115
		BC Mobile	5133	2422	14898	6074	2700
	No Area C	**BC Fixed**	5779	393	17638	5585	4119
		BC Mobile	5779	2121	26994	7897	3992
Afternoon	**Area C**	**BC Fixed**	2598	2245	6388	4188	1226
		BC Mobile	2598	2653	7632	4582	1135
	No Area C	**BC Fixed**	3054	1978	7395	4431	1370
		BC Mobile	3054	3593	13966	6625	1873

Table 3:4 Descriptive statistics for morning's and afternoon's fixed and mobile BC inside and outside Area C.

3.1.2 PNC data processing

The original recorded datasets were firstly manually analysed in order to detect error codes due to instrumentation malfunctioning. Data characterized by an error code were deleted and not further taken in account. Particle number concentration data (PNC), were originally sampled at a 1-second time resolution at both sampling site. In order to permit a correct comparison with BC concentration data (sampled at a 10-second time resolution), a 10 second averaging algorithm was applied on the original PNC dataset of both sampling sites. On the averaged PNC dataset, statistical analyses and potential outliers detection were carried out.

Main statistical parameters of the data distributions for the overall datasets and for the morning and afternoon datasets separately are reported in Table 3.5: data from the stationary instrument at the urban background site are reported as "PNC fixed" whereas those recorded along the pedestrian route as "PNC mobile". The box-plots of Figure 3.12 summarize the morning and afternoon datasets for the fixed and mobile instrument in terms of the median values, interquartile ranges, extreme values and outliers; morning and afternoon average values, together with 95% confidence intervals are plotted in Figure 9.15 (Annex II).

Instrument		N	Minimum	Maximum	Mean	Std. Deviation
PNC Fixed	Overall	25433	5273	500000	27263	19026
	Morning	14913	5273	500000	33287	21553
	Afternoon	10520	6713	82100	18723	9603
PNC Mobile	Overall	26280	5958	224800	41899	23843
	Morning	15826	8313	224800	45972	24789
	Afternoon	10454	5958	161200	35732	20875

Table 3:5 Descriptive statistics for overall, morning's and afternoon's fixed and mobile PNC.

Overall, PNC fixed data are in the 5.2 x 10^3 – 5.0 x 10^5 Pt/cm^3 range, with an average of 2.7 x 10^4 Pt/cm^3 and a standard deviation of 1.9 x 10^4 Pt/cm^3: corresponding figures for PNC mobile data are 5.9 x 10^3 – 2.2 x 10^5 Pt/cm^3 , 4.1 x 10^4 Pt/cm^3, and 2.4 x 10^4 Pt/cm^3. Compared to fixed data, mobile data are shifted towards higher values, as highlighted by the significantly (α = 0.05) higher mean as shown in Fig 9.15 in Annex II (about 1.5 times higher than average PNC measured at the fixed sampling site); also mobile PNC standard deviation is 1.2 times higher than fixed standard deviation. Fixed data are characterized by a larger variability, as stated by the comparison of the values computed for the coefficient of variations (CV = 0.70 for PNC fixed vs. 0.57 for PNC mobile).

3.1.2.1 Daily variability

PNC mobile data are significantly higher than fixed data also when separately considering the morning and the afternoon route: the mean values for the PNC mobile datasets are 4.6 x 10^4 and 3.6 x 10^4 respectively (1.2 and 1.3 times higher than those of the BC fixed on morning and afternoon subsets). Differently as for BC concentration data, PNC data variability is not always larger in the morning. While for fixed PNC data variability is larger during morning hours (for fixed PNC, $CV_{morning}$ = 0.65 vs. $CV_{afternoon}$ = 0.51), on the mobile PNC dataset the opposite trend is observable (for mobile PNC, $CV_{morning}$ = 0.54 vs. $CV_{afternoon}$ = 0.58).

For fixed PNC dataset, highest and lowest values were recorded in the morning; otherwise, mobile PNC dataset recorded lowest value during the afternoon and the highest concentration level in the morning.

The comparison between morning and afternoon values shows that during the morning hours concentration levels are significantly higher for both the fixed and mobile instrument: on the average, morning concentration is 1.8 times higher than in the afternoon for PNC fixed and 1.3 times higher for PNC mobile. Mobile average PNC data are always greater than those measured at the background measuring station; 1.4 times in the morning and 1.9 times in the afternoon, respectively. Absolute extreme values (minimum and maximum) were recorded on the fixed measuring station during morning hours. Morning's standard deviation of the fixed P-trak is 2.2 times higher than in the afternoon, while considering mobile P-trak ratio is 1.2.

PNC box-plot in Fig 3.12 shows how potential outliers are much numerous compared to BC dataset outlier and mostly present in the morning hours, especially for the fixed measuring station. Applying an accurate data label analysis, potential outliers of the fixed PNC dataset can be grouped into individual events which took place on December 13th and 17th. Considering mobile PNC dataset outliers, differences between morning and afternoon are less marked. In both cases, peaks along the monitoring route were observed in correspondence of busy crossroads or fast accelerating vehicles. As described for BC dataset, outlier detection is a merely statistical procedure intend to recognize those values that are inconsistent (i.e.: anomalous) with the whole dataset. Nevertheless, such anomalous values may be the result of very peculiar environmental conditions that, even though very infrequent and rarely occurring, are at the same time likely to happen. It is not surprising that the recognized potential outliers were mainly detected in the BC mobile dataset: indeed, the closer exposition to traffic exhaust emissions and peculiar environmental conditions from the emission standpoints (i.e.: queue of idling vehicles, busy crossroads, emission plume for fast accelerating vehicles) can determine short-time concentration peaks.

Higher values in the morning rush hours are probably due to the lower height of the atmospheric mixing layer combined to the more intense traffic and the higher portion of cold started vehicles. Daily variations are more evident on the fixed PNC dataset, suggesting an higher contribution of secondary particle formation during morning hours.

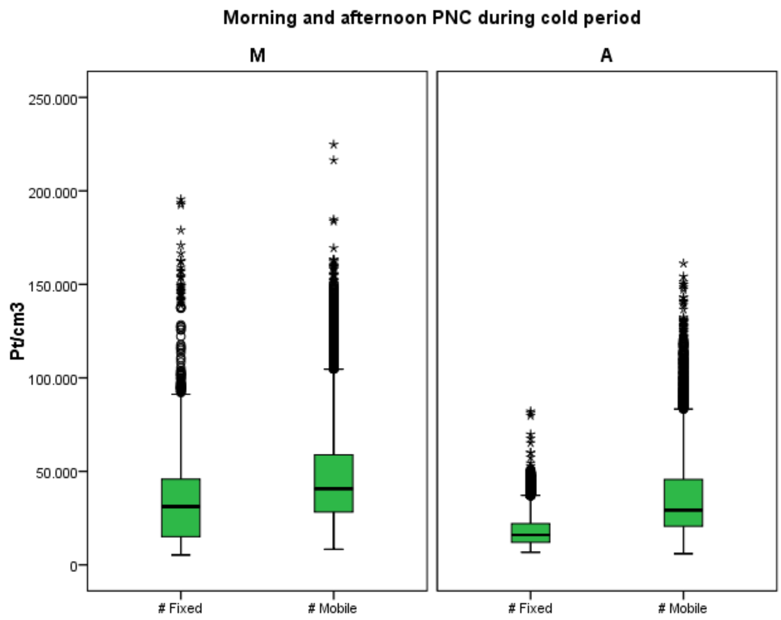

Figure 3:12 Box-plot of morning's and afternoon's fixed and mobile BC. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.1.2.2 Weekly variability

As for BC concentration data, also for PNC, datasets were further stratified by kind of the day, namely separately analysing data collected on working days and on Saturdays; additionally, data from one working day (Wednesday 5th March) when a public transport service strike occurred were extracted from the working days subset and separately analysed. Corresponding distributions of the PNC concentration levels are plotted in the box-plot of Figure 3.13.

In all cases, as for BC, average mobile PNC along the monitoring route is significantly higher than those at the fixed monitoring station, as shown in Figure 3.13. On normally working days, in the average, mobile PNC values is 42419 Pt/cm^3, 1.5 times greater than background average PNC levels, and vary in the 5.9 x 10^3 – 2.2 x 10^5 Pt/cm^3 range. Highest instantaneous peaks on the mobile P-trak were recorded during working days; lower peaks were recorded also on Saturdays ad strike day. Fixed PNC values on work days vary in the 5.3 x 10^3 – 5.0 x 10^5 Pt/cm^3 range with an average of 27656 Pt/cm^3.

Urban background average PNC levels are comparable during working days and Saturdays, even if on Saturdays no outliers were recorded, and range of Saturday's fixed PNC values is more restricted (average: 28276 Pt/cm^3; range 7.4 x 10^3 – 2.8 x 10^4 Pt/cm^3). In terms of daily average background PNC, values are therefore slightly higher on Saturdays than during normally week days. Outliers on the fixed PNC dataset are only present on working days. Considering average mobile PNC, no relevant statistical differences were observed between working days and Saturdays values (average: 41861 Pt/cm^3; range 8.3 x 10^3 – 1.6 x 10^5 Pt/cm^3) as shown in Figure 9.16 (Annex II). Strike days interquartile range is comparable with Saturdays background levels. Fixed average PNC data vary in the 5.9 x 10^3 – 3.2 x 10^4 Pt/cm^3 with an average value of 15166 Pt/cm^3. Statistical differences between strike day and other days were observed on average mobile PNC. On strike day, mean mobile PNC value is 29445 Pt/cm^3 and values vary in the 9.4 x 10^3 – 1.4 x 10^5 Pt/cm^3 range. Lowest maximum value were recorded on strike day.

During work days, fixed PNC dataset is characterized by a greater variability than mobile PNC dataset, as stated by the comparison of the values computed for the coefficient of variations (CV = 0.71 for PNC fixed vs. 0.56 for PNC mobile). Opposite trends are observable comparing Saturdays and strike days fixed and mobile PNC values. On Saturdays, CV = 0.51 for PNC fixed and 0.59 for PNC mobile, while on strike day CV = 0.39 for PNC fixed and 0.63 for PNC mobile. Mobile PNC interquartile value on strike day is comparable whit fixed PNC interquartile range on Saturdays. Outliers of working days on the fixed measuring station are part of a single event happened on 13th of December, while outliers of the mobile instrument were observed crossing busy roads for all kind of analysed days. As for BC concentration data, also for PNC data, same considerations must be taken into account considering strike day implications on urban traffic. Weekly differences are less marked for PNC than for BC during the cold period.

Main descriptive statistics are summarized in Table 3.6.

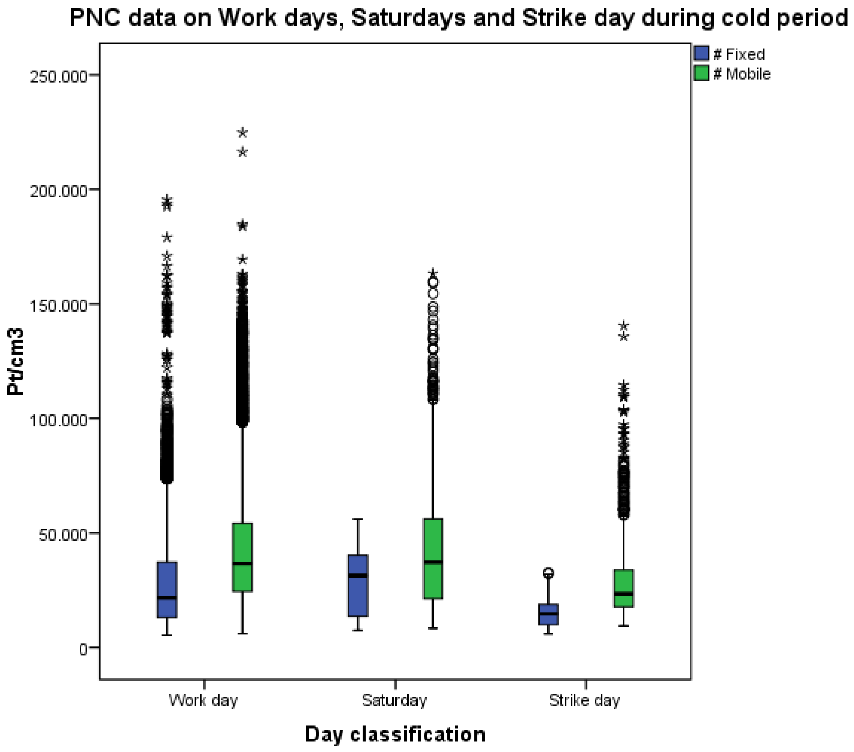

Figure 3:13 Box-plot of fixed and mobile PNC for each day type (Work days, Saturdays and strike day occurred on March the 5th. Boxes represent the median values, interquartile ranges, extreme values and outliers.

		N	Minimum	Maxiumum	Mean	Std.Deviation
Work day	**PNC Fixed**	21767	5273	500000	27656	19709
	PNC Mobile	22614	5958	224800	42419	23796
Saturday	**PNC Fixed**	2730	7367	56010	28276	14520
	PNC Mobile	2730	8313	163300	41862	24685
Strike day	**PNC Fixed**	936	5868	32470	15166	5880
	PNC Mobile	936	9363	140500	29447	18507

Table 3:6 Descriptive statistics of fixed and mobile PNC for each day type (Work days, Saturdays and strike day occurred on March the 5th.

3.1.2.3 *Spatial variability*

Subdivision of the monitoring route into different areas as described in Section 2.3.1 shows off differences between urban areas. The box-plots of Figure 3.14 summarize for each urban zone datasets for the fixed and mobile instrument in terms of the median values, interquartile ranges, extreme values and outliers; 95% confidence intervals for mean values are plotted in Figure 9.17 (Annex II). As for BC concentration, highest mobile PNC concentrations were recorded in an area without traffic limitation (out of Area C). Highest PNC average value was recorded in Corso Buenos Aires (AV), mobile PNC have an average value of 49642 Pt/cm^3 (1.7 times background average PNC value) and vary in the 7.9 x 10^3 – 2.2 x 10^5 Pt/cm^3. CV comparison indicates an higher data variability for fixed PNC dataset (CV_{fixed} = 0.71 vs. CV_{mobile} = 0.54). Differently as for BC, comparable high PNC were observed in Corso Porta Venezia (VB), where values vary in the range of 6.9 x 10^3 – 1.8 x 10^5 Pt/cm^3 with an average value of 45228 Pt/cm^3 (1.7 times higher than background PNC). Also in this case, even if less marked, CV comparison indicate a larger data variability on fixed PNC dataset (CV_{fixed} = 0.67 vs. CV_{mobile} = 0.60).

Entering in the pedestrian zone, average mobile PNC becomes lower. Mean mobile PNC value in Corso Vittorio Emanuele (BD) is 29680 Pt/cm^3 (1.2 times higher than fixed PNC at the same time period) and included in the 9.1 x 10^3 – 1.5 x 10^5 Pt/cm^3. High mobile PNC peaks were also observed in this zone, probably due to instantaneous local sources as cigarette smoke or soot coming from street food shops. Data variability in in pedestrian zone is the lowest of all city zones as suggested by comparison of computed CV values (CV_{fixed} = 0.49 vs. CV_{mobile} = 0.70). Lowest standard deviation was observed in pedestrian zone.

Differently as for BC data, lightly higher mean mobile PNC values were recorded in Via Mazzini (DM); values vary in the 9.0 x 10^3 – 1.5 x 10^5 Pt/cm^3 range, with an average of 31664 Pt/cm^3 (1.2 times higher than average background levels). High mobile PNC values were observed when public transportation or tourist busses passes. In Corso Porta Romana (MR) mobile PNC values increases reaching an average of 38705 (1.5 times higher than average fixed PNC); data vary in the 5.9 x 10^3 – 1.6 x 10^5 Pt/cm^3 range and CV comparison suggest an higher data variability for fixed PNC compared to mobile PNC values (CV_{fixed} = 0.63 vs. CV_{mobile} = 0.55).

As opposed to mobile BC concentration data, highest average mobile PNC data were not found in section RC. Despite the absence of any kind of traffic limitations, average mobile PNC value is lower than in Corso Porta Venezia (subjected to Area C), reaching a value of 42902 Pt/cm^3 (1.5 times average fixed PNC). Mobile data vary in the 7.3 x 10^3 – 1.8 x 10^5 Pt/cm^3. As for all other sections, fixed PNC data are characterized by a larger data variability compared to mobile PNC dataset as suggested by the computed CV values (CV_{fixed} = 0.73 vs. CV_{mobile} = 0.52).

As for BC, potential outlier detection on the mobile PNC dataset showed that these values are mostly present in most crowded urban zones. In all those sections, traffic represent the main primary source. According to Dons et al, (Dons, Temmerman, Van Poppel, Bellemans, Wets, & Int Panis, 2013) pedestrian exposure increase during traffic peak hours. As for mobile BC, extremely high PNC peaks were observed close to main crossroads and in presence of idling traffic or close to roadworks. Major traffic contribution on mobile PNC values is shown by the significantly (α = 0.05) higher means of those zones Figure 9.18 (Annex II).

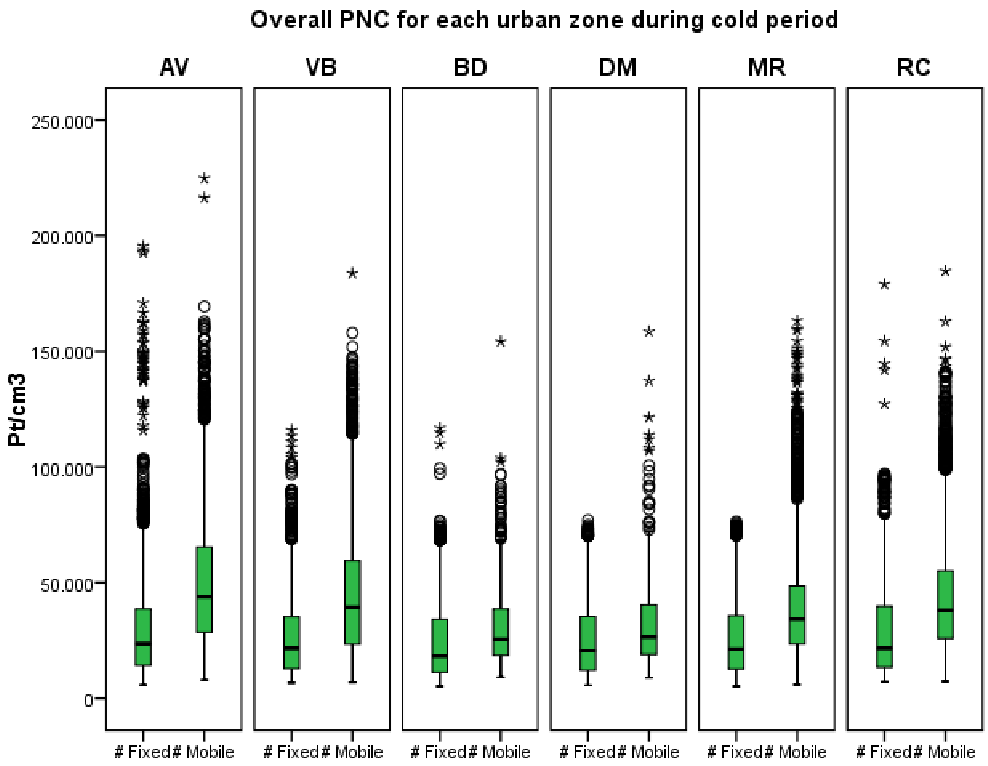

Figure 3:14 Box-plot of fixed and mobile PNC for each city zone. Boxes represent the median values, interquartile ranges, extreme values and outliers

Section	instrument	N	Minimum	Maximum	Mean	Std. Deviation
AV	PNC Fixed	5209	5868	195500	28782	20460
	PNC Mobile	5353	7942	224800	49642	26958
VB	PNC Fixed	3524	6727	115900	26549	17727
	PNC Mobile	3637	6884	183700	45228	27361
BD	PNC Fixed	2628	5280	116880	24738	17277
	PNC Mobile	2715	9118	154210	29680	14574
DM	PNC Fixed	1271	5674	77050	25838	17148
	PNC Mobile	1301	8975	158600	31664	17128
MR	PNC Fixed	4685	5273	76380	26300	16471
	PNC Mobile	4858	5958	163300	38705	21244
RC	PNC Fixed	8116	6739	500000	28195	20606
	PNC Mobile	8416	7358	184700	42902	22386

Table 3:7 Descriptive statistics for fixed and mobile PNC for each city zone.

Considering only morning's mobile PNC values along the monitoring route with those measured at the fixed station, except for the pedestrian zone where the difference is minimally, mobile average data are always higher than urban background data. Along the first stretch of road (AV), mobile PNC concentrations vary in the 9.1 x 10^3 – 2.2 x 10^5 Pt/cm^3range, with an average concentrations of 54548 Pt/cm^3; 1.6 times higher than the background levels. Compared to BC afternoon's values (average: 42518; range: 7.9 x 10^3 – 1.6 x 10^5 Pt/cm^3), morning's average value is 1.3 times higher. Relative diurnal differences are more marked for PNC than for BC concentration data. Morning fixed PNC data result to be characterized by an higher data variability than morning mobile PNC data, while the opposite trend is observable considering afternoon's PNC data as suggested by the comparison of computed CV values. . Morning's mobile PNC CV values vary in the 0.45 – 0.52 range vs. morning fixed CV values vary in the 0.57 – 0.69 range, while afternoon's mobile CV values vary in the 0.47 – 0.59 range vs. afternoon's fixed PNC CV values vary in the 0.46 – 0.52 range. In both cases (morning and afternoon) highest CV values on mobile PNC dataset were observed outside Area C zones (AV and RC), while lowest values were observed in the pedestrian zone (BD).

High average mobile PNC values were also observed in Corso Venezia (VB). Despite traffic limitations and the proximity to a city park, morning's mobile PNC vary in the 8.3 x 10^3 – 1.8 x 10^5 Pt/cm^3range with an average value of 50470 Pt/cm^3, 1.6 times greater than morning's fixed PNC and 1.4 higher than afternoon's average mobile PNC.

A marked reduction of mobile average PNC was observed in the pedestrian zone (BD). As shown in Figure 3.15, average mobile PNC values are comparable with average fixed PNC during morning hours, while during the afternoon, mobile average PNC is clearly higher. Morning mobile PNC data vary in the 9.1 x 10^3 – 1.0 x 10^5 Pt/cm^3 range with an average value of 33523 Pt/cm^3, 1.0 times fixed average PNC and 1.3 times higher afternoon's average mobile PNC in the same zone. Corresponding afternoon values are 9.7 x 10^3 – 1.5 x 10^5 Pt/cm^3 and 25175 Pt/cm^3, 1.5 times afternoon's average background PNC level. As for BC, PNC peaks in pedestrian zone are less numerous than in other city zones.

Differently as for mobile BC, mobile PNC values in Via Mazzini (DM) are 1.2 and 1.3 times higher than fixed PNC values, in the morning and in the afternoon respectively. Morning's mobile dataset vary in the 9.0 x 10^3 – 1.6 x 10^5 Pt/cm^3range with an average of 37010 Pt/cm^3. Corresponding afternoon values are 8.9 x 10^3 – 1.1 x 10^5 Pt/$cm^3$and 23427 Pt/cm^3, lower than in pedestrian zone.

Compared to fixed PNC, on average, mobile PNC in Corso Porta Romana are 1.4 and 1.8 times higher in the morning and in the afternoon respectively. Mobile PNC data are characterized by an average of 42228 Pt/cm^3 and a data 8.8 x 10^3 – 1.6 x 10^5 Pt/cm^3 range, while in the afternoon by an average of 33178 Pt/cm^3 and a data 5.9 x 10^3 – 1.5 x 10^5 Pt/cm^3 range. Compared to via Mazzini, Increasing of average exposure to PNC in Corso Porta Romana is probably linked to the major traffic intensity and higher travel speed. As for BC data, high peaks were sampled in proximity to main road intersections, particularly intersection with Via Sforza.

High PNC peaks were also observed in section RC. Compared to fixed PNC data, mobile PNC data are 1.3 and 2.0 times greater in the morning and in the afternoon respectively. Morning's mobile PNC data vary in the 9.2 x 10^3 – 1.8 x 10^5 Pt/cm^3 range with an average of 45808 Pt/cm^3. Corresponding afternoon's value are 7.4 x 10^3 – 1.4 x 10^5 Pt/cm^3 and 38224 Pt/cm^3. As for BC, high peaks were observed mainly close to Piazzale Corvetto and mostly during morning hours, but also in correspondence of stop-and-go traffic caused by traffic lights along Corso Lodi. Except for pedestrian zone, overall maximum mobile PNC levels were recorded during morning hours. Decreasing average PNC in the afternoon hours are probably explainable by the lower traffic volume which causes a reduction of idling traffic. It should be also noted that atmospheric turbulence increase usually in the afternoon hours and an increasing of the mixing layer height causes a reducing of pollution concentration levels.

Except for zone BD and DM, in all other zones, standard deviation values are comparable getting around values of 2.2 – 2.8 x 10^4 Pt/cm^3 vs. 1.0 – 1.8 x 10^4 Pt/cm^3 of the inner city zones.

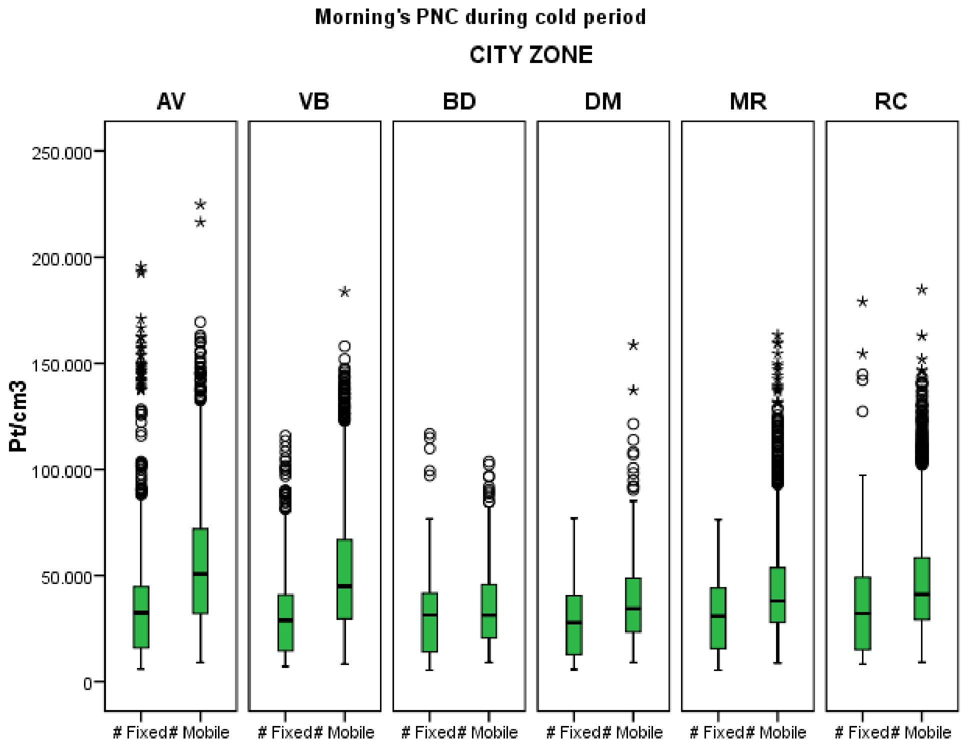

Figure 3:15 Box-plot for morning's fixed and mobile PNC for each city zone. Boxes represent the median values, interquartile ranges, extreme values and outliers.

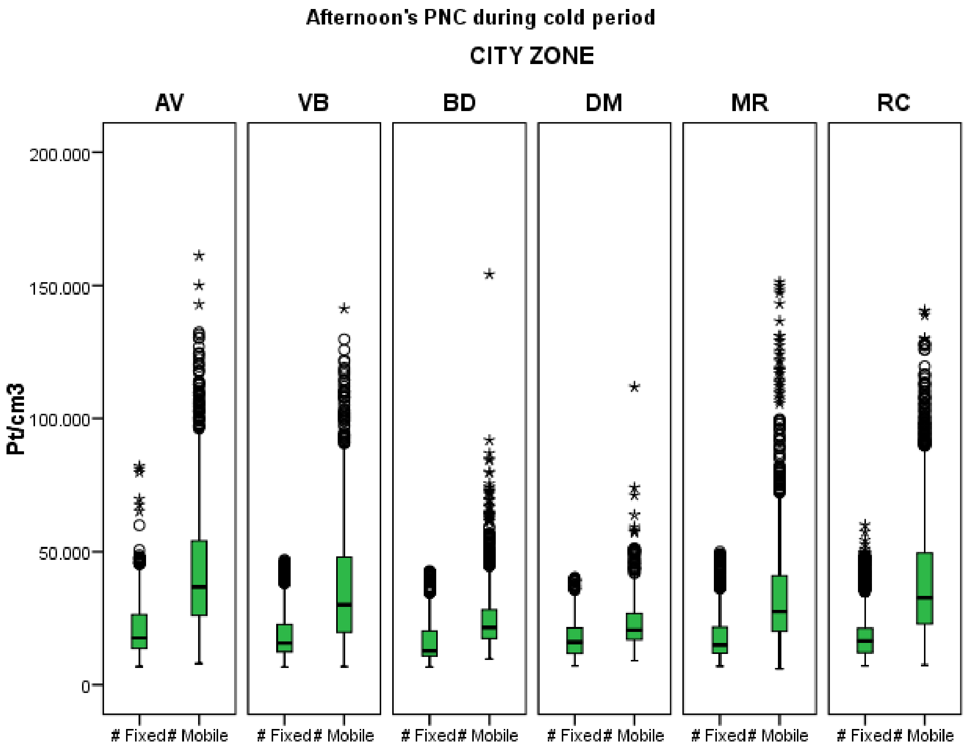

Figure 3:16 Box-plot for afternoon's fixed and mobile PNC for each city zone. Boxes represent the median values, interquartile ranges, extreme values and outliers.

As described decribed in section 2.3.1, also for the cold period mobile PNC dataset, a detailed route subdivision was applied with the aim to identify internal differences in terms of pollutants concentrations for each urban zone.

Corso Buenos Aires (AV) was divided into three parts: 1A, 1B and 1C. In the first section (1A) average mobile PNC concentration value is 45875 Pt/cm^3 and the dataset vary in the 7.9 x 10^3 – 1.7 x 10^5 Pt/cm^3 range. Higher values were observed in section 1B (average 51402 Pt/cm^3; range 9.9 x 10^3 – 2.2 x 10^5 Pt/cm^3) and in section 1C (average 53119 Pt/cm^3; range 8.3 x 10^3 – 1.6 x 10^5 Pt/cm^3). Oppositely to what observed for BC average concentrations, mobile average values at the end of Corso Buenos Aires (close to Porta Venezia) are 1.2 times higher than in section 1A. However, as shown in Fig 9.20, no relevant statistical differences (α=0.05) were found between average mobile PNC concentrations in the three subclasses. Observing the computed CV values, data variability decreases progressively from section 1A to section 1C (CV_{1A} = 0.58, CV_{1B} = 0.55, CV_{1C} = 0.48). Highest peaks were observed in street section 1B (in particular close to crossroad with Viale Tunisia), while number of probably outlier is less numerous in section 1C.

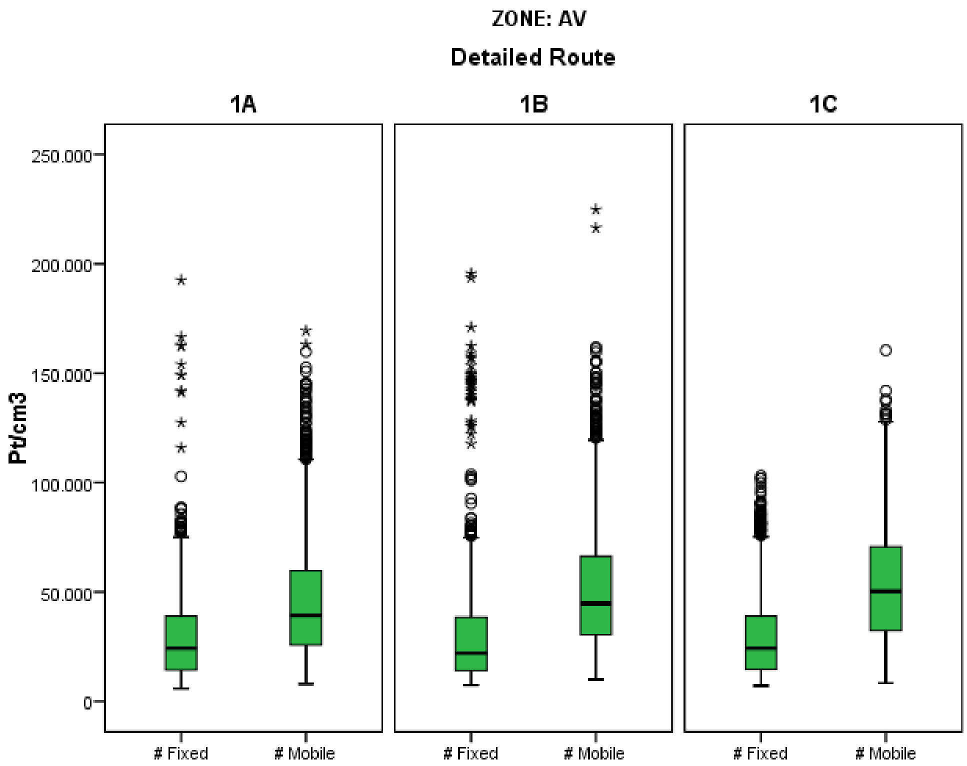

Figure 3:17 Box-plot of fixed and mobile PNC in city zone AV. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Corso Porta Venezia (VB) was divided into two sections. Boundary of the two section is the intersection whit Via Senato, an important main road of the inner city circle. Considering mobile average PNC, differences between the two sections are less marked than those observed for mobile BC. Despite the proximity to a city park (Giardini Indro Montanelli) and the larger street, also in this case it is possible to perceive an higher PNC average value of 46476 Pt/cm^3 and results to have an average value 1.1 times higher than the less crowded but narrower street section 2E (average 42797 Pt/cm^3). Mobile PNC vary in the 6.9 x 10^3 – 1.5 x 10^5 Pt/cm^3 in section 2D, while data in section 2E vary in 8.3 x 10^3 – 1.8 x 10^5 Pt/cm^3 range. Comparing CV values, data variability is higher in section 2D (CV_{2D} = 0.61 and CV_{2E} = 0.58).

Pedestrian zone (BD) and the traffic limited Via Mazzini (DM) were not further divided due to the absence of significant discontinuity along the monitoring route and formerly described (Annex II).

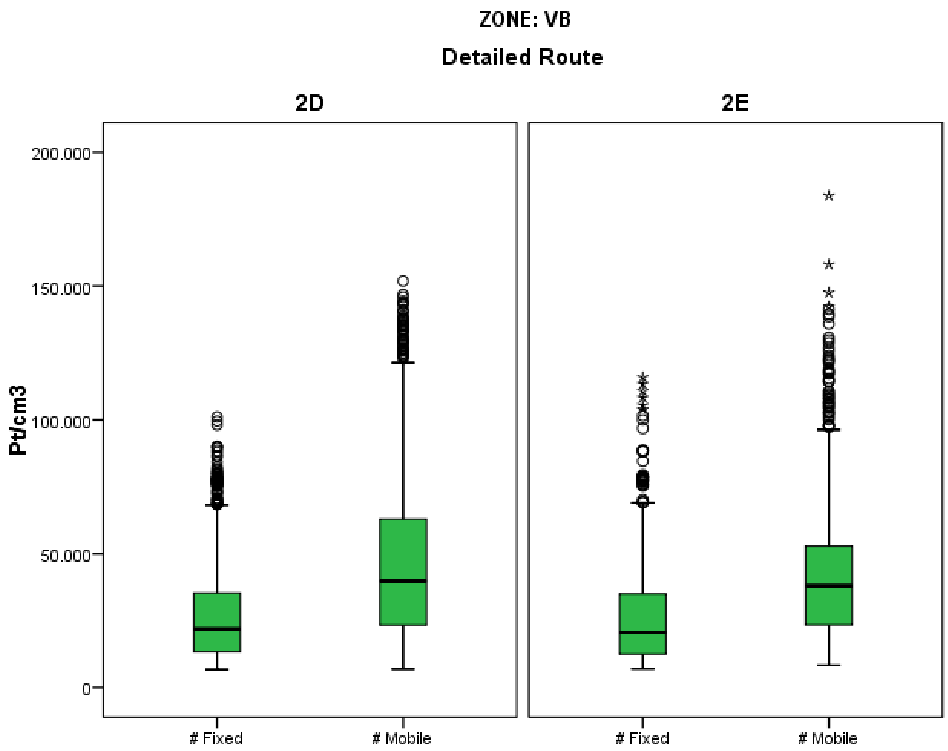

Figure 3:18 Box-plot of fixed and mobile PNC in city zone VB. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Until reaching the intersection whit Via Sforza (5H), Corso Porta Romana is less crowded then the second section (5I). Both sections are covered by public surface transport lines, and are made by cobblestones. However also in this case minimal differences between average mobile PNC values not suggest significant statistical differences, as highlighted in graph 4.19. In street section 5I mobile PNC data vary in the 5.9 x 10^3 – 1.6 x 10^5 Pt/cm^3, while average PNC concentration result to be 38000 Pt/cm^3. Corresponding vales for street section 5H are: 9.2 x 10^3 – 1.6 x 10^5 Pt/cm^3.

Differently as for BC, CV values suggest an higher data variability on the second street section (CV_{5H} = 0.53 vs. CV_{5I} = 0.56). As for BC, PNC peaks were observed close to the intersection with Via Sforza.

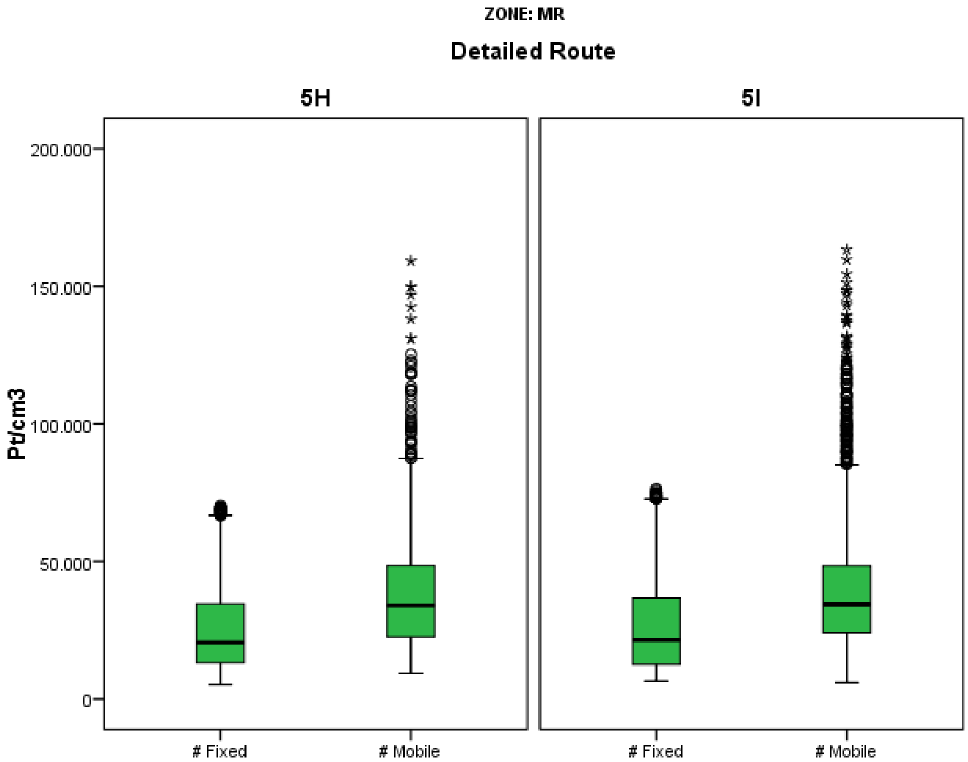

Figure 3:19 Box-plot of fixed and mobile PNC in city zone MR. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Section RC was divided into four parts: 6L, 6M, 6N and 6O. Same trend observed for BC is reflected by mobile PNC data. Highest average concentrations were observed in Piazzale Corvetto (6O) with a value of 52964 Pt/cm^3 (range: 8.6 x 10^3 –

1.8×10^5 Pt/cm^3). The first part of Corso Lodi (6L) is characterized by the presence of access roads implying a greater distance between kerbside an motorized traffic. This results in lower average concentrations (average: 40485 Pt/cm^3; range: 8.0×10^3 – 1.6×10^5 Pt/cm^3)which are 0,8 times those measured in Piazza Corvetto. Significant statistical differences on the average PNC were not found between section 6M (average: 43865 Pt/cm^3; range: 7.5×10^3 – 1.7×10^5 Pt/cm^3) and 6N (average: 41319 Pt/cm^3; range: 7.3×10^3 – 1.4×10^5 Pt/cm^3), both characterized by idling traffic. High outliers were observed in all analysed sections.

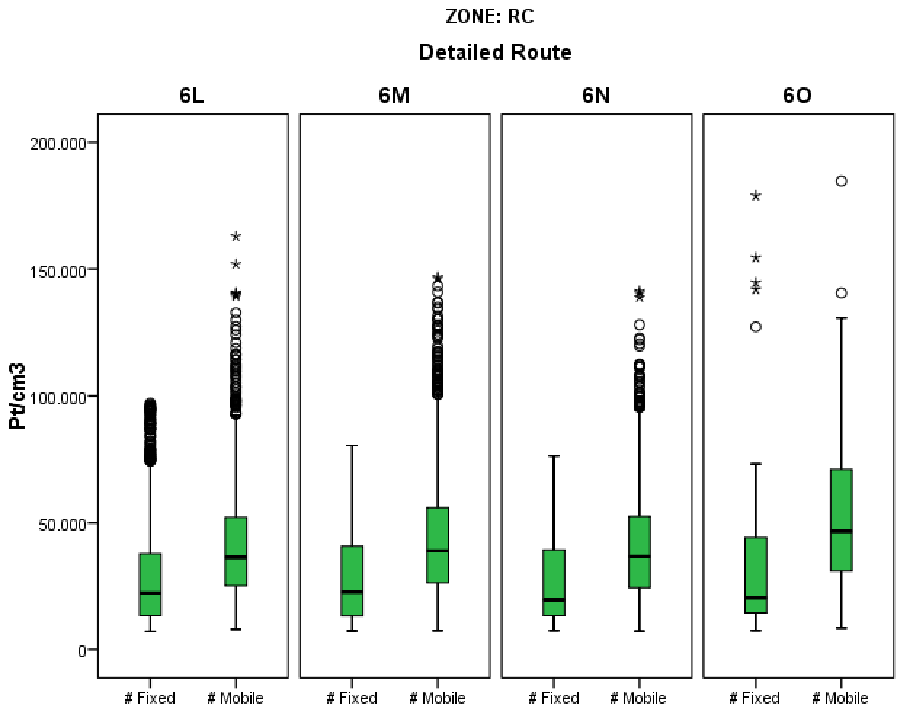

Figure 3:20 Box-plot of fixed and mobile PNC in city zone RC. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.1.2.4 Congestion charge effects

Outside Area C, average PNC values are 1.4 and 2.0 times higher than background PNC, respectively for morning and afternoon hours. In urban areas with restricted traffic access (VB, BD, DM and MR), mobile PNC are 1.3 and 1.7 times higher than those measured at the fixed station, respectively in the morning and afternoon hours. During afternoon hours, ratio between inside and outside Area C average PNC is 0.78 , while in the morning the difference is less marked (ratio 0,86). During public strike days, sampled data are all referred to No Area C category.

Comparing morning's mobile PNC data inside traffic limitation zone Area C with those outside Area C, even if less marked than for BC, average concentration values are higher in non-traffic limited urban areas, as shown in graph 3.21. Out of Area C, mobile PNC morning average concentration is 49121 Pt/cm^3 (1.3 times higher than average fixed PNC and 1.2 times higher than average PNC in Area C zone) and data vary in the 9.2 x 10^3 – 2.2 x 10^5 Pt/cm^3 range. Area C average mobile PNC is 42444 Pt/cm^3 (1.3 times average background concentration) and vary in the 8.3 x 10^3 – 1.8 x 10^5 Pt/cm^3 range. Observing computed coefficient of variation for each dataset, mobile PNC data outside Area C are characterized by a lower variability than inside Area C data ($CV_{Area\ C}$ = 0.55vs. $CV_{No\ Area\ C}$ = 0.52).

Considering afternoon's average mobile BC values, inside Area C, PNC is on the average 1.7 times background levels (average mobile PNC: 31203 Pt/cm^3; range: 5.9 x 10^3 – 1.5 x 10^5 Pt/cm^3). More marked is the difference between afternoon's average BC level Out of Area C and average fixed PNC, where the ratio with the fixed measurement station is 2.1 (average mobile PNC: 39958 Pt/cm^3; range: 7.3 x 10^3 – 1.6 x 10^5 Pt/cm^3). Afternoon's average mobile PNC out of Area C restrictions results to be 1.3 times higher than in the inner city circle. Differently to BC data and morning mobile PNC data, afternoon PNC Area C data are more variable than No Area C data ($CV_{Area\ C}$ = 0.61 vs. $CV_{No\ Area\ C}$ = 0.54).

Compared to BC, effects of a congestion charge area are less marked on PNC.

			N	Minimum	Maximum	Mean	Std. Deviation
Morning	**Area C**	**PNC Fixed**	7040	5273	116880	31817	19085
		PNC Mobile	7464	8313	183700	42444	23404
	No Area C	**PNC Fixed**	7868	5868	195500	34357	21289
		PNC Mobile	8362	9123	224800	49121	25555
Afternoon	**Area C**	**PNC Fixed**	5067	6713	49890	17880	8939
		PNC Mobile	5046	5958	154210	31203	19082
	No Area C	**PNC Fixed**	5453	6739	82100	19506	10119
		PNC Mobile	5408	7358	161200	39958	21579

Table 3:8 Descriptive statistics of fixed and mobile PNC inside and outside Area C for morning's and afternoon's values.

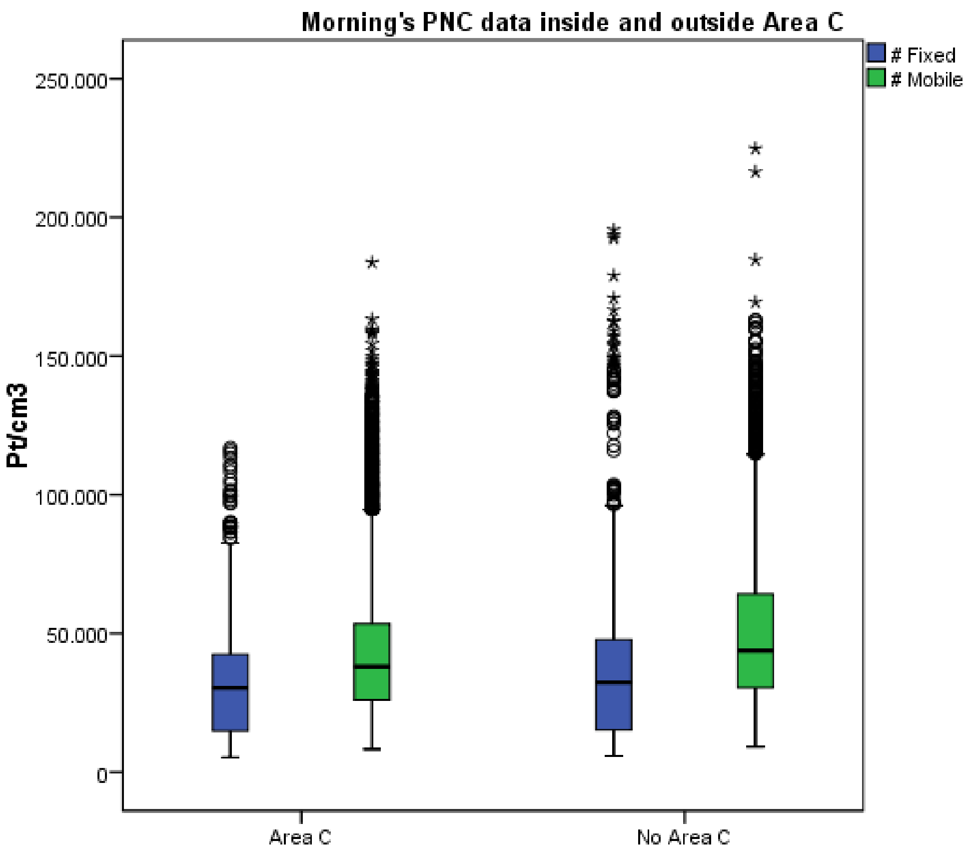

Figure 3:21 Box-plot for morning's fixed and mobile PNC ionside and outside Area C. Boxes represent the median values, interquartile ranges, extreme values and outliers.

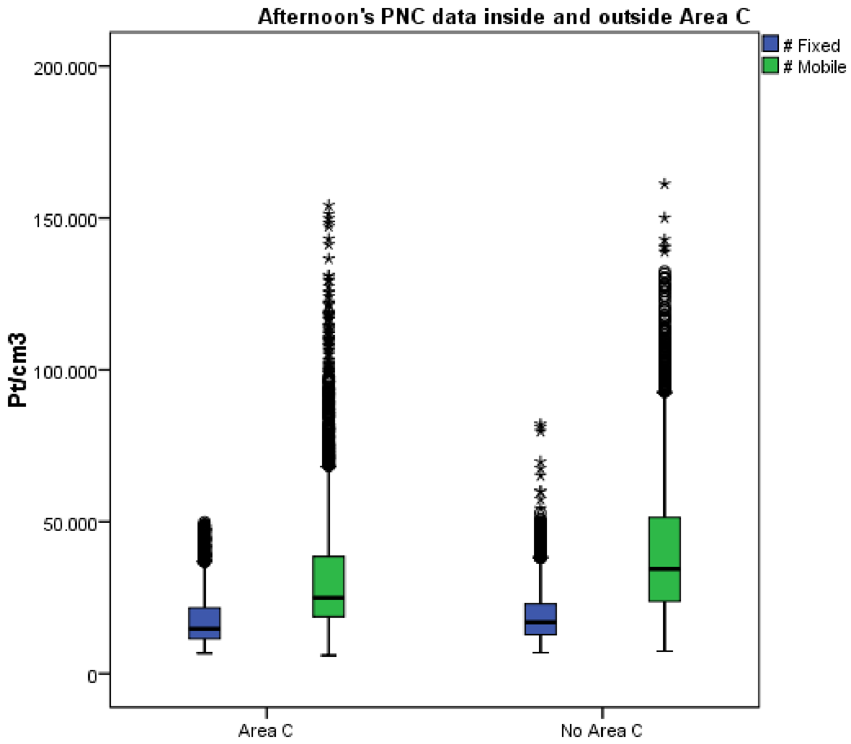

Figure 3:22 Box-plot for afternoon's fixed and mobile PNC ionside and outside Area C. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.1.3 Pollutants correlation

Observing time trends for mobile BC and for fixed BC relative to the cold period, given in Fig 3.23, similar pattern can be individuated. Analysing the result of individual runs, days with high background BC levels are characterized with high mobile BC levels. This trend is particularly evident for 22th and 23th January, both distinguished by particularly high fixed and mobile BC concentrations. Even when daily average BC urban background concentrations are low, a decrease in daily averaged mobile BC concentration is observable, particularly evident on Fridays and Saturdays when traffic intensity decreases. In order to quantify the degree of correlation between fixed and mobile BC values, daily averaged data of both instruments were plotted on a scatterplot, firstly without separation by type and then distinguished between morning and afternoon data.

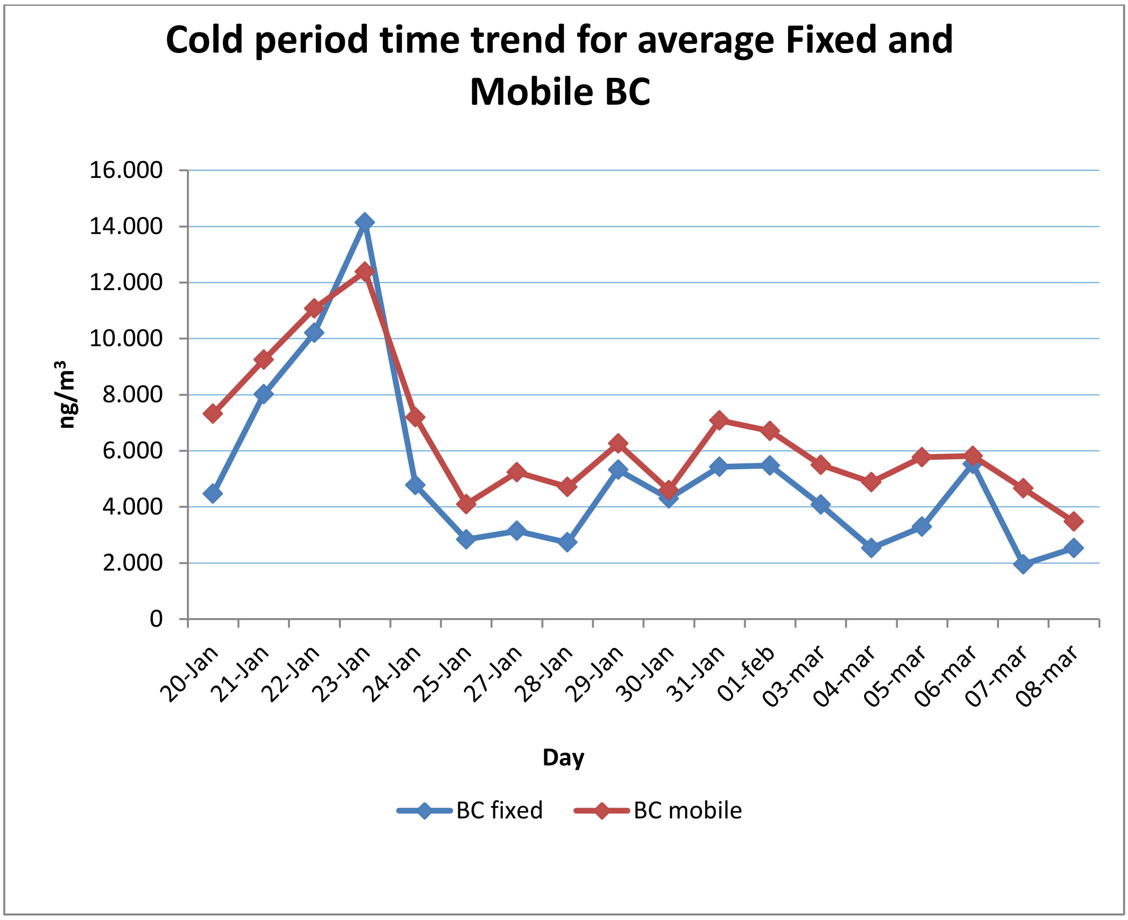

Figure 3:23 Time trend of daily averaged fixed and mobile BC during cold period.

As shown in Fig 3.24 a good correlation (R^2 = 0.8982) was found between overall daily averaged fixed BC levels and mobile BC concentrations. To find out in which part of the day the values are more correlated, morning and afternoon data were separately analysed.

By the comparison of R^2 values, morning mobile BC data result to be clearly more correlated with fixed BC data than afternoon's; respective values are R^2 = 0.9117 in the morning and R^2 = 0.6879 during afternoon hours. The difference is probably due to the higher mixing height and the consequent increase in atmospheric turbulence.

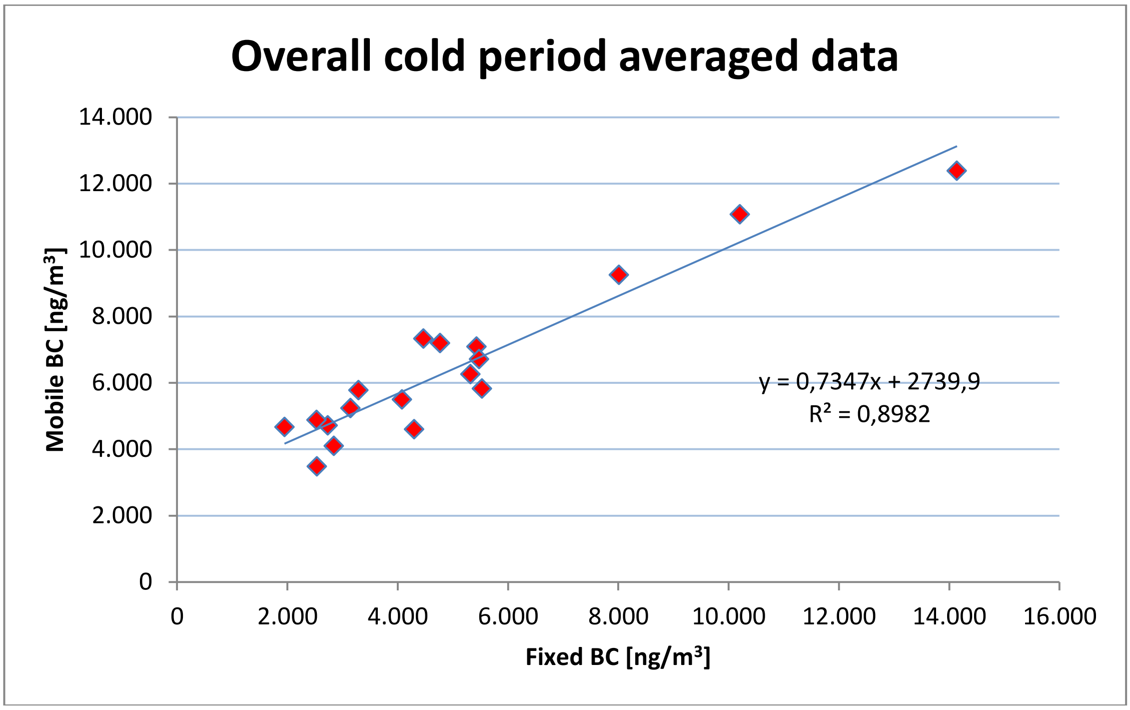

Figure 3:24 Linear correlation between overall fixed and mobile BC daily averaged data during cold period. R2=0.8982

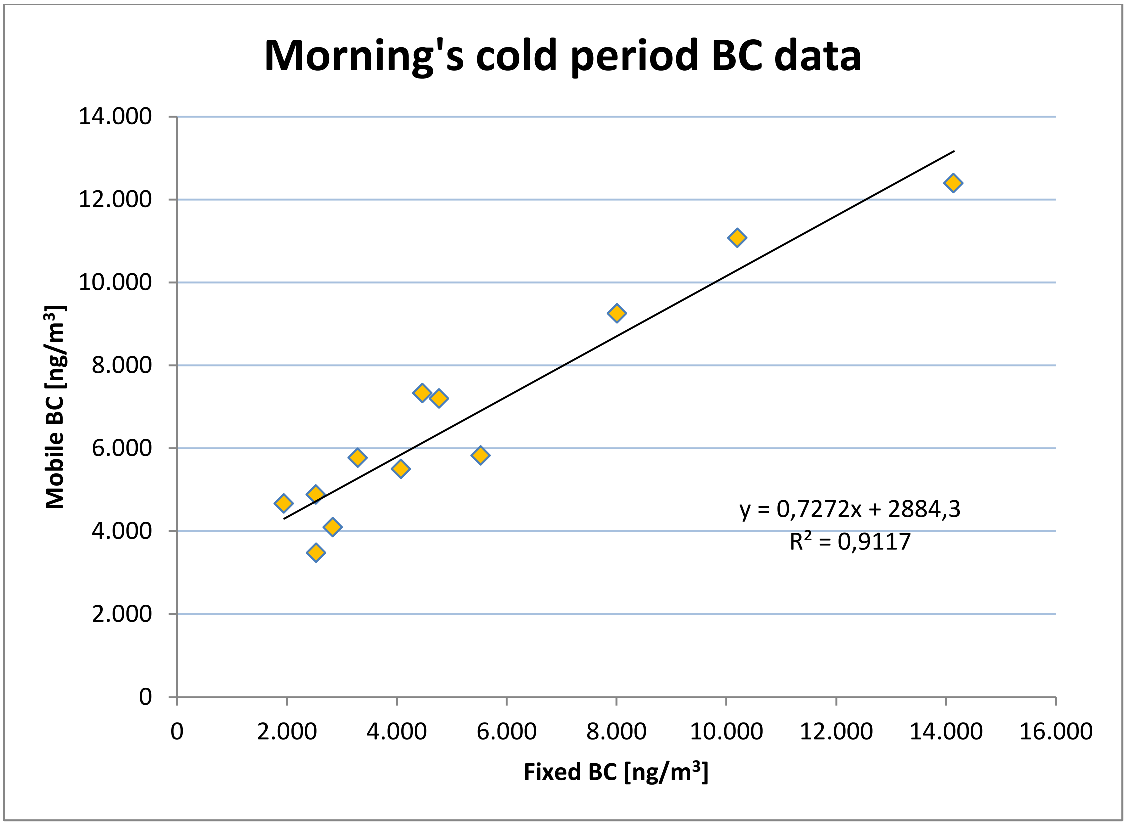

Figure 3:25 Linear correlation between morning's fixed and mobile BC daily averaged data during cold period. R2=0.9117

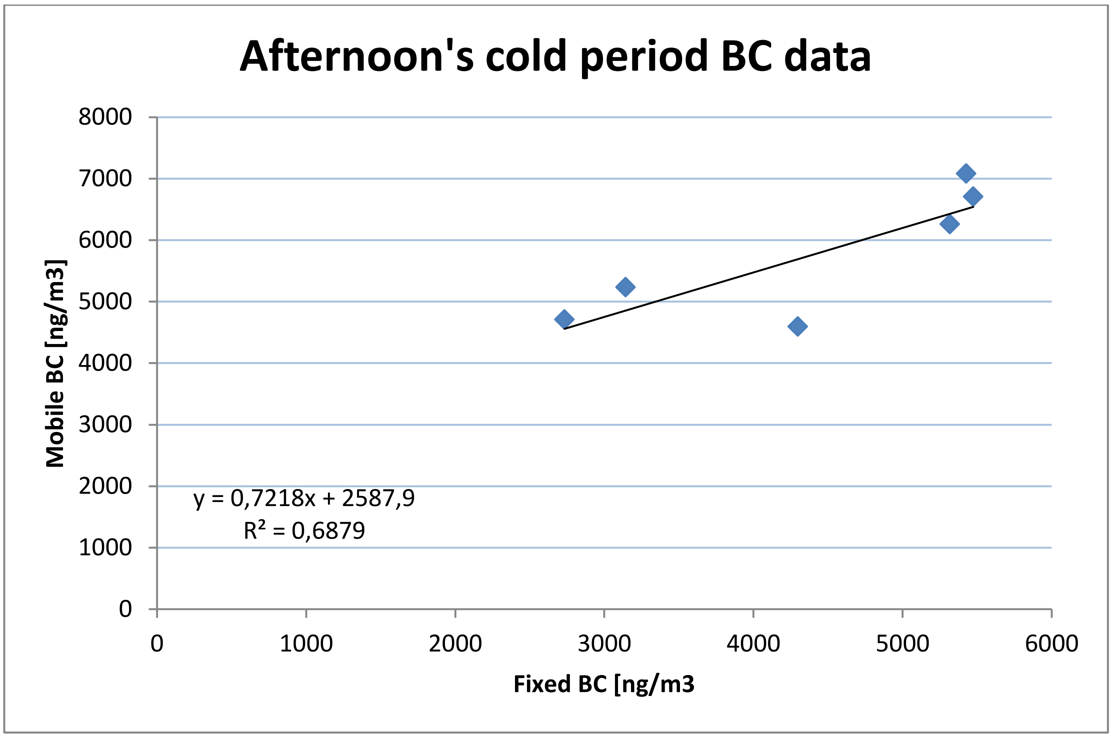

Figure 3:26 Linear correlation between afternoon's fixed and mobile BC data during cold period. R2=0.6879

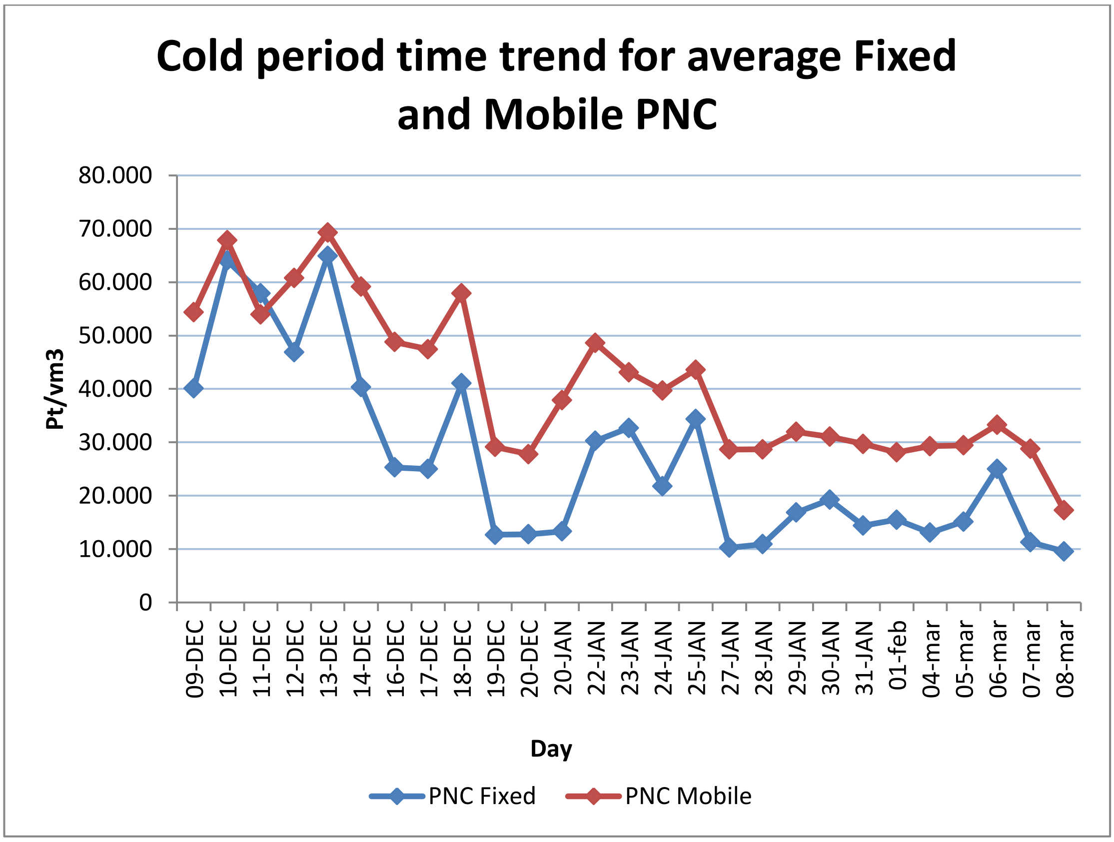

Figure 3:27 Time trend of daily averaged fixed and mobile PNC during cold period.

Analysing the averaged mobile and fixed PNC time trends for the cold period, similar pattern can be observed. Days with particularly high background concentration are characterized by high daily average mobile PNC values, and vice versa, days with lower background concentrations are characterized with lower average mobile PNC . This trend is particularly evident from the 13th to the 19th December, but also from 20th to the 28th January and March 6th. Difference between mobile and fixed PNC is in the average included in the 1 – 2 x 10^4 range except for December the 10th and 11th, where mobile and fixed averaged PNC values are comparable. Plotting averaged PNC data on a scatterplot permits to obtain the degree of correlation between mobile and fixed PNC. Overall cold period daily averaged data are given in Fig 3.28. The obtained linear interpolation reflect a good correlation (R^2 = 0.8664) between urban background measured data and mobile PNC. Also in this case, to find out in which part of the day the values are more correlated, morning and afternoon data were separately analysed on analogous scatterplots. Morning's averaged cold period PNC data evidence the same correlation (R^2 = 0.8664), while afternoon's correlation is quite higher obtaining an R^2 = 0.8937.

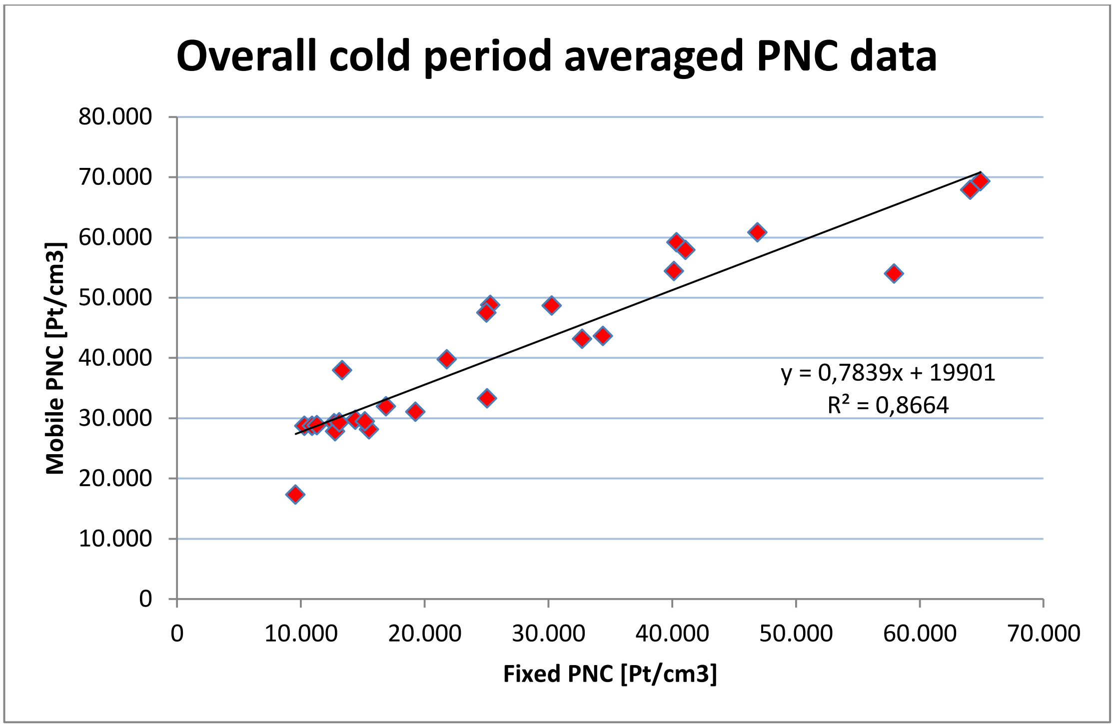

Figure 3:28 Linear correlation between overall fixed and mobile PNC data during cold period. R2=0.8664

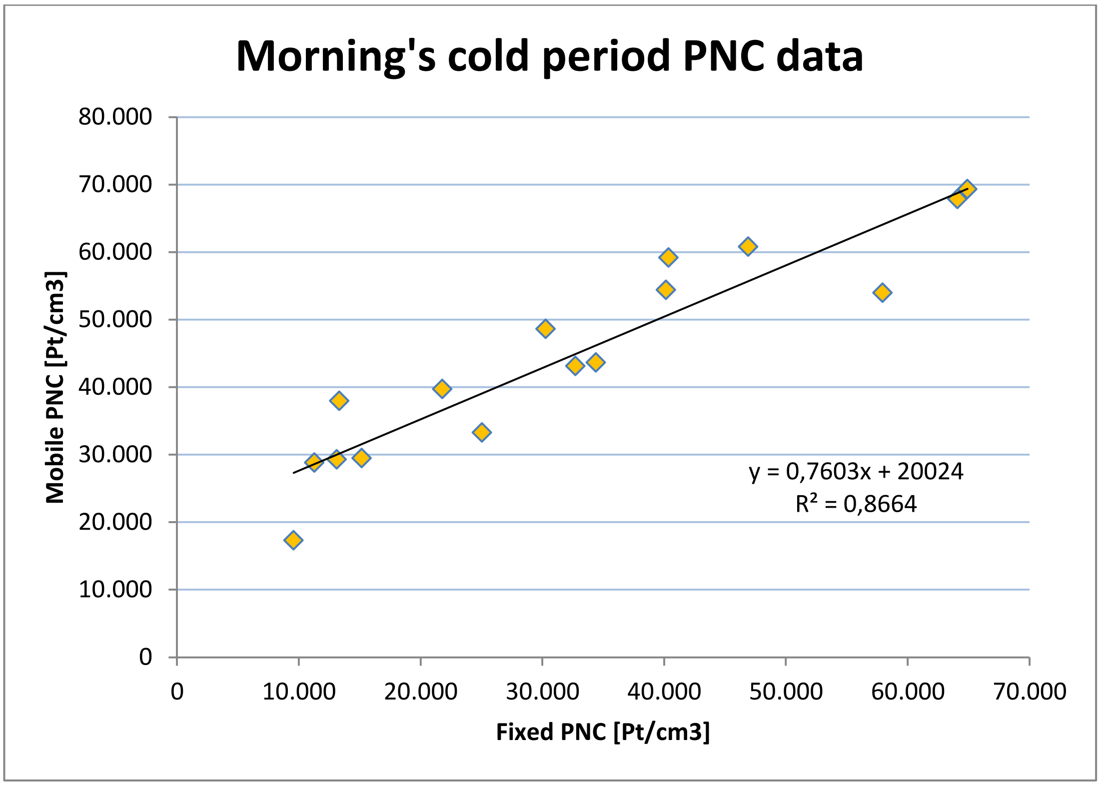

Figure 3:29 Linear correlation between morning's fixed and daily averaged mobile PNC data during cold period. R2=0.8664

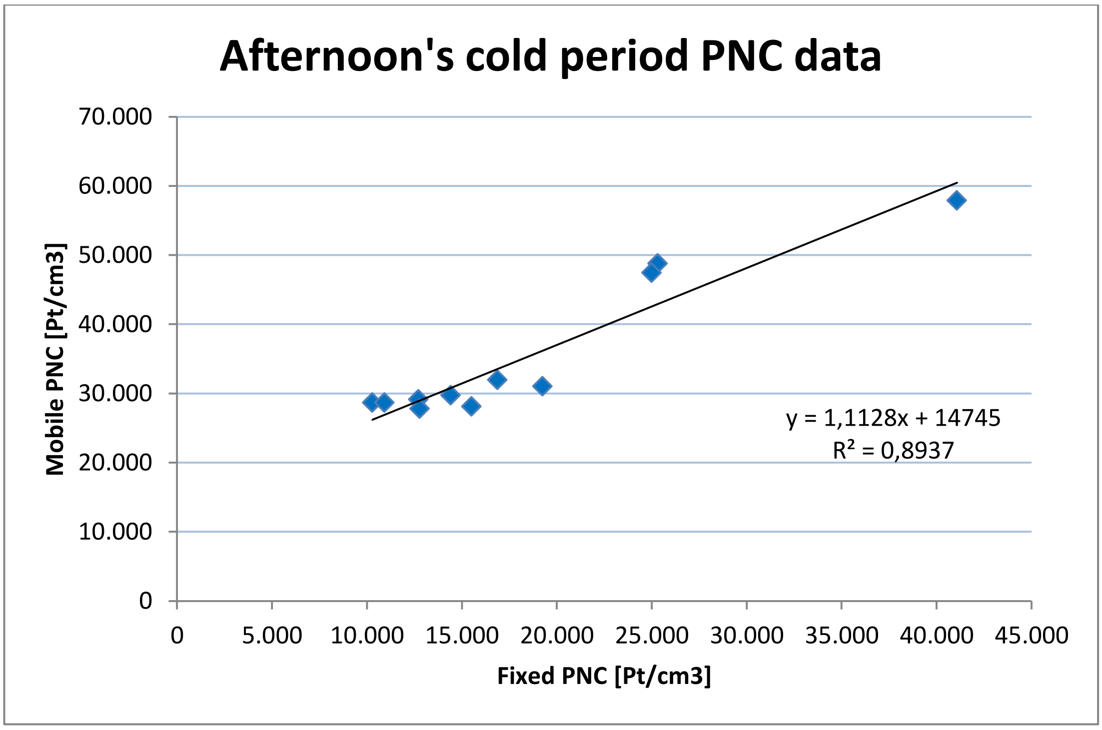

Figure 3:30 Linear correlation between afternoon's fixed and daily averaged mobile PNC data during cold period. R2=0.8937

Similar pattern for both pollutants were observed in the different city zones and in the urban background station, therefore correlation between mobile PNC recorded data and mobile BC values was examined. Daily averaged mobile data of each zone were plotted on a scatterplot and linearly interpolate computing R^2 value and linear equation of the trend-line. During December aethalometers were not available, therefore only mobile PNC data from January, February and March were included in data correlation analysis. Mobile PNC data (and consequently mobile BC data) from March 3th were excluded due to an instrumental malfunctioning .

In the underlying scatterplots, mobile PNC – Mobile BC linear correlation is shown for each city zone. Highest correlations were found in the most traffic congested zones. In section RC, R^2 = 0.6099 (Fig 3.36), the highest correlation of the entire route. High correlation suggest a commune origin for both pollutants. In section AV (R^2 = 0.4291, Fig 3.31) correlation between the two pollutants is less marked. Section VB is characterized by an R^2 value of 0.3946 (Fig 3.32) and 0.3573 in section MR (Fig 3.35). In pedestrian zone pollutants correlation is the lowest of the entire route (R^2 = 0.2584, Fig 3.33) while in Via Mazzini R^2 = 0.5358 (Fig 3.34), indicating a better correlation than in the pedestrian zone, probably due to the proximity to primary PNC and BC sources like motorized vehicles.

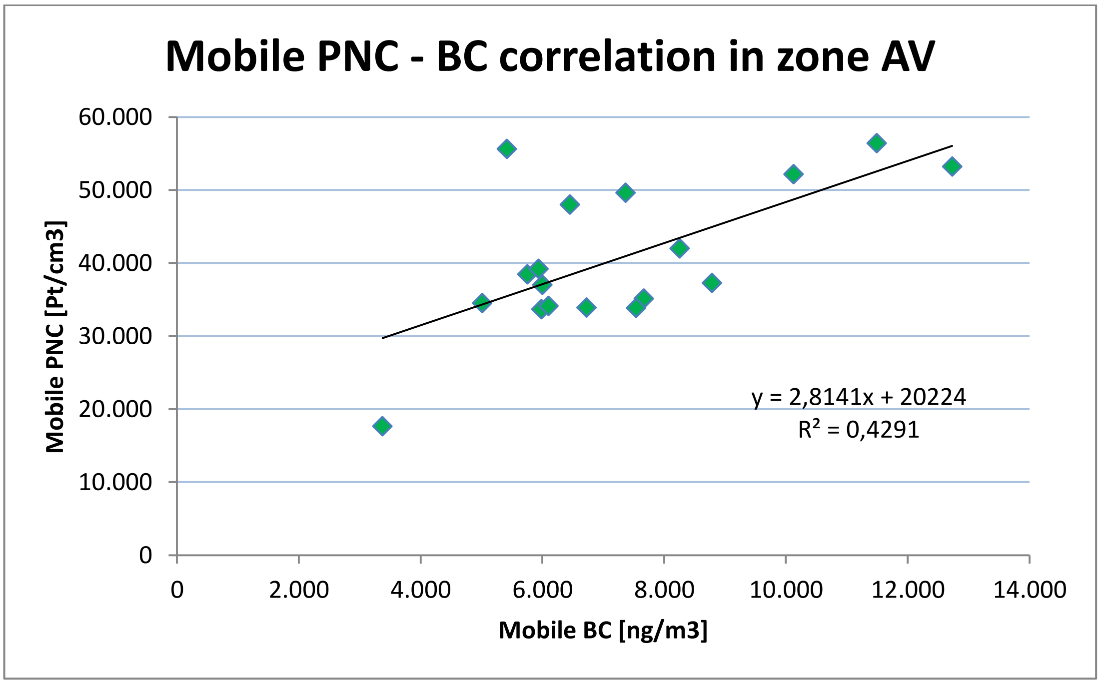

Figure 3:31 Mobile PNC-Mobile BC linear correlation in zone AV. R2=0.4291

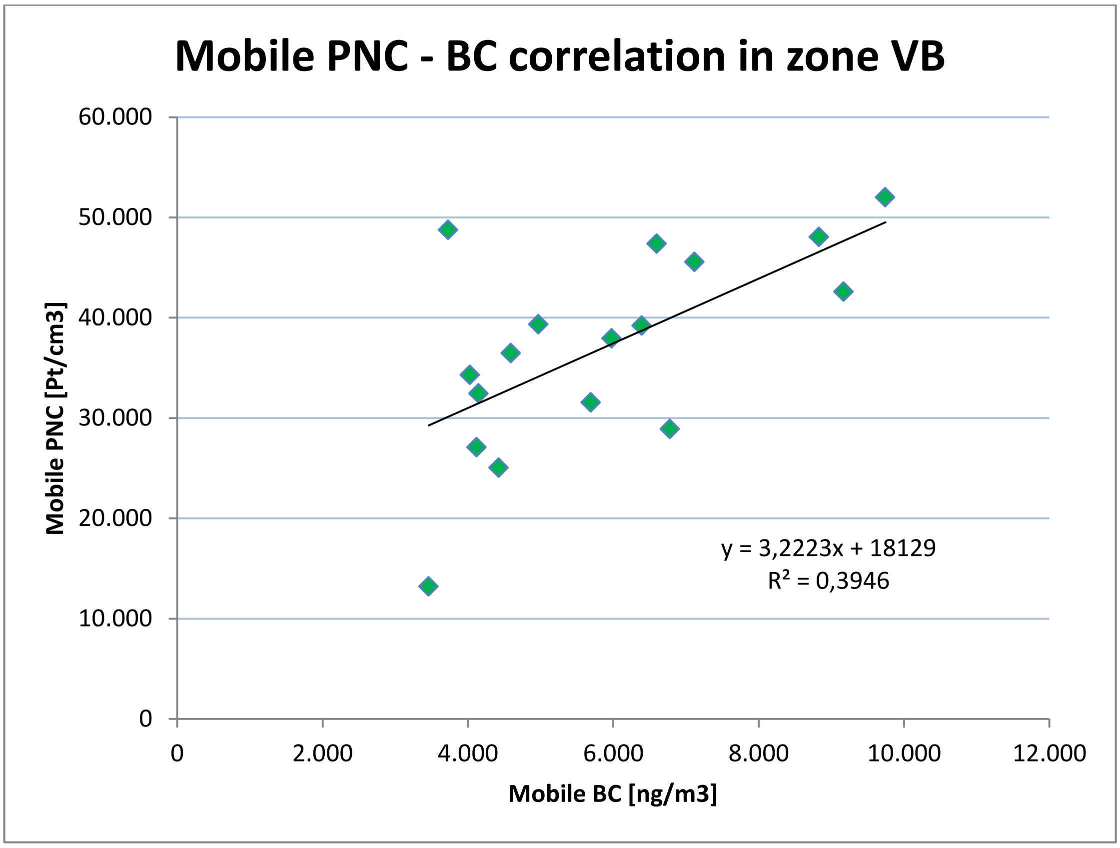

Figure 3:32 Mobile PNC-Mobile BC linear correlation in zone VB. R2=0.3946

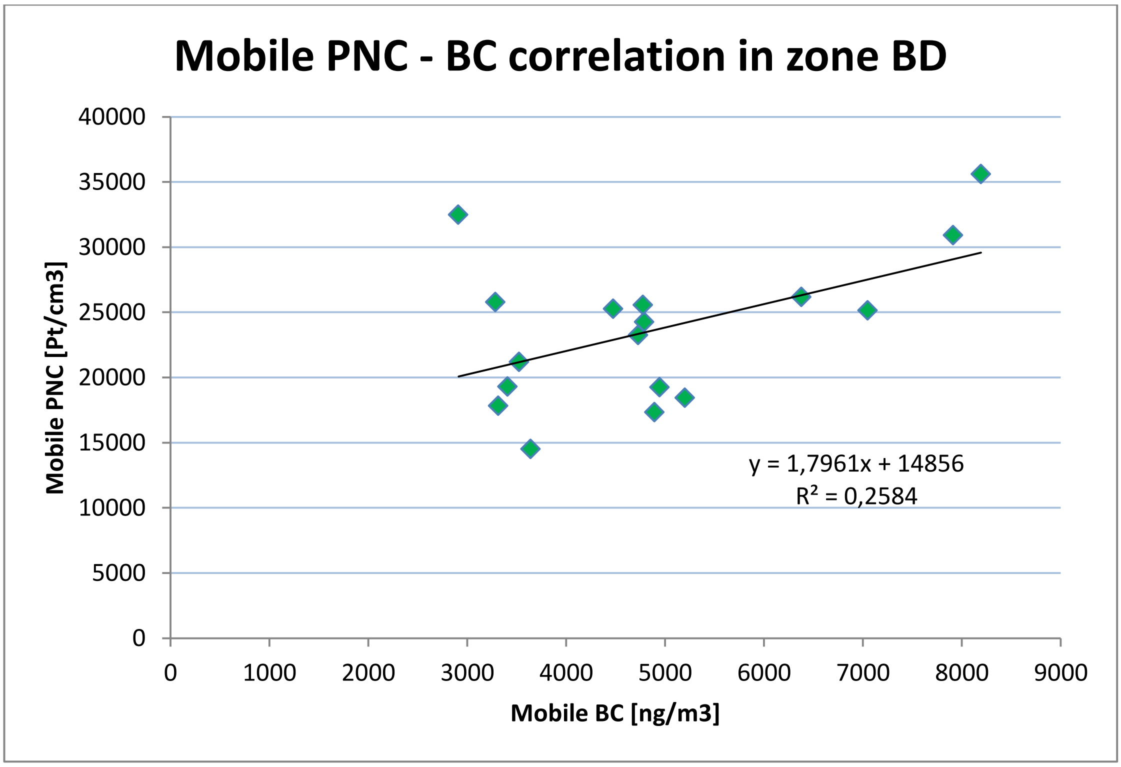

Figure 3:33 Mobile PNC-Mobile BC linear correlation in zone BD. R2=0.2584

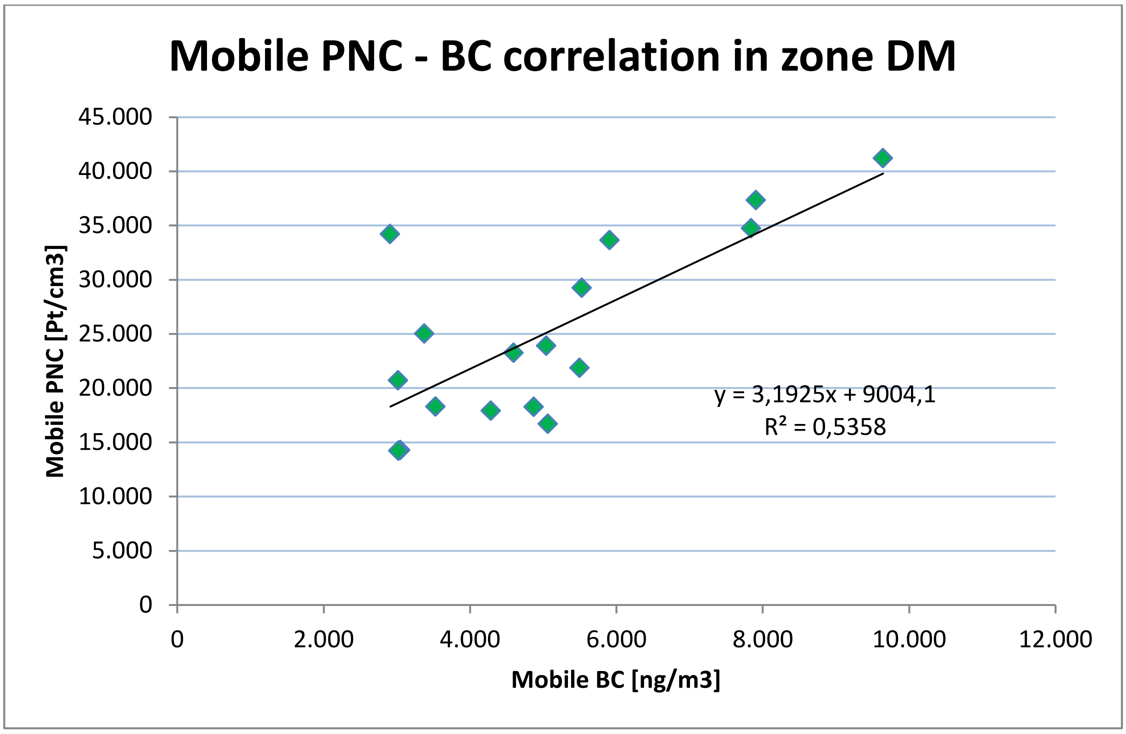

Figure 3:34 Mobile PNC-Mobile BC linear correlation in zone DM. R2=0.5358

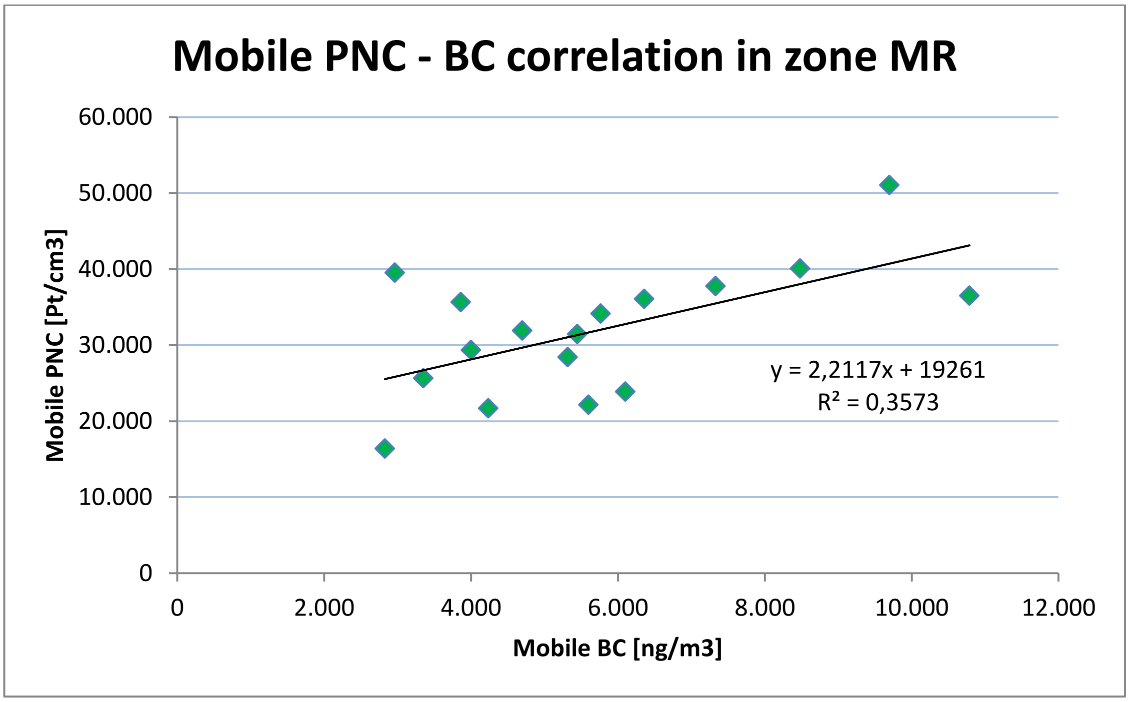

Figure 3:35 Mobile PNC-Mobile BC linear correlation in zone MR. R2=0.3573

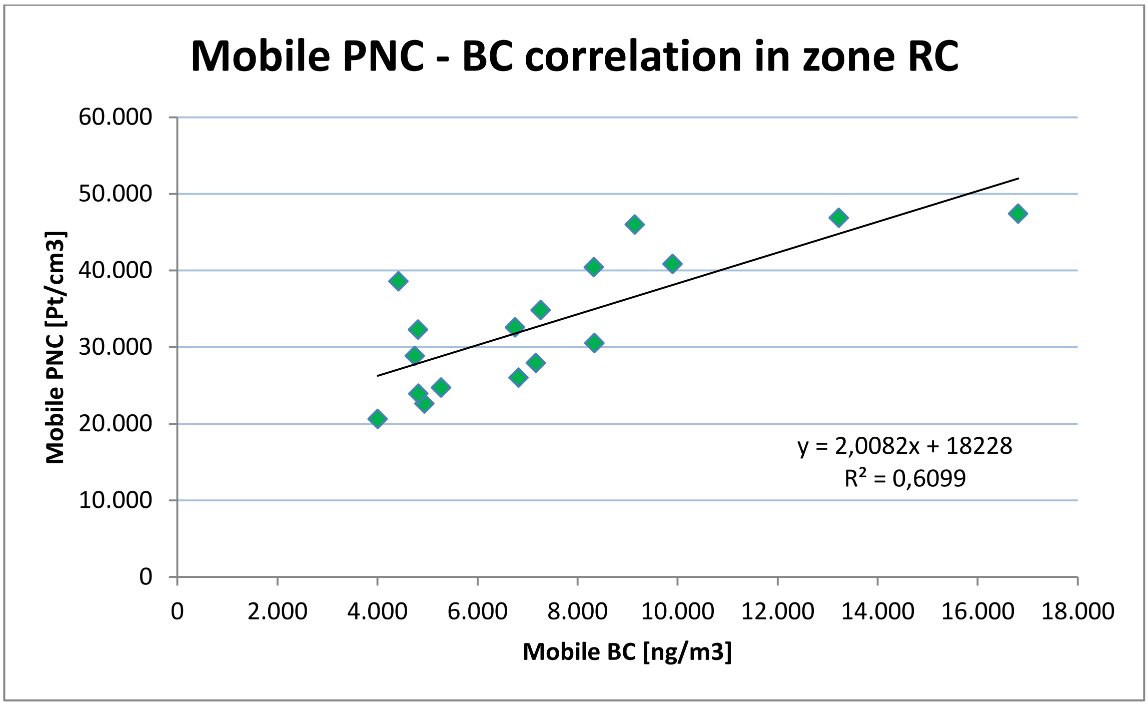

Figure 3:36 Mobile PNC-Mobile BC linear correlation in zone RC. R2=0.6099

Considering the entire cold period mobile PNC and BC dataset without zone classification, R^2 result to be 0.4488 as shown in Fig 3.37, comparable to values obtained in other similar works performed in Flanders (Peters, Bleux, & Van Poppel, Methodology for setup and data processing of mobile air quality measurements to assess the spatial variability of concentrations in urban environments, 2013) were an R^2=0.41 was obtained. Similar R^2 values was also obtained plotting fixed PNC and fixed BC on scatterplot of Fig 3.38 (R^2=0.4435).

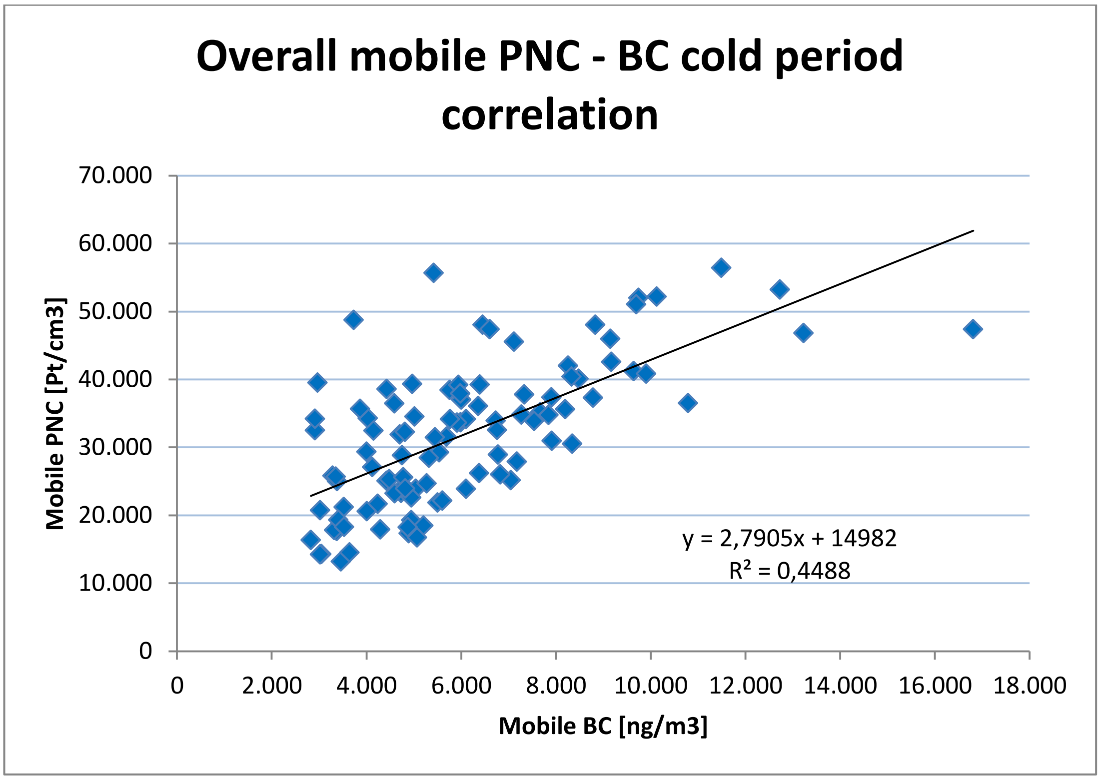

Figure 3:37 Mobile PNC-Mobile BC linear correlation on the entire route during cold period. R2=0.4488

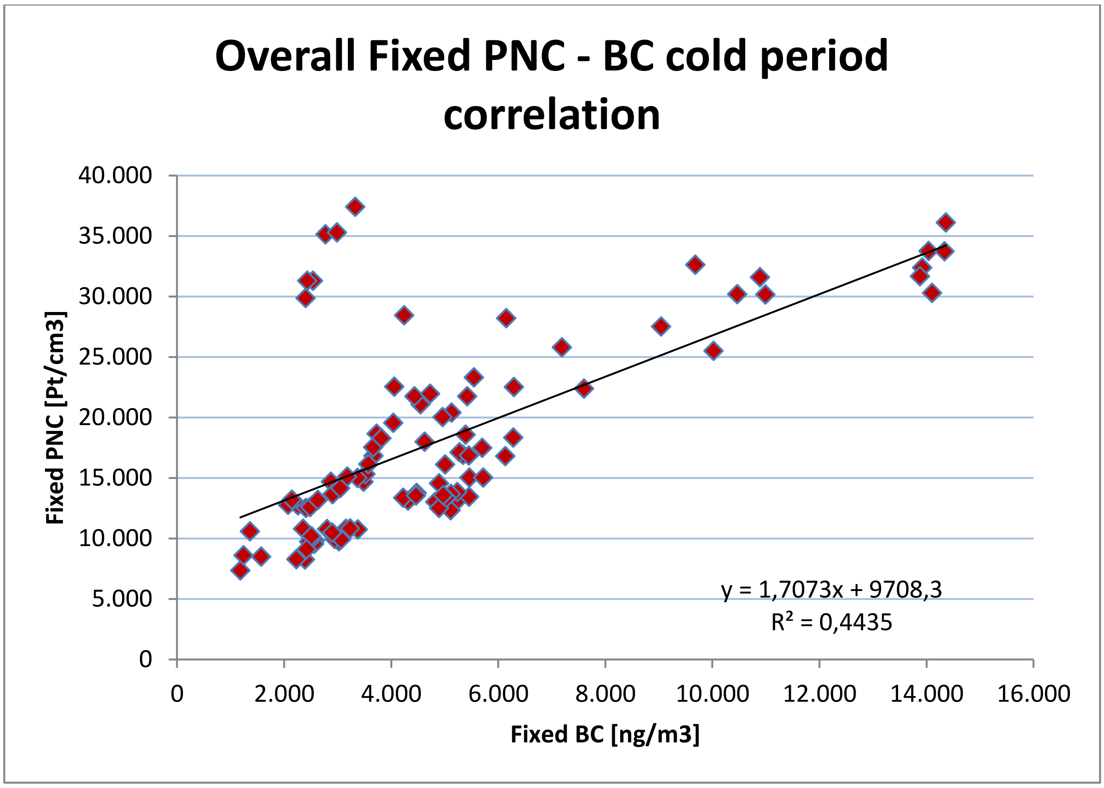

Figure 3:38 Fixed PNC-Fixed BC linear correlation during cold period.

3.2 Warm season

As for the cold period dataset, statistical presentation of the sampled PNC and BC concentration data during the warm period (March 31th – July 31th) is pictured through whiskers box-plots, representing median value, interquartile range and extreme cases of each single variable. Each box-plot is associated to a chart which display the 95% confidence interval for the average value of each considered variable (Annex III). Main descriptive statistics are summarized in tables.

During the warm season monitoring campaign, and after a manual data screening, 28875 Black Carbon (Fixed BC) data for the fixed Aethalometer and 33370 (Mobile BC) data for the mobile Aethalometer were collected at a 10-second time resolution.

Particle number concentration in the 20-1000 nm range ($PNC_{20-1000}$) data were initially more numerous due to the higher time resolution of the instrument (1-second). After applying a 10-secon averaging algorithm, 29347 data for the fixed P-trak and 28706 data for the mobile P-trak were available. Therefore, the entire warm period dataset consists of 120298 concentration data at a 10-second time resolution.

3.2.1 BC data processing

As for the cold period BC dataset, the original recorded warm period BC datasets (fixed BC and Mobile BC) were first processed with the ONA correcting algorithm (as explained in section 6) and then for statistical analyses and potential outlier detection. The main statistical parameters of the data distributions for the overall datasets and for the morning and afternoon datasets separately are reported in Table 8.13: data from the stationary instrument at the urban background site are reported as "BC fixed" whereas those recorded along the pedestrian route as "BC mobile". The box-plots of Figure 3.39 summarize the morning and afternoon datasets for the fixed and mobile instrument in terms of the median values, interquartile ranges, extreme values and outliers; morning and afternoon average values, together with 95% confidence intervals are plotted in Figure 10.1 (Annex III).

3.2.1.1 Seasonal variations

Overall, BC fixed data are in the 2 - 13721 ng/m^3 range, with an average of 1681 ng/m^3 and a standard deviation of 1753 ng/m^3: corresponding figures for BC mobile data are 225 - 144069 ng/m^3, 3212 ng/m^3, and 2987 ng/m^3. Compared to fixed data, mobile data are shifted towards higher values, as highlighted by both the min-max range and by the significantly ($\alpha = 0.05$) higher mean (about 1.9 times higher than that measured at the fixed sampling site); also mobile BC standard deviation is 1.7 times higher than for fixed BC dataset. Therefore, despite their restricted range, fixed data are characterized by a larger variability, as stated by the comparison of the values computed for the coefficient of variations (CV = 1.04 for BC fixed vs. 0.93 for BC mobile). Warm period BC concentrations average data are always higher than the respective cold period value. Average overall cold period data is 3.1 and 2.0 times higher than during the warm period, for BC fixed and BC mobile respectively. Seasonal variations are less marked during the morning hours and for BC mobile. Cold period's average BC mobile is 1.8 and 2.2 times higher than during the warm period, in the morning and in the afternoon respectively. Considering BC fixed, the respective ratios are 2.5 for the morning and 3.8 for the afternoon. While for cold period overall average BC fixed standard deviation is twice as during the warm period, no seasonal changes were noted for BC mobile standard deviation.

Due to the higher temperature than during the cold season, activity of primary emission sources is less intense. Domestic heating contribution to pollutants concentration could be considered non influential and vehicular traffic is less intense due to school-stop and summer holidays. Also the atmospheric conditions follows seasonal changes. During spring days atmospheric turbulence is in the average higher than during winter, and windy days are more frequent, even if not habitual.

Instrument		N	Minimum	Maximum	Mean	Std. Deviation
BC Fixed	Overall	28875	2	13721	1681	1753
	Morning	13708	92	13721	2278	2316
	Afternoon	15167	2	13041	1142	627
BC Mobile	Overall	33370	225	144069	3212	2987
	Morning	16579	429	144069	3827	3507
	Afternoon	16791	225	62926	2605	2202

table 3:9 Descriptive statistics for overall, morning's and afternoon's fixed and mobile BC data.

3.2.1.2 Daily variability

BC mobile data are significantly higher than fixed data also when separately considering the morning and the afternoon route: the mean values for the BC mobile datasets are 1.7 and 2.3 times higher than those of the BC fixed on morning and afternoon subsets, respectively. Data variability is always larger in the morning, and at the urban background site in particular (CV = 1.02 for BC fixed vs. CV = 0.92 for BC mobile), then in the afternoon when, conversely is larger for the BC mobile dataset (CV = 0.55 for BC fixed vs. CV = 0.85 for BC mobile). Same cold period daily trends are found in the warm period BC dataset. For both the fixed and mobile dataset the highest values were recorded in the morning, while lowest values were recorded in the afternoon.

The comparison between morning and afternoon values shows that during the morning hours concentration levels are significantly higher for both the fixed and mobile instrument: on the average, morning concentration are 2.0 times higher than in the afternoon for BC fixed and 1.5 times higher for BC mobile.

Morning's mobile BC dataset vary in the 429 - 144069 ng/m^3 with an average of 3827 ng/m^3. Respective fixed BC values are 92 – 13721 ng/m^3 and 2278 ng/m^3. Afternoon's mobile BC vary in the 225 – 62926 ng/m^3 range, while afternoon fixed BC vary in the 2 – 13041 ng/m^3 range with an average value of 1142 ng/m^3 and the lowest standard deviation of 627 ng/m^3(compared to the highest standard deviation of morning's mobile BC dataset: 3507 ng/m^3). As shown if Fig 10.2 (Annex III), afternoon's average mobile BC concentration is comparable to morning's average background BC concentration (α=0.05).

Potential outlier detection showed that these values are mostly present in the morning hours dataset for the mobile instrument and clearly higher compared to the cold period: in particular, data label analysis highlights that the morning highest outliers shown in Figure 8.68 were recorded on April 5th and May 17th and 21th whereas afternoon outliers of the mobile instrument were recorded on May 5th and 7th and April 7th . In the fixed instrument dataset number of potential outliers were lower than for the mobile instrument and higher for the morning hours than for the afternoon hours. For graphic reasons, 18 mobile BC data over 30.000 ng/m^3 were not taken in account during graph creation. However those data were taken in account during statistical analysis.

Also in this case, outlier detection must be considered as a merely statistical procedure intend to recognize those values that are inconsistent (i.e.: anomalous) with the whole dataset. Nevertheless, such anomalous values may be the result of very peculiar environmental conditions that, even though very infrequent and rarely occurring, are at the same time likely to happen. It is not surprising that the recognized potential outliers were mainly detected in the BC mobile dataset: indeed, the closer exposition to traffic exhaust emissions and peculiar environmental conditions from the emission standpoints (i.e.: queue of idling vehicles, busy crossroads, emission plume for fast accelerating vehicles) can determine short-time concentration peaks. Highest values were observed on the mobile instrument which is directly exposed to traffic related pollutants and the lowest value was sampled at the fixed station.

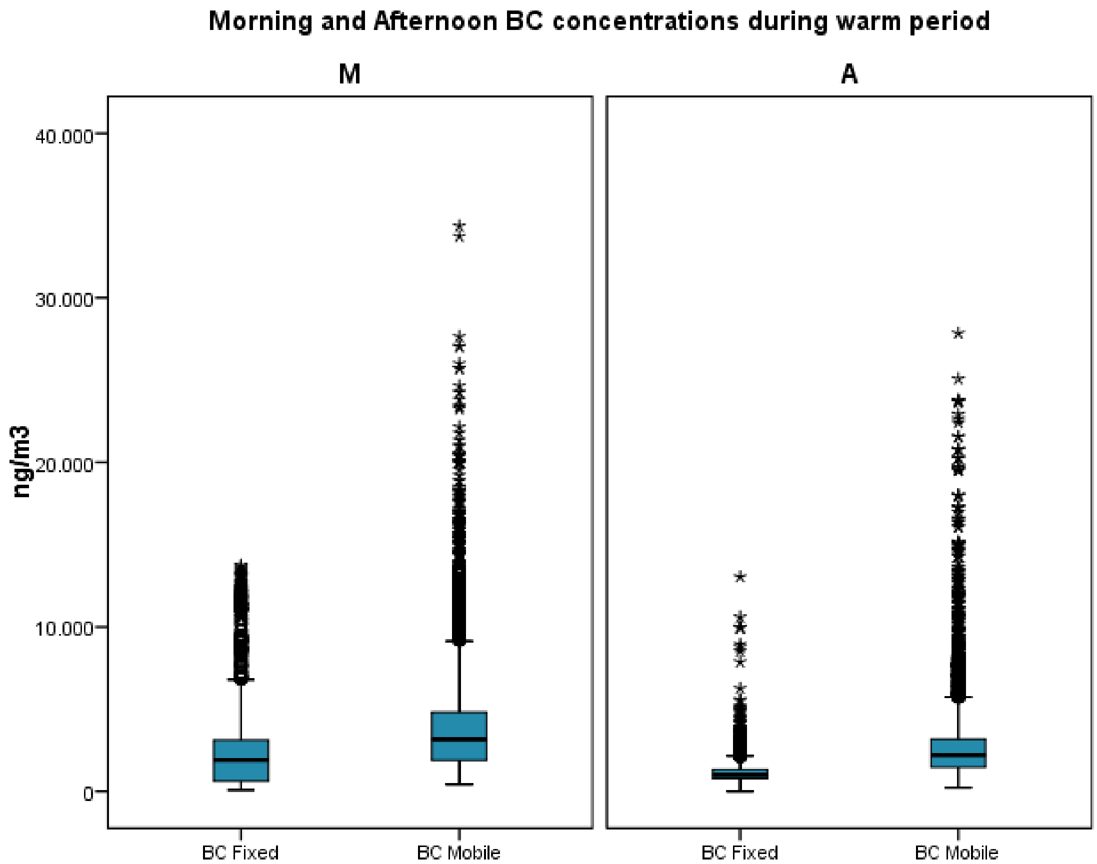

Figure 3:39 Box-plot for morning's and afternoon's fixed and mobile BC warm period data. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.2.1.3 Weekly variations

BC datasets were further stratified by kind of the day, namely separately analysing data collected on working days and on Saturdays; additionally. Differently as for the cold period, no public transport service strike occurred during the warm season monitoring campaign. Corresponding distributions of the BC concentration levels are plotted in Figure 3.40.

		N	Minimum	Maximum	Mean	Std. Deviation
Work day	**BC Fixed**	27112	2	13721	1687	1756
	BC Mobile	31607	225	144069	3219	2950
Saturday	**BC Fixed**	1763	258	8758	1578	1709
	BC Mobile	1763	594	68252	3084	3585

Table 3:10 Descriptive statistics for fixed and mobile BC data during warm period work days and Saturdays

In all cases average BC data along the monitoring route are significantly higher than those at the fixed monitoring station, namely by a 1.90 factor on working days and by a 1.95 factor on Saturdays. Background BC working days data are in the 2 – 13721 ng/m^3 range with an average of 1687 ng/m^3 and a standard deviation of 1756 ng/m^3. Mobile BC corresponding values are 225 - 144069 ng/m^3, 3219 ng/m^3 and 2950 ng/m^3. Working days fixed BC data turn out to be characterized by a larger variability than mobile BC data (CV_{fixed} = 1.04 vs CV_{mobile} = 0.92).

Saturday's fixed BC data are in the 258 - 8758 ng/m^3 range, with an average of 1578 ng/m^3 and a standard deviation of 1709 ng/m^3. Saturday's average background levels result to be 0.9 times lower than during work days. Mobile BC data on Saturdays are characterized by a 2827 – 10170 ng/m^3 range and an average value of 3084 ng/m^{3}and standard deviation of 3585 ng/m^3. On Saturdays BC data variability turn out to be higher for the mobile instrument (CV_{fixed} = 1.08 vs. CV_{mobile} = 1.16).

Average BC background concentration approximately the same during working days and Saturdays. This trend is also observable on the mobile instrument where the ratio between working days and Saturdays BC concentration is 1.0. As shown in Fig. 3.40, highest outliers are mostly referred to working days. Traffic contribution to mobile average BC concentration seems to be the same during working days and Saturdays, as suggested in Fig 10.2 (Annex III).

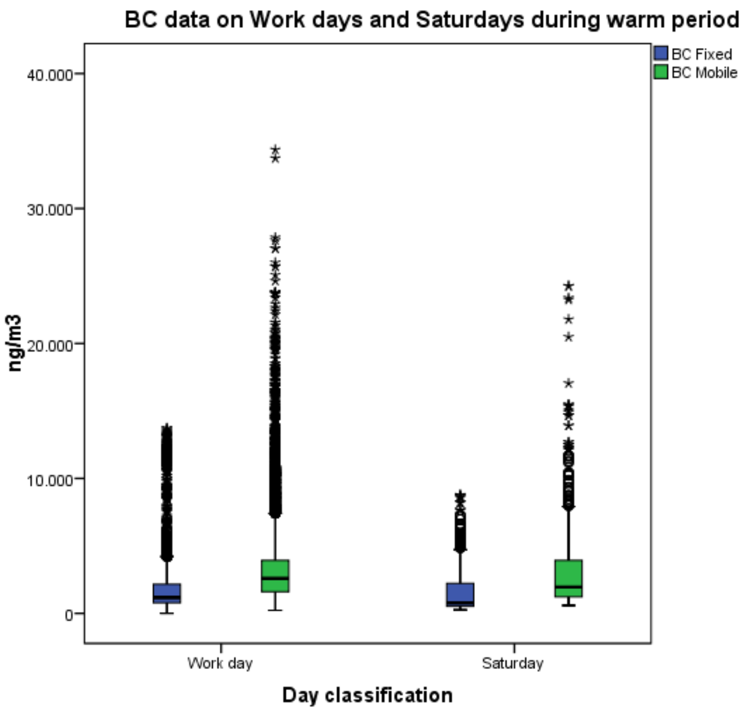

Figure 3:40 Box-plot for fixed and mobile BC warm period data during work days and saturdays. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.2.1.4 Spatial variability

Subdivision of the monitoring route into different zones as described in Section 2.3.1 shows off differences between urban areas. The box-plots of Figure 3.41 summarize for each urban zone datasets for the fixed and mobile instrument in terms of the median values, interquartile ranges, extreme values and outliers; 95% confidence intervals for mean values are plotted in Figure 10.3 (Annex III). Highest BC concentrations were recorded in the areas without traffic limitation (out of Area C, AV and RC). In Corso Buenos Aires (AV), mobile BC concentration data vary in the range of 225 - 144069 ng/m^3, with an average BC concentration of 4275 ng/m^3, which is 2.6 times higher than the urban background levels at the same time period (average 1668 ng/m^3; 41 - 11318 ng/m^3 range). Comparable high BC concentrations were observed in Corso Lodi (RC), where values vary in the range of 275 - 62926 ng/m^3 with an average value of 3619 ng/m^3 (2.1 times background BC concentrations) and a standard deviation of 3296 ng/m^3. It must be noticed that the adopted methodology imply that traffic peaks has been always verify in Corso

Buenos Aires, whereas in Corso Lodi traffic was less intense, this is reflected in lower average BC concentrations. Data variability result to be larger for mobile BC data in RC site than mobile BC data in AV sites stated by the comparison of the values computed for the coefficient of variations (CV_{AV} = 0.97 vs. CV_{RC} = 0.0.91).

Entering in areas subjected to Area C traffic limitations (VB, BD, DM and MR), average mobile BC concentrations becomes lower. The mean value for the BC mobile datasets in Corso Venezia (VB) is 2856 ng/m^3 (1.7 times higher than mean fixed BC value and 0.7 times average BC in zone AV) and data vary in the 225 – 39678 ng/m^3 range, with a standard deviation of 2287 ng/m^3. CV_{VB} for mobile BC decreases to 0.80

BC mobile data are significantly higher than fixed data also in Corso Porta Romana (MR) where average BC mobile data is 2647 ng/m^3 (1.7 time higher than average fixed BC) and vary in the 275 - 32220 ng/m^3 with a standard deviation of 1876 ng/m^3. Highest minimum BC mobile value was recorded in MR site. Observing CV values, as for VB, also considering MR, fixed data results to have a larger variability (CV_{fixed} = 0.97 vs. CV_{mobile} = 0.71).

Route		N	Minimum	Maximum	Mean	Std. Deviation
AV	BC Fixed	6062	41	11318	1668	1727
	BC Mobile	6688	225	144069	4275	4129
VB	BC Fixed	4290	2	11318	1700	1724
	BC Mobile	4844	225	39678	2856	2287
BD	BC Fixed	2533	7	11309	1692	1908
	BC Mobile	2886	330	17443	1969	1759
DM	BC Fixed	1315	22	11309	1551	1469
	BC Mobile	1557	330	14720	2124	1419
MR	BC Fixed	5932	3	11817	1603	1553
	BC Mobile	7242	275	32220	2647	1876
RC	BC Fixed	7974	8	13721	1723	1970
	BC Mobile	9384	275	62926	3619	3296

Table 3:11 Descriptive statistics for overall fixed and mobile warm period BC data for each city zone.

Absolute lowest average concentration was observed in the pedestrian zone (BD): mean value result to be 1969 ng/m^3 ; 1.2 times fixed BC average value. Mobile BC data vary in the 330 - 17443 ng/m^3 range and a standard deviation of 1759 ng/m^3. Analysis of coefficient of variance shows a major data variability on the fixed BC (CV_{fixed} = 1.13 vs. CV_{mobile} = 0.89).

Comparable values are obtained also in Via Mazzini (DM) where mean mobile BC concentration data is 2124 ng/m^3 , 1.4 times average background levels. Mobile BC data vary in the 330 - 14720 ng/m^3 as BD zone; while standard deviation is 1419ng/m^3. As for BD, also for DM zone, Fixed BC results to be characterized by a greater data variability (CV_{fixed} = 0.95 vs. CV_{mobile} = 0.67).

As for the cold period, potential outlier detection on the mobile BC dataset showed that these values are mostly present in most crowded urban zones: in particular, high outliers were recorded on the most traffic exposed road sections during the morning rush hours. Major traffic contribution on mobile BC values is shown by the significantly (α = 0.05) higher means of those zones in Fig 10.3 (Annex III).

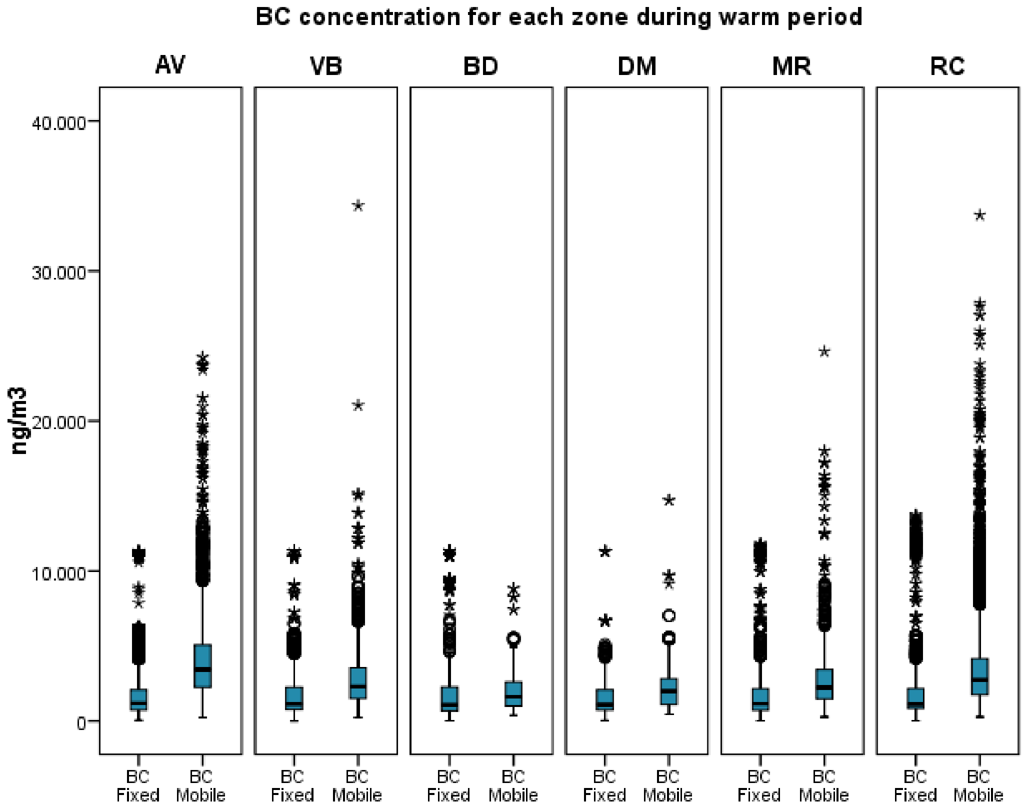

Figure 3:41 Box-plot for fixed and mobile BC warm period data for each city zone.. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Comparing only morning's mobile BC values along the monitoring route with those measured at the fixed station, differently as for the cold period dataset, mobile average data are always higher than urban background data.

Along the first stretch of road (AV), BC concentrations vary in the 429 - 144069 ng/m^3 range, with an average concentration of 5097 ng/m^3 ; 2.2 times higher than the background levels and 2.1 higher than in the pedestrian zone (BD), where the lowest average mobile BC concentration was recorded. Compared to BC afternoon's values (225 - 61569 ng/m^3 range; average 3471 ng/m^3), morning's average value is 1.5 times higher. Afternoon's average mobile BC concentration is 3.2 times greater than background concentration levels. Observing CV values, mornings mobile BC values are characterized by an higher variability only in zone AV, compared to afternoon values. Morning's mobile BC CV values vary in the 0.62 (DM) – 1.01 (AV) range, while afternoon's mobile CV values vary in the 0.53 (BD) – 0.95 (RC) range.

Proceeding on Corso Porta Venezia (VB), morning's mobile BC average level is 3321 ng/m^3 , 0.6 times lower than in Corso Buenos Aires (AV) but 1.5 times higher than average urban background levels. Mobile morning's BC data vary in the 429 - 34355 ng/m^3 while afternoon's levels in the 225 - 39678 ng/m^3 with an average value of 2352 ng/m^3, 2.2 times greater than average fixed BC concentration. Morning BC values are in the average 1.4 times higher than in the afternoon.

Lowest morning's average BC levels were sampled along the pedestrian zone (2475 ng/m^3) were the ratio with background levels is 1.062. Mobile BC morning data vary in the 466 - 17443 ng/m^3. Afternoon's BC levels vary in the 330 - 7428 ng/m^3 range with an average of 2475 ng/m^3; 0.6 times lower than morning's average values and 1.4 times higher than background levels. Instantaneous peaks are mainly due to cigarette smoke and soot coming from street food shops, especially during the Christmas period and in morning hours.

BC concentrations in Via Mazzini (DM) are 1.2 and 1.7 times higher than background levels, respectively in the morning and in the afternoon. Due to the low travel speed of public transport vehicles along this road, increasing of average concentrations (morning average 2534 ng/m^3 and afternoon average 1742 ng/m^3) is lower compared to other crowded zones.

An increasing of average exposure concentration is observed in Corso Porta Romana, probably linked to the increasing traffic intensity and higher traffic speed. Average mobile BC value is 3302 ng/m^3 in the morning and 1984 ng/m^3 in the afternoon. Morning values vary in the 592 - 32220 ng/m^3 range, while afternoon's values vary in the 275 - 17994 ng/m^3 range. Comparing mobile CV values in MR zone, data variability results to be the same during morning hours and afternoon hours ($CV_{morning}$ = 0.64 = $CV_{afternoon}$). Analysing outliers shown in Fig. 8.72, concentration peaks were sampled in proximity to main road intersections, particularly intersection with Via Sforza.

In Corso Lodi, during morning hours, mobile BC average concentration is 4219 ng/m^3; 1.8 and 1.7 times higher than background's and pedestrian's zone average BC levels. BC dataset vary in the 469 - 62228 ng/m^3 range in the morning and in the 275 - 62926 ng/m^3. Afternoon's average mobile BC concentration (2960 ng/m^3) is 2.2 times higher than urban background levels, and 0.7 times lower than morning's average mobile BC data. High peaks were observed mainly close to Piazzale Corvetto and mostly during morning hours, but also in correspondence of stop-and-go traffic caused by traffic lights along Corso Lodi.

Decreasing average BC concentrations in the afternoon hours are probably explainable by the lower traffic volume which causes a reduction of idling traffic. It should be also noted that atmospheric turbulence increase usually in the afternoon hours and an increasing of the mixing layer height causes a reducing of pollution concentration levels. Diurnal differences seems to be more marked for the warm period compared to those from the cold period.

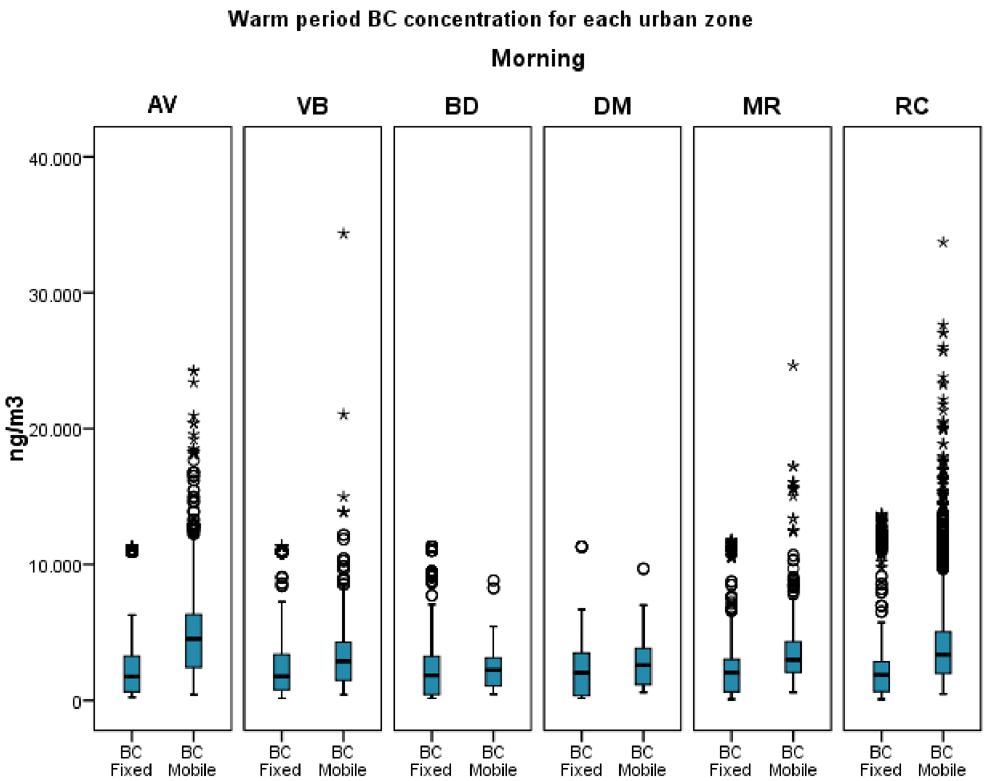

Figure 3:42 Box-plot for morning's fixed and mobile BC warm period data for each city zone.. Boxes represent the median values, interquartile ranges, extreme values and outliers.

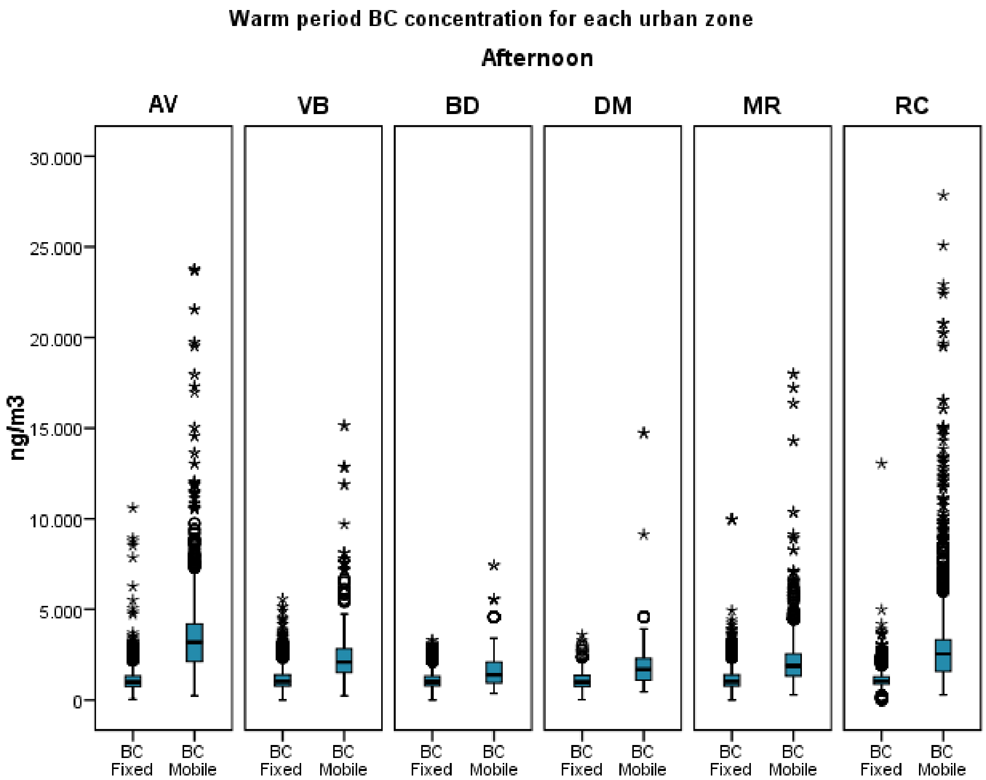

Figure3:43 Box-plot for afternoon's fixed and mobile BC warm period data for each city zone.. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Subdividing each section in subclasses as for the cold period dataset, it is possible to better ivestigate relevant internal differences in terms of pollutants concentrations for each urban zone.

Corso Buenos Aires (AV) was divided into three parts (1A, 1B and 1C) as described in section 2.3.1. In the first section (1A) average mobile BC concentration value is 4337 ng/m^3 and the dataset vary in the 645 - 68252 ng/m^3 range. Analogous values were observed in section 1B (average 3974; range 645 - 32186 ng/m^3) and in section 1C (average 3495 ng/m^3; range 429 - 61568 ng/m^3). As observed for the cold period BC dataset, lower average values were found at the end of Corso Buenos Aires (close to Porta Venezia), probably due to the fact that the street reach a large square, getting out of the street canyon environment. However, no relevant statistical differences were found between average mobile BC concentrations in the three subclasses (Fig 10.6, Annex III). Observing CV values, data variability is higher close to Porta Venezia (CV_{1A} = 0.78, CV_{1B} = 0.70, CV_{1C} = 0.88). Highest peaks were observed in the first street section, as found for the cold period.

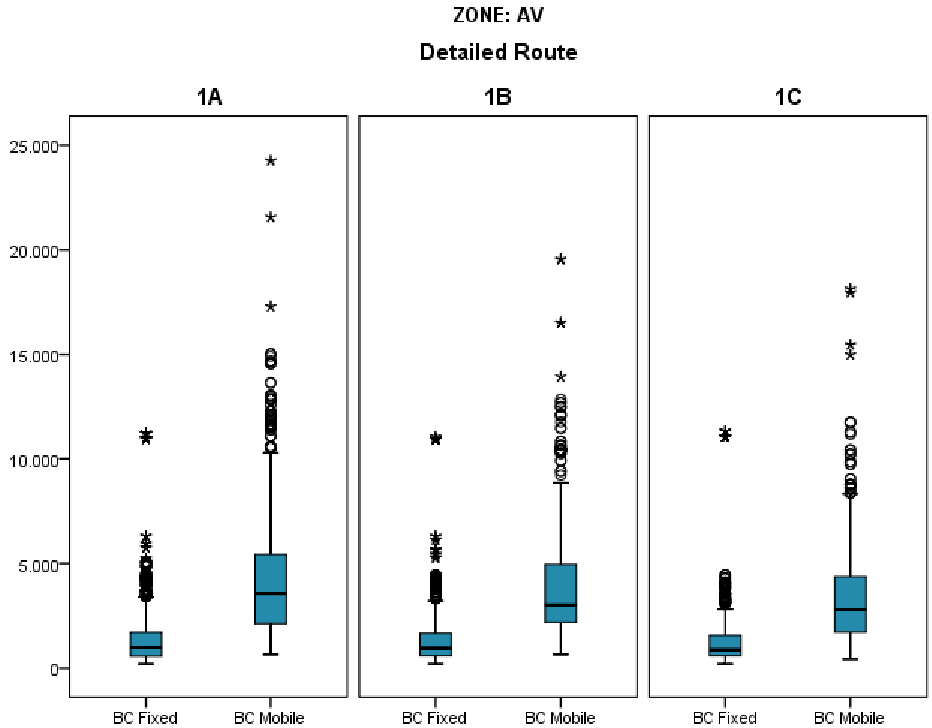

Figure 3:44 Box-plot of fixed and mobile BC in city zone AV. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Corso Porta Venezia was divided into two sections. Boundary of the two section is the intersection whit Via Senato, an important main road of the inner city circle.
Despite the proximity to a city park (Giardini Indro Montanelli) and the larger street, section and results to have an average value of 2619 ng/m^3, comparable to the average value of the less crowded but narrower street section 2E (average 2618 ng/m^3). Mobile BC vary in the 429 - 39678 ng/m^3 in section 2D (highest peak reached close to Porta Venezia), while data in section 2E vary in the 429 – 12851 ng/m^3 range. Comparing CV values, data variability is higher in the first section (CV_{2D} = 0.93 and CV_{2E} = 0.64).

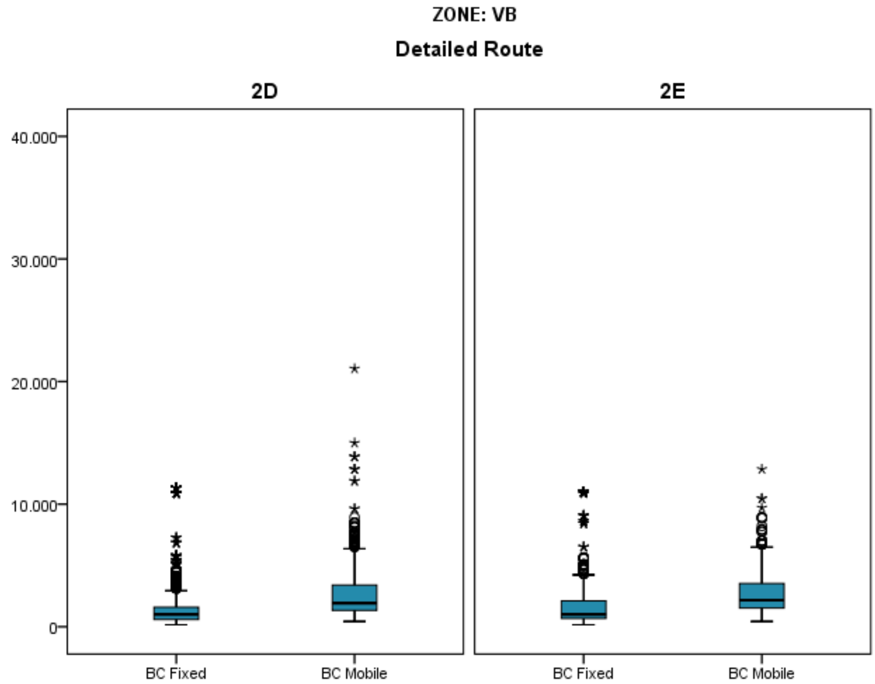

Figure 3:45 Box-plot of fixed and mobile BC in city zone VB. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Pedestrian zone (BD) and the traffic limited Via Mazzini (DM) were not further divided due to the absence of significant discontinuity along the monitoring route and formerly described. Highest peaks in section VB, BD and DM were all recorded during March 31th morning.
Considering section MR, until reaching the intersection whit Via Sforza (5H), Corso Porta Romana is less crowded then the second section (5I). Both sections are travelled by public surface public transport lines, and are covered by cobblestones.

However, also in this case differences between average BC values not suggest significant statistical differences, as highlighted in Fig. 3.46. In section 5I mobile BC data vary in the 737 - 32220 ng/m^3, while average BC concentration result to be 2591 ng/m^3, only 5% higher than in section 5H (average value: 2455 ng/m^3; range: 592 – 16366 ng/m^3).

Traffic contribution seems to be the same in both sections (Fig. 10.12, Annex III). CV values suggest an higher data variability on the second section (CV_{5H} = 0.73 vs. CV_{5I} = 0.88). High BC concentration peaks were observed close to the intersection with Via Sforza, as during the cold period.

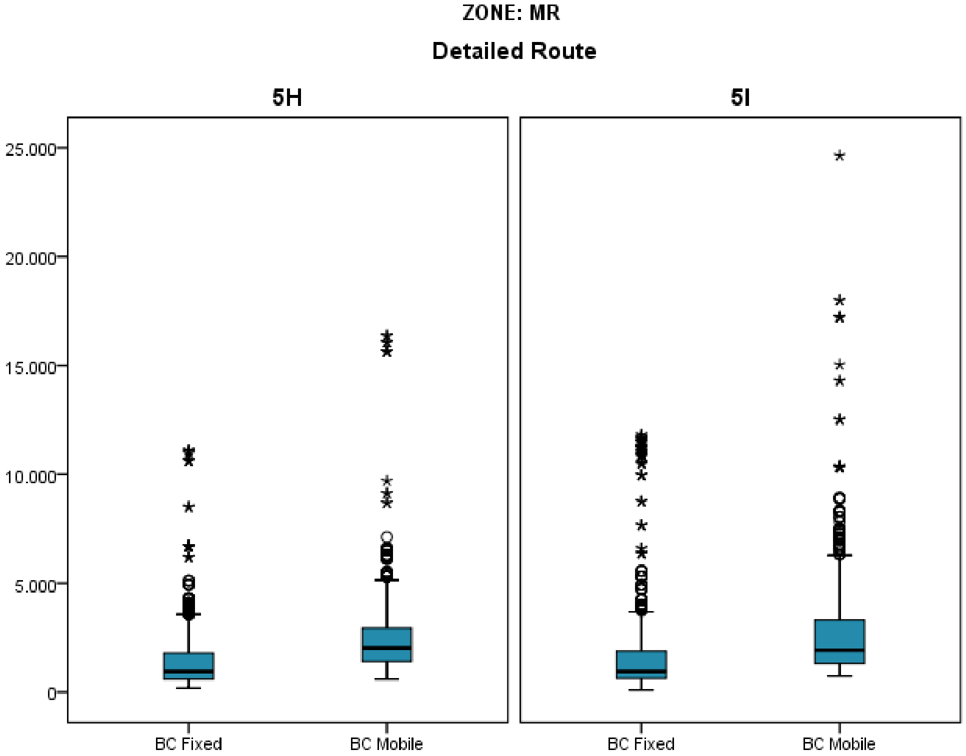

Figure 3:46 Box-plot of fixed and mobile BC in city zone MR. Boxes represent the median values, interquartile ranges, extreme values and outliers.

The longest section (RC) was divided into four parts (6L, 6M, 6N and 6O). As observed during the cold period, highest average concentrations were observed in Piazzale Corvetto (6O), an important junction with the south-east suburbs. The first part of Corso Lodi (6L) is characterized by the presence of access roads, implying a greater distance between kerbside and motorized traffic. This results in lower average concentrations (average: 3099 ng/m^3; range: 469 - 22637 ng/m^3) which are

0,6 times those measured in Piazza Corvetto (average: 5356 ng/m^3;range: 785 - 37241 ng/m^3). Significant statistical differences on the average BC concentration were not found between section 6M (average: 3914 ng/m^3; range: 469 - 62926 ng/m^3) and 6N (average: 3679 ng/m^3; range: 696 - 30645 ng/m^3), both characterized by idling traffic. Differently as during cold period, highest BC concentration was recorded in section 6M.Main descriptive statistics of all subclasses are summarized in Annex I.

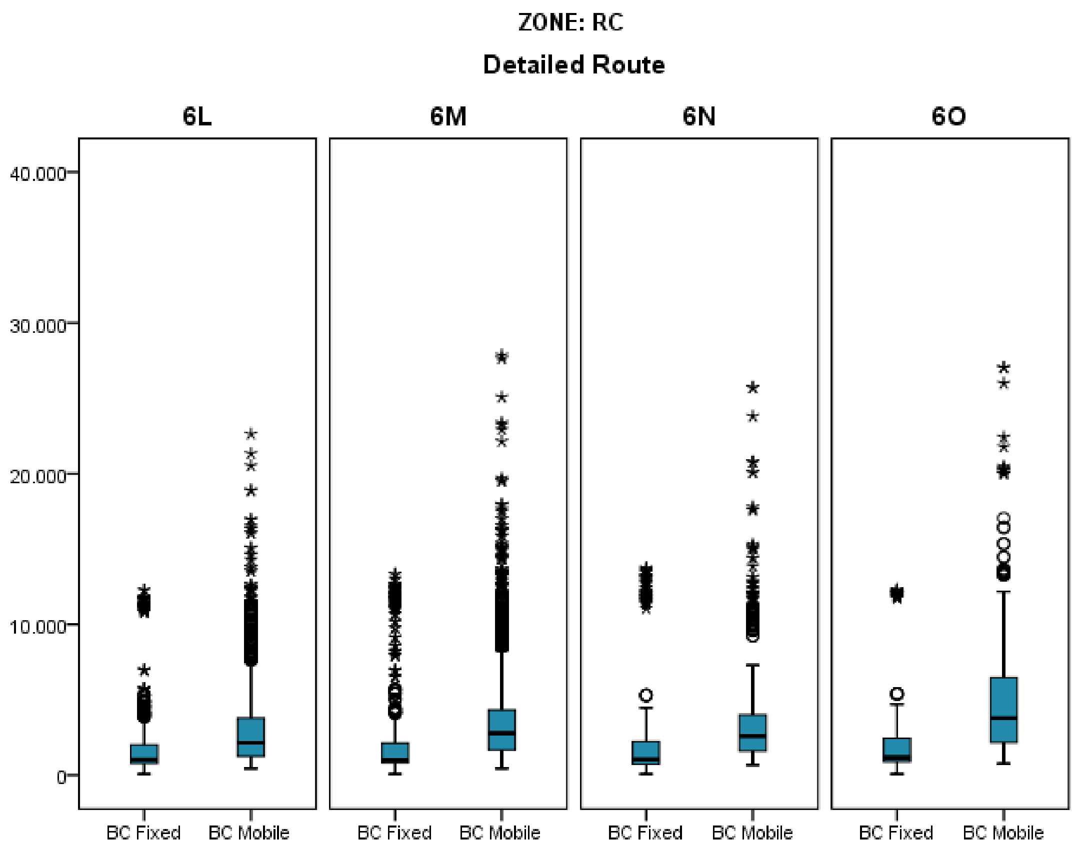

Figure 3:47 Box-plot of fixed and mobile BC in city zone RC. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.2.1.5 Congestion charge effect

Comparing morning's mobile BC data inside traffic limitation zone Area C with those outside Area C, average concentration values are significantly higher in non-traffic limited urban areas, as shown in Fig 3.48 and 10.14 ($\alpha = 0.05$; Annex I). Out of Area C, mobile BC morning average concentration is 4573 ng/m^3 (2.0 times average fixed BC concentration and 1.5 times higher than average mobile BC concentration in Area C zone) and data vary in the 429 - 144069 ng/m^3. Area C average mobile BC concentration is 3095 ng/m^3 (1.4 times average background concentration) and vary in the 429 - 34355 ng/m^3 range. As for the cold period BC dataset, computing coefficient of variation for each dataset, mobile BC data outside Area C are characterized by a larger variability than inside Area C data ($CV_{Area\ C}$ = 0.73 vs. $CV_{No\ Area\ C}$ = 0.94). Outliers shown in Fig 3.48 are mainly referred to April 5th and May 12th.

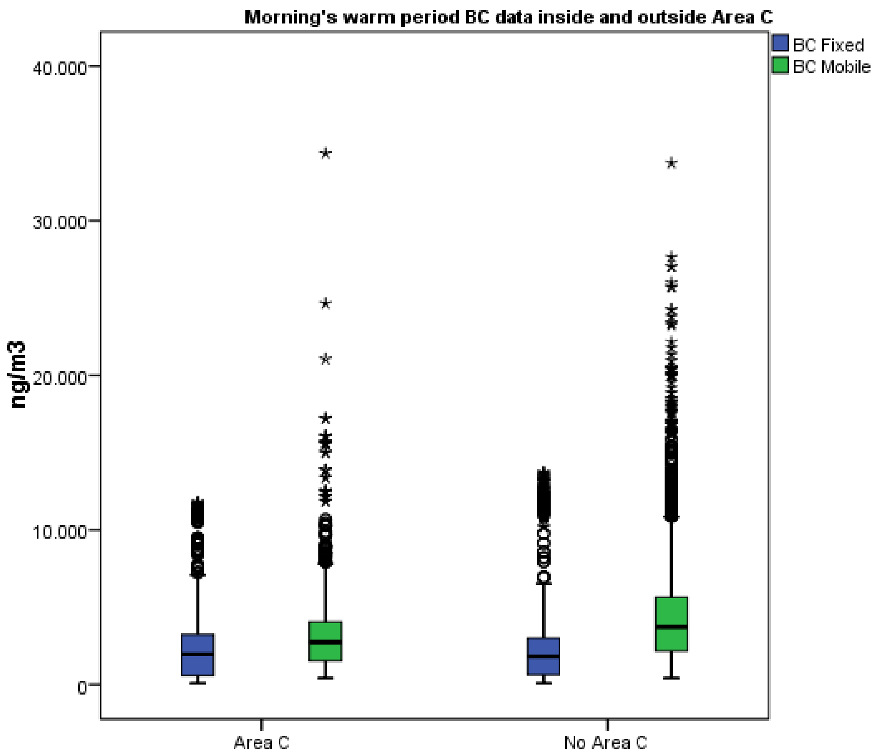

Figure 3:48 Box-plot for morning's fixed and mobile BC warm period data inside and outside Area C.. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Considering afternoon's average mobile BC values, inside Area C, BC concentrations are 1.8 times background levels (average mobile BC: 2048 ng/m^3; range: 225 - 39678 ng/m^3). More marked is the difference between afternoon's average BC level Out of Area C and average fixed BC concentration, where the ratio with the fixed measurement station is 2.8 (average mobile BC: 3190 ng/m^3; range: 225 - 62926 ng/m^3). Afternoon's average mobile BC out of Area C results to be 1.558 times higher than in the inner city circle. Also in this case, Area C data are less variable than No Area C data ($CV_{Area\ C}$ = 0.70 vs. $CV_{No\ Area\ C}$ = 0.84). However, despite the lower mean values, warm period BC concentrations data result to be more variable than during the cold season in both zones.

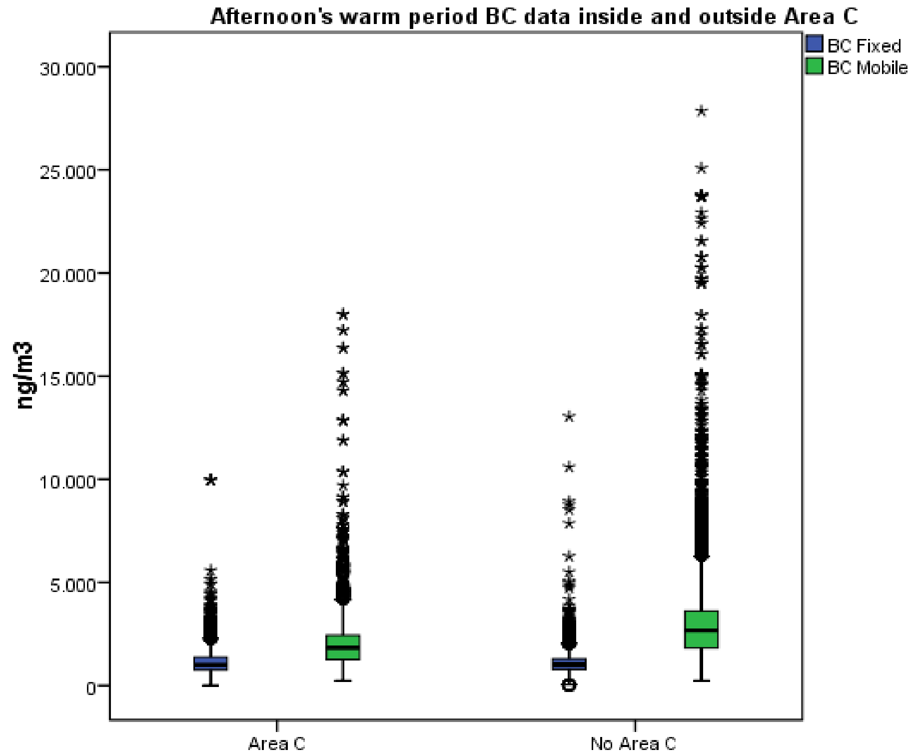

Figure 3:49 Box-plot for afternoon's fixed and mobile BC warm period data inside and outside Area C.. Boxes represent the median values, interquartile ranges, extreme values and outliers.

			N	Minimum	Maximum	Mean	Std. Deviation
Morning	**Area C**	**BC Fixed**	6826	92	11817	2249	2162
		BC Mobile	8364	429	34355	3095	2270
	No Area C	**BC Fixed**	6882	92	13721	2306	2459
		BC Mobile	8215	429	144069	4573	4298
Afternoon	**Area C**	**BC Fixed**	7682	2	9962	1133	637
		BC Mobile	8603	225	39678	2048	1436
	No Area C	**BC Fixed**	7485	8	13041	1150	617
		BC Mobile	8188	225	62926	3190	2667

table 3:12 Descriptive statistics for morning's and afternoon's fixed and mobile BC data inside and outside Area C [ng/m^3]

3.2.2 PNC data results

The original recorded datasets were firstly manually analysed in order to detect error codes due to instrumentation malfunctioning as for the cold period PNC dataset. Data characterized by an error code were deleted and not further taken in account. Particle number concentration data (PNC), were originally sampled at a 1-second time resolution at both sampling sites. In order to permit a correct comparison with BC concentration data (sampled at a 10-second time resolution), a 10 second averaging algorithm was applied on the original PNC dataset of both sampling sites. On the averaged PNC dataset, statistical analyses and potential outliers detection were carried out.

As for the BC dataset, main statistical parameters of the data distributions for the overall PNC datasets and for the morning and afternoon datasets separately are reported in Table 3.13: data from the stationary instrument at the urban background site are reported as "PNC fixed" whereas those recorded along the pedestrian route as "PNC mobile". The box-plots of Figure 3.50 summarize the morning and afternoon datasets for the fixed and mobile instrument in terms of the median values, interquartile ranges, extreme values and outliers; morning and afternoon average values, together with 95% confidence intervals are plotted in Figure 10.16 (Annex III).

Instrument		N	Minimum	Maximum	Mean	Std. Deviation
PNC Fixed	Overall	29347	1412	500000	9475	11654
	Morning	15191	1412	500000	10979	13858
	Afternoon	14156	2467	429000	7862	8395
PNC Mobile	Overall	28706	3027	254110	19487	15661
	Morning	15060	3027	254110	22263	17810
	Afternoon	13646	3554	183500	16423	12166

Table 3:13 Descriptive statiscs of overall, morning's and afternoon's fixed and mobile PNC during warm period

3.2.2.1 Seasonal variability

Overall, PNC fixed data are in the 1.4 x 10^3 – 5.0 x 10^5 Pt/cm^3 range, with an average of 9.5 x 10^3 Pt/cm^3 and a standard deviation of 1.1 x 10^4 Pt/cm^3: corresponding figures for PNC mobile data are 3.0 x 10^3 – 2.5 x 10^5 Pt/cm^3 ,1.9 x 10^4 Pt/cm^3, and 1.6 x 10^4 Pt/cm^3. As observed for the cold period, compared to fixed data, mobile data are shifted towards higher values, as highlighted by the significantly (α = 0.05) higher mean (about 2.1 times higher than average PNC measured at the fixed sampling site); also mobile PNC standard deviation is 1.3 times higher than fixed standard deviation. Fixed data are characterized by a larger variability, as stated by the comparison of the values computed for the coefficient of variations (CV = 1.23 for PNC fixed vs. 0.80 for PNC mobile). As observed for BC, cold period average PNC values are from 2.2 to 2.9 times higher than during the warm season, for fixed and mobile PNC respectively. Mornings cold period PNC are 3.0 and 2.1 times higher than in the warm period, for the fixed and mobile PNC respectively.

3.2.2.2 Daily variations

PNC mobile data are significantly higher than fixed data also when separately considering the morning and the afternoon route: the mean values for the PNC mobile datasets are 2.2 x 10^4 and 1.6 x 10^4 respectively (2.0 and 2.1 times higher than those of the BC fixed on morning and afternoon subsets). PNC data variability is not always larger in the morning. Fixed PNC data variability is larger during morning hours (for fixed PNC, $CV_{morning}$ = 1.26 vs. $CV_{afternoon}$ = 1.07), on the mobile PNC dataset the same trend is observable (for mobile PNC, $CV_{morning}$ = 0.80 vs. $CV_{afternoon}$ = 0.74). For both fixed and mobile PNC dataset, highest and lowest values were recorded in the morning (differently as during the cold season). The comparison between morning and afternoon values shows that during the morning hours concentration levels are significantly higher for both the fixed and mobile instrument: on the average, morning concentration is 1.4 times higher than in the afternoon for PNC fixed and 1.3 times higher for PNC mobile. Mobile average PNC data are always greater than those measured at the background measuring station; 2.0 times in the morning and 2.1 times in the afternoon, respectively. Absolute extreme values (minimum and maximum) were recorded on the fixed measuring station during morning hours. Morning's standard deviation of the fixed P-trak is 1.7 times higher than in the afternoon, while considering mobile P-trak ratio is 1.5.

PNC box-plot in Fig 3.50 shows how potential outliers are much numerous compared to BC dataset outlier, especially for the fixed measuring station. Applying an accurate data label analysis, potential outliers of the fixed PNC dataset can be grouped into individual events which took place on March 31th and May 6th. Considering mobile PNC dataset outliers, differences between morning and afternoon are less marked. In both cases, peaks along the monitoring route were observed in correspondence of busy crossroads or fast accelerating vehicles. As described for BC dataset, outlier detection is a merely statistical procedure intend to recognize those values that are inconsistent (i.e.: anomalous) with the whole dataset. Nevertheless, such anomalous values may be the result of very peculiar environmental conditions that, even though very infrequent and rarely occurring, are at the same time likely to happen. It is not surprising that the recognized potential outliers were mainly detected in the BC mobile dataset: indeed, the closer exposition to traffic exhaust emissions and peculiar environmental conditions from the emission standpoints (i.e.: queue of idling vehicles, busy crossroads, emission plume for fast accelerating vehicles) can determine short-time concentration peaks.

Higher values in the morning rush hours are probably due to the lower height of the atmospheric mixing layer combined to the more intense traffic and the higher portion of cold started vehicles.

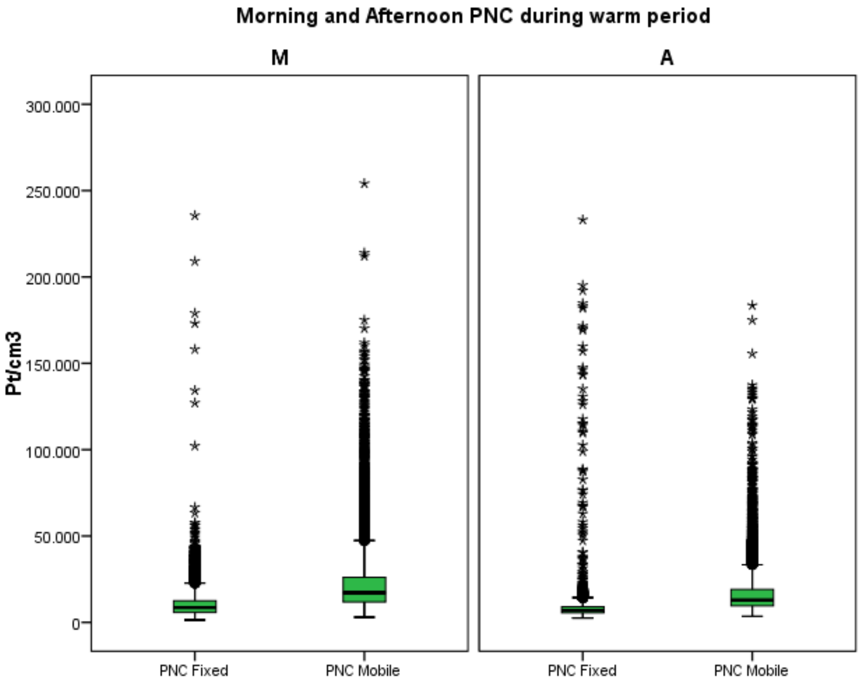

Figure 3:50 Box-plot for morning's and afternoon's fixed and mobile BC warm period data. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.2.2.3 Weekly variations

As for BC concentration data, also for PNC, datasets were further stratified by kind of the day, namely separately analysing data collected on working days and on Saturdays; differently as during the cold period, no public transport service strike occurred during the warm period monitoring campaign. Corresponding distributions of the PNC concentration levels are plotted in the box-plot of Figure 8.96.

In all cases, as for BC, average mobile PNC along the monitoring route is significantly higher than those at the fixed monitoring station, as shown in Figure 3.51. On normally working days, in the average, mobile PNC values is 19599 Pt/cm^3, 2.1 times greater than background average PNC levels, and vary in the 3.0 x 10^3 – 2.5 x 10^5 Pt/cm^3 range. Highest instantaneous peaks on the mobile P-trak were recorded during working days; lower peaks were recorded on Saturdays. Fixed PNC values on work days vary in the 1.4 x 10^3 – 5.0 x 10^5 Pt/cm^3 range with an average of 9517 Pt/cm^3.

		N	Minimum	Maximum	Mean	Std. Deviation
Work day	**PNC Fixed**	27584	1412	500000	9517	11953
	PNC Mobile	26943	3027	254110	19599	15796
Saturday	**PNC Fixed**	1763	2917	56090	8821	5021
	PNC Mobile	1763	3745	133620	17769	13303

table 3:14 Descriptive statistics for fixed and mobile PNC during warm perod's work days and Saturdays.

Urban background average PNC levels are comparable during working days and Saturdays, even if on Saturdays less outliers were recorded, and range of Saturday's fixed PNC values is more restricted (average: 8821 Pt/cm^3; range 2.9 x 10^3 – 5.6 x 10^4 Pt/cm^3). In terms of daily average background PNC, values are therefore slightly higher during normally week days than on Saturdays by a factor of 1.1. Outliers on the fixed PNC dataset are mostly present on working days. Considering average mobile PNC, no relevant statistical differences were observed between working days and Saturdays values (Saturday's mobile PNC average: 17769 Pt/cm^3; range 3.7 x 10^3 – 1.3 x 10^5 Pt/cm^3).

During work days, fixed PNC dataset is characterized by a greater variability than mobile PNC dataset, as stated by the comparison of the values computed for the coefficient of variations (CV = 1.26 for PNC fixed vs. 0.81 for PNC mobile). As during cold period, opposite trends are observable on Saturdays, CV = 0.57 for PNC fixed and 0.75 for PNC mobile. Main descriptive statistics are summarized in Table 3.14.

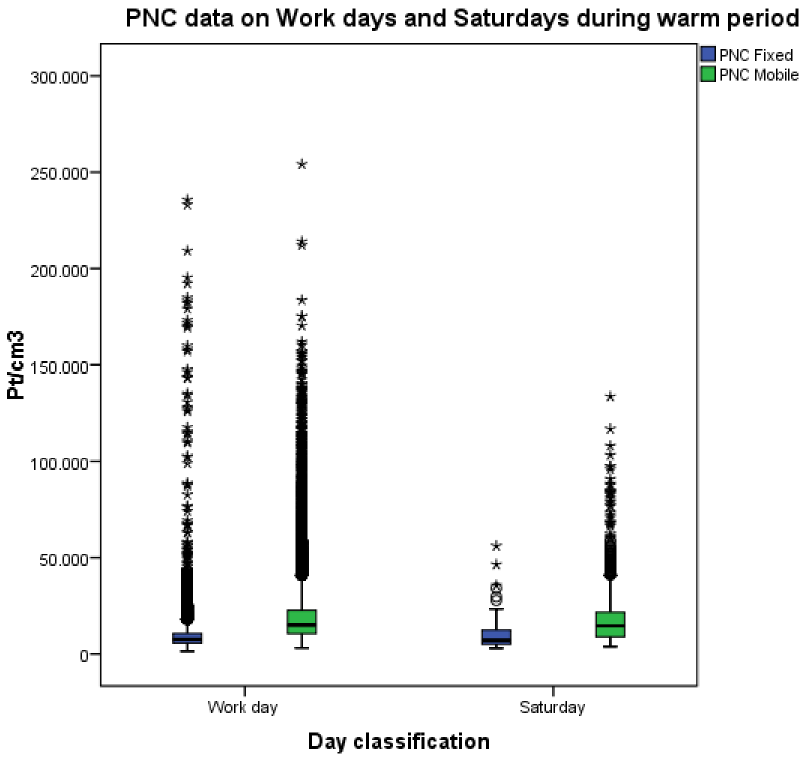

Figure 3:51 Box-plot for fixed and mobile BC warm period data during work days and saturdays. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.2.2.4 Spatial variability

Subdivision of the monitoring route into different areas as described for the cold season dataset, shows off differences between urban areas. The box-plots of Figure 3.52 summarize for each urban zone datasets for the fixed and mobile instrument in terms of the median values, interquartile ranges, extreme values and outliers; 95% confidence intervals for mean values are plotted in Figure 10.19 (Annex III). As for BC concentration, highest mobile PNC concentrations were recorded in an area without traffic limitation (out of Area C, AV and RC). Highest PNC average value was recorded in Corso Buenos Aires (AV), mobile PNC have an average value of 25465 Pt/cm^3 (2.670 times background average PNC value) and vary in the 3.9 x 10^3 – 1.5 x 10^5 Pt/cm^3. CV comparison indicates an higher data variability for mobile PNC dataset (CV_{fixed} = 0.64 vs. CV_{mobile} = 0.68). Differently as for BC, comparable high PNC were observed in Corso Porta Venezia (VB), where values vary in the range of 3.7 x 10^3 – 2.1 x 10^5 Pt/cm^3 with an average value of 24227 Pt/cm^3 (2.6

times higher than background PNC). Also in this case, CV comparison indicate a larger data variability on mobile PNC dataset (CV_{fixed} = 0.71 vs. CV_{mobile} = 0.88) and higher compared to the cold period values.

Entering in the pedestrian zone, average mobile PNC becomes lower. Mean mobile PNC value in Corso Vittorio Emanuele (BD) is 14766 Pt/cm^3 (1.6 times higher than fixed PNC at the same time period) and included in the 3.3 x 10^3 – 1.4 x 10^5 Pt/cm^3. High mobile PNC peaks were also observed in this zone, probably due to instantaneous local sources as cigarette smoke or soot coming from street food shops. Data variability in pedestrian zone is the lowest of all city zones as suggested by comparison of computed CV values (CV_{fixed} = 0.65 vs. CV_{mobile} = 0.54). Lightly lower mean mobile PNC values were recorded in Via Mazzini (DM); values vary in the 3.7 x 10^3 – 7.9 x 10^4 Pt/cm^3 range, with an average of 13691 Pt/cm^3 (1.5 times higher than average background levels). As during the cold period, high mobile PNC values were observed when public transportation or tourist busses passes.

In Corso Porta Romana (MR) mobile PNC values increases reaching an average of 16567 (1.6 times higher than average fixed PNC); data vary in the 3.4 x 10^3 – 1.7 x 10^5 Pt/cm^3 range and CV comparison suggest an higher data variability for fixed PNC compared to mobile PNC values (CV_{fixed} = 1.97 vs. CV_{mobile} = 0.82).

Highest average mobile PNC data were not found in section RC. Despite the absence of any kind of traffic limitations, average mobile PNC value is lower than in Corso Porta Venezia (subjected to Area C), reaching a value of 17511 Pt/cm^3 (1.9 times average fixed PNC). Mobile data vary in the 3.0 x 10^3 – 2.5 x 10^5 Pt/cm^3. Fixed PNC data are characterized by a larger data variability compared to mobile PNC dataset as suggested by the computed CV values (CV_{fixed} = 1.12 vs. CV_{mobile} = 0.75).

As for BC, potential outlier detection on the mobile PNC dataset showed that these values are mostly present in most crowded urban zones. In all those sections, traffic represent the main primary source. According to Dons et al, (Dons, Temmerman, Van Poppel, Bellemans, Wets, & Int Panis, 2013) pedestrian exposure increase during traffic peak hours. As for mobile BC, extremely high PNC peaks were observed close to main crossroads and in presence of idling traffic or close to roadworks. Major traffic contribution on mobile PNC values is shown by the significantly (α = 0.05) higher means of those zones (Annex III).

Route		N	Minimum	Maximum	Mean	Std. Deviation
AV	PNC Fixed	6000	1419	52180	9539	6113
	PNC Mobile	5824	3915	146800	25465	17377
VB	PNC Fixed	4370	1538	57630	9341	6637
	PNC Mobile	4282	3745	213900	24227	21373
BD	PNC Fixed	2708	2331	67360	8991	5871
	PNC Mobile	2667	3312	139970	14766	8046
DM	PNC Fixed	1397	2296	102690	9049	6944
	PNC Mobile	1376	3692	79360	13691	7377
MR	PNC Fixed	6298	1418	500000	10104	19857
	PNC Mobile	6121	3407	175100	16567	13586
RC	PNC Fixed	8574	1412	429000	9260	10370
	PNC Mobile	8436	3027	254110	17511	13130

table 3:15 Descriptive statistics for overall fixed and mobile PNC for each city zone

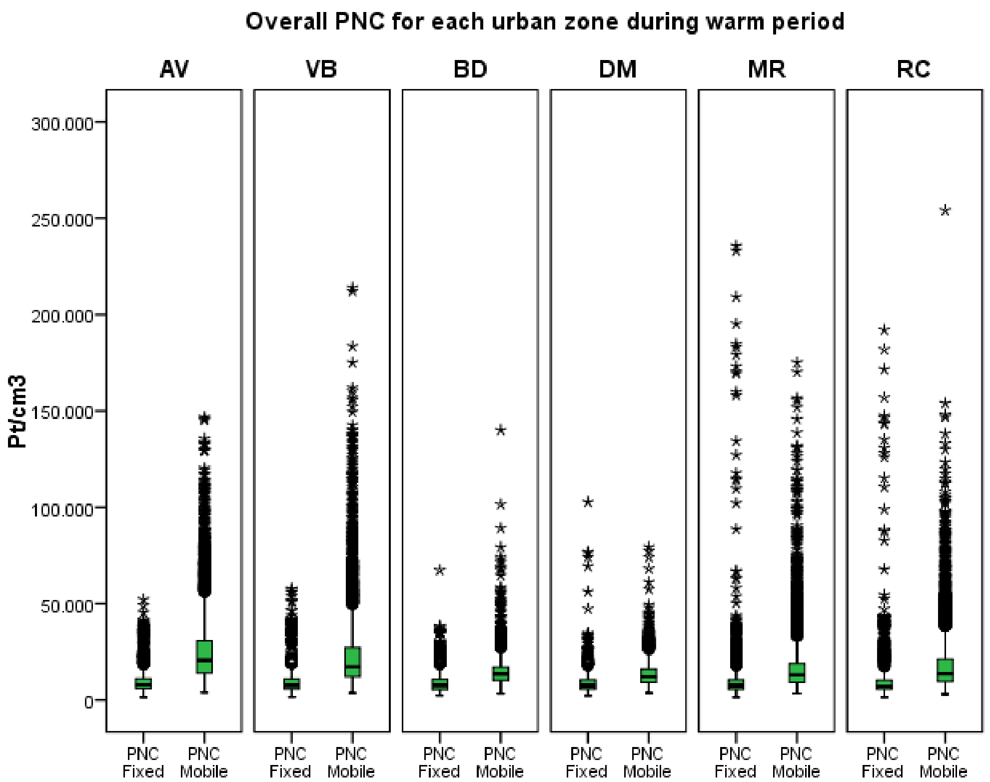

Figure 3:52 plot for fixed and mobile BC warm period data for each city zone. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Considering only morning's mobile PNC values along the monitoring route with those measured at the fixed station, mobile average data are always higher than urban background data. Along the first stretch of road (AV), mobile PNC vary in the 4.2 x 10^3 – 1.5 x 10^5 Pt/cm^{3}range, with an average concentration of 27649 Pt/cm^3; 2.6 times higher than the background levels. Compared to BC afternoon's values (average: 23192; range: 3.9 x 10^3 – 1.4 x 10^5 Pt/cm^3), morning's average value is 1.2 times higher. Morning fixed PNC data result to be characterized by an higher data variability than morning mobile PNC data (except for zone VB), while the opposite trend is observable considering afternoon's PNC data in zones AV, VA and BD as suggested by the comparison of computed CV values. . Morning's mobile PNC CV values vary in the 0.57 – 0.85 range vs. morning fixed CV values vary in the 0.64– 2.08 range, while afternoon's mobile CV values vary in the 0.41 – 0.81 range vs. afternoon's fixed PNC CV values vary in the 0.33 – 1.54 range. In both cases (morning and afternoon) highest CV values on mobile PNC dataset were observed outside Area C zones, while lowest values were observed in zone DM in for the morning and in zone AV for the afternoon.

Differently as for the cold period, highest average mobile PNC value was observed in Corso Venezia (VB). Despite traffic limitations and the proximity to a city park, morning's mobile PNC vary in the 3.7 x 10^3 – 2.1 x 10^5 Pt/cm^3 range with an average value of 28659 Pt/cm^3, 2.6 times greater than morning's fixed PNC and 1.5 higher than afternoon's average mobile PNC (average: 19071 Pt/cm^3; range: 4.1x 10^3 – 1.8 x 10^5 Pt/cm^3).

A marked reduction of mobile average PNC was observed entering in the pedestrian zone. Morning mobile PNC data vary in the 3.3 x 10^3 – 1.4 x 10^5 Pt/cm^3 range with an average value of 14824 Pt/cm^3, 1.4 times fixed average PNC and the same of afternoon's average mobile PNC. Corresponding afternoon values are 4.6 x 10^3 – 4.9 x 10^4 Pt/cm^3 and 14703 Pt/cm^3, 1.9 times afternoon's average background PNC level. As for BC, PNC peaks in pedestrian zone are less numerous than in other city zones.

Mobile PNC values in Via Mazzini (DM) are 1.5 and 1.5 times higher than fixed PNC values, in the morning and in the afternoon respectively. Morning's mobile dataset vary in the 3.7 x 10^3 – 7.9 x 10^4 Pt/cm^3 range with an average of 15499 Pt/cm^3. Corresponding afternoon values are 4.2 x 10^3 – 4.9 x 10^4 Pt/cm^{3}and 11878 Pt/cm^3, lower than in pedestrian zone.

Compared to fixed PNC, on average, mobile PNC in Corso Porta Romana are 1.6 and 1.8 times higher in the morning and in the afternoon respectively. Morning mobile PNC data are characterized by an average of 19466 Pt/cm^3 and a included in the 3.4 x 10^3 – 1.7 x 10^5 Pt/cm^3 range, while in the afternoon by an average of 13571 Pt/cm^3 and a 3.5 x 10^3 – 1.1 x 10^5 Pt/cm^3 range. Compared to via Mazzini, Increasing of average exposure to PNC in Corso Porta Romana is probably linked to the major traffic intensity and higher travel speed. As for BC data, high peaks were sampled in proximity to main road intersections, particularly intersection with Via Sforza.

High PNC peaks were also observed in section RC. Compared to fixed PNC data, mobile PNC data are 2.0 and 1.7 times greater in the morning and in the afternoon respectively. Morning's mobile PNC data vary in the 3.0 x 10^3 – 2.5 x 10^5 Pt/cm^3 range with an average of 20754 Pt/cm^3. Corresponding afternoon's value are 3.6 x 10^3 – 1.3 x 10^5 Pt/cm^3 and 13694 Pt/cm^3. As for BC, high peaks were observed mainly close to Piazzale Corvetto and mostly during morning hours, but also in correspondence of stop-and-go traffic caused by traffic lights along Corso Lodi. As observed for the cold period, except for pedestrian zone, overall maximum mobile PNC levels were recorded during morning hours. Decreasing average PNC in the afternoon hours are probably explainable by the lower traffic volume which causes a reduction of idling traffic. It should be also noted that atmospheric turbulence increase usually in the afternoon hours and an increasing of the mixing layer height causes a reducing of pollution concentration levels.

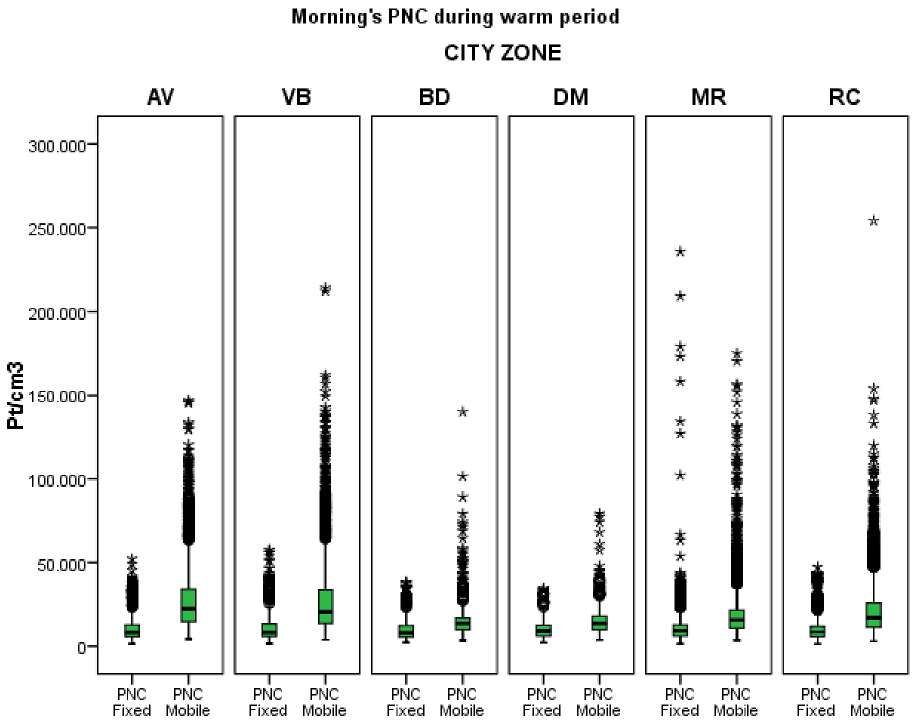

Figure 3:53 Box-plot for morning's fixed and mobile BC warm period data for each city zone. Boxes represent the median values, interquartile ranges, extreme values and outliers.

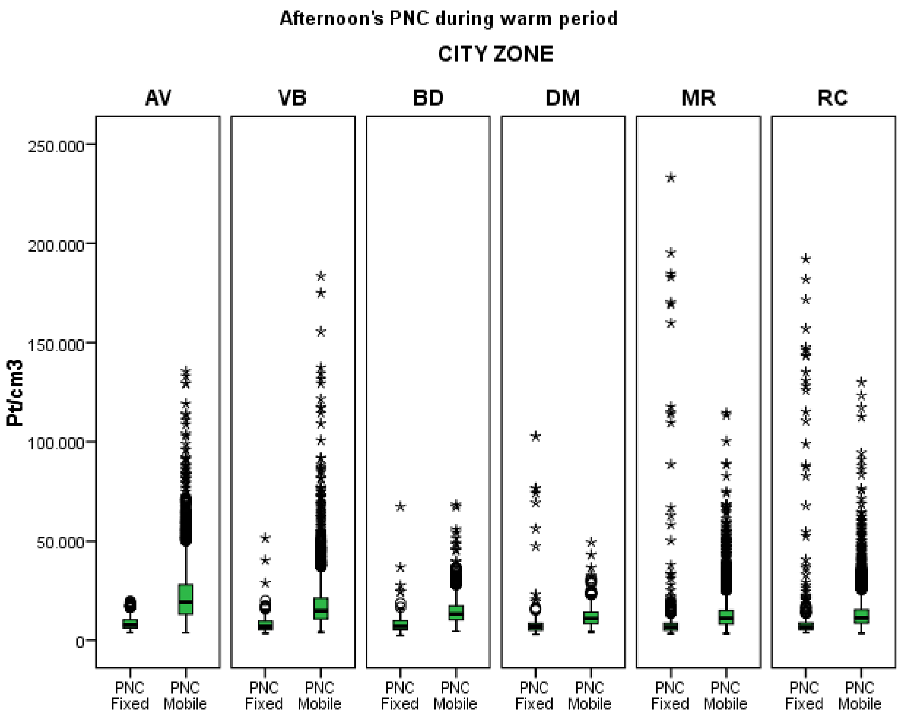

Figure 3:54 Box-plot for afternoon's fixed and mobile BC warm period data for each city zone. Boxes represent the median values, interquartile ranges, extreme values and outliers.

As described decribed in section 2.3.1, also for the warm period mobile PNC dataset, a detailed route subdivision was applied with the aim to identify internal differences in terms of pollutants concentrations for each urban zone. Box-plots and confidence intervals for the detaled route divisions are given in Annex III. Corso Buenos Aires (AV) was divided into three parts: 1A, 1B and 1C. In the first section (1A) average mobile PNC concentration value is 26467 Pt/cm^3 and the dataset vary in the 4.2 x 10^3 – 1.5 x 10^5 Pt/cm^3 range. As observed for the cold period PNC dataset, highest concentrations were sampled in section 1B (average 27560 Pt/cm^3; range 5.0 x 10^3 – 1.3 x 10^5 Pt/cm^3) and lowest in in section 1C (average 24733 Pt/cm^3; range 4.4 x 10^3 – 1.3 x 10^5 Pt/cm^3). Differently as for the cold period PNC mobile data, average PNC values at the end of Corso Buenos Aires (close to Porta Venezia) are 0.9 times lower than in section 1A. However, as shown in Fig 10.21., no relevant statistical differences (α=0.05; Annex III) were found between average mobile PNC concentrations in the three subclasses. Observing the computed CV values, data variability decreases in the most polluted section (1B), while in section 1A and 1B data variability is comparable (CV_{1A} = 0.72, CV_{1B} = 0.63, CV_{1C} = 0.73). Highest peaks were observed in street section 1B (in particular close to crossroad with Viale Tunisia), while number of probably outlier is less numerous in section 1C.

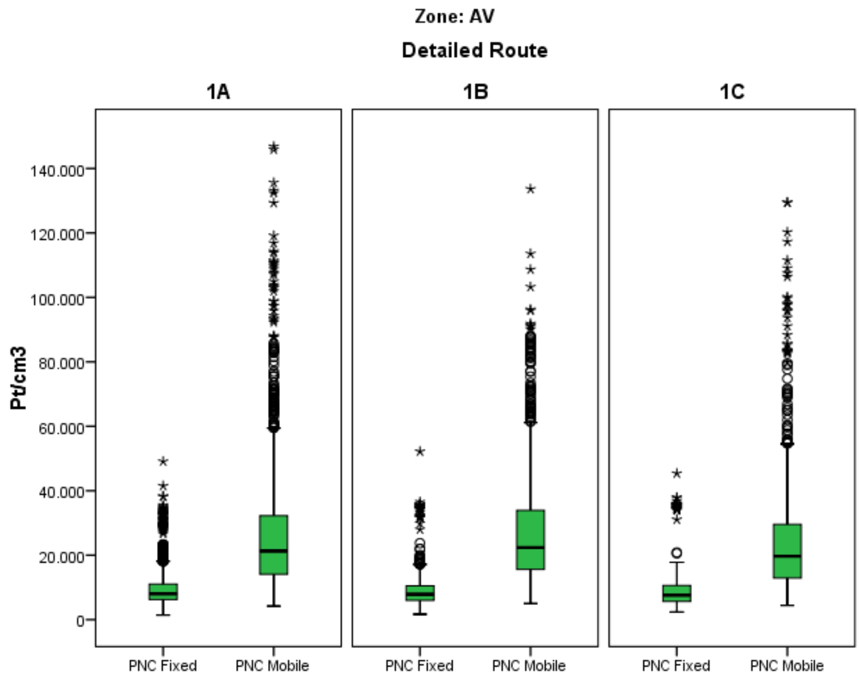

Figure 3:55 Box-plot of fixed and mobile PNC in city zone AV. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Corso Porta Venezia was divided into two sections. Considering mobile average PNC, no relevant differences between the two sections were observed. Despite the proximity to a city park (Giardini Indro Montanelli) and the larger street, also in this case it is possible to perceive a slight higher PNC average value of 25015 Pt/cm^3 and results to have an average value 1.1 times higher than the less crowded but narrower street section 2E (average 22327 Pt/cm^3). Mobile PNC vary in the 3.7 x 10^3 – 2.1 x 10^5 Pt/cm^3 in section 2D, while data in section 2E data vary in 4.6 x 10^3 – 1.6 x 10^5 Pt/cm^3 range. Comparing CV values, data variability is higher in section 2D (CV_{2D} = 0.92 and CV_{2E} = 0.71), as observed for the cold period.

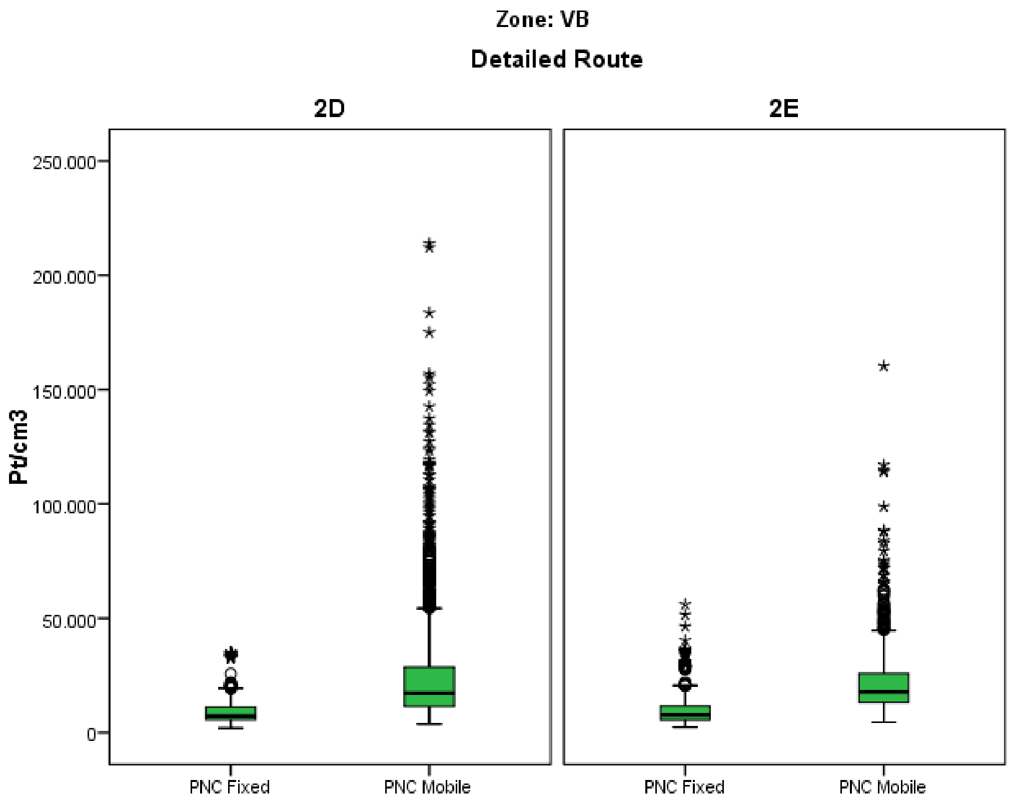

Figure 3:56 Box-plot of fixed and mobile PNC in city zone VB. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Pedestrian zone (BD) and the traffic limited Via Mazzini (DM) were not further divided due to the absence of significant discontinuity along the monitoring route and formerly described (Annex III).

Until reaching the intersection whit Via Sforza (5H), Corso Porta Romana is less crowded then the second section (5I). Both sections are served by public surface transport lines, and are covered by cobblestones. However also in this case minimal differences between average mobile PNC values not suggest significant statistical differences, as highlighted in Fig. 10.30 (Annex III). In street section 5I mobile PNC data vary in the 4.0 x 10^3 – 1.6 x 10^5 Pt/cm^3 , while average PNC concentration result to be 15997 Pt/cm^3. Corresponding values for street section 5H are: 3.4 x 10^3 – 1.7 x 10^4 Pt/cm^3. CV values suggest an higher data variability on the second street section (CV_{5H} = 0.80 vs. CV_{5I} = 0.82), as observed during the cold period. As for BC, PNC peaks were observed close to the intersection with Via Sforza.

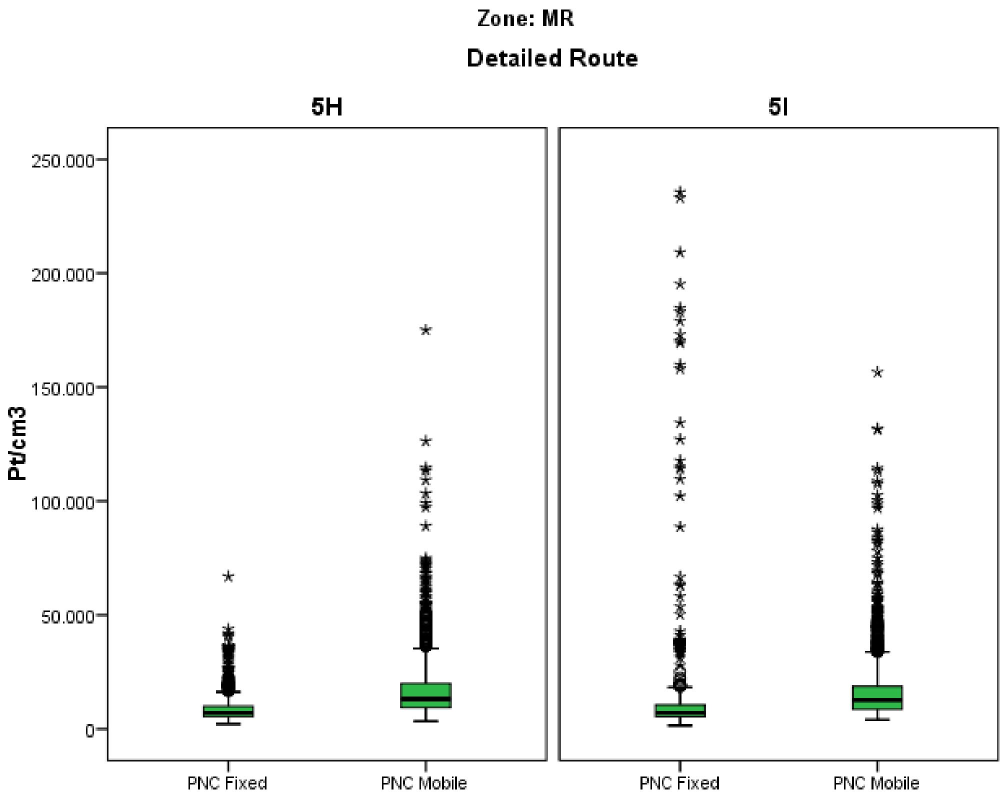

Figure 3:56 Box-plot of fixed and mobile PNC in city zone MR. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Section RC was divided into four parts: 6L, 6M, 6N and 6O. Same trend observed for BC and for cold period PNC is reflected by mobile PNC data. Highest average concentrations were observed in Piazzale Corvetto (6O) with a value of 21557 Pt/cm^3 (range: 4.0 x 10^3 – 1.5 x 10^5 Pt/cm^3). The first part of Corso Lodi (6L) is characterized by the presence of access roads implying a greater distance between kerbside an motorized traffic. This results in lower average concentrations (average:

16584 Pt/cm^3; range: 3.0 x 10^3 – 2.5 x 10^5 Pt/cm^3) which are 0.8 times those measured in Piazza Corvetto. Significant statistical differences on the average PNC were not found between section 6M (average: 17199 Pt/cm^3; range: 3.4 x 10^3 – 1.5 x 10^5 Pt/cm^3) and 6N (average: 16208 Pt/cm^3; range: 3.9 x 10^3 – 1.5 x 10^5 Pt/cm^3), both characterized by idling traffic. High outliers were observed in all analysed sections due to direct traffic exposure.

Main descriptive statistics of all subclasses are summarized in Annex III.

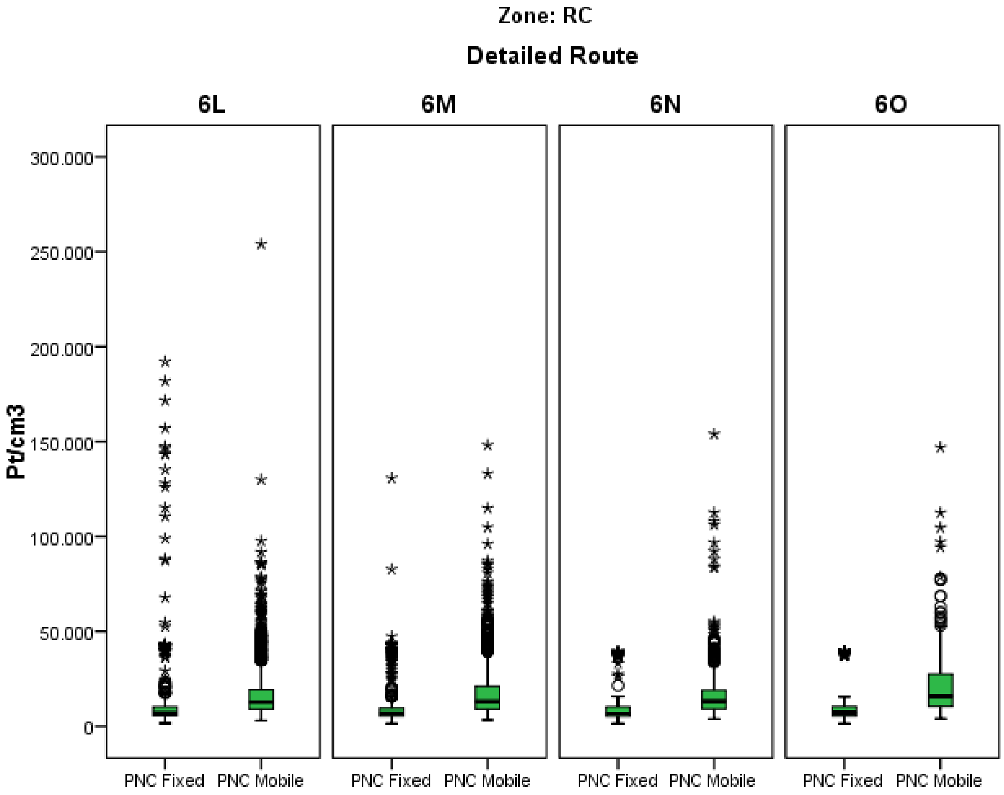

Figure 3:57 Box-plot of fixed and mobile PNC in city zone AV. Boxes represent the median values, interquartile ranges, extreme values and outliers.

3.2.2.5 Congestion charge effect

Outside Area C, average mobile PNC values are in the average 2.22 and 2.20 times higher than background PNC, respectively for morning and afternoon hours. In urban areas with restricted traffic access, mobile PNC are 1.9 and 2.0 times higher than those measured at the fixed station, respectively in the morning and afternoon hours. During afternoon hours, ratio between inside and outside Area C average PNC is 0.8, while in the morning the difference is less marked (ratio 0.9).

Comparing morning's mobile PNC data inside traffic limitation zone Area C with those outside Area C, even if differences are less marked than for BC, average concentration values are higher in non-traffic limited urban areas, as shown in Fig 3.58. Out of Area C, mobile PNC morning average concentration is 23473 Pt/cm^3 (2.220 times higher than average fixed PNC and 1.115 times higher than average PNC in Area C zone) and data vary in the 3.0 x 10^3 – 2.5 x 10^5 Pt/cm^3 range. Area C average mobile PNC is 21053 Pt/cm^3 (1.849 times average background concentration) and vary in the 3.3 x 10^3 – 2.1 x 10^5 Pt/cm^3 range. Observing computed coefficient of variation for each dataset, mobile PNC data outside Area C are characterized by a lower variability than inside Area C data ($CV_{Area\ C}$ = 0.88 vs. $CV_{No\ Area\ C}$ = 0.73).

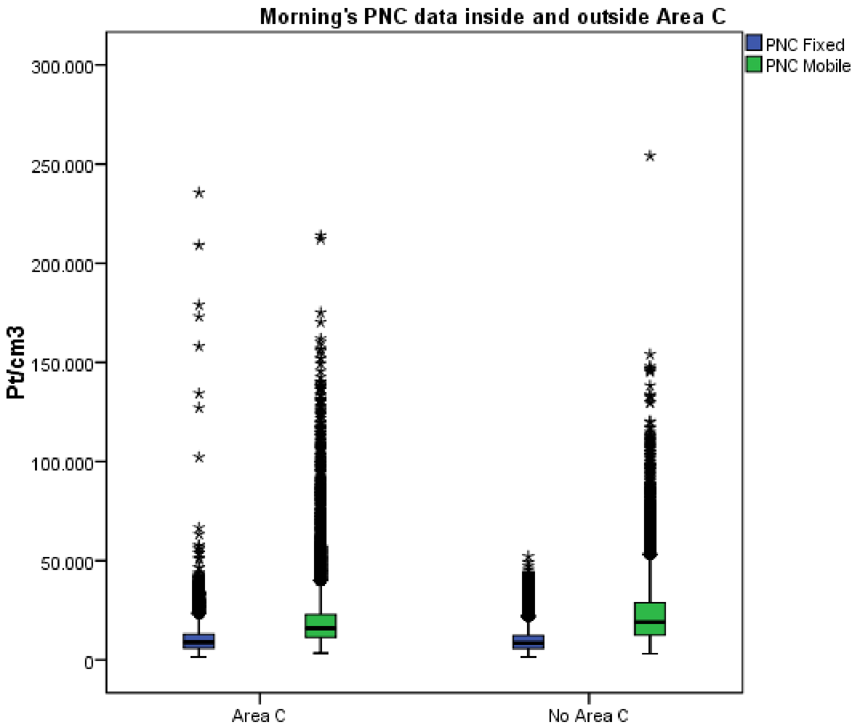

Figure 3:58 Box-plot for morning's fixed and mobile BC warm period data inside and outside Area C. Boxes represent the median values, interquartile ranges, extreme values and outliers.

Considering afternoon's average mobile BC values, inside Area C, PNC is on the average 1.977 times background levels (average mobile PNC: 15159 Pt/cm^3; range: 3.5 x 10^3 – 1.8 x 10^5 Pt/cm^3). As observed for the cold period, also for the warm season, the difference between afternoon's average BC level Out of Area C and average fixed PNC result to be more marked; ratio with the fixed measurement station is 2.198 (average mobile PNC: 17722 Pt/cm^3; range: 3.6 x 10^3 – 1.4 x 10^5 Pt/cm^3). Afternoon's average mobile PNC out of Area C restrictions results to be 1.169 times higher than in the inner city circle. Afternoon PNC Area C data are more variable than No Area C data ($CV_{Area\ C}$ = 0.74 vs. $CV_{No\ Area\ C}$ = 0.73).

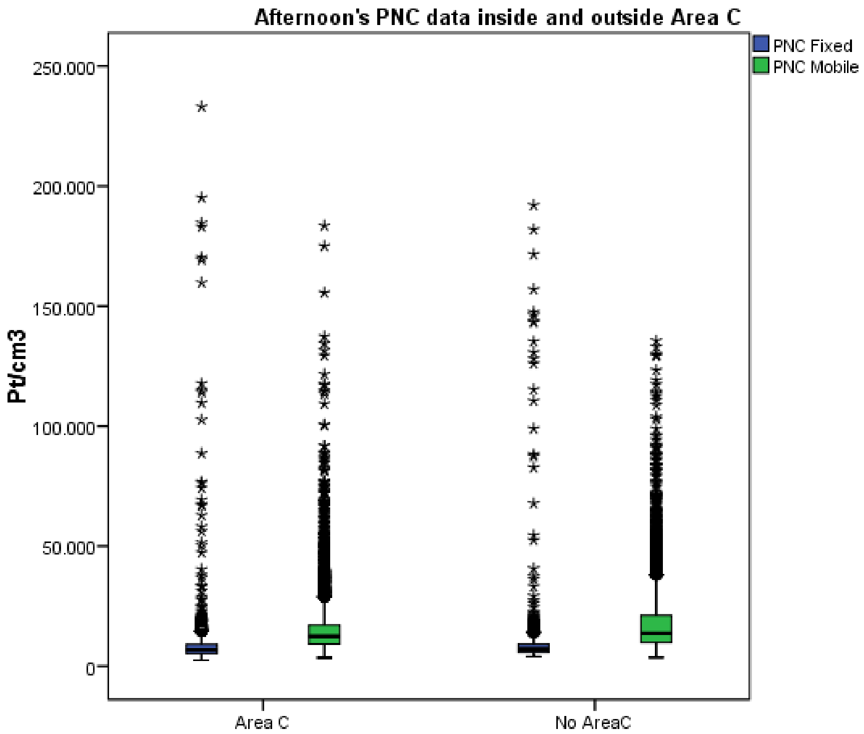

Figure 3:59 Box-plot for afternoon's fixed and mobile BC warm period data inside and outside Area C. Boxes represent the median values, interquartile ranges, extreme values and outliers.

			N	Minimum	Maximum	Mean	Std. Deviation
Morning	Area C	PNC Fixed	7568	1418	500000	11388	17856
		PNC Mobile	7529	3312	213900	21053	18482
	No Area C	PNC Fixed	7623	1412	52180	10573	8114
		PNC Mobile	7531	3027	254110	23473	17027
Afternoon	Area C	PNC Fixed	7205	2467	233100	7670	7220
		PNC Mobile	6917	3554	183500	15159	11198
	No Area C	PNC Fixed	6951	2605	429000	8061	9457
		PNC Mobile	6729	3605	135600	17722	12959

Table 3:16 Descriptive statistics of morning's and afternoon's fixed and mobile PNC inside and outside Area C.

3.2.3 Pollutants correlation

Observing time trends for mobile BC and for fixed BC relative to the warm period, similar tendencies can be noted. Analysing the result of individual runs, days with high background BC levels are characterized with high mobile BC levels. This trend is particularly evident for 3th 5th April, 7th and 21th May, which are distinguished by particularly high fixed and mobile BC concentrations. Even when daily average BC urban background concentrations are low, a decrease in daily averaged mobile BC concentration is observable, particularly evident on Fridays and Saturdays when traffic intensity decreases. In order to quantify the degree of correlation between fixed and mobile BC values, as for the cold period dataset, daily averaged data of both instruments were plotted on a scatterplot, firstly without separation by type and then distinguished between morning and afternoon data. Differently as observed for the cold period, during the warm period, daily average mobile BC concentration is always higher than average fixed BC concentration.

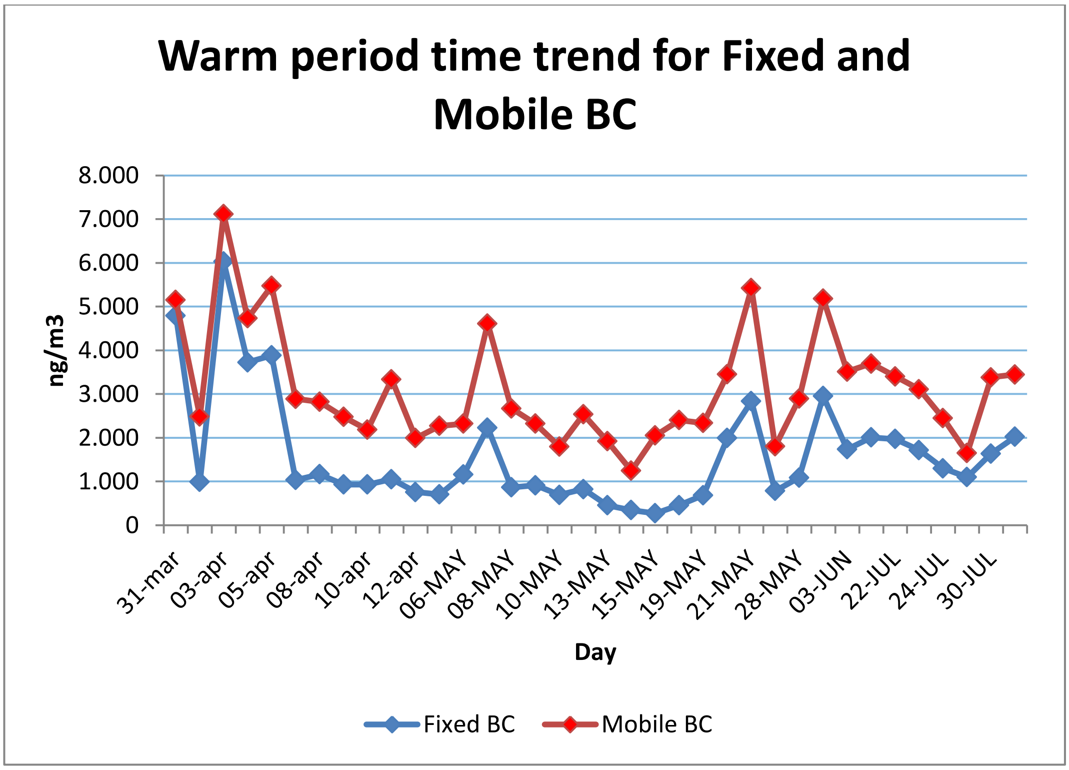

Figure 3:60 Time trend for fixed and mobile daily averaged BC during warm period.

As shown in Fig 3.61 a good correlation (R^2 = 0.8734), but quite lower than during the cold period, was found between overall daily averaged fixed BC levels and mobile BC concentrations. To find out in which part of the day the values are more correlated, morning and afternoon data were separately analysed.

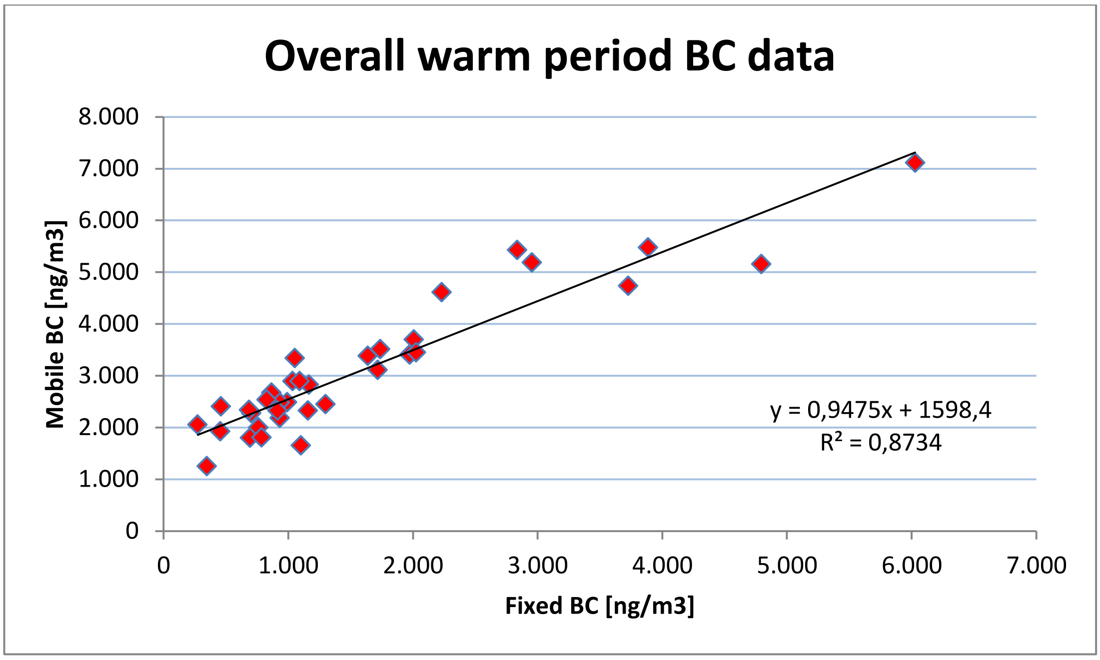

Figure 3:61 Linear correlation between overall fixed and mobile BC data during warm period. R2=0.8734

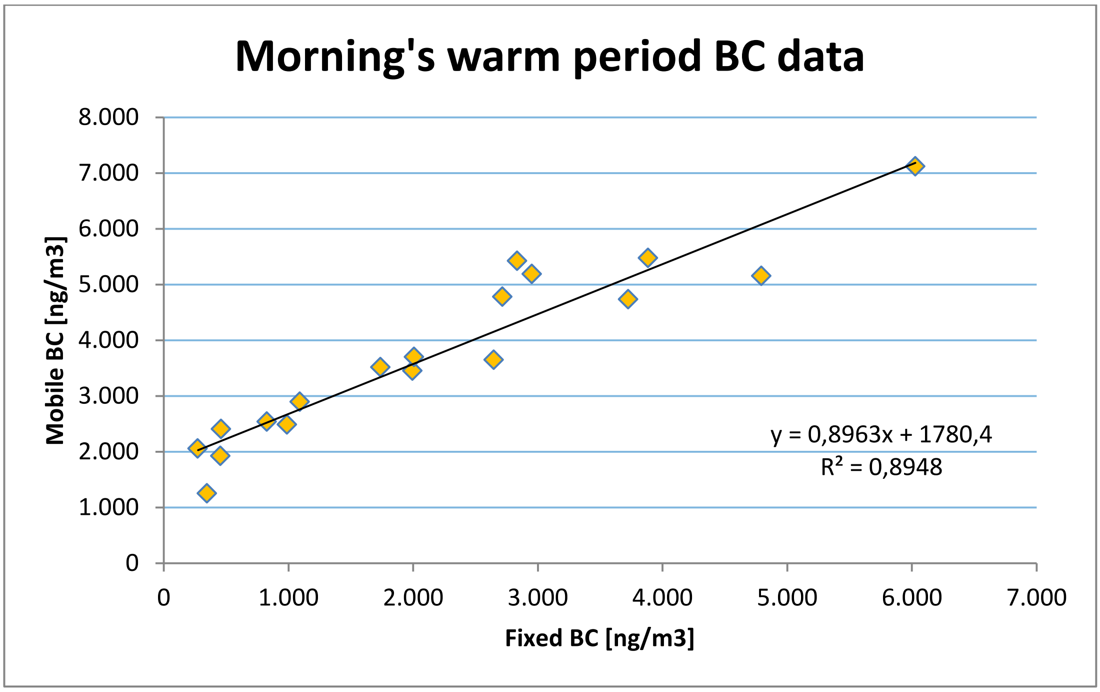

Figure 3:62 Linear correlation between morning's fixed and mobile BC data during warm period. R2=0.8948

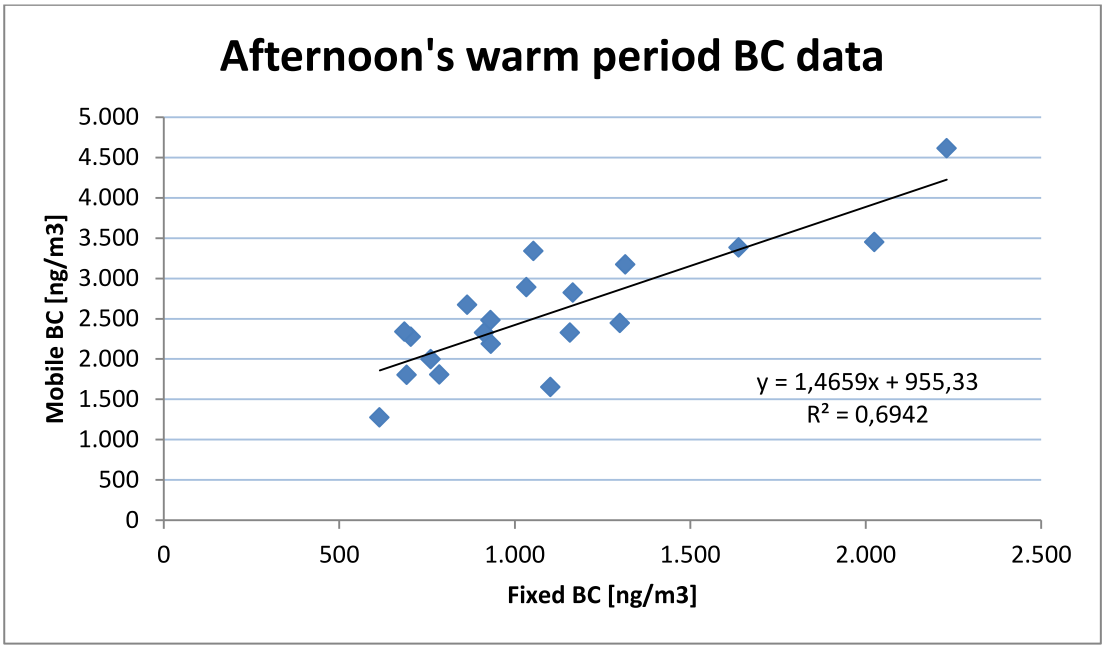

Figure 3:63 Linear correlation between afternoon's fixed and mobile BC data during warm period. R2=0.6942

By the comparison of R^2 values, morning mobile BC data result to be clearly more correlated with fixed BC data than afternoon's coherently with cold period results. Morning's computed R^2 value is 0.8948, lower than during the cold season. Warm season afternoon R^2 value is 0.6942, quite higher than cold period afternoon's value. Similar pattern can be therefore observed for both seasons.

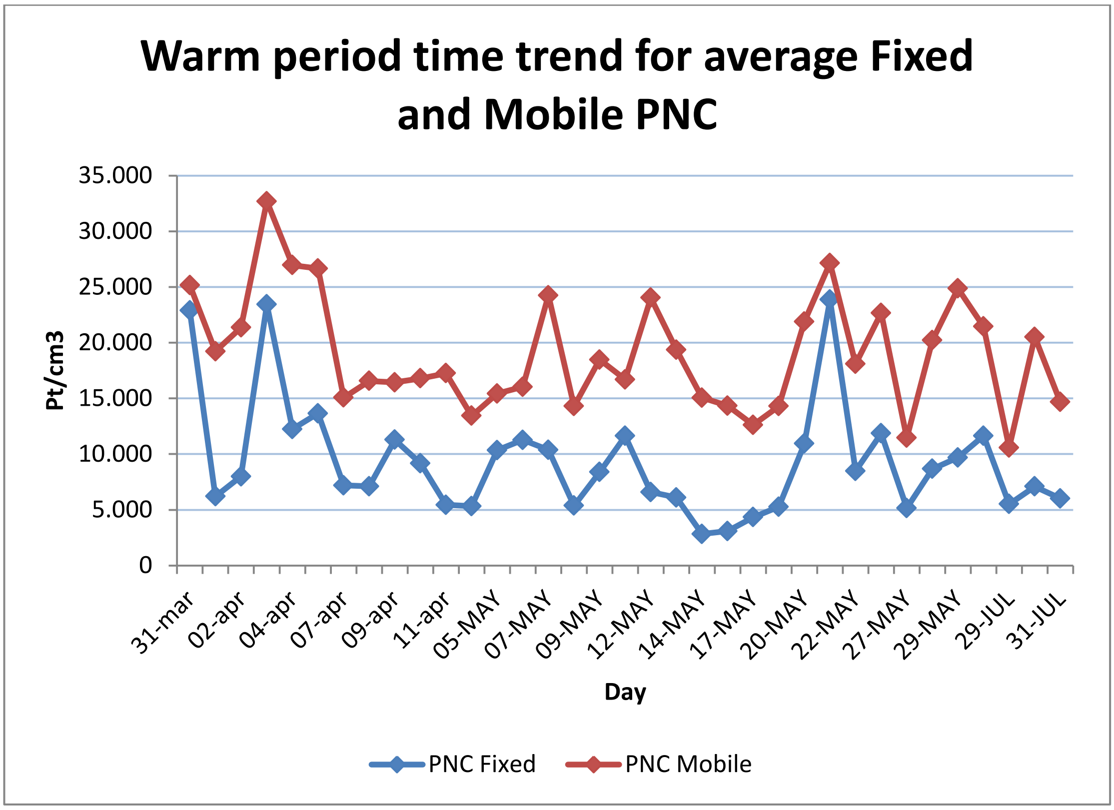

Figure 3:64 Time trend for fixed and mobile daily averaged PNC during warm period.

Also analysing the averaged mobile and fixed PNC time trends for the cold period, similar pattern can be observed. Days with particularly high background concentration are characterized by high daily average mobile PNC values, and vice versa, days with lower background concentrations are characterized with lower average mobile PNC . This trend is particularly evident from the 1th to the 5th April. As observed during the cold period, differences between mobile and fixed PNC is in the average included in the 1 – 2 x 10^4 range except for March the 31th and May 21th, where mobile and fixed averaged PNC values are comparable.

Plotting averaged PNC data on a scatterplot permits to obtain the degree of correlation between mobile and fixed PNC. Overall warm period daily averaged data are given in Fig 3.65. The obtained linear interpolation reflect a clearly lower correlation (R^2 = 0.5681) than for the cold period between urban background measured data and mobile PNC. Also in this case, to find out in which part of the day the values are more correlated, morning and afternoon data were separately analysed on analogous scatterplots. Morning's averaged cold period PNC data evidence an higher correlation (R^2 = 0.6724), but clearly lower than respective cold period value. Afternoon's correlation of R^2 = 0.2540 reflects the lowest computed correlation between average mobile PNC and background levels.

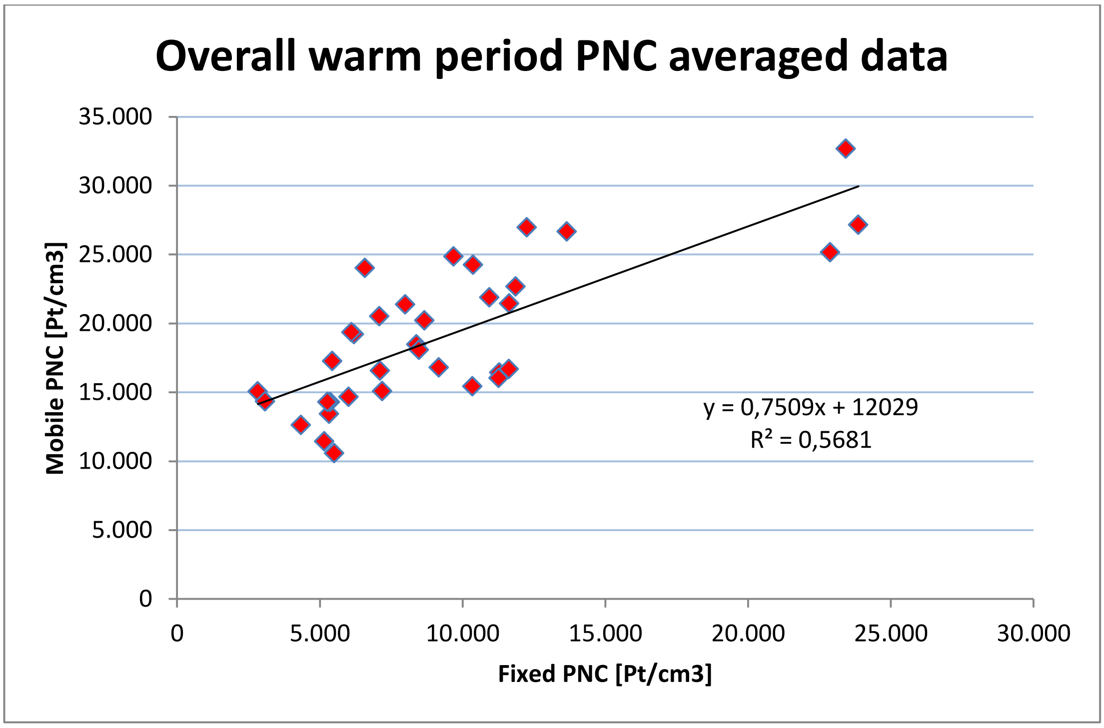

Figure 3:65 Linear correlation between overall fixed and mobile PNC data during warm period. R2=0.5681

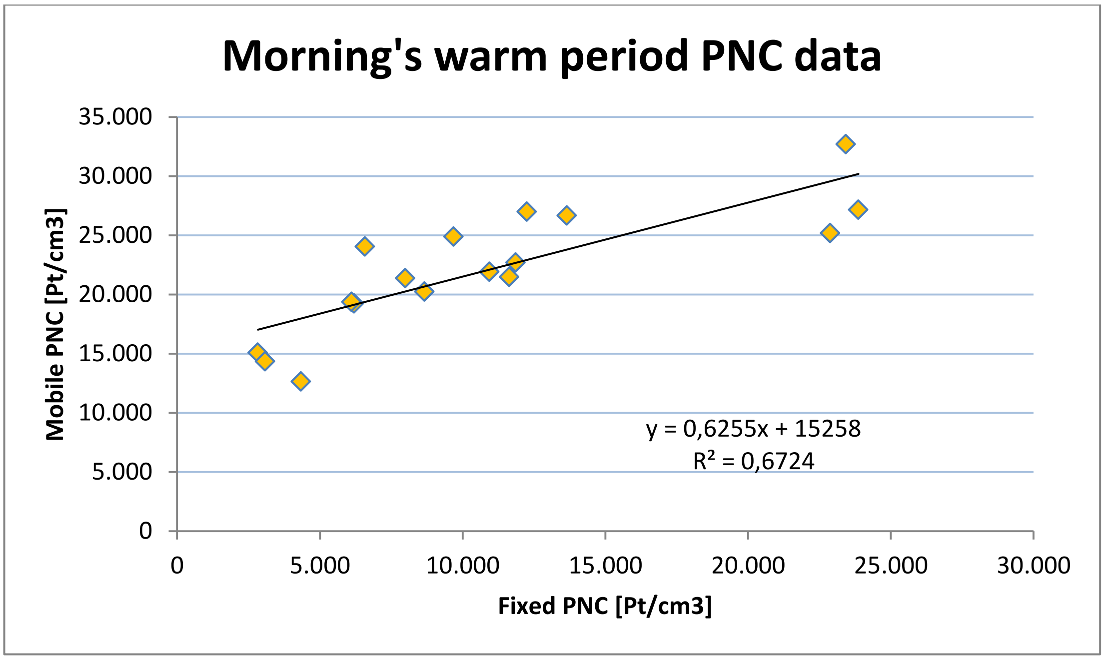

Figure 3:66 Linear correlation between morning's fixed and mobile PNC data during warm period. R2=0.6724

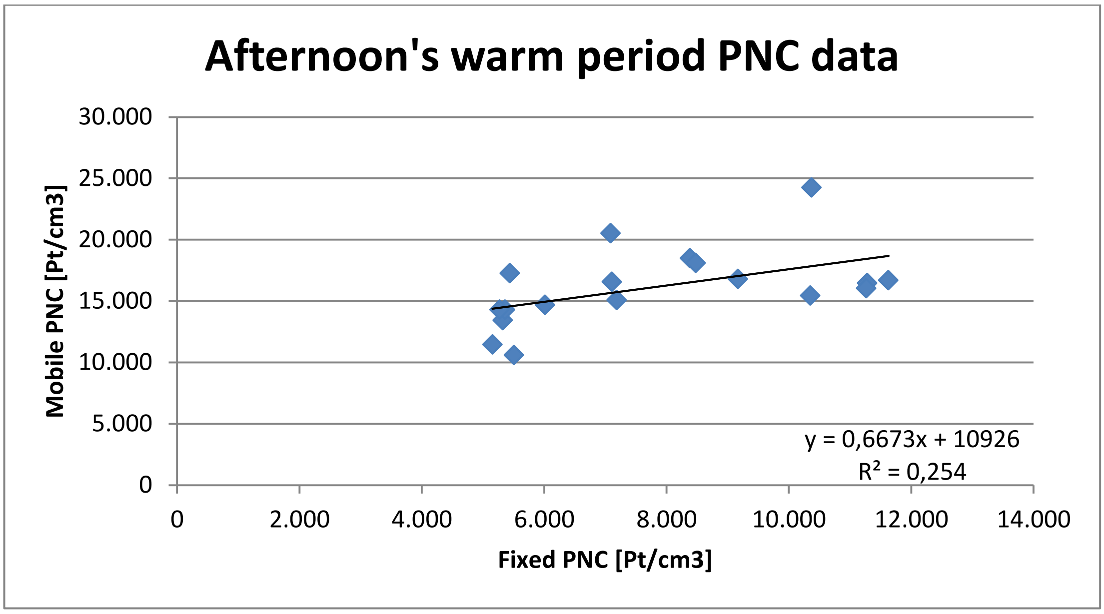

Figure 3:67 Linear correlation between afternoon's fixed and mobile PNC data during warm period. R^2=0.2540

Similar pattern for both pollutants were observed in the different city zones and in the urban background station, therefore correlation between mobile PNC recorded data and mobile BC values was examined. As for the cold period, also for the warm period dataset, daily averaged mobile data of each zone were plotted on a scatterplot and linearly interpolate computing R^2 value and linear equation of the trend-line. Mobile PNC data (and consequently mobile BC data) from April 1th and May 22th – 23th were excluded due to an instrumental malfunctioning.

In the underlying scatterplots, mobile PNC – Mobile BC linear correlation is shown for each city zone. Highest correlations were found in the most traffic congested zones, as observed during the cold season. In section RC, R^2 = 0.6949, higher than during cold period and the highest correlation value of the entire route. In section AV (R^2 = 0.5644) correlation between the two pollutants is less marked, but also higher than during cold season. Relative high R^2 values were found in section MR, characterized by an R^2 value of 0.598. In section VB, R^2 = 0.4931 while in pedestrian zone pollutants correlation is the lowest of the entire route (R^2 = 0.3089). Via Mazzini (DM) R^2 = 0.4117, is the only zone in which warm period computed correlation is lower than cold period's correlation. Also for the warm period, highest correlation were found in the most crowded street sections (RC and AV), while lowest correlation were found in pedestrian zone (BD).

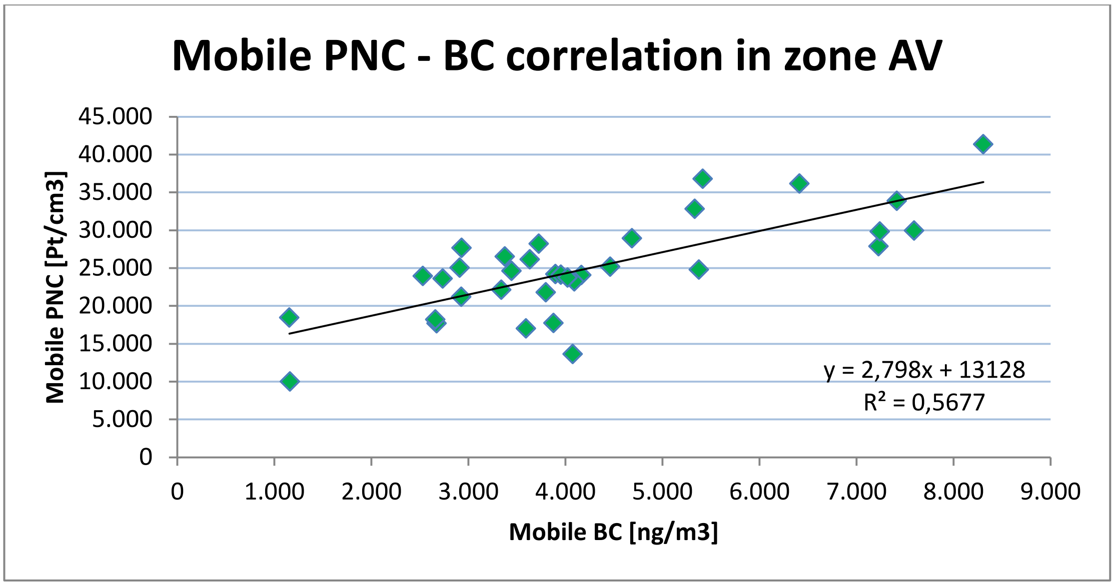

Figure 3:68 Mobile PNC-Mobile BC linear correlation in zone AV. R^2=0.5677

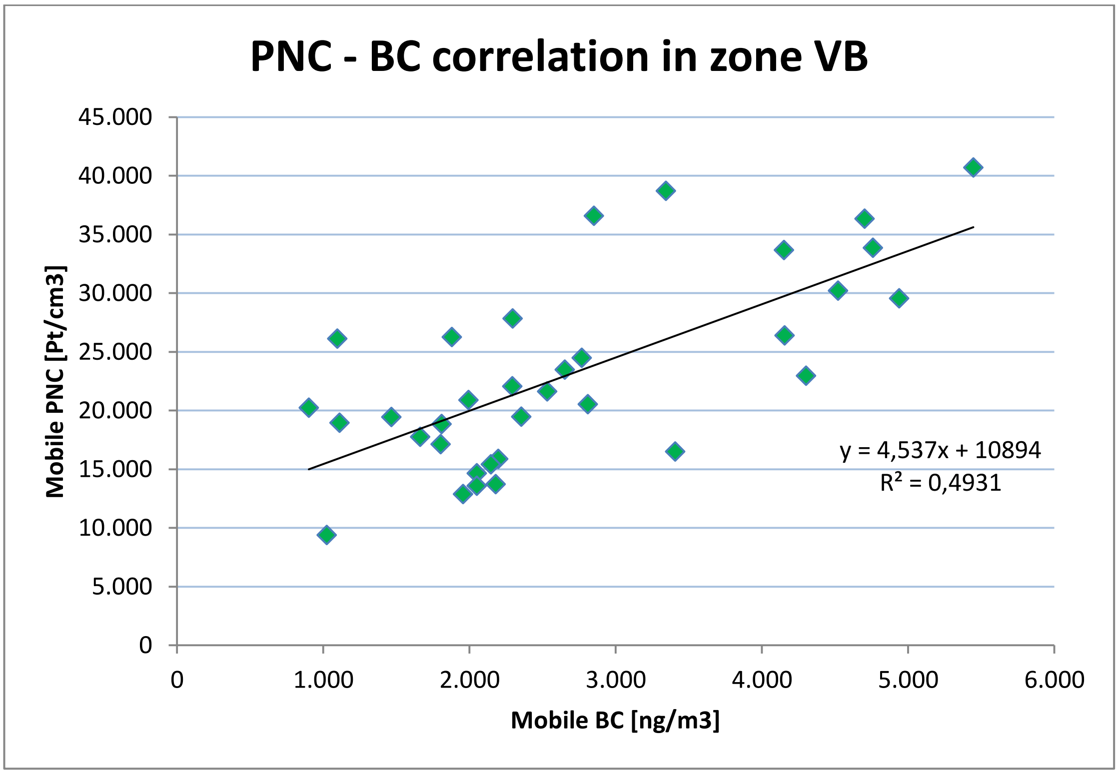

Figure 3:679 Mobile PNC-Mobile BC linear correlation in zone VB. R^2=0.4931

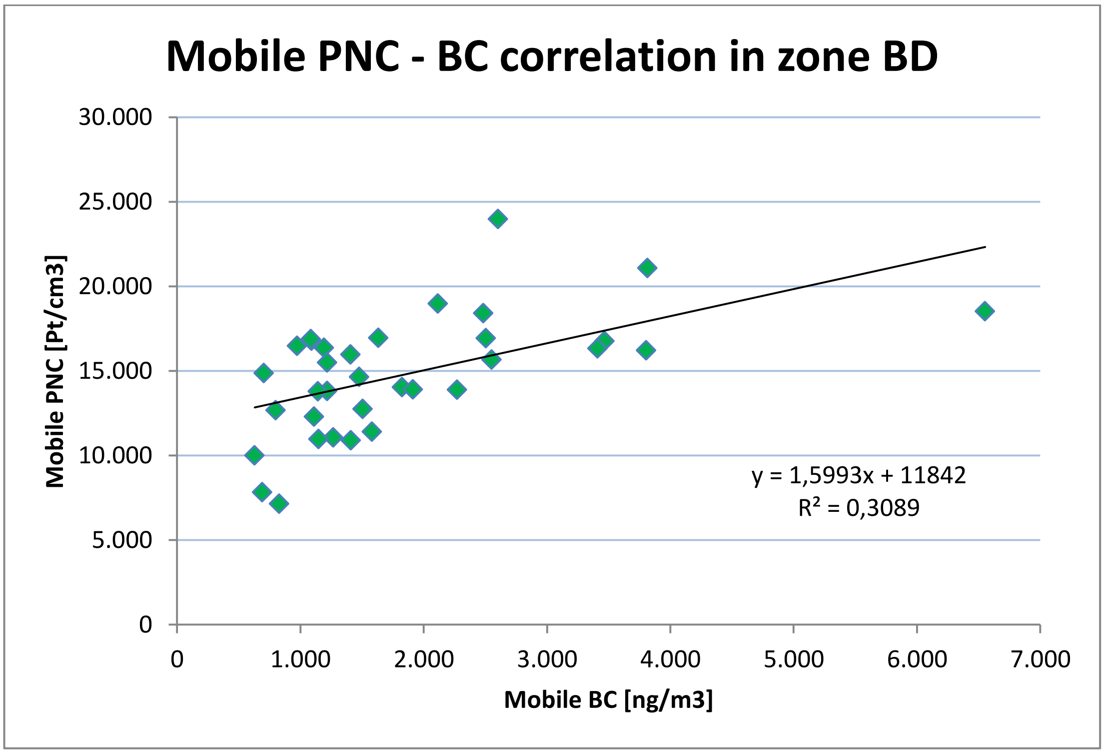

Figure 3:7068 Mobile PNC-Mobile BC linear correlation in zone BD. R^2=0.3089

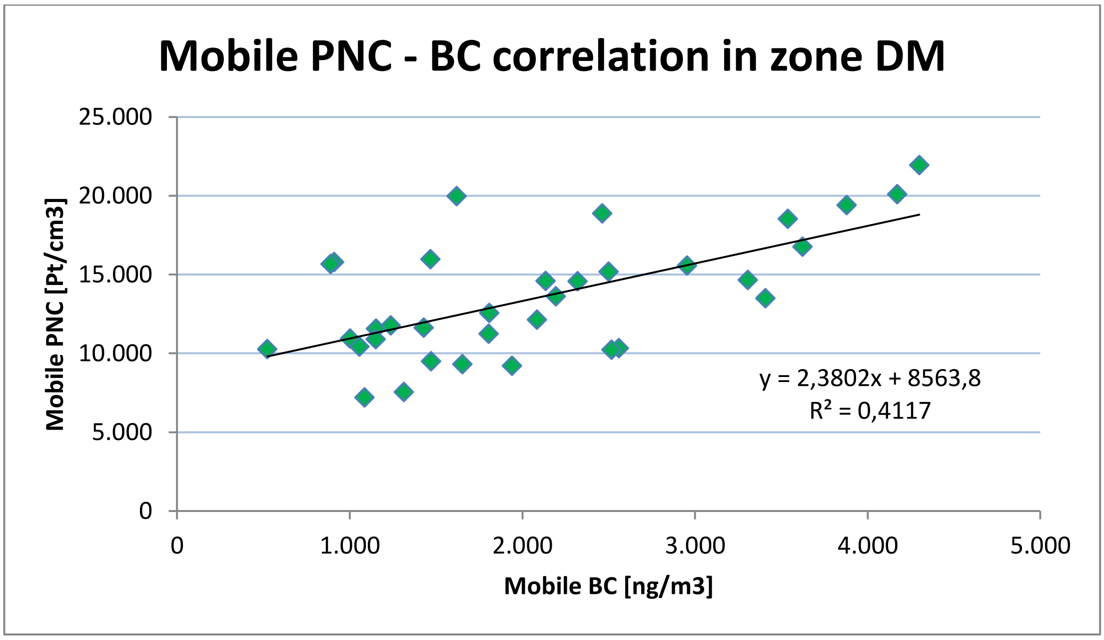

Figure 3:71 Mobile PNC-Mobile BC linear correlation in zone DM. R^2=0.4117

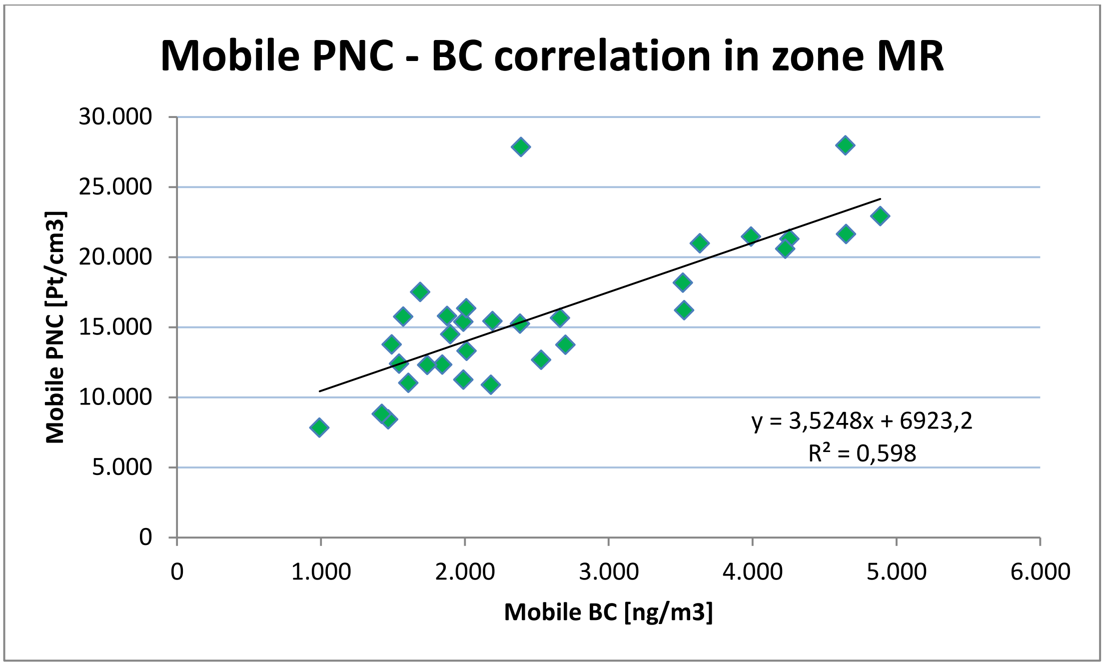

Figure 3:72 Mobile PNC-Mobile BC linear correlation in zone MR. R^2=0.5980

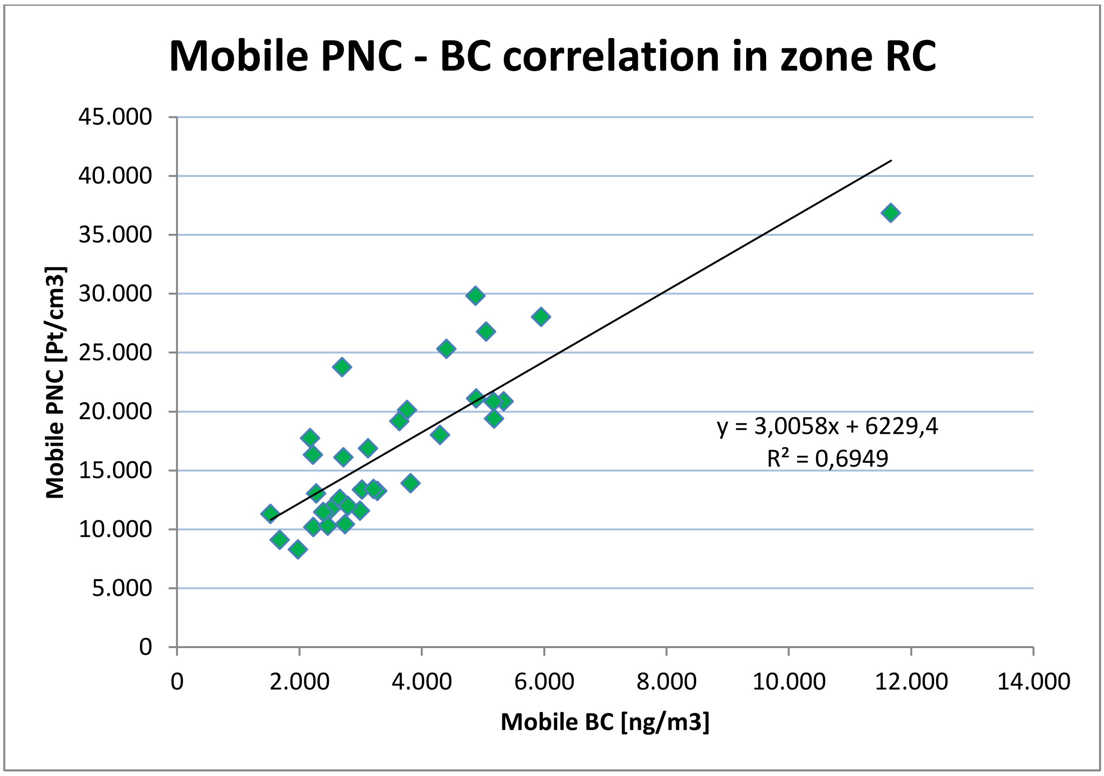

Figure 3:69 Mobile PNC-Mobile BC linear correlation in zone RC. R^2=0.6949

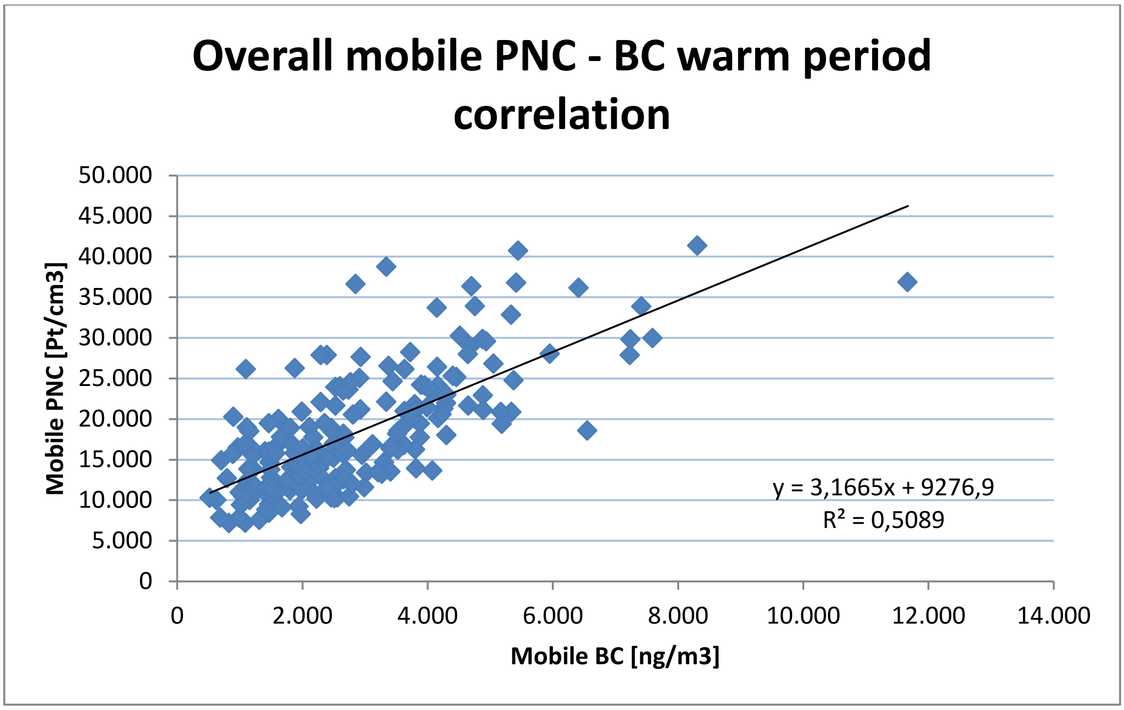

Figure 3:704 Overall Mobile PNC-Mobile BC linear correlation. R^2=0.508

Considering the entire warm period mobile PNC and BC dataset without zone classification, R^2 result to be 0.5089 as shown in Fig 3.74, and higher than during the cold period. Similar R^2 values was also obtained plotting fixed PNC and fixed BC on scatterplot of Fig 3.75 (R^2=0.5337), indicating a quite better correlation for background levels than for mobile pollutants concentration. The better correlation is probably due to the lower instrumental noise of a fixed monitoring station compared to stress noise which are subjected mobile instruments.

Compared to cold period, during the warm period a better correlation was found between PNC and BC for both the fixed and the mobile instruments.

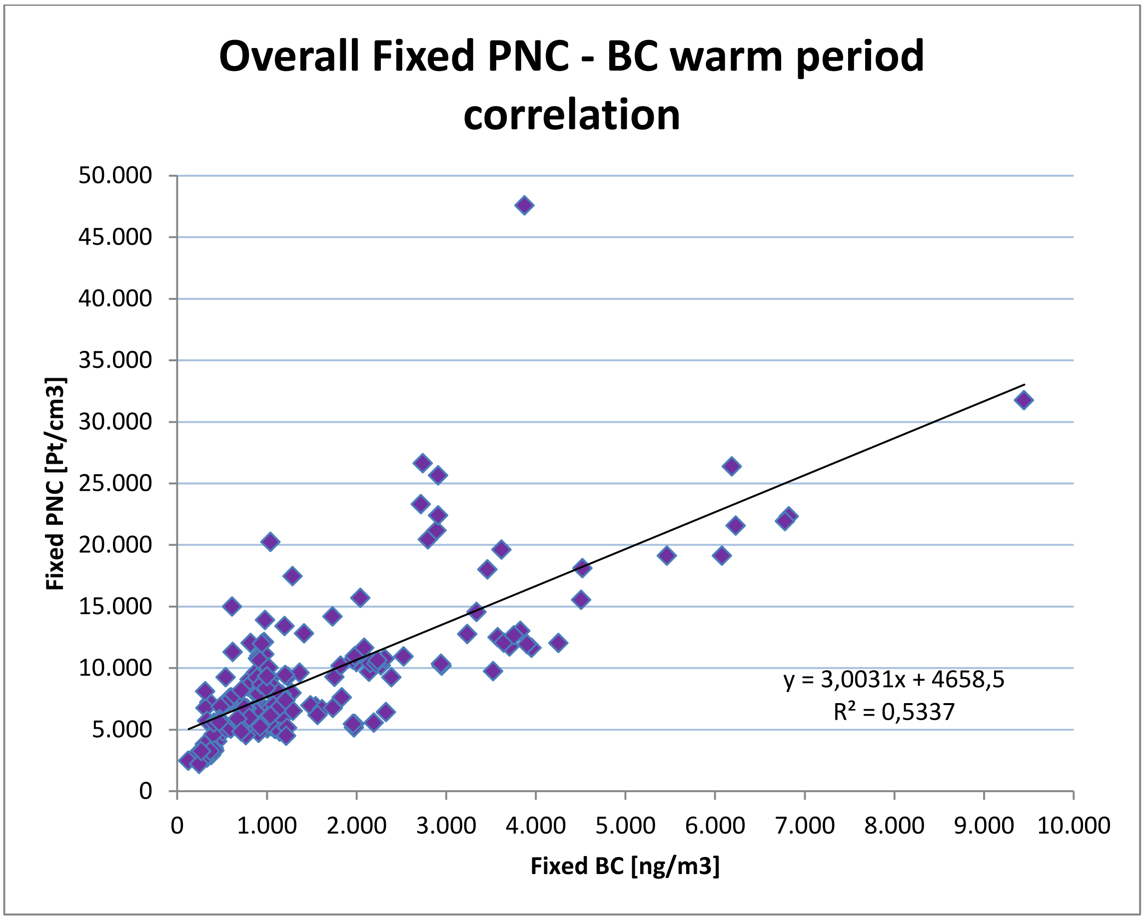

Figure 3:75 Overall Mobile PNC-Mobile BC linear correlation at urban background site during warm period. R^2=0.5337

4 Summary and conclusions

In Milan, Italy, atmospheric black carbon (BC) concentrations and particle number concentration were measured during December 2013 and July 2014 at two different sampling sites: an urban background site and a 17 Km long city track. The resulting dataset was divided into a cold season (84841 BC and PNC data) and warm season dataset (120298 BC and PNC data), covering an overall distance of approximately 1200 Km. Samplings took place during morning hours (8:30 – 12:00) and during afternoon hours (15:00 – 18:00) and during all week days except Sundays. In order to ensure the correct instrument functioning, two condensation particle counter (TSI P-trak model 8525) and two micro-aethalometers (AE51) were tested side-by-side for a total of 26 hours in side-by-side tests at the fixed AQ sampling site before starting with the monitoring campaign. After applying noise reduction algorithm on raw data, instruments show a good agreement, $R^2_{P\text{-}trak} = 0.924$ and $R^2_{AE} = 0.993$.

During cold period, primary sources of BC and PNC are characterized by a strong intensity. Main sources in urban environments are traffic and domestic heating emissions. The typically stable atmospheric winter conditions limit pollutants dispersion, causing higher concentration values in the lower atmosphere. Differently, during the warm season primary sources intensity decrease. Traffic is less intense due to the good weather conditions (incentive for active travellers) and to the school-stops during summer holidays. Domestic heating contribution can be considered insignificant and higher atmospheric turbulence promote pollutants dispersion.

Overall cold season average morning BC background concentrations are 5162 ng/m^3, while mobile overall BC is in the average 1.3 times higher reaching the value of 6578 ng/m^3.

During the cold period, average fixed BC is 3.1 times higher than the respective value for the warm season (1681 ng/m^3). Seasonal differences are less marked considering mobile BC, where the ratio between cold period and warm period is 2.0 (3212 ng/m^3).

Also considering PNC, seasonal variations are evident. Cold period PNC are 2.9 and 2.2 times higher than during the warm period, for the fixed and for the mobile instrument respectively.

Strong diurnal differences were observed in both seasons and on both pollutants. Morning's average concentrations are always higher than afternoons. Considering the BC dataset, daily variability is higher during the warm period and for BC fixed. During cold period, morning average BC values are 1.3 and 1.2 times higher than in the afternoon, for BC fixed and BC mobile respectively. Corresponding ratios for the warm season are 2.0 and 1.5. Extreme values were always recorded during morning rush hours. Morning's BC dataset evidence numerous statistical outliers due to instantaneous concentration peaks, while only few were recorded in the afternoon.

Daily differences are more marked for the PNC. Cold period's morning average values are 1.8 and 1.3 times higher than during the afternoon, for the fixed and mobile PNC respectively. Same daily variability was observed during the warm period for fixed and mobile PNC; morning's average PNC are 1.4 times higher than in the afternoon for both instruments.

Those daily variations are probably due to the daily evolution of the mixing height. During warm period days, mixing height grows more rapidly than during the typical cold period day, causing an higher dispersion of pollutants and consequently lower average concentrations during the afternoon hours. Afternoon's rush hours are spread over an larger time period, thus contributing to lower afternoon mobile concentrations, for both BC and PNC.

Weekly variations between normally working days, Saturdays and anomalous days (public transport strike day) were investigated for each season and for both pollutantants. During cold season, working days are characterized by 1.4 times higher mobile BC than during Saturdays and 1.2 times higher than during strike day. Considering cold period PNC dataset, in the average no differences were noted on mobile and fixed PNC values between working days and Saturdays. Compared to strike day, working days are in the average characterized by an 1.4 higher mobile PNC values. Despite the supposed higher private traffic volume during the strike day, mobile concentration levels are lower than during working days, probably due to the backward shifting of the commute rush hours.

During the warm season, no strike days occurred, and weekly differences in terms of average mobile concentrations are less marked. Saturdays average mobile BC are approximately the same than during working days, while considering mobile PNC the ratio is 1.1.

For further investigating the influence of traffic source on exposure concentrations, mobile monitoring route was divided into six street sections. The classification is based on traffic restrictions and street characteristics. Observing overall cold period BC concentration, as expected, the sections without traffic limitations (AV and RC) turn out to be the most polluted. An average BC concentration of 7522 ng/m^3, 1.5 times higher than average background levels is observed in section RC. Section AV is characterized by an average BC concentration of 7365 ng/m^3. Lower values were found on sections subjected to a congestion charge (VB, BD, DM and MR). Overall average concentrations of 5977 ng/m^{3}and 5735 ng/m^3 were found in sections VB and MR respectively. Comparable to background BC concentration values were recorded in pedestrian zone and in Via Mazzini (DM), 4922 ng/m^{3}and 5060 ng/m^3 respectively, both slightly lower than average background levels measured at the fixed station. Highest peaks were monitored on the most crowded street sections AV and RC (2.6 x 10^4 ng/m^3). Lower standard deviation was observed in pedestrian zone, about the half of section RC. Strongest diurnal variation were found in sections with lower traffic intensity (DM, MR and BD). In those sections morning’s mean value are 1.4 higher than in the afternoon. Lower diurnal variations were found in the most crowded zones, probably due to the lower diurnal traffic variation intensity and to the proximity to primary emission sources. Morning’s average BC concentration in section RC, VB and AV are 1.2, 1.2 and 1.1 times higher than respective afternoon values.

Sections AV, VB, MR and RC were further subdivided in order to detect internal differences in terms of average BC concentrations. In section AV no significant statistical differences were found, while the first stretch of section VB is characterized by 1.2 times higher average BC concentration than in the second stretch, despite the proximity to a city park. Higher values are probably explainable with the major traffic intensity and higher number of fast accelerating vehicles . Subdivision of section RC highlights absolute highest average BC concentration in Piazzale Corvetto with an average value of 8944 ng/m^3, 1.325 times higher than in the first stretch of Corso Lodi (RC) characterized by a clearly large street which implies a major distance between pedestrians and motorized traffic.

Same distinctions were also made for the particle number concentration data (PNC) collected during the cold period. Same pattern observed for BC concentration were also observed for PNC. Highest PNC average value was recorded in Corso Buenos Aires (AV), mobile PNC have an average value of 5.0 x 10^4 Pt/cm^3 (1.8 times background average PNC value). Differently as observed for BC, section VB results to have a comparable high average value of 4.5 x 10^4 Pt/cm^3 despite traffic limitations. High crowded section RC is characterized by 4.3 x 10^4 Pt/cm^3, while in section MR average mobile PNC is 3.9 x 10^4 Pt/cm^3. Lowest average mobile PNC were recorded in pedestrian zone and in section DM, 3.0 x 10^4 Pt/$cm^3$and 3.1 x 10^4 Pt/cm^3 (1.2 times background average PNC), respectively. Extremely high PNC peaks were observed close to main crossroads and in presence of idling traffic or close to roadworks. The further subdivision of the route evidence in the average 16% higher PNC at the beginning of section AV compared to the end of the street. Even if less marked than BC, the first stretch of section VB results to have in the average 9 % higher PNC than in the second stretch. Internal differences in section MR are less than 3%. Same trend observed for BC in section RC, was found also for PNC. Highest average PNC measured in Piazza Corvetto (mean 5.3 10^4 Pt/cm^3) were 31% higher than at the beginning of Corso Lodi (6L mean: 4.1 x 10^4 Pt/cm^3).

Considering warm period dataset and compared with background levels, mobile BC concentrations are from 1.6 (in the pedestrian zone) to 2.6 (in section AV) times higher. Concentration peaks are less numerous but more higher than those measured during the cold period. Section AV is characterized by the highest average BC concentration of 5097 ng/m^3 in the morning and 47% higher than in the afternoon (3471 ng/m^3). High average BC concentrations were also found in section RC with an average of 4219 ng/m3, 42% higher than in the afternoon (2960 ng/m^3). In the other sections, average BC data ranged from 2475 ng/m^3 (pedestrian zone) to 3321 ng/m^3 (zone VB). In the afternoon, values in those sections ranged from 1459 ng/m^3 (pedestrian zone) to 2352 ng/m^3 in zone VB.

Class internal analysis of warm period BC data points out same trend. Instantaneous peaks were observed at each main crossroad of all sections except for pedestrian zone. Differently as observed for the cold period, section VB and MR points out no significant differences. In section RC, highest average BC data were sampled in Piazza Corvetto, 73% higher than in correspondence of the access road at the beginning of Corso Lodi. Lowest differences with respective cold period average BC data are given in the first stretch of section AV and in the last stretch of section RC, the two most crowded sections of the entire monitoring route.

Analysing the congestion charge area (Area C) effect on pollutants concentrations, an higher variation vas observed for BC concentrations compared to PNC. Higher relative variations were found during afternoon values even if absolute values were higher during morning rush hours in both zones. In the average, considering cold period BC dataset, No Area C zones are characterized by 1.3 and 1.4 times higher concentrations than inside Area C, for the morning and the afternoon respectively. More marked is the difference considering warm period mobile BC data; corresponding ratios are 1.5 and 1.6.

The effect of the congestion charge area is less evident considering PNC dataset. During cold period, No area C zones have in the average 1.2 and 1.3 times higher PNC than inside Area C, in the morning and in the afternoon respectively. Warm period variations on PNC are less evident than during the cold season. Respective ratios for warm period mobile PNC are 1.1 and 1.2.

The lower effect of Area C on PNC compared to BC concentration is probably due to the duplicity of particle formation sources (traffic emissions and secondary formation).

The coefficient of correlation shows a high agreement between mobile and fixed instruments, for both the condensation particle counters and the aethalometers (R^2_{AE51} =0.8982 and $R^2_{P\text{-}trak}$ =0.8664). In both cases a better correlation was found in morning hour data.

Good agreement was also found between PNC and BC data. For the mobile instruments, during the cold period R^2_{Mobile} =0.44 while for the fixed R^2_{Fixed} = 0.44. Higher values of correlation coefficient were found in crowded sections (R^2_{RC} = 0.61) and lowest in the pedestrian zone (R^2_{BD} = 0.26). Those values suggest that traffic is the main common source of fine particulate matter and black carbon aerosols. A better agreement was found during the warm period between BC and

PNC. For the mobile instruments, during the cold period R^2_{Mobile} =0.51 while for the fixed R^2_{Fixed} = 0.53. As for the cold period, highest values of correlation coefficient were found in crowded sections and lowest in pedestrian zone (R^2_{RC} = 0.69; R^2_{RC} = 0.31). Higher R^2 values during the warm period indicate a lower contribution of secondary fine particle matter formation compared to the cold period.

The comparison of the concentration levels at the different sites points out that the highest values were observed in winter, when the meteorological conditions are typically very unfavourable for the atmospheric dispersion and primary emission sources are stronger. Lowest ones were recorded in summer, when the activity of the emission sources is reduced. Large variation in particle number and black carbon concentration indicates that multiple factors affect these concentrations. The analysis of both the intra-site seasonal differences and the inter-site differences for corresponding seasons of the year points out the relevant role of meteorological conditions and of the secondary sources, which are responsible for a diffused background concentration level when mixing layer is high. Observing the high diurnal differences, timing of a trip is an important parameter influencing pedestrian exposure to BC and fine particulate matter.

Unfortunately during the measuring campaign only few rainy days occurred and no statistical analysis of consequences of rainy events were made. However, the role of the traffic as the main primary source of the finest fractions of the particulate matter and black carbon aerosols clearly appears when considering the significant differences of average concentration values of the two sampling sites.

Research could be improved considering other relevant parameters like hourly traffic intensity of each street sections, data about the development of the mixing layer height, and other meteorological data. Data on regional winds measured every hour in a nearly situated fixed AQ measuring station is not sufficient to describe the variability in the wind field in the urban areas. As suggested by previous researches, traffic-induced turbulence is generally stronger than wind-induced turbulence in an urban street, except at times when strong prevailing and in-street air flows are present (rare situation in Milan) (Patra, et al., 2008).

Given the relatively spartan sampling equipment and approach, this study was quite successful from an operational standpoint, although an increased suite of measurement instrumentation would be useful in any ensuing work. Limitations of the present study included the absence of particle size distribution information and lack of traffic data coincident with the measurement periods . Particle size distribution (including possible impacts of ambient air temperature) and chemical composition could both be assessed. Development of emission factors and examination of the mechanical condition may also be useful (Knibbs, de Dear, Morawska, & Mengersen, 2009).

This work aims to be a support of decision makers in evaluating abatement strategies, urban planning (building constructions, ventilation systems, traffic management). Since local traffic has a very large share in the total UFP and BC concentrations, those can be used as a sensitive parameter to evaluate long or short term local air quality management strategies.

5 Table Index

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7 Bibliography

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