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Assessment of Portable and Miniaturized Sensors for the Monitoring of Human Exposure to Air Pollutants

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Content Index

ABBREVIATIONS

AB	AirBeam
AR	Augmented Reality
BLE	Bluetooth Low Energy
CC	CairClip
CI	Confidence Interval
CPC	Condensation Particle Counter
DSC	Diffusion Size Classifier
EPA-WINS	EPA Well Impactor Ninety-Six
FRMs	Federal Reference Methods
GC/MS	Gas Chromatography/Mass Spectrometry
GIS	Geographic Information System
GPS	Global Positioning System
HI	Harvard Impactor
INSIDE	INdividual air pollution exposure, extracellular vesicles Signaling and hypertensive disorder DEvelopment in pregnancy)
IoT	Internet of Things
IVN	Intelligent Vehicle Network
LOD	Limit Of Detection
LUR model	Land Use Regression model
m	Slope

MAPS MI	Mapping Air Pollution in a School catchment area of MIlan
MEs	Micro-Environments
MMs	Miniaturized Monitors
MPPD model	Multiple-Path Particle Dosimetry model
MSUs	Micro Sensing Unit
OPC	Optical Particle Counters
PBL	Planet Boundary Layer
PCIS	Personal Cascade Impactor Samplers
PHOTs	Photometers
PM	Particulate Matter
PNC	Particle Number Concentration
PRISMA	Preferred Reporting Items for Systematic reviews and Meta-Analysis
PS	Participatory Sensing
PTFE	Polytetrafluoroethylene
q	Intercept
R	Pearson correlation coefficient
RF	Radio Frequency
RH	Relative Humidity
SD	Standard Deviation

SE	Standard Error
T	Temperature
TAD	Time Activity Diary
TSP	Total Suspend Particles
UFP	Ultrafine Particle
VE	Ventilation rate
VOC	Volatile Organic Compounds
WDESN	Wireless Distribute Environmental Sensor Network
WSNs	Wireless Sensor Networks

SUMMARY

Background and aims

Air pollution can cause adverse effects on the human health and on the environments: for these reasons air quality monitoring is required by national and international regulations. The environmental monitoring is also used for the exposure assessment of the general population to different air pollutants. Instruments and methods traditionally used to measure exposure levels and to meet air quality international standards are characterized by high cost and can provide accurate data only for selected and restricted areas. This last feature is critical in the field of personal exposure assessment, especially in urban environments, because measurement at adequate spatial scales are essential in heterogeneous environments, where emission sources are many and varied. On the contrary, portable and miniaturized monitors can provide exposure data with high spatial and temporal resolution and allow to measure human exposure at an individual (the exposure constantly measured in proximity -3m- to the subject) or personal level (the exposure measured in the breathing zone of the subject).

In the last years, several in-field campaigns have been conducted using portable and miniaturized monitors to evaluate the personal exposure to different pollutants. In general, this kind of monitors are characterized by worse metrological performance (i.e. accuracy, precision and maximum measurable concentrations) if compared to the traditional standard methods. Despite this disadvantage, portable and miniaturized monitors could be easily used across different applications, because their advantageous features, such as the capability to provide real-time measurement, the high spatial and temporal resolution of acquired data, the ability to adapt to different experimental designs and, especially, the ability to follow the subject in any activity. Finally, portable and miniaturized instruments can provide data acquired in the respiratory zone of the subject, following therefore the practices for a correct exposure assessment. Obviously, the best compromise between the analytical gold standard (in terms of precision, accuracy and instrumental sensitivity) and the gold standard in regard to the exposure assessment should be chosen.

Therefore, in brief, principal aims of this thesis are (i) to evaluate the on-field performances of portable and miniaturized monitors for gaseous pollutants and airborne PM and (ii) to use these monitors in exposure assessment studies and (iii) to understand if data acquired via portable and miniaturized monitors could be useful in other fields of application, such as epidemiological studies or toxicological studies, in which the evaluation of the inhaled dose of pollutants could play a key role.

Materials and methods

As reported at the beginning of this thesis, the work is developed in different parts, briefly described below: The first part of the introduction (Chapter 1) provides the definition of the background and the objectives of the thesis, in addition to the methods used. The first results are indeed reported in Chapter 2 (state of the art) and in Chapter 3 (evaluation of accuracy and precision of portable and miniaturized monitors). Chapter 4 reports studies regarding the exposure assessment of susceptible subjects, through the use of portable and miniaturized sensors (commuters - Chapter 4.1, pregnant - Chapter 4.2 - 4.3 and children, even if only as a reference, in Chapter 4.4). In the Chapter 5 the aims and the methods used for the development of a LUR models (land use regression model) for the city of Milan are reported. The discussions (Chapter 6) are supplemented by sub-section relating to future developments and to the limits and advantages of this thesis work.

First, a study of the current literature about miniaturized sensors was conducted via a systematic review, using outcomes from three different scientific databases (ISI Web of Knowledge, PubMed and Scopus), using a search query defined a priori for all databases. Papers were detected and selected using well-defined inclusion and exclusion criteria. The whole process of literature reviewing was based on the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) criteria.

Performance evaluation of portable instruments was performed during N=16 repeated 8-h sessions. Tested and used instrument refers to (i) direct-reading instruments (UFP and size-fractionated PM) and filter-base PM sampling. Performances of portable monitors were tested against reference instrumentation or against widely used direct-reading instruments. In

particular, the comparability and the predictability between instruments were tested evaluating the regression parameters (R^2, slope and intercept). To assess absolute errors and error trends, the instruments comparisons were evaluated via Bland-Altman plots.

Performance evaluation of co-located $PM_{2.5}$ miniaturized monitors was performed during two different periods (warm and cold), during N=20 repeated 8-h sessions. Again, the performances of miniaturized monitors were tested against reference instrumentation or against widely used portable direct-reading instruments. Different tests were used for the performance evaluation and in particular: (i) precision and uncertainty evaluation between co-located miniaturized monitors; (ii) comparisons among miniaturized monitors and the reference gravimetric methods via Mann-Whitney tests and Spearman's correlation and regression analysis; (iii) evaluation of error trends (Bland-Altman plot evaluation and analysis of relative error). Finally, (iv) the impact of meteorological variables on measurement errors was tested.

Two exposure assessment studies were carried out. The first work refers to the measurement of selected pollutants (PM and NO_2) during a typical commuter's route (home-workplace and return). The route was fixed a-priori, considering different traffic microenvironments. Experimental data were collected over 4 working weeks (Monday-Friday), in two different seasons (winter and summer). Different portable and miniaturized monitors (direct-reading and filter-based) were used for the collection of exposure data. The evaluation of physiological parameters (heartbeat) acquired continuously during the whole monitoring period, was used to calculate the inhaled dose of pollutants across the different environments visited by the subject.

N=84 pregnant women were recruited for the second exposure assessment study, during two consecutive winter periods. Subjects were asked to wear personal and portable monitors for the measurement of their personal exposure to the same air pollutants (PM and NO_2) in different traffic (and non-traffic) microenvironments. The evaluation of differences in pollutant exposure across the considered microenvironments was performed via non-parametric tests (Kruskal-Wallis and Mann-Whitney tests). Moreover, bivariate correlation and change in R^2 and level of significance was assessed

considering all pollutants among different environments. Again, the evaluation of the inhaled dose among visited environments was performed.
Finally, data acquired during the latter exposure assessment study were used to develop a land-use regression model for the city of Milan. Even if this work is currently under development, a brief description of the methods used is reported below. Input variables used for the development of the model, via regression analysis and geo-statistical methods, consist in personal and direct-reading exposure measurements and geographical information (i.e.: traffic, population density, altitude, and land use information).

Results and Discussions

In the first part of the thesis (Chapter 1), the relevance of portable and miniaturized monitors in exposure assessment studies has been assessed. Moreover, the importance of the spatial and temporal resolution of human exposure data was reported. Articles reviewed in Chapter 2 substantially agree on the practicality of miniaturized sensors in different studies and across different applications, even if their performances (in terms of accuracy) are worse than reference methods for exposure assessment. Comparison test reported in Chapter 3 confirm the presence of an error bias associated with data collected via portable and miniaturized monitors. Thus, this chapter deals also with the data management for this kind of data (i.e. use of correction factor, applicable at posteriori). Finally, exposure assessment studies performed in the framework of this thesis (Chapter 4) demonstrate the ability of portable and miniaturized monitors to be used across different kind of application. For example, an evaluation of exposure concentrations among different traffic microenvironments, as well as the calculation of the inhaled dose of pollutants was performed.
Finally, even if the results are in the re-analysis and verification stage, a LUR model has been developed (starting from data obtained from portable and miniaturized monitors), with the aim of verifying the potential use of portable and miniaturized monitors in other and wider applications, such as in epidemiological studies.

1. INTRODUCTION

1.1. Problem Statement

Fixed air quality stations are usually adopted for the measurement of air pollutant concentrations and are characterized by an excellent data quality, while portable instruments are affected by intrinsic measurement errors. On the contrary, miniaturized monitors (MMs) consist in novel, very small and lightweight instruments whose measurement performance has not yet been adequately addressed in the scientific literature. Nevertheless, portable monitors and MMs are currently and commonly used across several applications, thanks to the following benefits and potentials.

(i) Technical characteristics: reduced dimensions and weight, other than the reduced noise;
(ii) Reduced costs of purchase and maintenance;
(iii) Ability to provide real-time continuous measurement, useful to characterize spatial and temporal variabilities;
(iv) The ability to be used both indoor/outdoor and across different environment (where, on the other hand, it is not always possible to use fixed monitoring stations);
(v) The possibility (due to reduced dimensions and weight, as well as ease of use) to be used for (or by) different kind of subjects, such as susceptible subjects or workers.

Although not previously evaluated in terms of instrumental performance, the use of MMs is increasing for the reasons reported above. Therefore, the current needs in this research field concern primarily the in-depth evaluation of MMs before their use and the improvement of data quality. In addition, due to the great potential of these monitors, it would be advisable to identify research fields where MMs can best be used.

1.2. Research Objectives and Contributions of the Thesis

The final goal of this thesis is the evaluation and the use of miniaturized monitors (for NO_2 and PM) in exposure assessment studies for selected populations. A further aim is to understand if MMs can be effectively used

for the spatial modelling of air pollution to be used in epidemiological studies.

In particular, the first aim of the study was to provide an overview regarding the use and the availability of MMs and studies that previously used these monitors in the field. This part of the work allowed to explore and understand the advantages and possible application of MMs, other than disadvantages of their use in exposure assessment studies. The rest of the work focused on the evaluation and use of selected portable monitors and MMs, based on all the issues emerged in this first phase.

The instrumental evaluation phase comprised:

i. The evaluation of comparability/predictability of these instruments to each other, to other widely-used portable instruments or to the gravimetrical techniques (evaluation of precision and accuracy);
ii. The occurrence of biases and their evaluation in specific environmental conditions;
iii. The evaluation of instrumental performances across different environmental conditions;
iv. The evaluation of suitability of portable monitors and MMs for exposure assessment.

The selected instruments were first tested, then used in exposure assessment studies on some categories of subjects (commuters, pregnant women and children).

The principal aims of the commuter study were to:

i. Evaluate exposure concentration across different transport micro-environment frequented by subjects;
ii. Calculate the inhaled dose of pollutant across different transport micro-environment frequented by the subjects;
iii. Evaluate which parameter used for the estimate of the inhaled dose (exposure concentration, time spent in an environment,

pulmonary ventilation rate) has the major impact on inhaled dose values;

iv. Understand in which transport MEs (among those usually used by commuters) higher exposures and inhalation doses occur.

The aims of the pregnant women study are similar to the previous ones. The hypothesis was again that visiting particular MEs (mainly traffic MEs) can contribute to high exposure levels and inhaled dose values. Results regarding the exposure assessment study on children are not reported here in detail: are only briefly cited in Chapter 4.4 (to highlight that portable and miniaturized instruments can be used on different populations) as they are the results of another Ph.D. project.

The last aim of this project was to use personal exposure data for the development of a land-use regression model for the city of Milan, using an innovative geostatistical methodology. Personal measurements can also be used to validate this (or other) exposure models. Another goals were, finally, to explore the usefulness of monitoring campaigns performed via MMs for epidemiology and evaluate if this kind of monitors can be useful as an alternative to traditional and fixed air quality station, especially because their higher spatial and temporal data resolution.

1.3. Thesis Overview

Background and information regarding the current knowledge about MMs are reported in Chapter 2, which shows the results obtained from a systematic review of the scientific literature on this topic. Chapter 3 describes the findings of two inter-comparison campaigns, designed and performed to test the performances of portable (Paragraph 3.1) and miniaturized (Paragraph 3.2) sensors. These tests focused on the evaluation of sensor's performances, in terms of precision and accuracy. Comparisons were performed at an urban background station (Como, Italy) and vs filter-based techniques and other widely used direct-reading instruments. The aims of this chapter are to assess instrumental performances across different meteorological conditions and to identify

the parameters mostly affecting the measurement error. Chapters 4 reports different exposure assessment studies of selected populations through the use of the portable and MMs evaluated in Chapter 3. In paragraph 4.1 the exposure assessment of a commuter was investigated using different instruments (for the evaluation of UFP, PM and NO_2) in repeated monitoring campaigns and along a fixed route. The aim of this work was to assess the exposure across different typical traffic (other than indoor) microenvironments. Moreover, an evaluation of the inhaled dose of pollutants was attempted, considering some physiological parameters (heartbeat and then pulmonary ventilation rate) and the time spent across different MEs. This approach was used to identify those parameters mainly influencing the inhaled dose, micro-environments. The second part of this chapter (4.2) focused on the exposure assessment to different pollutants (NO_2 and size-fractionated particulate matter) of a selected and susceptible population (pregnant women). Again, besides the evaluation pollutant exposure levels, the estimation of the inhaled dose was performed across the different MEs visited by subjects. Finally (4.4), even if not directly related to this project, an exposure assessment on another selected and susceptible population (children) was performed in the city of Milan, using some instruments selected and tested in this project. Chapter 5 describes the first stages of development of a land-use regression model for the city of Milan, using data collected in the previous monitoring campaigns (and in particular those collected in the framework of the INSIDE project - Chapter 4.2). Finally, in the last chapter (Chapter 6) the discussions and conclusions of the dissertation are reported. Passible future developments, as well as the drawbacks and advantages of this study, are then presented.

2. STATE OF THE ART

This chapter is based and published on: Borghi et al. Miniaturized Monitors for Assessment of Exposure to Air Pollutants: A Review.
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PREFACE

Low-cost and miniaturized monitors (MMs) are becoming increasingly available; due to several practical advantages (as discussed in this chapter), the use of this kind of sensors is increasingly widespread, both in citizen-science initiatives and in the scientific community [1-5]. The aim of the systematic review presented in the following chapter is to identify and report scientific studies that have used portable and miniaturized gas and PM sensors and the new integrated technologies (such as Global Positioning System - GPS), wireless communication module and web/smartphone application, to provide an exhaustive overview about studies regarding this issue. Because of the relative recent implementation of these MMs and to their growing use, at the time of writing of the following chapter [6], no other scientific literature review was available (a new review study, focused on the measurement performance of low-cost sensors, was published more recently [7]).

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3. Hasenfratz, D.; Saukh, O.; Walser, C.; Hueglin, C.; Fierz, M.; Arn, T.; Beutel, J.; Thiele, L. Deriving high-resolution urban air pollution maps using mobile sensor nodes. Pervasive Mob. Comput. 2015.
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to observation web with environmental enablers in the future internet. Sensors 2011.
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7. Karagulian, F.; Barbiere, M.; Kotsev, A.; Spinelle, L.; Gerboles, M.; Lagler, F.; Redon, N.; Crunaire; Borowiak, A. Review of the Performance of Low-Cost Sensors for Air Quality Monitoring. Atmosphere 2019.

Air quality has a huge impact on different aspects of life quality, and for this reason, air quality monitoring is required by national and international regulations. Technical and procedural limitations of traditional fixed-site stations for monitoring or sampling of air pollutants are also well-known. Recently, a different type of miniaturized monitors has been developed. These monitors, due to their characteristics (e.g., low cost, small size, high portability) are becoming increasingly important for individual exposure assessment, especially since this kind of instrument can provide measurements at high spatial and temporal resolution, which is a notable advantage when approaching assessment of exposure to environmental contaminants. The aim of this study is indeed to provide information regarding current knowledge regarding the use of miniaturized air pollutant sensors. A systematic review was performed to identify original articles: a literature search was carried out using an appropriate query for the search of papers across three different databases, and the papers were selected using inclusion/exclusion criteria. The reviewed articles showed that miniaturized sensors are particularly versatile and could be applied in studies with different experimental designs, helping to provide a significant enhancement to exposure assessment, even though studies regarding their performance are still sparse.

2.1. Introduction

Air pollution may result in huge impacts, causing different effects on human health, on the environment (e.g., ecosystem damage) and on the economy of industrialized and developing countries [1,2,3]. For these reasons, air quality monitoring is typically required by national and international regulations to assess systematically the environmental exposure of the general population to multiple environmental contaminants [3,4].

The equipment used to meet international standards regarding air quality/air pollution measurement is, at present, characterized by high cost and a high level of maintenance [3,5]. For example, the purchase and installation of single gas-analyzer can cost between £10,000 and £15,000 while the purchase and installation of particulate monitoring devices in existing station can cost between £10,000 to £25,000. Finally, the purchase of a multi-pollutant analyzer can cost £50,000–£80,000 [6,7]. In addition to the economic issue, traditional air quality stations are placed at strategic fixed-site locations and can provide accurate data only for a restricted area. This is a disadvantage because measurements at adequate spatial scales are essential for monitoring

air pollution in heterogeneous environments such as the urban environment, characterized by different emission sources [6,8,9,10]. High spatial (and temporal) resolution data are especially important in the air pollution field, due to the highly location-dependent concentration of atmospheric pollutants, particularly in the urban environment, which is characterized by high variability in terms of point pollutant concentrations [11]. Other disadvantages related to the use of fixed-site monitoring stations are related to the necessity of other support infrastructures (e.g., secure enclosures, power supply, etc.) [6,11]), of a dedicated area, and the need for maintenance and of continuous power consumption [12,13]. However, since traditional stationary sampling devices are usually expensive and complex to use, the development of portable sensors for the measurement of airborne pollutant concentrations has provided data with high temporal resolution characterized by a real-time response [14]. These portable instruments have been widely used in several studies, significantly improving the assessment of human exposure to atmospheric pollutants, since these instruments are able to measure exposure at an individual level (defined as the exposure constantly measured in proximity - within 3 m - to the subjects) or at personal level (which is preferable for assessing human exposure, as it is representative of the contaminant concentration in the breathing zone) [15,16].

Moreover, personal monitors can provide air pollutant exposure concentrations for specific and selected subject categories (e.g., susceptible individuals, workers, etc.) and, furthermore, can be used both indoors and outdoors. Several in-field campaigns have been conducted in the last years, using portable measurement devices, to evaluate the individual or personal exposure to different air pollutants and across different scenarios [17,18,19,20,21,22,23]. At present, the main limitation of these monitors is that portable devices are generally characterized by worse performance in terms of accuracy than the commonly used standard techniques [24]. Therefore, in summary, the quality of future exposure assessment studies depends strongly on the improvement of direct-reading portable sensors for airborne pollutant measurements, in terms of their compactness, portability, reliability, accuracy, and costs [25]. In recent years, a new kind of extremely portable air pollutant monitor has been developed [26,27]; these sensors are generally manufactured using micro-fabrication techniques and contain

micro-electro-mechanical systems (made of microfluidic, optical and nanostructured elements), allowing them to be compact, lightweight, inexpensive, and energy-efficient, with extremely low-power consumption. These devices are usually also completed by advanced computing power for data handling and by software packages for data elaboration and visualization [28]. Then, miniaturized sensors devices are usually low cost (i.e., ~£100–£5000), easy to use and easily portable, and they can provide data with high spatial and temporal resolution [29,30] and real-time continuous measurement of air pollutants [26]. These devices are continuously being improved, and their use is becoming increasingly widespread [29,30,31,32,33] because of the several previously described advantages. Considering the growing use of these miniaturized air pollutant monitors, the aim of this review is to identify and report studies that have used portable airborne gaseous pollutants and particulate matter (PM) sensors and the new integrated technologies such as Global Positioning System (GPS), wireless communication module and web/smartphone applications and to present the principal results provided by these studies. Although a recent paper [34] reported the characteristics and applications of portable gaseous air pollution monitors, there are no systematic review regarding the use on field of miniaturized PM and gas sensors and regarding the benefits arising the use of integrated technologies abovementioned.

The paper identification process used for the systematic review of the literature is described in Section 2. The results reported by article selection and screening are illustrated in the initial part of Section 3 while in the second part of this section are presented the new technologies to support individual and personal monitoring (GPS; wireless communication module, web or smartphone application). Principal results show how miniaturized monitors are continuously improved and how their use is becoming increasingly widespread, having the potential to improve human exposure assessment studies.

2.2. Materials and Methods

We conducted a systematic review using outcomes in three different databases (ISI Web of Knowledge, PubMed and Scopus). For each database, we used a list of keywords, which was the same for the three databases (Table 1). The keywords and the query structure were arranged as a function of the writing rules required by the selected database.

Database	**Search query**
ISI Web of Knowledge	(TS=("air quality")) AND (TS=("sensor network" OR "wearable sens*" OR "crowd sensing" OR "participatory sensing" OR "mobile sensor node" OR "low cost sensor" OR "citizen science"))
PubMed	air quality AND (sensor network) OR wearable sens*) OR crowd sensing) OR participatory sensing) OR mobile sensor node) OR low cost sensor) OR citizen science)
Scopus	(TITLE-ABS-KEY ("air quality")) AND (TITLE-ABS-KEY ("sensor network" OR "wearable sens*" OR "crowd sensing" OR "participatory sensing" OR "mobile sensor node" OR "low cost sensor" OR "citizen science"))

Table 1. Query used for the search in three different databases: ISI Web of Knowledge, PubMed and Scopus.

We found a total of 56 papers in ISI Web of Knowledge, 65 papers in PubMed and 122 papers in Scopus (last search: 19/12/2016). Papers were detected and then selected following chosen inclusion and exclusion criteria. First, we decided not to use time filters regarding year of publications and to consider only scientific papers written in the English language. For this reason, data concerning conference proceedings were not reported. Other exclusion criteria considered concerned the kind of the study: we decided to consider only studies conducted in the field with mobile monitors (e.g., mobile monitors used in fixed locations were not considered). Moreover, only "miniaturized" sensors (i.e., with the greater dimension smaller than 20 cm) were selected. Notably, the proposed dimensional criteria were not confirmed in the scientific literature, but it was an arbitrary subdivision with a certain level of subjective decisions. Unfortunately, it was not possible to make a

selection according to the price of the sensor because papers did not report costs and because several instruments were developed by universities so prices would not be available in any case. Finally, since several miniaturized sensors able to measure different environmental parameters (e.g., temperature, relative humidity, noise, pollutants) are available on the market, we considered only papers concerning environmental pollutants, with no other restrictions about kind of pollutant. After a selection in accordance with the aforementioned inclusion/exclusion criteria, only 13 papers were found to be suitable for the present review. Therefore, to provide an overview as accurate as possible about studies that used miniaturized monitors in the field, we decided to extend the number of papers considering also those articles reported as references in the 13 selected studies. The reported literature was consequently analyzed following the same inclusion/exclusion criteria. Four papers were added in this way, and a total of 17 papers was finally reported in the present review A. flowchart of the literature research and review process (modified from Moher et al [35]) is reported in Figure 1.

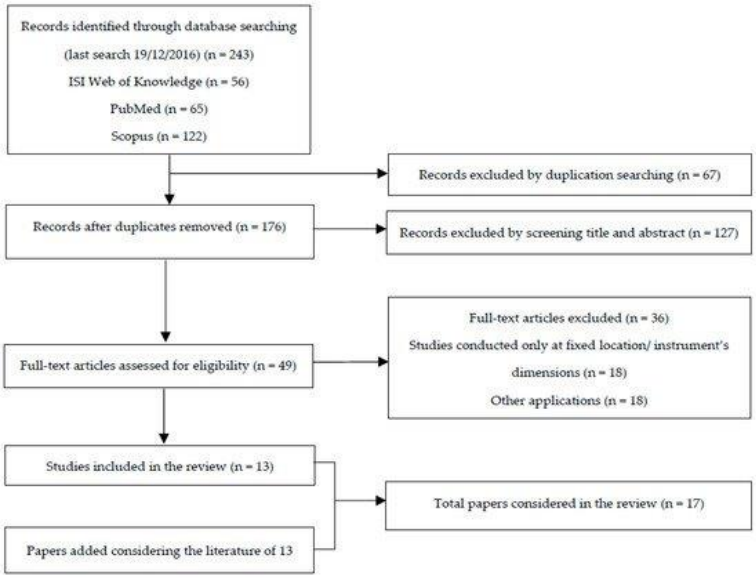

Figure 1. Flowchart of literature searched and reviewed (modified from Moher et al. [35]).

2.3. Results and Discussion

The next paragraphs report studies relative to campaigns in the field that used miniaturized sensors for PM and gas in air quality monitoring campaign and instrument validation. We also report technical and instrumental innovations (GPS, wireless communication and web/smartphone applications), the use of which is becoming increasingly common. As evidence, the scientific community is increasingly attentive to these topics and the number of scientific studies regarding these matters is rising.

The number of papers analyzed in this work, total raw results and selection by publication year is reported in Table 2. There is a positive trend concerning the number of articles per publication year, which could be interpreted as an increased scientific interest in the topic.

Publication Year	Sum of Papers	Papers Considered in This Review
(1977)	(1)	(0)
2004	1	0
2005	0	0
2006	5	0
2007	0	0
2008	12	1
2009	6	1
2010	11	1
2011	12	2
2012	17	3
2013	26	0
2014	39	3
2015	57	3
2016	56	3

Table 2. Number of papers analyzed per publication year. The sum of all papers resulting from raw research within ISI Web of Knowledge, PubMed and Scopus (inclusion/exclusion criteria not considered) were reported in the second column. The number of papers selected and present in this work was reported in the third column. The only paper published before 2004 is reported in brackets.

2.3.1. Particulate Matter Sensors

The present subsection is focused on studies regarding particulate matter (PM) sensors [3,5,31,36,37]. Sensor characteristics are reported in Table 3, whereas summary information about the experimental design are reported in the supplemental material (Tables S1 and S2).

Numeration	Study	Pollutant	Sensor/Instrument	Dimensions and Weight	Measuring Principle	Operational Range	Sensitivity
37	Al- Ali et al., 2010	CO NO_2 SO_2	All sensors: Alphasense	n.a.	*All senors: electrochemical*	CO: 0 - 1000 ppm NO_2: 0 - 20 ppm SO_2: 0 - 20 ppm	CO: <1.5 ppm NO_2: 0.02 ppm SO_2: <0.1 ppm
28	Castell et al., 2015	O_3 CO CO_2 NO NO_2 SO_2	All sensors: Alphasense (Series B)	*All sensors: 32 mm (sensor diameter)*	All sensors: electrochemical	All sensors: concentration typically found in urban environment	n.a.
44	Chen et al., 2012	VOCs	n.a.	Not much larger than common smartphone (< 300 g)	n.a.	4 ppb - 1000 ppb	Resolution < 4 ppb
39	Eisenman et al., 2009	CO_2	7001 CO_2/Temperature monitor (Telaire)	*150x70 mm*	*Absorption Infrared*	*0-2500 ppm or 0-4000 ppm*	*± 1 ppm*
40	Fu et al., 2012	CO_2	K-30 Probe (CO_2 meter)	*80x60x30 mm*	*Non-Dispersive Infrared (NDIR)*	n.a.	n.a.
41	Gall et al., 2016	CO_2	CM-0018 (CO_2 Meter)	*146x91x33 mm*	*Non-Dispersive Infrared (NDIR)*	*0-10000 ppm*	n.a.
38	Guevara et al., 2012	CO	MQ-7 Carmon Monoxide Semiconductor	*16 mm (sensor diameter)*	*Semiconductor*	*10-10000 ppm*	n.a.
29	Hasenfratz et al., 2015	UFP O_3 CO NO_2	UFP: DiSCsMini (Matter Aerosol) O_3: MiCS-OZ-14 (e2v) CO: CO-B4 (Alphasense) NO_2: NO_2-B4 (Alphasense)	UFP: 40x90x180 mm (700 g) O_3: n.a. *CO: 32 mm (sensor's diameter)* *NO_2: 32 mm (sensor diameter)*	*UFP: unipolar charger* O_3: semiconductor CO: electrochemical NO_2: electrochemical	UFP: 10^3 - 10^6 particle/cm^3 *O_3: 20-200 ppb* CO: n.a. NO_2: n.a.	n.a.
42	Hu et al., 2011	CO_2	H-550 EV	*38x32x12 mm (sensor)*	*Non-Dispersive Infrared (NDIR)*	0 - 5000 ppm	n.a.
43	Kanjo et al., 2008	CO	n.a.	n.a.	n.a.	n.a.	n.a.
9	Lo Re et al., 2014	O_3 CO CO_2 NO_2	n.a.	n.a.	n.a.	n.a.	n.a.

6	Mead et al., 2013	CO NO NO_2	CO: CO-AF (Alphasense) NO: NO-A1 (Alphasense) NO_2: NO_2-A1 (Alphasense)	All sensors: 183x95x35 mm (445 g)	All sensors: Electrochemical	n.a.	n.a.
35	Mueller et al., 2016	UFP O_3 CO	UFP: DiSCsMini (Matter Aerosol) *O_3: MiCS-OZ-14 (e2v)* *CO: CO-B4 (Alphasense)*	UFP: 40x90x180 mm O_3: n.a. *CO: 32 mm (sensor diameter)*	UFP: Unipolar diffusion charger *O_3: electrochemical* *CO: electrochemical*	UFP: 10^3 - 10^6 particle/cm^3 *O_3: 20-200 ppb* CO: n.a.	n.a.
45	Negi et al., 2011	Hydrocarbon and acid	n.a.	Dimension comparable with a common smartphone (< 250 g)	n.a.	n.a.	n.a.
7	Pokrić et al., 2015	PM O_3 CO CO_2 NO	PM: OPC-N1 (Alphasense) O_3: O_3-B4 (Alphasense) CO: CO-B4 (Alphasense) CO_2: CO_2-IRC-AT (Alphasense) NO: NO-B4 (Alphasense)	*PM: n.a.* *O_3: 32 mm* *CO: 32 mm* *CO_2: 20 mm* *NO: 32 mm*	O_3: electrochemical CO: electrochemical CO_2: infrared NO: electrochemical	O_3: 0 - 2 ppm CO: 0 - 50 ppm CO_2: 0 - 5000 ppm NO: 0 - 20 ppm	n.a.
3	Velasco et al., 2016	PM_{10} O_3	GPY21010AU0F (Sharp) MiCS-2610 (e2v Technologies Ltd)	*PM_{10}: 46x30x17 mm* *O_3: 9 mm*	PM_{10}: Light scattering O_3: n.a.	PM_{10}:0 - 0.5 mg/m^3 O_3:10 - 1000 ppb	PM_{10}: 5 V (0.1 mg/m^3) O_3: 2-4 ohm
36	Wong et al., 2014	$PM_{2.5}$	GP2Y1010AU0F (Sharp)	89x113 mm	Light scattering	n.a.	n.a.

Table 3. Particulate and gas sensor characteristics as reported in the selected papers. Data that were not directly acquired from the paper are reported in italics. In the case of missing data within the reference papers, data were acquired from the literature cited in bibliography or from external sources (retailer's site).

Regarding the experimental design of the selected studies, miniaturized sensors were often placed on public and private transport devices such as vehicles, bicycles, and public transportation, but only for a limited amount of time, probably due to the battery life problems, commonly related to PM sensors. In such cases, the use of a secondary power supply with customized voltage regulation (and/or supplemental batteries) can contribute to extend the duration of monitoring, even if this can significantly affect portability of the instruments. Velasco et al. [3] conducted a study focused on the use of a high-portability mobile sensor network system, with easy data acquisition and maintenance. The sensor network included commercial PM_{10} and O_3 sensors. In this study, different tests were carried out in various locations: tests were performed in controlled environments (indoor/outdoor locations) and during different field campaigns (e.g., urban/rural locations) in mobile and static tests. The results arising from mobile tests (the system was mounted on a bicycle) showed that measurements did not suffer significant variation compared to the measurements made with instruments used as fixed monitors. Additionally, during long-run mobility tests, the prolonged use of the device did not reveal relevant problems. In conclusion, the authors asserted that measurements carried out with the use of a mobile sensor network are less accurate than reference instruments used at fixed locations by the Regional Environmental Agency. However, this kind of sensor has the potential to provide insight about air pollution and to complement data acquired from official and reference monitoring stations. The authors also reported and highlighted how mobile wireless systems may be able to improve spatial and temporal resolution, thus improving exposure assessment studies. Other authors [37] conducted field tests in different environments, measuring $PM_{2.5}$ concentration, both indoors and outdoors, on a bus journey and during walking. The results arising from field tests showed that the sensor provided a good performance for immediate measurement in living environments. Moreover, a comparison between instruments used and the reference instruments used at fixed locations by the Hong Kong Environmental Protection Department showed that $PM_{2.5}$ data were characterized by a reasonable accuracy. As a further result, the authors considered that an extensive use of this kind of sensor could contribute to

raising the public awareness regarding air quality in microenvironments. Another way to assess the human exposure to air pollutants is through the use and interpretation of pollutant maps or models, which can also be developed on the basis of concentration results obtained by miniaturized sensors. For example, Hasenfratz et al. and Mueller et al. [31,36] reported results from a two-year campaign conducted in Zurich, measuring ultrafine particles (UFP), O_3, CO and NO_2. In this campaign, a land-use regression model was developed to create maps of air pollutant concentrations with high temporal and spatial resolution, monitoring the pollutant concentrations using 10 sensor nodes installed on top of public transport vehicles. The results showed that despite the accuracy of the obtained maps being influenced by the relatively small number of measurements, these maps could be useful for a detailed exposure assessment because of their high spatial and temporal resolution. Finally, [5] described an innovative approach for the integration of physical and digital worlds through aggregation of Internet of Things (IoT), demonstrating how IoT and Augmented Reality (AR) could provide a new way for sharing data. Additionally, in this case, the authors thought that this new approach would promote environmental issues, increasing interaction between general population and environmental data.

2.3.2. Gas Sensors

A larger number of papers concerning gas sensor monitoring were found. Sensor characteristics are reported in Table 3, while a study summary is reported in the supplemental material (Tables S1 and S2). Most of the selected papers were related to the monitoring of CO [5,6,9,29,31,36,38,39], CO_2 [5,9,29,40,41,42,43,44], O_3 [3,5,9,29,31,36] and NO_2 [6,9,29,31,38], even though other pollutants were sometimes considered, such as NO [5,6,29], SO_2 [29,38]; VOC [45], and hydrocarbons and acids [46]. Several studies reported results regarding wearable sensors provided to pedestrians. For example, Chen et al. [45] presented a wearable VOC sensor able to provide information about indoor and outdoor concentrations of selected pollutants. In this study, the sensor was validated under real-world conditions and across different scenarios (i.e., different works and applications). The results regarding field tests demonstrated the goodness of data obtained and the

ability of this kind of sensor to greatly improve knowledge of personal exposure to environmental contaminants. In particular, the VOC sensor performance was validated using gas chromatography and selected ion flow tube mass spectrometry as reference methods, showing accuracy higher than 81%. Moreover, a comparison conducted outdoors showed results with accuracy values higher than 84%, demonstrating the capability of the tested sensor to provide reliable measurements in outdoor environments. Similar results concerning the development and testing of wearable devices for hydrocarbons and acids were reported by Negi et al. [46]. Additionally, in this case, portable monitors provided accurate and real-time measurements. The validation of sensor performance was carried out in different scenarios, involving operators from different working fields and using GC/MS (gas chromatography/mass spectrometry as a reference method. The authors reported comparison data characterized by a high degree of correlation and with a relative error of 2% ($r^2 = 0.99$). The authors also highlighted that wearable sensors can be used for remotely detecting the risk of potential toxic exposure, helping to better understand the nature of the exposure. The potential of miniaturized sensor networks in the urban environment and their ability to provide data at an adequate scale has also been highlighted by Mead et al. [6]. In this study, the authors performed measurements (concerning NO, NO_2 and CO concentrations) via portable devices (held by pedestrians and cyclists) and via static stations, across different urban environments. Moreover, laboratory tests and validations were carried out. The authors remarked first the inability of fixed stations to fully characterize the urban environment and the necessity to use environmental networks characterized by high spatial and temporal resolution in this kind of heterogeneous environment. Second, Mead and collaborators showed that air quality sensor networks are now feasible for widespread use for monitoring at an environmental level, complementing other measurement methods. Other authors [42,44] conducted analogous monitoring campaigns and field tests, reporting similar results. Personal and continuous CO_2 monitoring was used by Gall et al. [42] in both indoor and outdoor campaigns, to understand levels and influencing factors in personal exposure to the selected pollutant. Kanjo et al. [44] provided an evaluation of the CO sensor in a school environment,

demonstrating the feasibility of an extensive environmental monitoring with the use of mobile sensing devices.

As for PM sensors, several studies considered the use of gas sensors on private or public transports. For example, Lo Re et al., Al-Ali et al. and Guevara et al. [9,38,39] placed environmental sensors on public transport and reported similar results, namely, that mobile monitors were characterized by good performance. The authors also highlighted how vehicular sensor networks must be considered as an innovative approach to environmental monitors. In addition to the public transport support, other kinds of transport have been used in reported studies. In a study conducted by Eisenman and collaborators [40] monitors were presented and tested during bicycle trips on different routes while test and field campaigns with positioning of monitors on different transports were reported by different authors [29,41,43]. Other studies, already reported in the previous paragraph referring to particulate matter sensors, refer also to gas monitoring [3,5,31,36] and, for this reason, they have not been reported in this paragraph.

2.3.3. Accessibility of Data

At present, the way to communicate and share scientific data is changing. In the opinion of the authors, three implementations in personal exposure assessment are particularly interesting and often reported in selected studies: (i) Integration of personal monitoring with Global Positioning System (GPS); (ii) Communication and data transfer via wireless; (iii) Data communication via web or smartphone applications. The simultaneous use of these implementations could help the citizen-scientist to have more awareness about atmospheric pollution, to share data and to try to mitigate their exposure conditions, raising community awareness about air quality [5,39]. Furthermore, sensors coupled with an efficient delivery of sensed information could provide benefits to society, improving emergency response [39]. Moreover, the simultaneous use of miniaturized sensors and, in particular, GPS can become a great support to different and innovative studies (e.g., innovative approach in the epidemiological research). These new and innovative support elements (wireless, GPS and web/smartphone applications) and their important contribution in exposure assessment studies

will be further discussed below. A first and general overview of their use in the considered papers is reported in Table 4.

Study	GPS	Wireless	Application
Al-Ali et al., 2010 [37]	Yes	Yes	Yes
Castell et al., 2015 [28]	Yes	Yes	Yes
Chen et al., 2012 [44]	Yes	Yes	Yes
Eisenman et al., 2009 [39]	Yes	Yes	Yes
Fu et al., 2012 [40]	Yes	Yes	Yes
Gall et al., 2016 [41]	No	No	No
Guevara et al., 2012 [38]	Yes	Yes	Yes
Hasenfratz et al., 2015 [29]	Yes	Yes	No
Hu et al., 2011 [42]	Yes	Yes	No
Kanjo et al., 2008 [43]	Yes	Yes	Yes
Lo Re et al., 2014 [9]	Yes	Yes	No
Mead et al., 2013 [6]	Yes	No	No
Mueller et al., 2016 [35]	Yes	No	No
Negi et al., 2011 [45]	No	Yes	Yes
Pokrić et al., 2015 [5]	Yes	Yes	Yes
Velasco et al., 2016 [3]	Yes	Yes	No
Wong et al., 2014 [36]	Yes	Yes	Yes

Table 4. Presence or absence of GPS, wireless and web/smartphone application technologies in reported studies.

At present, geo-referencing of data is becoming increasingly important, due to the possibility of understanding pollution patterns and pollution hotspots. Furthermore, the use of geo-referred data may define the human exposure more accurately. Fifteen articles out of the total 17 studies considered in the present review (equal to 88% of the total) used a GPS in the study protocol. Different kinds of GPS have been used, both connected to a mobile phone or as separate instruments. Characteristics (e.g., acquisition/navigation/tracking sensitivity, hot and cold start time, positional accuracy error and speed accuracy) may obviously change, and even provided data can be different [3]. Clearly,

the fundamental data are related to the position (normally given as longitude and latitude), but other information can be supplied such as data validity checksum, velocity, heading, date, magnetic variation and direction, mode and checksum [38]. Other than coordinates, other kinds of information can be derived from GPS system results. For example, [41] used an activity classification model to determine the transportation mode (e.g., staying position, walking, driving). In this case, the system used results from activity classification as inputs to the emission factor model, to generate estimates regarding human exposure. In several studies, the main problem encountered in the use of GPS was closely related to the number and position of GPSs and related satellites. Position accuracy could not be very good since the GPS signal could be blocked by buildings or when the GPS signal results were totally blocked due to the overhead cover [37]. GPS also seems not always to be functional in some common environments such as among tall buildings or under dense overgrowth (tree canopy) [40].

Regarding communication and data transfer via wireless, 14 articles out of 17 (82% of the total) and 10 articles of 17 (59% of the total) were endowed, respectively, with wireless communication mode and smartphone/web application. Few studies used smartphone connected to pollutant sensors to collect data, but this innovative approach could be very useful. Kanjo et al. [44] highlighted three advantages of using a mobile phone: (i) mobile phones are carried around by a large percentage of population; (ii) the mobile phones can be used to process, store and transfer other kinds of data (such as photos and messages), and (iii) collection using mobile phones should be more energy efficient, because data are sent directly to the phone bypassing the entire sensor network. Moreover, a wireless network may be created, with the aim of providing real-time information about environmental and human health hazards [45] and, using smartphone and associated wireless technology, data can be transferred and shared more easily, and exposure data can be obtained remotely [46]. Furthermore, several authors highlighted how Wireless Sensor Networks (WSNs) can simplify the use of sensors. WSNs can eliminate barriers related to installation, remove connectors and increase scalability. Guevara et al. [39] showed typical obstacles and barriers in an Intelligent Vehicle Network (IVN) system: bundles of lead wires are subject

to breakage, and they represent a significant installation and long-term maintenance cost. Further problems reported by authors referred to the scalability of the sensors, which is limited by vendor-specific protocols. Analysis of selected papers shows that different kinds of communication protocols can be used for personal monitoring purposes. Standards such as 802.15.1 (Bluetooth), 802.15.4 (ZigBee), 802.11 (Wi-Fi), 3G/GPRS, GSM/GPRS, Bluetooth Low Energy (BLE), standard IEEE 1451 family, 802.15.4 (Intra-BAN) and Radio Frequency (RF) communication are commonly adopted as viable wireless interfaces [3,37,39]. However, most of the selected studies adopted the Bluetooth module for wireless communications, probably because Bluetooth has been recognized as an effective mode for short range data communication due to its relatively low power consumption and low-cost [37]. Obviously, a wireless communication module is necessary for the development and the use of web or smartphone applications, due to the type of real-time data. Data returned by the web or smartphone applications are of different kinds: normally the applications characterized by a user-friendly interface show data concerning date, time, pollutant monitoring, position and concentration results. Different applications also have a notification service that warns if the environmental readings exceed threshold values. Data summary, elaborations, precautionary measures to adopt and download functions are also commonly provided by the system. Often, applications are also able to provide data concerning the status of the monitor (e.g., pump, valves and battery life) while in other applications, users can select different application scenarios (e.g., industrial solvent, motor vehicle emission).

2.3.4. Impact on the Assessment of Human Exposure

We observed that both traditional and new miniaturized monitoring devices present advantages, especially related to the capability of providing continuous and real-time data characterized by high spatial and temporal resolution. Traditional fixed-site monitoring stations provide data characterized by good quality but, due to high costs and several position problems, the number of these stations is reduced and, consequently, data provided lacks an adequate spatial coverage. New miniaturized and low-cost

devices generally have worse data quality (for the time being), but they are able, also thanks to the new paradigm of monitoring "citizen-science", to have higher spatial and temporal resolution, which is fundamental in complex environments such as urban environments. The aim of this review was not to evaluate the performance of miniaturized sensors, even if, after a preliminary analysis, they seemed to be less accurate as compared with reference methods. Moreover, a comparison between sensor performance was not possible because the considered studies used different sensors and sampling protocols, across various scenarios and, furthermore, only a few papers reported data concerning the comparison between miniaturized sensors and reference methods. For this reason, the evaluation of miniaturized sensor performances should be considered in future specific studies, to establish appropriate methods for evaluation and validation, as well as to provide adequate operating procedures to ensure the obtaining of accurate data. Moreover, performance and reliability of these sensors have yet to be fully evaluated, especially for long-term measurements [26]. Particularly, performance in areas with poor air quality, cross interferences and influences of temperature and relative humidity should be evaluated [26,47]. In this regard, the intercomparison and the performance evaluation (especially as regards the field performance) of miniaturized sensors is necessary, because if sensor performance results are to be validated (e.g., via comparison with reference methods), these miniaturized sensors could be used as support to fixed air quality monitoring networks to achieve a broader spatial coverage, to provide a more representative characterization of exposure [48]. However, despite this possible lack in their accuracy, and due to the abovementioned advantages, miniaturized monitors are becoming increasingly important in community and individual exposure assessment studies and can potentially be used in different application, such as outdoor/indoor air pollution monitoring and community/individual exposure [26]. In this review, we also wanted to emphasize the increasingly innovative role of miniaturized pollutant sensors and their different applications. We first found how, at present, different miniaturized sensing devices are available on the market, and how improvements in sensor technologies are currently emerging. Overall, there is a need to develop

personal environmental monitoring systems, especially integrating measurement devices, mobile application on smartphones and GPS data [37]. Second, we found how miniaturized sensors could support or become a new way for human exposure assessment, especially due to their capability to measure air pollutant concentrations at adequate spatial and temporal scale and to their great versatility (such as the ability to adapt to different experimental designs). Reviewed papers reported that measurements conducted at high spatial and temporal resolution could contribute to scientific understanding and address economic, policy and regulatory issues, as well as air quality and human exposure [6]. All these positive features may lead to the effective use of these sensors in different environmental and human health fields. Moreover, when sensors are used by the general population, they can be useful to report data relative to an immediate surrounding or to a selected location, and this knowledge will help citizens make the decision regarding quality of life [29]. In particular, if connected in networks, these sensors can provide data representative of high spatial and temporal variability in pollutant concentrations for a wider area, unlike traditional monitoring stations [49]. Moreover, Micro Sensing Units (MSUs) can gather high spatial and temporal resolution data from numerous nodes [2], especially if they are connected by a Wireless Distribute Environmental Sensor Network (WDESN).

An example of this use is the "Citizen Science". Citizen-scientists are described as citizens involved in collecting, categorizing, transcribing or analyzing scientific data [26,47,50]. Citizen-science is presently considered an important implementation to scientific studies, especially because it can increase the spatial coverage and time resolution data, also thanks to the increasing use of personal devices such as smartphones [1]. According to the "Participatory Sensing" (PS) definition, users can acquire and make available to other people data of interest, such as data regarding air quality, pollutant concentrations (e.g., environmental data, weather and traffic information, also related to geographical position and time of data collection, intelligent transportation and route planning) [12,13,51]. Data are subsequently reported to a central server through wireless communication. Data analyzed and processed by the server are presented and displayed on participant

smartphones in different forms (e.g., graphical representation or maps) [12]. This innovative approach might be able to satisfy the increasing interest in mobile air quality sensor network applications, as noticed by different studies [4] and provide increased coverage of monitored areas (in time and space), in addition to facilitating learning and increasing citizen awareness of environmental issues [10].

In addition, the importance of Internet in the environmental research field should be emphasized. Traditional dissemination channels such as television and radio contribute to a common sense but often do not provide update data, and even data are not directly accessible by users [32]. With progress in mobile, miniaturized and on-line technologies, more environmental data can be spread and characterized by higher spatial and temporal resolution. In this way, users can receive personalized information (in terms of time, area of interest and kind of environmental data request). At present, several initiatives promote tests of environmental sensor devices that are coupled with smartphones and that can connect to web portals [52]. Then, principal pro and cons of Miniaturized Monitors (MMs) which resulted from this review are reported in Table 5.

Finally, we have chosen not to report data relative to pollutant sensors used at fixed stations, but it is important to remember their importance in air quality measurement and exposure assessment, especially if they are connected in a network of sensors. As reported by Castell et al., 2015 [29], the combination of mobile sensors and fixed stations might be able to foster the development of spatial models, helping to create a new approach to the human exposure assessment. Finally, we found three different innovations that have the potential to significantly improve human exposure assessment studies. These innovations are related to the integration of GPS, wireless communication mode and smartphone or web applications.

Disadvantages
MMs seemed to be less accurate as compared with reference methods
Performance and reliability of MMs have yet to be fully evaluated
Advantages
MMs have the capability of providing continuous and real-time data
Data acquired via MMs are characterized by high spatial resolution
Data acquired via MMs are characterized by high temporal resolution
MMs can potentially be used in different application (indoor/outdoor air quality monitoring; community/individual exposure)
MMs can adapt to different experimental designs

Table 5. Disadvantages and advantages related to the use of MMs.

2.4. Conclusions

Due to their characteristics, miniaturized sensors for the measurements of airborne gaseous pollutants and PM could provide a significant enhancement in exposure assessment studies, increasing the spatial and temporal resolution of human exposure data and incrementing the awareness and the data-sharing process. The articles that were reviewed also showed that miniaturized sensors are particularly versatile and could be applied in studies with different experimental design, helping to ensure high quality and in high-sensitivity exposure assessments (particularly in participatory and ubiquitous monitoring campaigns), even though studies regarding their accuracy or the comparison between miniaturized sensors and reference methods still seem to be sparse.

Supplementary Materials

Table S1. Studies' characteristics. Data that were not directly acquired from the paper are reported in italics. In the case of missing data within the reference papers, data were acquired from the literature cited in bibliography or from external sources (retailer's site).

Numeration	Study	Monitoring Site	Period	Pollutants	Mobile/Stationary	Indoor/Outdoor	Dimension and Weight	Wireless	GPS	Application	Power	Measurement Range	Response Time
[37]	Al-Ali et al., 2010	Sharjah	n.a.	CO NO_2 SO_2	Mobile	Outdoor	n.a.	Yes	Yes	Yes	n.a.	CO: 0 - 1000 ppm NO_2: 0 - 20 ppm SO_2: 0 - 20 ppm	CO <25s NO <60s SO_2 <25s
[28]	Castell et al., 2015	Oslo	n.a.	O_3 CO CO_2 NO NO_2 SO_2	Mobile	Outdoor	*32 mm (sensor diameter)*	Yes	Yes	Yes	Platform will be mounted on an electrical bicycle and the power of the platform will be supplied from the	Concentrations typically found in urban environment	*O_3 <45s* *CO <25s* *CO_2 n.a.* *NO <45s* *NO_2 <60s* *SO_2 <30s*

											bicycle battery			
[44]	Chen et al., 2012	Phoenix San Diego	n.a.	VOC	Mobile	Indoor Outdoor	Not much larger than a common smartphone (<300 g)	Yes	Yes	Yes	10 hours	Environmental: 0 - 1 ppm Industrial: 1 - 1000 ppm	Raw data: 1 s per measurement Calibrated concentration: 3 min per data point
[39]	Eisenman et al., 2009	Hannover	August 2006 - August 2007	CO_2	Mobile	Outdoor	*150x70 mm*	Yes	Yes	Yes	*10 hours (4 AA batteries)*	*0-2500 ppm or 0-4000 ppm*	*< 60s*
[40]	Fu et al., 2012	Singapore	n.a.	CO_2	Mobile Stationary	Outdoor	*80x60x30 mm*	Yes	Yes	Yes	n.a.	n.a.	*Warm up time: <60s*
[41]	Gall et al., 2016	Singapore	May - December 2015	CO_2	Mobile	Indoor Outdoor	*146x91x33 mm*	No	No	No	*AA Batteries*	*0-10000 ppm*	1 min
[38]	Guevara et al., 2012	Asuncion	n.a.	CO	Mobile	Outdoor	*16 mm (sensor diameter)*	Yes	Yes	Yes	n.a.	*10-10000 ppm*	n.a.
[29]	Hasenfratz et al., 2015	Zurich	April 2012 - April 2014	UFP O_3 CO NO_2	Mobile	Outdoor	UFP: 40x90x180 mm (700g) O_3: n.a. *CO: 32 mm (sensor diameter)* *NO_2: 32 mm (sensor diameter)*	Yes	Yes	No	UFP: 20 hours	UFP: 10^3 - 10^6 particles/cm^3	n.a.
[42]	Hu et al., 2011	Hsinchu	n.a.	CO_2	Mobile	Indoor Outdoor	*38x32x12 mm*	Yes	Yes	No	n.a.	0-5000 ppm	30 s

[43]	Kanjo et al., 2008	Bristol	n.a.	CO Noise	Mobile	Indoor Outdoor	n.a.	Bluetooth	Yes	Yes	n.a.	n.a.	n.a.
[9]	Lo Re et al., 2014	Palermo	n.a.	O_3 CO CO_2 NO_2	Mobile	Outdoor	n.a.	Yes	Yes	No	n.a.	n.a.	n.a.
[6]	Mead et al., 2013	Cambridge London Cranfield Valencia Kuala Lampur Lagos	2010	CO NO NO_2	Mobile Stationary	Outdoor	183x95x35 mm	No	Yes	No	14 hours	n.a.	n.a.
[35]	Mueller et al., 2016	Zurich	July - September 2013 December 2013 - February 2014	UFP O_3 CO	Mobile Stationary	Outdoor	UFP: 4x9x18 cm (700g) O_3: n.a. *CO: 32 mm (sensor diameter)*	No	Yes	No	*UFP: 20 h*	UFP: 10^3 - 10^6 particles/cm^3	n.a.
[45]	Negi et al., 2011	n.a.	n.a.	Hydrocarbons and acid	Mobile	Indoor Outdoor	Size comparable with a smart cell phone (<250 g)	Yes Bluetooth	No	Yes	9h	n.a.	n.a.
[5]	Pokrić et al., 2015	n.a.	n.a.	PM_1 $PM_{2.5}$ PM_{10} O_3 CO CO_2	Mobile Stationary	Indoor Outdoor	n.a.	Yes	Yes	Yes	n.a.	O_3: 0 - 2 ppm CO: 0 - 50 ppm CO_2: 0 - 5000 ppm NO: 0 - 20	n.a.

				NO NO_2								ppm NO_2: 0 - 20 ppm	
[3]	Velasco et al., 2016	Turin	n.a.	PM_{10} O_3	Mobile	Outdoor	*PM_{10}: 46x30x17 mm* *O_3: 9mm*	Yes	Yes	No	n.a.	PM_{10}: 0 - 0.5 mg/m^3 O_3: 10 - 1000 ppb	30 s
[36]	Wong et al., 2014	Hong - Kong	April 2014	$PM_{2.5}$	Mobile	Indoor Outdoor	113x89 mm	Bluetooth	Yes	Yes	30 hours	n.a.	1 s

Table S2. Summary of selected papers. Aim of the study, methods and principal results are reported.

Numeration	Study	Aim of the Study	Methods	Principal Results
[37]	Al-Ali et al., 2010	Design, implementation and test of a wireless distributed mobile air pollution monitoring system	The system was placed on a university bus	Data transmitted and available on Internet shows pollution level and their conformance to local air quality standards
[28]	Castell et al., 2015	Present a new approach for the development of information chain	Measurement were conducted outdoor, using mobile vehicles (e.g. bicycles, bus)	Main results not reported but authors, demonstrating the feasibility of mobile sensor network explains how this kind of data can contribute to understanding about air quality issue
[44]	Chen et al., 2012	Present a wearable sensor able to provide improvement in understanding of indoor and outdoor personal exposure assessment to VOC Validation of VOC sensor in real-word environments and in different scenarios	Validation of VOC sensor's performance using Gas Chromatography and Selected Ion Flow Tube e mass Spectrometry reference Methods in different environments (indoor/outdoor, traffic…) and scenarios (e.g. different work, paint remodeling…) Calibration and validation of the VOC sensor in real-word environments Different tests were conducted: fields tests, inter laboratory tests and validation with commercial instruments	Field test validated the instrument's performance Field test demonstrate high temporal and spatial pollutants information provided by this innovative monitor The sensor correlates well or outperforms similar VOC sensor The sensor provides an accuracy higher than 81% The sensor may be able to improve knowledge about personal exposure, protecting human health

[39]	Eisenman et al., 2009	Authors presents design, implementation and evaluation of a mobile sensing system	Reported implementation were tested during bicycle trips on different routes	The study reported is the first to quantify cyclist experience (personal performance and shared sampling)
[40]	Fu et al., 2012	Reports design of environmental monitoring system and related critical issue	Light-weight and low-cost sensors were installed on mobile vehicles (e.g. cars, scooters, bicycle) and placed in outdoor fixed stations	Three critical issues related design of environmental monitoring have been reported: efficiency of sensors, coverage of monitoring area, validity of sensed data
[41]	Gall et al., 2016	An exposure study was conducted, in order to understand levels, dynamics and influencing factors of personal exposure to CO2	Personal, portable and continuous monitoring characterized by high time resolution were used for indoor and outdoor campaign	Some determinants of CO_2 exposure were found
[38]	Guevara et al., 2014	Describes design and implementation of an environmental wireless sensor network The study reports the development of the sensor network and results obtained	Sensor network was tested following selected routes of public transports	Environmental monitors were characterized by good performance
[29]	Hasenfratz et al., 2015	Development of a land-use regression model in order to create pollution maps, characterized by high spatial resolution	Measurement carried out on the top of public vehicles	Accuracy of pollution maps (characterized by sub-weekly temporal resolution) suffers from the reduced number of measurement available Maps generate with this new approach are characterized by higher spatial and temporal resolution and are useful to general population as well environmental scientist and epidemiologist
[42]	Hu et al., 2011	Propose a vehicular sensor network architecture Development of a Zig-Bee based prototype in order to monitor carbon dioxide in urban areas	Measurement conducted outdoor and indoor, via vehicular sensor node (characterized by internal and external sensors)	Reported results are related to simulation data and prototype experience
[43]	Kanjo et al., 2008	Describes a monitor system able to monitors using mobile phones	Evaluation of sensor in a school environment	Authors demonstrate the feasibility of developing an environmental sensing monitors using mobile sensing devices

[9]	Lo Re et al., 2014	Show and discuss different approach to environmental monitoring	Use of mobile monitor device as implementation of vehicular sensor network Monitors used outdoor on public busses	Vehicular sensor network is an innovative approach to environmental monitoring and it is considered as an interesting development in wireless and mobile networking The main advantage of this approach is relative to the economy and to the simplicity of the system
[6]	Mead et al., 2013	Provide evidence about performance of electrochemical sensor network	Measurement via portable devices held by pedestrian and cyclist/drivers and via static devices in outdoor Different test carried out in urban environments Laboratory test and validation carried out using standard gas	The study showed that urban environment cannot fully characterized using static networks Networks characterized by high spatial and temporal resolution are required in urban air quality measurements In field measurement, the sensor baseline signal depends on environmental conditions (temperature and relative humidity) Sensor operate without significant gain attenuation over long period The work demonstrate the potential of miniaturized and low-cost sensor network system utilized in urban environment and its ability to provide data at appropriate scale
[35]	Mueller et al., 2016	Show performance of electrochemical sensor in urban environment Present a method to modelling pollutant concentrations in urban environments relying on georeferred data acquired via mobile sensor network	Measurements were carried out both with stationary and mobile devices Mobile monitors were installed on the roof of public transports Model validation with data from fixed stations	Sensor used in monitor test showed low noise and high linearity The modelling approach proposed reasonably predict the main features of the investigated pollutant
[45]	Negi et al., 2011	Paper reports development and test of a wearable monitor	Validation of function and performance in different scenarios, involving operator from different working fields Sensor validation was carried out with chromatography-mass spectrometer (GC-MS) and performances were compared with commercial instrument	Monitors provide accurate and real-time measurement and it is immune to environmental changes (e.g. humidity, temperature…)

[5]	Pokrić et al., 2015	Describes an approach to integration of physical and digital worlds Demonstrate how Internet of Things (IoT) and Augmented Reality (AR) could provide a new way to present and share digital information in real world	Different kind of application in real-word (stationary/mobile and indoor/outdoor)	Several users find that this new approach promotes environmental issue and that the game proposed was educational an entertaining
[3]	Velasco et al., 2016	The paper describes a mobile wireless sensor network with the aim to complement existing air quality monitoring system	PM10 and O3 sensors were tested in controlled environments (outdoor/indoor) and during different on-field campaigns (urban and rural locations), principally using bike sharing support and static stations	This system, due to its high portability, may be able to improve spatial resolution and resolution of data Test conducted on field showed that sensors are able to provide accurate data, under adequate calibration and maintenance conditions Measurement conducted via proposed sensor were less accurate than reference methods
[36]	Wong et al., 2014	Development and evaluation of an Integrated Environmental Monitoring System	Field test conducted in different environments and locations both outdoor (e.g. road repair work, bus stop) and indoor	The system illustrated worked well during field test and provide an important platform, raising the public awareness regarding environmental quality in micro environments GPS performance are related to the number and the position of GPS satellites

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3. ACCURACY AND PRECISION OF PORTABLE AND MINIATURIZED MONITORS FOR HUMAN EXPOSURE ASSESSMENT TO AIRBORNE POLLUTANTS

The following chapters are based and published on:

(3.1) Spinazzè et al. Field comparison of instruments for exposure assessment of airborne ultrafine particles and particulate matter. Atmospheric Environment 2017, 154, 274-284; doi: 10.1016/j.atmosenv.2017.01.054

(3.2) Borghi et al. Precision and Accuracy of a Direct-Reading Miniaturized Monitor in $PM_{2.5}$ Exposure Assessment. Sensors 2018, 18, 3089; doi:10.3390/s18093089

PREFACE

Different studies [1-7], evaluated the measurement performances of portable monitors through laboratory tests and results shows that, in general, this kind of instruments is characterized by worse performance if compared to reference technique. Only a few studies [8-15] were aimed to evaluate the performance of these monitors in the field and in real-world conditions. Studies regarding the evaluation of MMs in the laboratory and in-field are even less. Thus, many of these monitors are neither well evaluate in the scientific literature nor compared with reference methods. The aims of the following chapters are therefore to: (i) evaluate the metrological performances (in terms of precision and accuracy) of portable (firstly) and miniaturized (secondly) direct-reading monitors against filter-based sampling techniques; (ii) compare metrological performances of portable and miniaturized monitors against widely used direct-reading instruments; (iii) highlight the environmental factors (such as temperature, relative humidity and pollution levels) that can have a negative effect on the measurement error associated with the different tested instruments; (iv) evaluate the applicability of the selected portable and miniaturized instruments in future research, in particular for the evaluation of the exposure assessment of susceptible subjects/selected population (commuters, pregnant, children). Following the writing of this chapter, some similar studies were published [16, 17].

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3.1. PORTABLE MONITORS

This chapter is based and published on Spinazzè et al. Field comparison of instruments for exposure assessment of airborne ultrafine particles and particulate matter Atmospheric Environment 2017, 154, 274-284; doi: 10.1016/j.atmosenv.2017.01.054

The objective of this study was to compare the use of co-located real-time devices and gravimetric samplers to measure ultrafine particles (UFP) and size-fractionated PM mass concentrations. The results contribute to evaluating the comparability of different monitoring instruments for size-fractionated PM concentrations. Paired light scattering devices and gravimetric samplers were used to measure the PM_1, $PM_{2.5}$, $PM_{4/5}$, PM_{10} and TSP mass concentrations during 8-h monitoring sessions in an urban background site (Como, Italy) in winter. A total of 16 sampling sessions were performed: measurements were analyzed using linear regression analysis. Absolute deviations between techniques were calculated and discussed. The UFP concentrations measured using a condensation particle counter were clearly overestimated compared with the reference instrument (portable diffusion charger), with an absolute deviation that appeared to increase with the UFP concentration. The comparison of different light scattering devices (photometers - 'PHOTs') indicated an over-estimation of two of the tested instruments (PHOT-2 and PHOT-3) with respect to the one used as the reference (PHOT-1) regarding the measurement of the size-fractioned PM, with the only exception being $PM_{4/5}$. Further, the comparison of different light-scattering devices with filter-based samplers indicated that direct-reading devices tend to over-estimate (PHOT-2, PHOT-3) or under-estimate (PHOT-1) the PM concentrations from gravimetric analysis. The comparison of different filter-based samplers showed that the observed over-estimation error increased with increasing PM concentration levels; however, the good level of agreement between the investigated methods allowed them to be classified as comparable, although they cannot be characterized as having reciprocal predictability. Ambient relative humidity was correlated with the absolute error resulting from the comparison of direct-reading vs. filter-based techniques, as well as among different filter-based samplers for the same PM fraction.

3.1.1. Introduction

Particulate Matter (PM) is considered to be one of the main air pollutants [1,2]. Epidemiological and toxicological studies show that a number of negative effects on human health are possibly related to PM exposure [3]. The health effects strongly depend on different factors of PM, such as the

chemical composition [4,5], assumption rate [6] and size [7]. Recently, scientific attention has moved toward ultrafine particles ('UFP': particles < 100 nm) because these particles can easily enter the human respiratory system and deposit in the deepest areas of the lungs, carrying toxic compounds. A number of recent studies have related particle effects on health to the number of particles [8–10] and surface area concentrations [10–15]. Concern about health risks related to PM and UFP exposure in urban populations is growing rapidly [16–18]. Further, concern about the inadequacy of current air quality monitoring approaches is also growing, due to limitations in the consolidated measurement approaches. The existing measurement networks exhibit poor spatial and temporal resolutions and are often inadequate for characterizing the exposure of a population, identifying pollution hotspots and providing real-time information suitable for modeling and prediction purposes [19]. Traditional stationary sampling device are usually expensive and complex to use, but currently, this paradigm is changing. The introduction and development of portable sensors for the measurement of concentrations airborne pollutants have provided data with high temporal resolution characterized by a real time response [20]. In this regard, the quality of future exposure assessment studies depends strongly on the improvement of routine applications of direct-reading, portable monitors and sensors for PM and UFP measurements, in terms of their compactness, portability, reliability, accuracy, and costs. Portable devices are usually characterized by a worse metrological performance than the commonly used standard techniques in aerosol research in terms of their accuracy, minimum detectable particle diameter and maximum measurable concentrations [21]. For this reason, previous studies have intensively tested newly developed portable direct-reading devices; however, most of them have tested the instruments under laboratory conditions, testing the instruments with purposely generated aerosol [22–29]. Fewer studies have tested the instruments in real-world operating conditions [30–36]. In the present work, portable direct-reading instruments were field tested in an urban background scenario, with ambient UFP and PM concentrations being measured. The aim was to compare their performance against widely used 'reference' direct-reading instruments or versus filter-based sampling techniques for gravimetrical analysis. The performance of the portable monitors is assessed in terms of the particle

number concentration (UFP) and size-fractionated PM mass concentration (PM_1; $PM_{2.5}$; PM_5; PM_{10}; TSP - Total Suspended Particles). The final goal is to evaluate whether the instruments under study are comparable to each other, to their reference (or widely accepted) counterparts and to gravimetrical techniques for outdoor air quality studies. If their performance is validated, these monitors could be viable additions to existing air quality monitoring networks to achieve a broader spatial coverage and a more representative characterization of exposure.

3.1.2. Methods

3.1.2.1. Study design

Experimental data were collected within the area of the University of Insubria in Como (Italy), during N=16 repeated 8-h sessions, performed over a one-month period (November - December 2015). Measurements were performed in winter, under different meteorological scenarios, which were characterized by main meteorological variables. The selected site for sampling could be classified as an urban background site, according to the Guidelines regarding the Air Quality Monitoring Network, provided by the Agency for the Environmental Protection and Technical Services [37]. Thus, the performed sampling could be considered representative of the average pollution levels in an urban environment (urban background concentration) resulting from the transport of air pollutants from outside the urban area and from emissions in the city itself, without dominating or prevailing emission sources, such as traffic or industrial activities [38]. The measurement design consists of the combination of (i) direct reading instruments (UFP and size-fractionated PM) and (ii) filter-based PM sampling used for the determination of size-resolved particles concentrations. Table 1 summarizes the monitoring design and strategy. The sampling equipment was placed in a dedicated sampling box, at street level, and sampling lines were placed with the air inlets at approximately 1.5 m above the ground, which approximately corresponds to the breathing zone of humans; sampling tubes were 50-cm long straight silicon tubing with 7-mm internal diameter (tubes were kept to a minimum to minimize diffusion losses). At the sampling site, the monitoring devices were far from obstructions and pollution sources. The direct-reading instruments were placed with sufficient distance from each other to avoid

interferences and sampled at approximately the same height. The clocks of all instruments were synchronized prior to the first measurement in each session; data were measured with a 1-min frequency (averaging time).

Type of measurement	**Instrument**	**PM size-fraction**	**Metric**
Direct reading *(time resolved)*	DSC* UPC (CPC)	UFP	Number concentration
	PHOT-1**	PM_1, $PM_{2.5}$, PM_5, PM_{10}, TSP	Mass concentration
	PHOT-2+	PM_1, $PM_{2.5}$, PM_4, PM_{10}, TSP	
	PHOT-3	$PM_{2.5}$	
Filter-based *(gravimetric – time-weighted average)*	HI***	$PM_{2.5}$ ($PM_{0.25}$; $PM_{0.5}$)	
	PCIS****	PM_1, $PM_{2.5}$, PM_{10}	
	PCIS- mod	$PM_{2.5}$, PM_{10}	
	PHOT-3 (nephelometer)	$PM_{2.5}$	

*Legend - reference instruments: *DSC for UFP; **PHOT-1 for size-fractionated PM (time-resolved); ***HI for $PM_{2.5}$ (gravimetric and time-resolved session-average values); ****PCIS for PM_1 and PM_{10} (gravimetric and time-resolved session-average values); + PM_4 (PHOT-2) and PM_5 (PHOT-1) were assimilated in this study (and referred to PM_5).*

Table 1. Environmental monitoring strategy and instruments contextually used for the measurement of UFP and different PM size fractions.

3.1.2.2. Direct-reading instruments

The concentrations of airborne UFP were measured using a miniature diffusion size classifier (DSC) (DiSCmini, Matter Aerosol AG, Wohlen AG, Swiss) and a portable condensation particle counter (CPC) (P-Trak Ultrafine Particle Counter model 8525; TSI Inc., Shoreview, MN, USA) to perform a field comparison among these two instruments. Both instruments can provide real time measurement of ultrafine particles (i.e., sub-micrometer), although each type of instrument has its own sensitivity to specific particle characteristics. DSC measures the number concentration of particles (10^3-10^6 particle/cm^3) in the size range of 10-700 nm. DiSCmini is based on the

unipolar charging of aerosol, which is followed by detection in two electrometer stages [23]. CPC quantifies the number concentration of particles (up to 5*105 particle/cm^3) in the size range of 0.02-1 mm, using isopropanol to artificially enlarge particles through the condensation of vapors on the particle surface. DSC was selected as a reference measurement method for UFP measurements because previous studies reported that the DiSCmini provides accurate particle number concentrations (PNC) in urban environments [39–41]. Size-Fractionated PM concentrations (PM_1; $PM_{2.5}$; $PM_{4/5}$; PM_{10}; TSP) were measured using two photometers, which both use an active sampling mode (flowrate = 2.83 L/min) and are based on the principle of light scattering of a linear radiation produced by a diode laser focused on the airflow to measure PNC (particle count-to-mass conversion). The first photometer used in this study (PHOT-1: Handheld 3016 IAQ, Lighthouse Worldwide Solutions, Fremont, Calif.; Counting Efficiency: 50% @ 0.3 mm; 100% for particles >0.45 mm) classifies PM into 7 different dimensional fractions ($PM_{0.3}$; $PM_{0.5}$; PM_1; $PM_{2.5}$; PM_5; PM_{10}; TSP), whereas the second PHOT used in this study (PHOT-2: Aerocet-831 Aerosol Mass Monitor, Met One Instruments, Inc., USA; Accuracy ±10% to calibration aerosol) classifies PM into 5 different dimensional fractions (PM_1; $PM_{2.5}$; PM_4; PM_{10}; TSP). Continuous measurements of outdoor $PM_{2.5}$ were also performed using a nephelometer (PHOT-3: Dust-Trak™ II Aerosol Monitor Model 8530, TSI Inc., Shoreview, MN, USA) operating at 3 L/min and equipped with a size-selective impactor for $PM_{2.5}$. PHOT-1 was selected as a reference measurement method for size-fractionated PM measurements based on inter comparison tests performed immediately before the study, in which PHOT-1 showed better performances (wider measurement range and higher sensibility) in comparison to PHOT-2.

All guidelines provided by the manufacturer were strictly followed to ensure that quality-controlled data were collected. All the photometers measurements were operated using the factory-supplied particle densities and calibration factors. Before and after each monitoring session, a zero calibration was performed with appropriate HEPA absolute filter (rated at 99.96% removal efficiency for 0.45 mm particles). During monitoring, the instruments were checked periodically to avoid flow rate errors. Immediately

before the study, all of the instruments were calibrated by factory services; further, the accuracy of the adopted instruments (±5%) was verified for a number of instruments of the same type (N = 4 CPC; N = 3 PHOT-1; N = 5 PHOT-2; N = 2 PHOT-3), by means of intercomparison tests against factory-calibrated instruments.

3.1.2.3. Filter-based PM sampling and gravimetric analysis

$PM_{2.5}$ concentrations were measured gravimetrically by means of a Harvard Impactor sampler (HI), which operates at a flow rate of 10 L/min and has a 50% cut-off point at 2.5 mm (collection substrate: PTFE w/PMP ring; diameter: 37 mm; porosity: 2 mm) [42]. HI was selected as a standard method for $PM_{2.5}$ measurements, due to its documented agreement with $PM_{2.5}$ Federal Reference Methods (FRMs) [43,44]. Two Personal Cascade Impactor Samplers (PCIS) were also used [45]: PCIS is a miniaturized cascade impactor that operates at a flow rate of 9 L/min and consists of four impaction stages (collection substrates: PTFE s/PTFE filters; diameter: 25 mm; porosity: 0.8 mm), which are followed by an after-filter for particles < 0.25 mm (collection substrate: PTFE w/ PMP ring; diameter: 37 mm; porosity: 2 mm). This device was developed for the analysis of size-fractionated PM ($PM_{0.25}$; $PM_{0.5}$; PM_1; $PM_{2.5}$; PM_{10}). In this study, one PCIS was used following the guidelines provided by the manufacturer, whereas a second PCIS was modified ('PCIS-mod') to obtain a two-stage impaction device, which can be used for the sampling of $PM_{2.5}$ and PM_{10} only. Finally, the collection of $PM_{2.5}$ on PHOT-3 internal filters (collection substrate: PTFE w/PMP ring; diameter: 37 mm; porosity: 2 mm) was conducted in each sampling session to further assess the accuracy of the instrument ('PHOT-3-grav'). All the guidelines provided by the manufacturer were strictly followed to ensure that quality-controlled data were collected. Before and after each sampling, the impactors were cleaned and/or greased. The flow rates were calibrated before sampling and verified after sampling using the whole sampling train (with the impactor and representative filter in place), and a primary standard calibrator (DryCal Defender 520, International Corp., Butler, NJ, USA) was used to improve the accuracy of the sampling volume estimates and verify that considerable flux variations (CV% > 5%) did not occur during sampling. The PM mean mass concentrations (mg/m^3) were then determined by gravimetric analysis in

accordance with reference methods [46,47] and with the accepted standard practice. The net PM mass on the filters was measured by weighing the 48-h conditioned filters before and after sampling with a microbalance (Gibertini micro1000; Novate, Milan, Italy) in a temperature- and relative humidity-controlled (T: 20.0 ± 1.0 °C; RH: 50 ± 5%) environment. The filter weighting procedure consisted of three consecutive weighting (every 20") performed ensuring a standard deviation ± 3 mg, by a micro-balance with a readability of 1 mg (Gibertini 1000; Novate, Milan, Italy). An electrical C-shaped ionizer (HAUG GmbH & CO. KG, Germany) was used to eliminate electrostatic charges from the filter surfaces. This procedure was repeated before and after each sampling, and the particulate masses were determined by differential weighing. Laboratory blanks - two for each type of filter used - were always weighed under the same conditions to verify possible anomalies in the weighing room conditioning (e.g., temperature and humidity variations). The average blank filter masses were then used to correct the filter mass results for each test. Prior to the analysis, the microbalance was auto-calibrated, and a calibration check was performed using certified standard weights of 1 and 100, allowing deviations from the true value ≤ 3 mg and ≤ 5 mg, respectively. The quality of the weighing procedure was assessed using the ASTM D 6552 method. The weighing procedure was repeated on three filters of each type at least three times on the same day for twelve different days to obtain a representative number of repeated weighing for each type of collection substrate. Mass limits of detection (LODs) of 1.31 mg and 1.27 mg (a = 0.05) were calculated for 25-mm PTFE filters (PCIS, PCIS-mod) and 37-mm PTFE membranes (HI, PCIS, PHOT-3), respectively.

3.1.2.4. Meteorological data

An external weather station (BABUC-ABC, LSI Lastem, Milan, Italy) was also used to characterize and record on-line meteorological conditions during the study period at the sampling site, particularly the temperature (T), relative humidity (RH), atmospheric pressure, wind velocity and direction. For each parameter, the weather station was programmed with an acquisition rate of 1 min and an elaboration rate of 60 min so that every hour, the acquired data point was processed using the programmed statistical mode, providing hourly averages. Rainfall data (hourly mean) were obtained by the nearest monitoring

station of the Regional Agency for Prevention and Environment of Lombardy, located 2.5 km NW from the sampling point. Planetary Boundary Layer (PBL) data related to the sampling location were recovered from the Regional Agency for Prevention and Environment of Emilia- Romagna.

3.1.2.5. Data treatment and statistical analysis

Data collected from direct-reading measurement were examined and handled to exclude zero, unreliable and missing data (case-wise deletion), following well-established practices in statistics [48]. The concentration distributions were truncated above the 99th percentile and below the 1st percentile to exclude unrealistic concentration values [49] (i.e., infrequent situations of high exposure concentrations). The performances of portable monitors were tested against a reference instrumentation, or against the most widely used instruments in the case of unregulated parameters (e.g., ultrafine particle number concentration) for which no reference is available [35]. Following Watson et al. [50], linear regression was used to evaluate the comparability between two measurement techniques as well as the predictability of one sampler's measurements from that of the other sampler (considering a reference sampler measurement as the independent variable and the investigated sampler measurement as the dependent variable). For example, regression slopes and intercepts (along with their standard errors) were used as indicators for each sampler pair [50]. In particular, two measurement techniques meet the requirement for comparability and predictability when (i) the slope equals unity within three standard errors, (ii) the intercept does not significantly differ from zero within three standard errors (SE), and (iii) the correlation coefficient exceeds 0.9. In this case the selection of independent and dependent variables is interchangeable [51,52]. When the correlation coefficient is greater than 0.9 but the slope and intercept criteria are not met, the investigated methods can be classified as comparable, but only the dependent variable can be predicted from the independent variable [50]. When the correlation coefficient is lower than 0.9, data from different instruments should be classified as not comparable. Obviously, the criteria for comparability are less stringent than those required for equivalence (Regression Slope = 1 ± 0.05; Intercept 0 ± 1 mg/m^3; Correlation = 0.97) [50]. Then, a linear regression was conducted separately for each PM fraction

(i) among continuous data deriving from direct reading instruments, (ii) among session-average data obtained from direct reading instruments and the corresponding session-average data obtained from gravimetrical techniques and (iii) among session-average data obtained from different gravimetrical techniques for the same PM fraction. Measurements taken with DSC and PHOT-1 were used as independent variables (reference value) for UFP and size-fractionated PM, respectively, for comparison among direct reading instruments. Measurements taken with HI were used as a reference for $PM_{2.5}$ (session-average values), whereas measurements taken with PCIS were used as reference for PM_1 and PM_{10} (session-average values) on the basis of previous evidences [33]. The concentrations measured using the other techniques were used as dependent variables in the regression analysis. To allow a better assessment of the absolute errors and possible error trends and to evaluate these errors as a function of the desired precision, the instrument comparisons were examined using Bland-Altman plots [53]. The plots (Supplemental material; Figs. S1eS19) were built based on the session-average data and report the absolute deviation (i.e., the difference) between the results of the reference instrument and the comparison instrument for each pair of measurements. The observed average errors and the relative upper and lower 95% limits of agreement (95%CI, calculated as the average difference ±1.96 standard deviation of the difference) are also reported in the following tables. Finally, bivariate correlation analysis was performed on registered absolute deviations and meteorological data: in every model, the mean absolute deviations calculated among values deriving from different techniques were singularly included as dependent variables and meteorological variables were included as predictors (mean values). Data were analyzed using SPSS Statistics 20.0 (IBM, Armonk, NY, USA); a significance level of 0.05 was used for all statistical tests.

3.1.3. Results

Repeated UFP and size-fractionated PM outdoor monitoring (N = 16 session; > 120 h sampling) was performed within an urban background area in the period of November to December 2015. In each session, samples were taken by means of each type of filter-based PM sampling for gravimetric analysis, and a total of N > 8000 data observations were collected from each

direct reading instrument; after data cleaning, between 5787 and 7388 pieces of data were used for the statistical analysis.

A general synopsis of UFP, PM and meteorological session-average data is provided in Table 2. The UFP mean concentrations (mean ± SD) were similar for DSC (21373 ± 8631 particle/cm^3) and CPC (23,974 ± 9061 particle/cm^3). Contrarily, PM_1 session-average concentrations are subject to a great variability as a function of the adopted measurement technique: the PHOT-2 results (40.0 ± 24.1 mg/m^3) were on average similar to PCIS samplings results (39.3 ± 21.1 mg/m^3), whereas PHOT-1 shows an underestimation (30.8 ± 18 mg/m^3). $PM_{2.5}$, according to the reference measured method (HI), resulted in a mean concentration of 38.8 ± 25.2 mg/m^3; the other measurement techniques appear to introduce an over-estimation, ranging from a slight increase (PHOT-1: 39.4 ± 21 mg/m^3) to a gross error (PHOT-3: 124.4 ± 86.9 mg/m^3). PM4 (PHOT-2) and PM5 (PHOT-1), which were assimilated in this study (and referred to $PM_{4/5}$), showed very similar mean concentrations. PM_{10} showed an opposite trend, highlighting relevant differences among filter-based sampling and direct-reading instruments results (with PHOT-1 and PHOT-2 showing an over-estimation). Further, also in the case of PM_{10} and TSP concentrations, the two direct reading devices used in this study did not show agreement. It must be noted that such high concentrations of UFP and PM could be explained by the particular meteorological condition of the sampling period; in fact, the study area was characterized by peculiar meteorological conditions (high atmospheric stability, total absence of rainfall, high atmospheric pressure and low mixing layer height) that promoted the accumulation of air pollutants in the lower atmosphere. These conditions were briefly interrupted, with a reduction in PM concentration levels, before the previous atmospheric conditions were restored [54].

Parameter	Measurement Method	Measurement Technique	Mean	SD	Min	Max
UFP	DSC*	DR	21373	8631	8992	40137
[particle/cm^3]	CPC	DR	23974	9061	10364	44703
PM_1 [µg/m^3]	PHOT-1*	DR	30.8	18	7.3	54.2
	PHOT-2	DR	40.0	24.1	9.2	80.4
	PCIS*	GA	39.3	21.1	10.4	78.9
$PM_{2,5}$ [µg/m^3]	PHOT-1*	DR	39.4	21	11.6	67.8
	PHOT-2	DR	55.0	34.1	13.3	114.7
	PHOT-3	DR	128.4	86.9	35.2	288.3
	PCIS	GA	44.6	21.2	17.6	85.2
	PCIS-mod	GA	48.2	26.0	13.5	95.5
	PHOT-3-grav	GA	47.3	27.2	12.1	96.7
	HI**	GA	38.8	25.2	10	89.7
PM_5 [µg/m^3]$^+$	PHOT-2	DR	63.5	36.8	18.1	125
	PHOT-1*	DR	60.4	26.7	23.8	103.2
PM_{10} [µg/m^3]	PHOT-1*	DR	67.4	26.7	29.6	116.7
	PHOT-2	DR	87.5	38	38.4	152.5
	PCIS**	GA	51.6	24.1	20.9	97.7
	PCIS-mod	GA	55.3	28.5	18.9	109.4
TSP	PHOT-1*	DR	87.8	30.9	47.5	158.1
[µg/m^3]	PHOT-2	DR	99.3	37.6	48.6	167.1
Sampling time [min]			466	49	345	519
Temperature [°C]			9.6	3.2	5.5	19.3
Relative Humidity [%]			72.8	13	51.2	97.5
Atm. Pressure [hPa]			1014.6	5	1006.8	1022.1
Wind Direction [°]			163.4	18.6	144.8	192.5
Wind Intensity [m/s]			0.3	0.2	0.1	0.8
Precipitations [mm]			0.0	0.0	0.0	0.0
PBL height [m]			210.5	96.1	92.9	351.6

*Legend: DR = direct reading instrument; GA: filter-base sampling for gravimetrical analysis; * reference instrument direct-reading measurement; * reference technique for filter-based measurement; $^+$ PM_4 (PHOT-2) and PM_5 (PHOT-1) were assimilated in this study (and referred to PM_5).*

Table 2. Environmental monitoring results as function of different measurement techniques. Data are referred to session-average and are reported as mean, standard deviation (SD), minimum (min) and maximum (max).

Linear regression was conducted separately for each PM fraction and among continuous data derived from direct reading instruments to assess the agreement between different monitoring methods as a function of the slope (m), intercept (q) and Pearson correlation coefficient (R), with the criteria mentioned above. The analysis was performed on the entire dataset (Rt; N > 7300 data pairs) and then repeated using partial datasets, derived from each measurement session (Rs; N = 16 partial datasets, each consisting of N > 350 data), to evaluate the differences between sampling sessions; a general summary of the results is reported in Table 3. In this study, UFP measurement instruments (DSC vs CPC) showed a good correlation coefficient for the overall dataset (Rt = 0.951), but wide variations occurred in different sampling session (0.566< Rs < 0.911). Similarly, PM_1 measurement devices (PHOT-1 vs PHOT-2) showed satisfactory correlation coefficient (Rt = 0.924), despite a large variability being observed between different sessions (0.278< Rs < 0.997). The reference instrument for direct reading instruments $PM_{2.5}$ was tested against two devices: the first (PHOT-2) showed an acceptable coefficient, despite a large variability in the correlation coefficients (Rt = 0.926; 0.479< Rs <0.995); contrarily, the second tested device (PHOT-3) showed an unsatisfactory performance (Rt = 0.823; 0.362< Rs < 0.995). Finally, an instrument comparison (PHOT-1 vs PHOT-2) for $PM_{4/5}$ (Rt = 0.930; 0.514< Rs < 0.984), PM_{10} (Rt = 0.936; 0.689< Rs < 0.979) and TSP (Rt = 0.913; 0.536< Rs < 0.974) showed acceptable, but highly variable, correlation coefficients. It must also be noted that none of the performed analysis satisfied the slope and intercept criteria; thus, none of the instrument comparison met the requirement for comparability and predictability. Nevertheless, pairs for which Rt as greater than 0.9 can be classified as comparable, although not reciprocally predictable.

PM fraction	Comparison	Data set*	Regression model**			Slope			Intercept		
			N	R	Adj r^2	m	SE	p	q	SE	p
UFP	DSC vs CPC	Total	7388	0.951	0.903	0.94	0.004	< 0.001	3709	99.8	< 0.001
		+	477	0.991	0.981	0.966	0.978	< 0.001	6559	178.4	< 0.001
		-	360	0.566	0.318	0.548	0.043	< 0.001	4770	455.1	< 0.001
PM_1	PHOT-1 vs PHOT-2	Total	7378	0.924	0.854	1.207	0.007	< 0.001	2.284	0.244	< 0.001
		+	467	0.997	0.993	1.642	0.006	< 0.001	0.567	0.087	< 0.001
		-	513	0.278	0.075	0.594	0.415	< 0.001	48.895	4.854	< 0.001
$PM_{2,5}$	PHOT-1 vs PHOT-2	Total	7373	0.926	0.857	1.484	0.008	< 0.001	-3.385	0.365	< 0.001
		+	467	0.995	0.990	1.598	0.008	< 0.001	0.116	0.113	0.384
		-	436	0.479	0.227	0.528	0.047	< 0.001	25.728	1.891	< 0.001
	PHOT-1 vs PHOT-3	Total	7307	0.823	0.677	3.329	0.03	< 0.001	-0.712	1.379	< 0.001
		+	469	0.995	0.989	4.077	0.02	< 0.001	-3.211	0.349	< 0.001
		-	500	0.362	0.085	1.223	0.362	0.107	35.064	10.739	0.004
PM_5	PHOT-1 vs PHOT-2	Total	7372	0.930	0.866	1.182	0.006	< 0.001	-8.796	0.424	< 0.001
		+	469	0.984	0.969	1.287	0.011	< 0.001	-5.550	0.312	< 0.001
		-	436	0.514	0.263	0.561	0.045	< 0.001	21.861	2.721	< 0.001
PM_{10}	PHOT-1 vs PHOT-2	Total	7347	0.936	0.876	1.678	0.008	< 0.001	-27.701	0.640	< 0.001
		+	469	0.979	0.958	1.388	0.014	< 0.001	-0.703	0.487	0.149
		-	512	0.689	0.473	0.822	0.039	< 0.001	66.246	4.178	< 0.001
TSP	PHOT-1 vs PHOT-2	Total	7370	0.913	0.833	2.058	0.012	< 0.001	-86.602	1.266	< 0.001
		+	451	0.974	0.949	0.644	0.010	< 0.001	14.875	1.059	< 0.001
		-	443	0.536	0.274	1.912	0.406	< 0.001	6.273	30.86	0.84

** Total: results from regression analysis on the entire dataset (16 sampling session); +, -: best and worst performance for a single monitoring session (based on regression analysis' R value); ** all the regression analysis models are statistically significant with $p < 0.001$.*

Table 3. Regression analysis results for the comparability among direct-reading instruments (continuous data).

PM Fraction	Comparison	Mean error (CI 95%) [μg/m³] #	Regression model*			Slope			Intercept		
			N	R	Adj r²	m	SE	p	q	SE	p
UFP #	DSC vs CPC	- 2600 (-6489; 1288)	16	0.976	0.949	1.025	0.061	< 0.001	2074	1402	0.161
PM_1	PHOT-1 vs PHOT-2	-11.2 (-30.3; 7.9)	15	0.924	0.843	1.239	0.142	< 0.001	1.784	5.032	0.729
$PM_{2,5}$	PHOT-1 vs PHOT-2	-18.4 (-51.5; 14.7)	15	0.906	0.807	1.474	0.191	< 0.001	-3.063	8.472	0.724
	PHOT-1 vs PHOT-3	-94.0 (-234.1; 46.1)	15	0.813	0.635	3.373	0.670	< 0.001	-4.564	229.7	0.880
PM_5	PHOT-1 vs PHOT-2	6.1 (-28.7; 41.0)	15	0.881	0.758	1.214	0.181	< 0.001	-9.795	11.900	0.425
PM_{10}	PHOT-1 vs PHOT-2	-23.4 (60.1; 12.3)	15	0.875	0.747	1.242	0.875	< 0.001	3.769	13.784	0.789
TSP	PHOT-1 vs PHOT-2	-14.9 (-57.4; 27.6)	15	0.804	0.619	0.980	0.201	< 0.001	13.236	18.651	0.490

** all the regression analysis models are statistically significant with $p < 0.001$* # UFP measured in particle/cm³.

Table 4: Regression analysis results for the comparability among direct-reading instruments (session-average data).

PM Fraction	Comparison	Mean error (CI 95%) [μg/m³]	Regression model*			Slope			Intercept		
			N	R	Adj r²	m	SE	p	q	SE	p
PM_1	PCIS vs PHOT-1	10.4 (-0.3; 31.9)	15	0.843	0.711	0.720	0.127	< 0.001	2.5	5.6	0.664
	PCIS vs PHOT-2	-0.7 (-17.5; 16.2)	16	0.937	0.869	1.073	1.303	< 0.001	-2.209	4.748	0.649
$PM_{2.5}$	HI vs PHOT-1	1.3 (-28.3; 25.6)	15	0.833	0.670	0.693	0.128	< 0.001	12.527	5.849	0.052
	HI vs PHOT-2	-16.2 (-43.0; 10.6)	16	0.937	0.869	1.268	0.126	< 0.001	5.807	5.791	0.333
	HI vs PHOT-3	-5.7 (-22.4; 10.9)	16	0.953	0.901	3.287	0.280	< 0.001	0.787	12.829	0.952
PM_{10}	PCIS vs PHOT-1	-14.5 (-40.1; 11.1)	15	0.873	0.745	0.969	0.150	< 0.001	17.420	8.481	0.061
	PCIS vs PHOT-2	-35.9 (-72.9; 1.2)	16	0.910	0.816	1.433	0.175	< 0.001	13.6	9.9	0.192

** all the regression analysis models are statistically significant with $p < 0.001$.*

Table 5: Regression analysis results for the comparability of gravimetrical methods and direct-reading instruments (session-average data).

PM Fraction	Comparison	Mean error (CI 95%) [µg/m³]	Regression model*			Slope			Intercept		
			N	R	Adj r^2	m	SE	p	q	SE	p
$PM_{2.5}$	HI vs PCIS	-5.7 (-22.4; 10.9)	16	0.947	0.899	0.798	0.072	< 0.001	13.6	3.3	0.001
	HI vs PCIS-mod	-9.0 (-26.6; 8.6)	15	0.939	0.872	0.933	0.095	< 0.001	11.641	4.348	0.019
	HI vs PHOT-3-grav	-6.6 (14.1; -27.2)	15	0.922	0.838	0.997	0.116	< 0.001	8.580	5.323	0.131
	PCIS vs PCIS mod	-2.0 (-19.8; 15.9)	15	0.940	0.874	1.149	0.120	< 0.001	-3.041	5.167	0.881
PM_{10}	PCIS vs PCIS mod	-1.7 (-17.3; 13.8)	15	0.963	0.922	1.137	0.091	< 0.001	-3.408	5.167	0.522

** all the regression analysis models are statistically significant with $p < 0.001$.*

Table 6: Regression analysis results for the comparability among gravimetrical methods (session average data).

Interestingly, when linear regression analyses were performed on the same instrument pairs considering the session-average concentrations as pairs of data (Table 4), only a few instrument comparisons, and in particular DSC vs CPC (UFP) and PHOT-1 vs PHOT-2 (PM_1, $PM_{2.5}$), respected the comparability criteria for R and slope (but not for the intercept). It also must be noted that the associated mean error between DSC and CPC confirmed the tendency of an over-estimation by CPC, also outlined by the Bland-Altman plot, which showed a negative, although not statistically significant, trend (Fig. S1). Similarly, PHOT-1 vs PHOT-2 showed a similar behavior for PM_1 (Fig. S2) and $PM_{2.5}$ (Fig. S3), with PHOT-2 tending to over-estimate the PHOT-1 measurement and a clear negative trend for increasing concentrations (proportional error). The other performed comparisons did not allow us to classify the pairs of data as comparable: it must be noted that a higher mean error was associated with PHOT-1 vs PHOT-3 for $PM_{2.5}$ measurements, for which a proportional error was also identified (Fig. S4). Interestingly, PHOT-2 tends to under-estimate PHOT-1 measurements when measuring $PM_{4/5}$ (Fig. S5), with an opposite trend with respect to finer (PM_1 and PM_2) and coarser (PM_{10}, TSP) fractions (Figs. S2, S3, S5-S7).

Linear regression analyses were then conducted for each PM fraction on data derived from direct reading instruments (session-average) and results from the corresponding gravimetrical reference techniques; these latter techniques were considered as the reference values for comparison (independent variable) (Table 5). PHOT-1 and PHOT-2 were tested versus HI ($PM_{2.5}$) and PCIS (PM_1, PM_{10}), which resulted in completely opposite behavior: PHOT-1 was non-comparable ($R < 0.9$), whereas PHOT-2 met the comparability criteria for R and slope (but not for the intercept). Similarly, the observed mean errors outlined the different responses of PHOT- 1 and PHOT-2: when compared to the gravimetrical analysis results for PM_1 and $PM_{2.5}$, PHOT-1 showed a non-systematic (casual) error (Fig. S8, S10) and tended to under-estimate higher concentrations than low concentrations. Contrarily, PHOT-2 showed proportional error trends (Fig. S9, S11) leading to an over-estimation, especially when measuring higher concentrations. Both PHOT-1 and PHOT-2 showed a similar over-estimation trend when compared to the gravimetrical analysis of PM_{10}. Finally, PHOT-3, tested against HI for $PM_{2.5}$,

also showed a good comparability performance (R = 0.953), even if the high slope value (m = 3.287) and the corresponding mean error (-86.6 mg/m^3) underline the possibility of a proportional error and of a systematic over-estimation of the actual $PM_{2.5}$ concentrations (Fig. S12). The comparability among different gravimetrical techniques was also assessed (Table 6). The reference method for $PM_{2.5}$ was tested against PCIS, PCIS-mod and PHOT-3-grav: all these comparisons showed met the comparability criteria for R, but none of the three respected the criteria for the slope and intercept simultaneously. The lowest observed mean error was associated with the use of PCIS, followed by PHOT-3-grav and PCIS-mod, although each of these instruments showed a typical error behavior (Fig. S15-S17). The comparison of PCIS vs PCIS-mod indicated in a low mean error both for $PM_{2.5}$ and PM_{10} (Fig. S18, S19), and the two techniques showed to be comparable (R > 0.9) but not reciprocally predictable.

Finally, bivariate correlation analysis was performed on the calculated absolute deviations and meteorological data, with the aim of investigating whether conditions could affect the performances of the study measurement instruments and, eventually, whether one of the considered parameters could contribute to the day-to-day variability observed in the regression analysis (Table 3). None of the considered meteorological parameters showed statistically significant correlations with the absolute error among pairs of direct-reading instruments (data not shown). Contrarily, the correlation analysis identified relative humidity as correlated ($p < 0.05$) with the absolute error resulting from the comparison of direct-reading vs filter-based techniques, as well as among different filter-based sampler for the same PM fraction.

3.1.4. Discussion

Portable direct-reading instruments were tested in the field, measuring UFP and PM concentrations, with the aim to assess their performance in an urban background environment and to compare their performance against filter-based sampling techniques.

DSC and CPC showed good agreement (Rt = 0.951; m = 0.940; q = 3.709); however, this accounts for an over-estimation effect of UFP by CPC (mean error: 2600 particle/cm^3). However, it should be considered that the comparison of results obtained by instruments operating with different measurement principles may pose some problems [27,55]. In fact, the present study, in spite of the good relationship between the two techniques, demonstrated that the average CPC particle counts were generally higher than DSC counts (Table 2), contrary to previous studies [23,39,40]. In this regard, a previous study [40] showed that DSC and CPC measured similar particle numbers with a high temporal resolution, allowing both devices to identify the same peak episodes during personal monitoring in urban traffic environments. Another study outlined that CPC presented a lack of accuracy at high concentrations, which is not expected to affect its capacity to measure short-term variations in the PNC in urban environments [56]. Previous studies have (i) discussed whether the under-estimation effect of CPC is an effect of the different cut-off diameters for detection (size-dependent efficiency) or, more likely, (ii) hypothesized that semi-volatile compounds of freshly emitted particles are not effectively detected by CPC [57]. Contrarily, other studies reported that (i) the lower detection limit of DSC in respect to CPC can introduce a bias that will not significantly affect the measurement results [25] and that (ii) the performance of DSC corresponds fairly well to traditional instruments used for UFP measurements and they are reproducible and in agreement with standard condensation particle counters and SMPS systems [23,25,35,39]. As seen from the results of the present study, however, both the instrument could be considered useful for measuring human exposure to UFP with an acceptable rate of comparability. However, due to relevant differences in the mutual performances of the two investigated devices for different UFP concentration, despite a clear error trend not being identified (Fig. S1), caution should be used when compare measurement taken with these two different devices.

A comparison with respect to PHOT-1 in the measurement of size-fractioned PM (PM_1, $PM_{2.5}$, PM_{10}, TSP), with the only exception being $PM_{4/5}$, for which an opposite trend was observed (Table 3, Table 4); this underestimation of $PM_{4/5}$ can be attributed to the fact that two different

fractions (i.e., PM_4 measured by PHOT-2 and PM_5 measured by PHOT-1) were assimilated in this study and referred to as $PM_{4/5}$. Further, a comparison of different light-scattering devices with filter-based samplers outlined that direct-reading devices tend to an important overestimation (PHOT-2, PHOT-3) or a slight underestimation (PHOT-1) of PM concentrations resulting from gravimetrical analysis (Table 5). It must be noted that Despite PHOT-1 showed better performances with respect to PHOT-2 in a series of preliminary intercomparison test (which leaded to the assumption that PHOT-1could be used as the reference method or size-fractionated PM direct-reading measurements), the results of the study showed an opposite behavior, leading to the conclusion that actually PHOT-1 was not to be the best performer with respect to gravimetric methods. This result emphasizes the importance of conducting detailed intercomparison analyses to properly evaluate the performance of direct-reading instruments. In this regard, as already discussed in [34], (i) a systematic bias between measurement devices can be outlined when the regression intercepts significantly differ from zero and (ii) a proportional bias between measurement devices can be identified when the regression slopes significantly differ from one [58]. Considering the regression analysis performed on the results of the direct-reading measurement, a proportional bias between measurement devices can be identified. This behavior was probably firstly caused by different PM properties of urban backgrounds compared to the calibration factors for which the devices are factory-calibrated [34]. In fact, differences in actual sampled airborne particle characteristics (e.g., density, size distribution, shape, reflectance properties) from the factory-calibrated settings can produce different scattering responses for identical masses of PM passing through direct reading devices [59]. For example, because urban particulates typically have a lower specific gravity than standard dust [40,60], a significant overestimation of concentrations is possible; in this regard, previous study noted that PM concentrations measured by photometers may be up to 5 times greater than the reference gravimetrical method [61]. Furthermore, airborne PM is typically characterized by irregular shapes [62,63], which, together with particle orientation and rotation in the air flow, can introduce errors in the size classification by optical instruments [64].

The error associated to the direct-reading measurement could be reduced by using custom calibration factors to correct real-time PM measurements; custom calibrations factors can be calculated by dividing the PM concentration obtained by means of a standard gravimetrical sampling technique using the mean PM concentration measured simultaneously with the direct-reading instrument [65]. For example, when considering $PM_{2.5}$ measurements by means of HI vs PHOT-3 in this study, the performance of the direct-reading instrument can be significantly improved if continuous data are corrected on the basis of PHOT-3-grav data (PHOT-3 integrated filter-based sampler), which shows a significantly better regression, i.e., more accurate and site-specific data; similar examples can be found in the scientific literature [34,60]. On this basis, it can be concluded that, to obtain reliable and accurate PM concentrations by direct-reading measurement, it is indispensable to apply case-specific calibration factors and/or a-posteriori correction procedures; this is obviously more efficient only in the case that a proportional (systematic) error is defined. The observed absolute errors showed an increasing trend for higher concentrations and for coarse particles, as already discussed in previous studies [66–68]. Further, the present study is coherent with previous literature data, which identified relative humidity as a possible error determining factor in light scattering devices [69–71]. In particular, ambient relative humidity could have a role in particle volume, shape and refractive index and, consequently, on light scattering properties [69], which are likely to cause uncertainties in the particle concentration and sizing measurements. Further, hydrated particles can have a density that differs from dry particles. To overcome this problem and achieve comparability between measurements, some studies [72,73] propose to limit the relative humidity by using conditioned inlet [71] or drying the sample aerosol (in order to keep RH below 40%, to minimize diameter changes due to hygroscopic growth); other studies provide a number of recommendations concerning a strategy to evaluate and manage the possible RH effect on PM measurement and, eventually, to correct the data recorded by means of photometers [70]. However, when using PHOTs for evaluating mass concentrations, it is necessary to take into account the RH effect and, possibly, use direct-reading instruments together with reference (i.e. gravimetric) methods, in order to check their response in the effective

operative conditions [71]. Again, the measurement principle of light-scattering devices is a strong function of the particle size and refractive index [74], so these measurements can differ from gravimetric measurements of airborne PM, especially when the size distribution of the airborne particles differs significantly from the size distribution of the test aerosol [75] or, for example, when the ultrafine fraction it is predominant [76]. In this regard, differences in correlation were also attributed to the PM composition rather than to the overestimation of the equivalent gravimetric sampler [44,77]. Spatial or temporal (i.e. daily or seasonal) variations in particle composition, could also lead to a change in the density and refractive index of particles, which also might introduce biases [33]. In this regard, it should be noted that the present study was performed only in winter: further sessions could be performed in other seasons, to consider changes in PM composition and investigate the potential effects on the observed measurement errors. However, more in general, since particle properties (i.e. refractive indices, shape, composition and size distribution) may vary enormously, photometers should be calibrated in-situ to obtain reliable results [33].

Finally, the comparison of different filter-based samplers showed that the absolute errors increased with increasing PM concentration levels. The results also showed that all the considered sampling techniques showed a slight over-estimation of $PM_{2.5}$ with respect to the reference method (HI). Similarly, the modified PCIS tends to over-estimate the PCIS used under the manufacturer operating conditions. Regarding these two last observations, it is known that photometers are typically more sensitive at low concentrations, since they are more efficient in detecting a change in a small light intensity (i.e. at low PM concentrations) than in a high intensity (i.e. at high PM concentrations) [66]. However, the good level of agreement between the investigated methods allowed them to be classified as comparable in the concentration range under investigation, even if not characterized by reciprocal predictability.

Another aim of this study is the applicability of the investigated direct-reading devices to exposure assessment studies; thus, it is interesting to consider the main advantages and disadvantages of the investigated devices. CPC is user friendly and quite easy to transport (this type of handheld device can fit into

a small backpack for personal exposure evaluation) [40,56,78]. The main disadvantage of CPC is that the instrument needs the intervention of an operator every few hours, to refill isopropanol and to recharge or change batteries (if used in battery-operated mode). The main advantages of DSC are the temporal resolution of the measurement (1 s), the compactness and portability (DSC can be easily used for personal exposure assessment studies) and the easiness with which the operator can perform measurements and data interpretation. Further, DSC provides real-time measurement of particle mean-diameter and lung-deposited surface areas of particles, other than particle number concentrations, which can further improve the data interpretation. A previous study already noted that DSC is less accurate than traditional aerosol instruments, such as condensation particle counters and scanning mobility particle sizer, even if this is often compensated for by its smaller size and easier handling [23]. Similarly, direct-reading devices for PM measurements are easy to operate and portable and provide continuous data with high temporal resolution. Although the standard methods - which are attested to be the most accurate methods - refer to the gravimetrical analysis of filter-based samples, these may present disadvantages compared to direct-reading instruments in terms of lower time and spatial resolutions and longer analysis time. In addition, it must be noted that, in the absence of standardized monitoring procedures, the indiscriminate use of direct-reading instruments can easily introduce relevant biases (in terms of accuracy) in exposure assessment studies. In conclusion, the characteristics of direct-reading instruments, when appropriately used (i.e., with reliable correction factors), could be applied in high-quality, low-cost, high-sensitivity exposure assessment studies, as well as to improve effective monitoring networks and to complete traditional gravimetric techniques. In addition, one of the most interesting developments for direct-reading instruments is the development of miniaturized instruments for participatory and ubiquitous monitoring strategies [79]. In this regard, different studies have showed how spatially and temporally appropriate measurements are essential for personal exposure assessments. In particular, studies characterized by high temporal and spatial resolutions are needed in heterogeneous environments, such as an urban environment [80]. Finally, standardized protocols need to be developed, and harmonization is needed in the performance evaluation of existing devices

[34]; further, other studies covering a wider range of ambient concentrations and/or a major number of measurement devices are requested.

3.1.5. Conclusions

Paired direct-reading devices and gravimetric samplers were used to measure the UFP number concentration and size fractionated PM mass concentrations in an urban background site. Pairs of measurements were recorded and analyzed using linear regression analysis.

The following conclusions can be drawn: firstly, the UFP concentrations measured using CPC were clearly overestimated compared with DSC, with an error that appears to increase with the UFP concentration. This is consistent with some literature evidence, which indicates that DSC is less accurate than traditional aerosol instruments, even if this is often compensated for by its smaller size and easier handling [23]. Although these two devices could be classified as comparable, relevant differences in the performances of the two investigated devices were observed. In addition, with respect to data from the literature, caution should be used when comparing measurements taken with these two devices.

The comparison of different light-scattering devices for PM measurement outlined an over-estimation of two of the tested instruments (PHOT-2 and PHOT-3) with respect to the one used as a reference (PHOT-1) in the measurement of size-fractioned PM (PM_1, $PM_{2.5}$, PM_{10}, TSP), with the only exception being $PM_{4/5}$, for which an opposite trend was observed. Further, a comparison of different light-scattering devices with filter-based samplers indicated that direct-reading devices tend to over-estimate (PHOT-2, PHOT-3) or under-estimate (PHOT-1) PM concentrations resulting from gravimetrical analysis. The results obtained by photometers should be interpreted carefully to quantify PM in urban background environments, when appropriate calibration factors are not used. Further, ambient relative humidity was correlated with the absolute error resulting from the comparison of direct-reading vs. filter-based techniques, as well as among different filter-based samplers for the same PM fraction.

Regarding this last point, the comparison of different filter-based samplers showed that the absolute errors increased with increasing PM concentration levels; however, despite an observed over-estimation effect, the good level of agreement between the investigated methods allowed them to be classified as comparable even if they are not characterized by reciprocal predictability. In conclusion, despite a general good level of comparability, relevant absolute errors were identified among different measurement and sampling techniques, which outlines the need to develop standardized protocols and harmonize performance evaluation criteria for existing devices.

Supplementary material

To allow a better assessment of the absolute errors and possible error trends, and to evaluate these errors as a function of the desired precision, the instrument comparisons were examined using Bland-Altman plots (Altman and Bland, 1983; Bland and Altman, 1986). The following graphs were built based on the session-average data and reports the absolute deviation (i.e. the difference) between the results of the reference instrument and the comparison instrument as function of the measured concentrations. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0), the solid black line represents the observed average error, whereas broken lines correspond to the upper and lower 95% limits of agreement (calculated as the average difference ± 1.96 standard deviation of the difference).

Figure S1. Comparison of UFP concentrations, measured with DSC (reference) and CPC (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-2600 particle/cm³); broken lines correspond to the upper and lower 95% limits of agreement (-6489; 1288 particle /cm³).

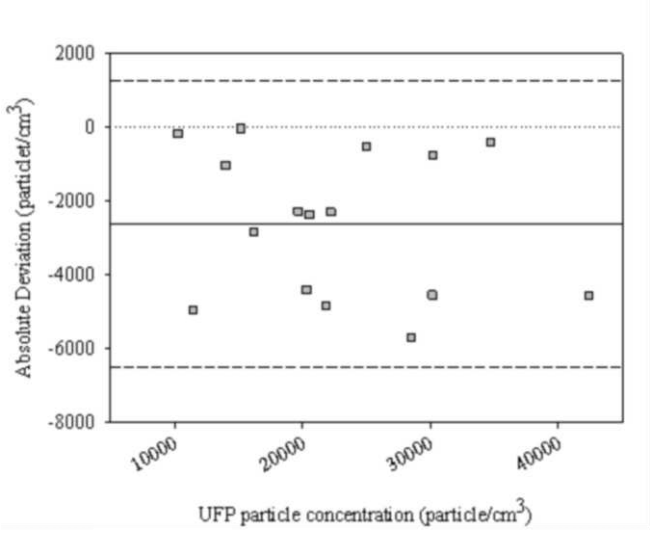


Figure S2. Comparison of PM_1 concentrations, measured with PHOT-1 (reference) and PHOT-2 (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-11.2 $\mu g/m^3$); broken lines correspond to the upper and lower 95% limits of agreement (-30.3; 7.9 $\mu g/m^3$).

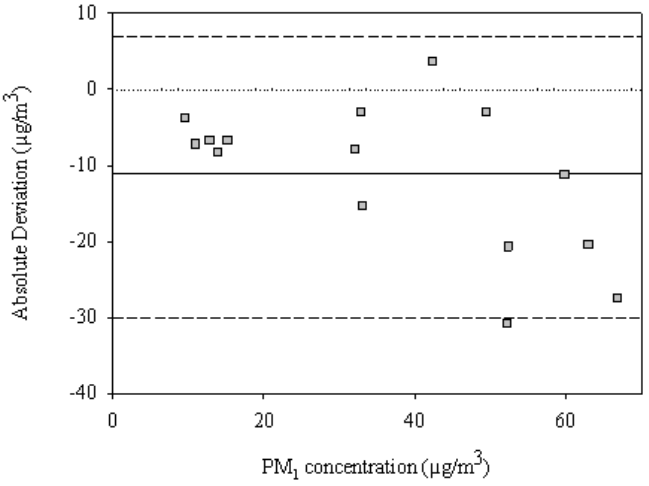


Figure S3. Comparison of $PM_{2.5}$ concentrations, measured with PHOT-1 (reference) and PHOT-2 (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-18.4 $\mu g/m^3$); broken lines correspond to the upper and lower 95% limits of agreement (-51.5; 14.7 $\mu g/m^3$).

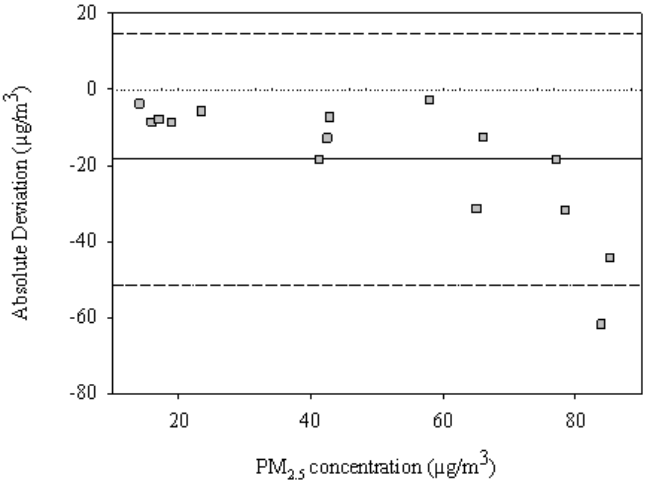


Figure S4. Comparison of $PM_{2.5}$ concentrations, measured with PHOT-1 (reference) and PHOT-3 (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-94.0 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-234.1; 46.1 μg/m³).

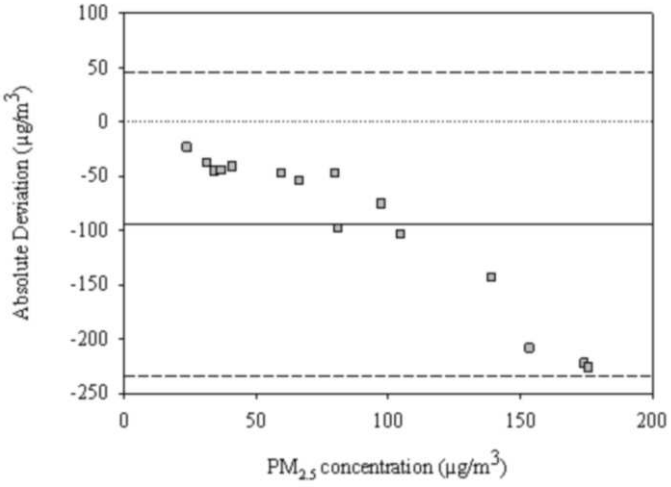


Figure S5. Comparison of $PM_{4/5}$ concentrations, measured with PHOT-1 (reference) and PHOT-2 (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (6.1 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-28.7; 41.0 μg/m³).

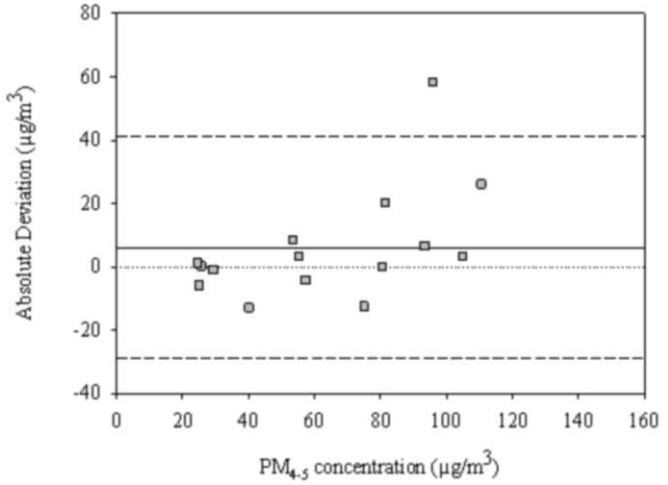


Figure S6. Comparison of PM_{10} concentrations, measured with PHOT-1 (reference) and PHOT-2 (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-23.4 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-60.1; 13.3 μg/m³).

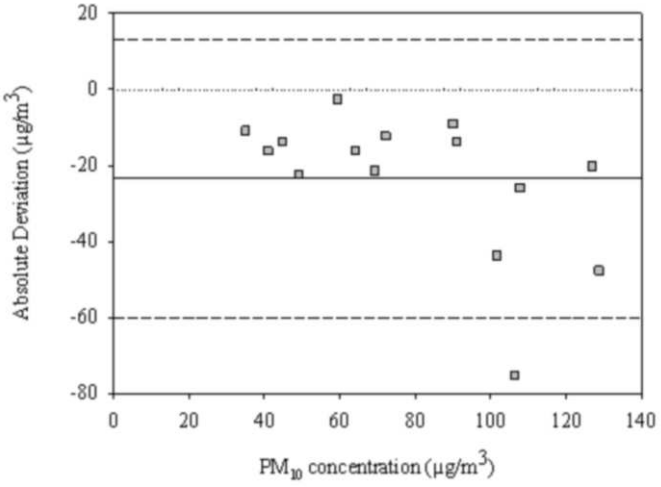


Figure S7. Comparison of TSP concentrations measured with PHOT-1 (reference) and PHOT-2 (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-14.9 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-57.4; 27.6 μg/m³).

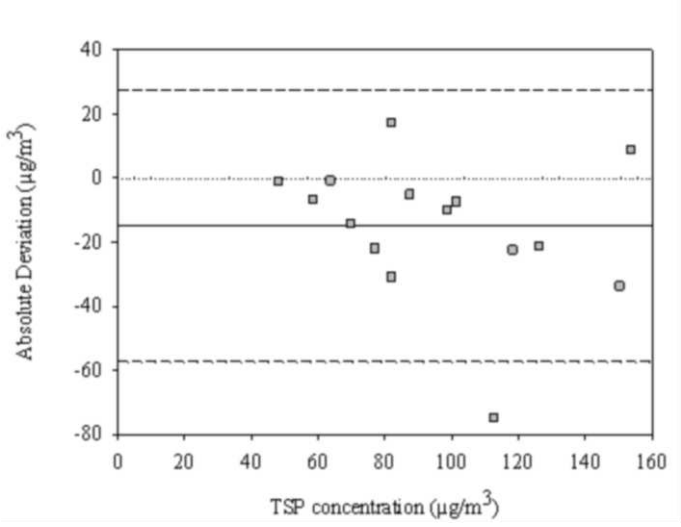


Figure S8. Comparison of PM_1 concentrations, measured with PCIS (reference) and PHOT-1 (comparison) using the Bland-Altman plot.
The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (10.4 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (0.3; 31.9 μg/m³).

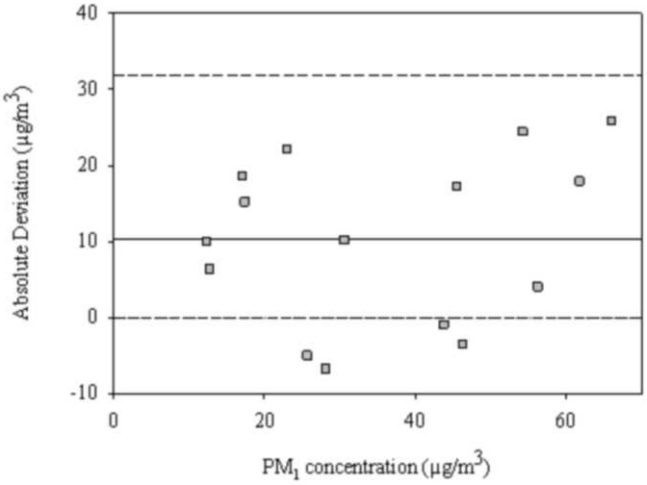


Figure S9. Comparison of PM_1 concentrations, measured with PCIS (reference) and PHOT-2 (comparison) using the Bland-Altman plot.
The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-0.7 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-17.5; 16.2 μg/m³).

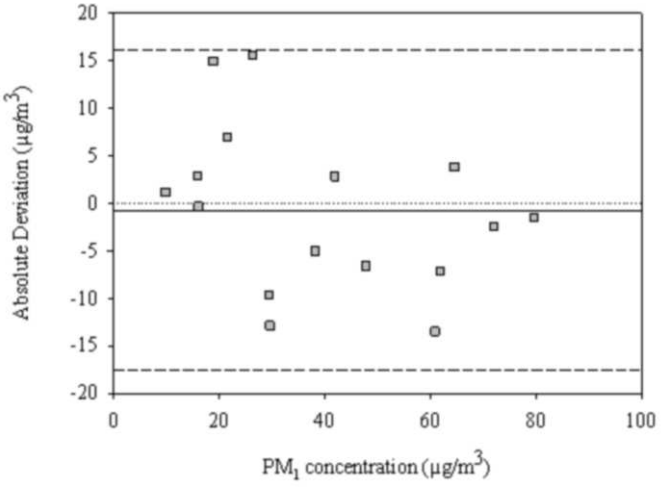


Figure S10. Comparison of $PM_{2.5}$ concentrations, measured with HI (reference) and PHOT-1 (comparison) using the Bland-Altman plot.
The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (1.3 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-25.6; 28.3 μg/m³).

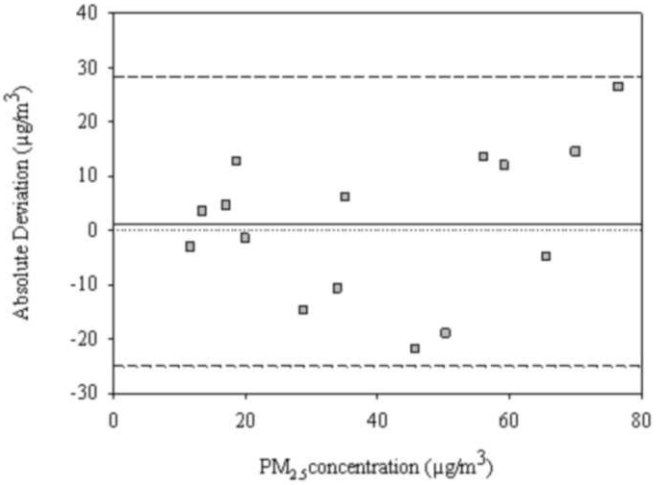


Figure S11. Comparison of $PM_{2.5}$ concentrations, measured with HI (reference) and PHOT-2 (comparison) using the Bland-Altman plot.
The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-16.2 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-43.0; 10.6 μg/m³).

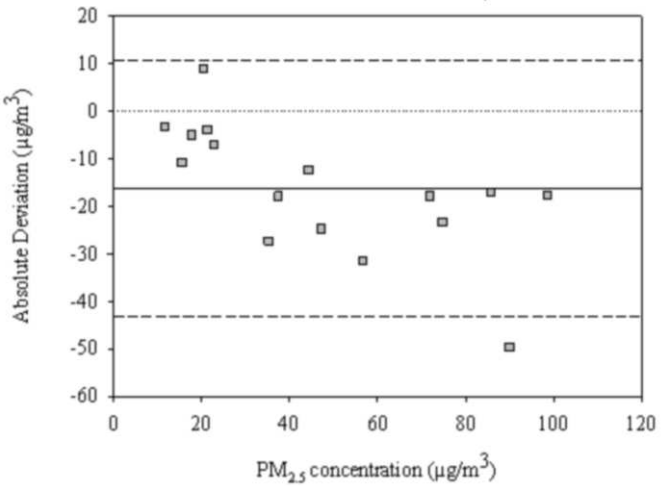


Figure S12. Comparison of $PM_{2.5}$ concentrations, measured with HI (reference) and PHOT-3 (comparison) using the Bland-Altman plot.
The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-89.6 μg/ m³); broken lines correspond to the upper and lower 95% limits of agreement (-213.7; 34.6 μg/ m³).

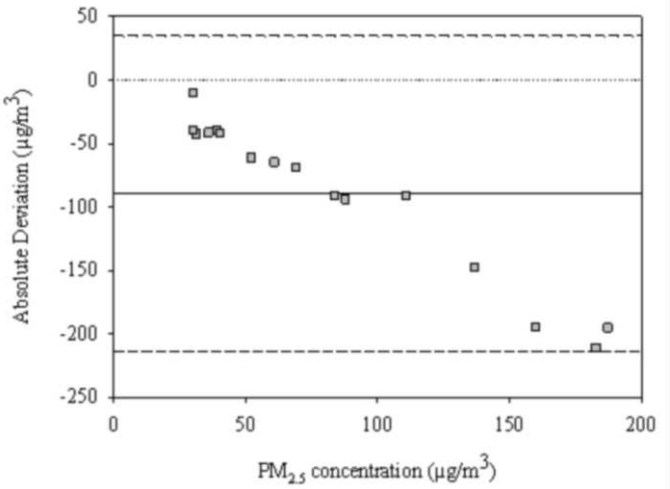


Figure S13. Comparison of PM_{10} concentrations, measured with PCIS (reference) and PHOT-1 (comparison) using the Bland-Altman plot.
The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-14.5 μg/ m³); broken lines correspond to the upper and lower 95% limits of agreement (-40.1; 11.1 μg/ m³).

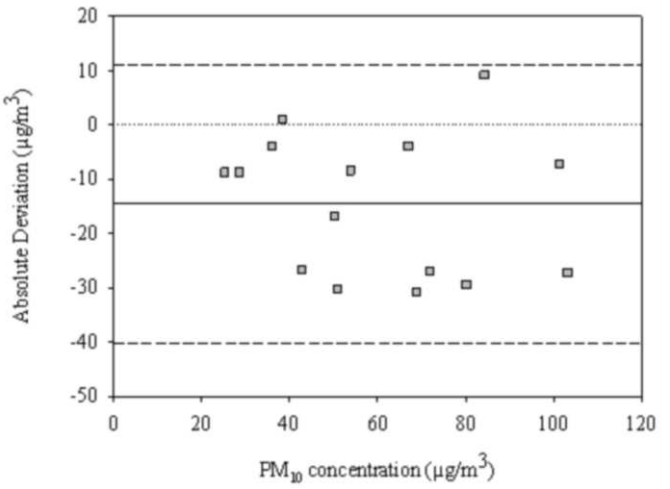


Figure S14. Comparison of PM_{10} concentrations, measured with PCIS (reference) and PHOT-2 (comparison) using the Bland-Altman plot.
The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-35.9 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-72.9; 1.2 μg/m³).

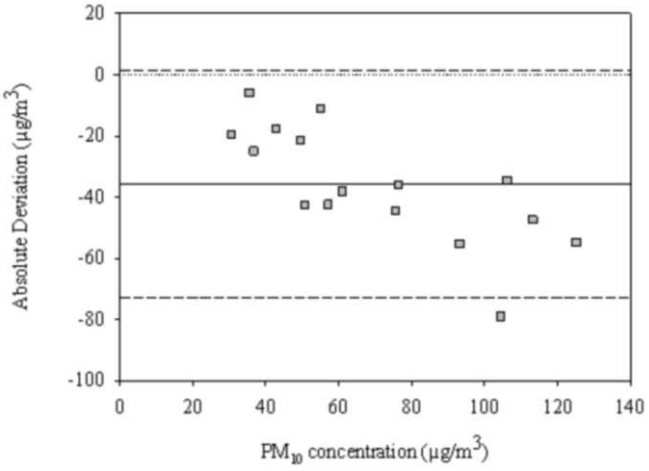


Figure S15. Comparison of $PM_{2.5}$ concentrations, measured with HI (reference) and PCIS (comparison) using the Bland-Altman plot.
The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-5.7 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-22.4; 10.9 μg/m³).

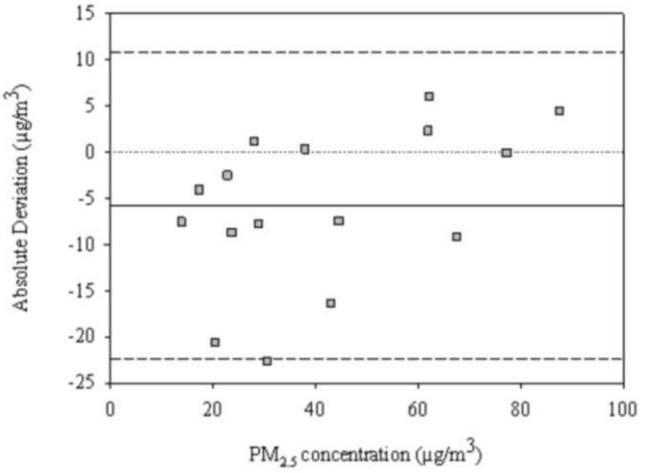


Figure S16. Comparison of $PM_{2.5}$ concentrations, measured with HI (reference) and PCIS (mod) (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-9.0 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-26.6; 8.6 μg/m³).

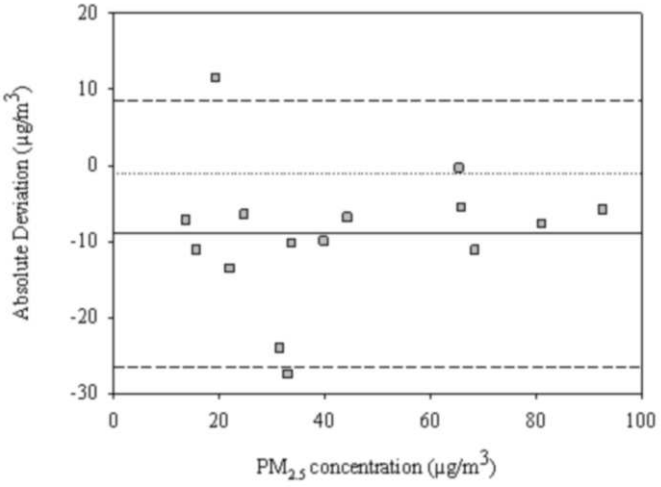


Figure S17. Comparison of $PM_{2.5}$ concentrations, measured with HI (reference) and PHOT-3-grav (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-6.6 μg/m³); broken lines correspond to the upper and lower 95% limits of agreement (-27.2; 14.1 μg/m³).

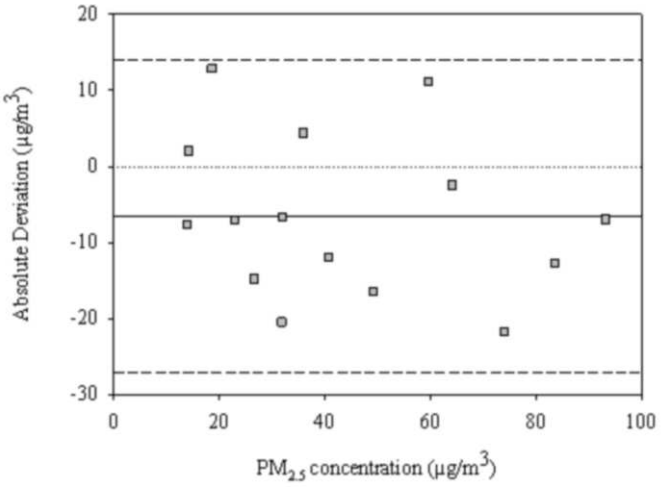


Figure S18. Comparison of $PM_{2.5}$ concentrations, measured with PCIS (reference) and PCIS(mod) (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-2.0 $\mu g/m^3$); broken lines correspond to the upper and lower 95% limits of agreement (-19.8; 15.9 $\mu g/m^3$).

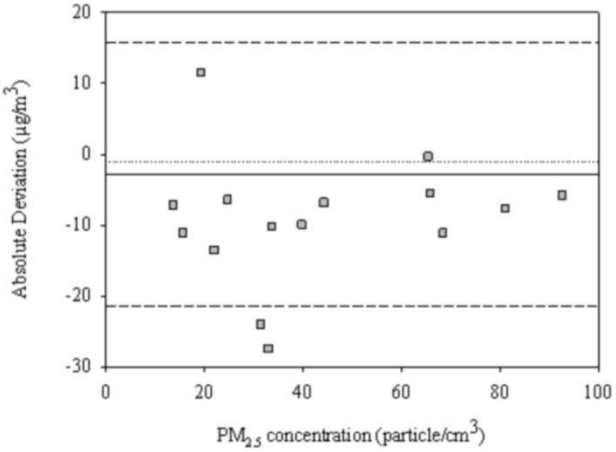
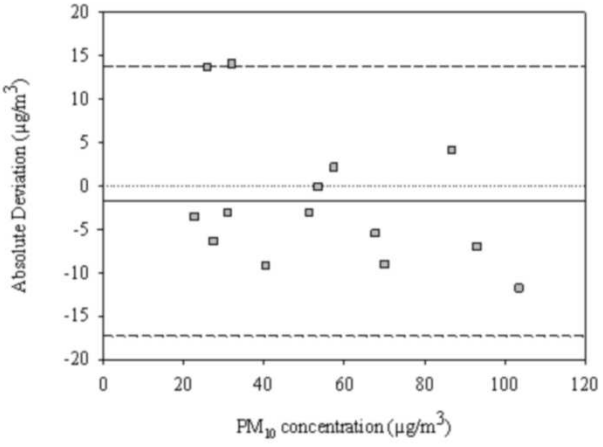


Figure S19. Comparison of PM_{10} concentrations, measured with PCIS (reference) and PCIS(mod) (comparison) using the Bland-Altman plot. The dotted line represents the perfect agreement between the two methods (absolute deviation = 0); the solid black line represents the observed average error (-1.7 $\mu g/m^3$); broken lines correspond to the upper and lower 95% limits of agreement (-17.3; 13.8 $\mu g/m^3$).



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sensors for monitoring urban air quality in low-cost, high-density networks. Atmos. Environ. 2013, 70, 186–203.

3.2. MINIATURIZED MONITORS

This chapter is based and published on Borghi et al. Precision and Accuracy of a Direct-Reading Miniaturized Monitor in $PM_{2.5}$ Exposure Assessment. Sensors 2018, 18, 3089; doi:10.3390/s18093089

The aim of this study was to evaluate the precision, accuracy, practicality, and potential uses of a $PM_{2.5}$ miniaturized monitor (MM) in exposure assessment. These monitors (AirBeam, HabitatMap) were compared with the widely used direct-reading particulate matter monitors and a gravimetric reference method for $PM_{2.5}$. Instruments were tested during 20 monitoring sessions that were subdivided in two different seasons to evaluate the performance of sensors across various environmental and meteorological conditions. Measurements were performed at an urban background site in Como, Italy. To evaluate the performance of the instruments, different analyses were conducted on 8-h averaged $PM_{2.5}$ concentrations for comparison between direct-reading monitors and the gravimetric method, and minute-averaged data for comparison between the direct-reading instruments. A linear regression analysis was performed to evaluate whether the two measurement methods, when compared, could be considered comparable and/or mutually predictive. Further, Bland-Altman plots were used to determine whether the methods were characterized by specific biases. Finally, the correlations between the error associated with the direct-reading instruments and the meteorological parameters acquired at the sampling point were investigated. Principal results show a moderate degree of agreement between MMs and the reference method and a bias that increased with an increase in $PM_{2.5}$ concentrations.

3.2.1. Introduction

Presently, particulate matter (PM) is considered as one of the main air pollutants [1], since several epidemiological and toxicological studies have reported associations between PM and its effects on human health [2,3,4,5]. Thus, air quality monitoring is frequently required by national and international regulations [6,7].

The inadequacy of traditional fixed air quality stations in assessing human exposure to PM has emerged in recent years and their main disadvantages are related to: (i) the inability to provide data at high spatial and temporal resolutions - a limitation essential in urban environments [8,9]; (ii) the necessity of technical and logistic infrastructures (power supply, protection structures,

etc.) [9,10]; and, (iii) the high cost/high level of maintenance [6,11]. Due to these limitations, several portable monitors have been developed which provide data (i) at high spatial and temporal resolutions; (ii) at individual or personal levels; (iii) characterized by real-time responses [12]; and, (iv) provide air pollutant exposure values for the selected subject. Previous studies have tested several portable monitors through laboratory tests with standard aerosol, outlining that such monitors are generally characterized by a worse performance than reference measurement methods [13,14,15,16,17,18,19]. Nevertheless, only few studies aimed at evaluating the performance of these monitors were conducted in field and in real-world conditions [20,21,22,23,24,25,26,27]. However, studies regarding the evaluation/comparison of miniaturized monitors (MMs) are few. MMs are characterized by several advantages because they are (i) compact; (ii) lightweight; (iii) inexpensive; (iv) energy-efficient; (v) easy to use and portable; and, (vi) are able to provide data at high spatial and temporal resolutions [28,29,30]. Presently, many of these monitors are neither well evaluated in the scientific literature nor compared with reference methods. Therefore, the aim of this study is to evaluate the performance of an MM for direct-reading (real-time) measurement of $PM_{2.5}$ (AirBeam, HabitatMap Inc., Brooklyn, NY, USA; particle sensor: Shinyei PPD60PV—abbreviated 'AB'). AB was selected among other sensors [28] mainly due to its practicability (as discussed in Section 4.1), since ABs are intended to be used in a future exposure assessment study by the authors. However, presently, scientific articles regarding the use of AB are few: for this reason, it was necessary to deepen the issue of AB's precision and accuracy and provide further information in this regard.

In particular, only three studies have been conducted to evaluate accuracy, precision, and reliability of such miniaturized and low-cost sensors in field and real-world conditions [31,32,33] (Table 1). Mukherjee et al. [31] evaluated the performance of the AB over a 12-week period in Cuyama Valley (California, USA). Contrariwise, Sousan et al. [32] evaluated performances of different consumer air quality monitors (including AB) in laboratory tests and over a wide range of mass concentrations. Finally, the multi-year CAIRSENSE project [33] tested different instruments in the field.

Reference	Monitoring period	Sampling point	Compared instruments	Performed analysis	Notes
[31]	12 weeks	Cuyama Valley (California, USA). Field test	◦ GRIMM 11-R ◦ Met One (BAM)	◦ Precision ◦ Accuracy ◦ Evaluation of sampling orientation ◦ Size distribution ◦ Meteorology and size distribution influence	◦ High precision between couple of ABs: $R^2 > 0.95$ ◦ Low R^2 for comparison between AB and BAM (< 0.33) ◦ Instruments were evaluated over different meteorological conditions and aerosol properties ◦ Authors used the default conversion algorithm that was used to convert counts to PM concentrations ($PM_{2.5}$: 0.518 + 0.0027 4 x particle count - hppcf)
[32]	n.a	Laboratory test	◦ Personal DataRAM 1500, Thermo Scientific	◦ Tests performed across different occupational settings ◦ Regression analysis ◦ Bias analysis ◦ Precision analysis	◦ R^2 from comparison with comparison instrument: 0.7–0.96 ◦ High precision: 2–9% ◦ Precision < 10% for all types of aerosol used (salt, welding fume, ARD) ◦ AB is not able to detect mass concentrations > 200 $\mu g/m^3$
[33]	2013–2014	USA. Field test	◦ Met One (BAM) ◦ FEM	◦ Regression analysis ◦ OLS regression	◦ R^2 ranges from 0.65 and 0.66

Table 1. Principal outcomes from other studies that evaluated AirBeam (AB). n.a.: not available.

It should be noted that studies that evaluated other types of MMs or measurement devices based on the Shinyei PPD60PV sensor [34,35] are not reported in Table 1, since the aim of this study is to specifically evaluate the AB monitor and its potential applicability for exposure assessment studies, wherein the performance depends not only on the kind of sensor but also on other factors, such as the type of hardware and software system, as well as calibration factors and correction algorithms used.

3.2.2. Materials and Methods

3.2.2.1. Study Design

This study consisted of a field campaign carried out to evaluate the performances of co-located MMs in comparison with a reference (gravimetric) method for $PM_{2.5}$ and with other widely used portable PM monitors. The campaign was performed during two different periods (warm period: 24 July 2017 - 8 August 2017; cold period: 10 January 2018 - 7 February 2018) at an urban background site described elsewhere [20,36]. An urban background site was chosen according to the Guidelines for Air Quality Monitoring Network provided by the Agency for Environmental Protection and Technical Services [37] to acquire data representative of the average pollution levels in the study area. Moreover, measurements were performed across different periods of the year to evaluate the performance of sensors under different meteorological and environmental conditions. In each season, 8-h long (8 AM to 4 PM) monitoring sessions (N = 10) were conducted. The sampling equipment was placed in a dedicated sampling station, which is approximately 1.5 m above the ground, far from obstructions, walls, and pollution sources. All the instruments were positioned at about 20 cm from each other to avoid possible interferences. Clocks for all the instruments were synchronized at the first measurement session and were checked at the beginning of each 8-h sampling (Figure S1). To ensure that quality-controlled data were collected, all the direct-reading instruments were operated following the manufacturer guidelines and using the factory-supplied calibration factors. Further, before and after each monitoring session, a zero calibration was performed for Optical Particle Counters (OPC) and Aerocet with appropriate HEPA absolute filter (rated at 99.96% removal efficiency for 0.45 mm particles). During monitoring, the

functionality of the instruments was checked hourly to avoid malfunctions or data loss. Immediately before the study, all of the instruments were checked by factory services to verify their compliance with the product specifications.

3.2.2.2. Instruments: PM

To assess the performance of the MM, direct-reading instruments and a reference filter-based technique were selected for comparison. Specifically, two Optical Particle Counters were used as direct-reading devices, and specifically a Handheld 3016 IAQ (abbreviated "OPC"—Lighthouse Worldwide Solutions, Fremont, CA, USA; counting efficiency: 50% at 0.3 nm; 100% for particles >0.45 nm;) and an Aerocet-831 (abbreviated "Aerocet"—Aerosol Mass Monitor, Met One Instruments, Inc., Grants Pass, OR, USA; accuracy ±10% to calibration aerosol). Both the instruments classify PM into different fractions, including $PM_{2.5}$, and they are based on the principle of light scattering while using an active sampling mode with a flow rate of 2.83 L/min.

The filter-based instrument for the gravimetric determination of $PM_{2.5}$ (used as reference method in this study) was an EPA Well Impactor Ninety–Six ("EPA WINS"; Federal Reference Method for $PM_{2.5}$) which operates using a sampling pump (Digit ISO, Zambelli, Milan, Italy) at a flow rate of 16.7 $L \cdot min^{-1}$. Particles were collected on 47 mm glass fiber filters (Whatman GF/D glass microfiber filters) and mass concentrations were determined via gravimetric analysis following a standard reference method [38,39]. The weighing filters were conditioned in a controlled environment (temperature: 20.0 ± 1.0 °C; relative humidity (RH): 50 ± 5%) for a minimum of 24-h following which the filters were weighed, before and after the sampling, with a microbalance (Gibertini Micro1000, Novate, Milan, Italy; readability: 1 μg). An electrical C-shaped ionizer (HAUG GmbH & Co. KG, Leinfelden-Echterdingen, Germany) was used to eliminate electrostatic charges from the filter surface. Two laboratory blanks were also weighed under the same conditions to identify the possible anomalies in the weighing room environment (temperature and humidity variations). To check the accuracy of the microbalance, certified masses of 1 and 100 mg were always weighed at the beginning and at the end of each weighing session, allowing for deviations of ≤3 and 5 μg, respectively, from the true value.

Finally, three ABs (instruments that reflect the MM characteristics reported above) represented the MMs to be evaluated in this study. The sensor is based on an Arduino board and can detect particles ranging from 0.5 to 2.5 μm and $PM_{2.5}$ concentrations up to 400 $\mu g/m^3$ [32,40]. These monitors are characterized by reduced dimensions (10.46 cm × 10.03 cm × 4.62 cm), low weight (198 g), and low costs (about USD 250, according to [31]). The air was drawn through the sensing chamber by means of an internal fan where an LED light source scattered off particles. The light scatter produced was then detected and the instrumental signal was converted to a mass concentration value while using a linear regression model [32]. The acquired data were sent via Bluetooth, approximately once per second, to an open source Android Application (AirCasting Android app, HabitatMap Inc., Brooklyn, New York, NY, USA), from which they can be downloaded [41].

3.2.2.3. Instruments: Meteorological Data

An external weather station (BABUC-ABC, LSI Lastem, Milan, Italy) was placed at the same sampling point to characterize the meteorological conditions. In particular, temperature (°C), RH (%), atmospheric pressure (hPa), wind intensity (m/s), and wind direction (°) data were acquired. The weather station was programmed with an acquisition rate of 1 min and an elaboration rate of 60 min. The acquired data were processed every hour to provide: (i) hourly averages; (ii) standard deviations (S.D.); (iii) maximum; (iv) minimum; and, (v) time of maximum and minimum values. Hourly mean rainfall data were obtained from the nearest monitoring station of the Regional Agency for Environmental Protection of Lombardy (Como, ARPA - Agenzia Regionale per la Protezione Ambientale -Villa Gallia) located 2.5 km NW from the sampling point.

3.2.2.4. Statistical Analyses and Data Treatment

Statistical analyses were performed while using SPSS Statistics 20.0 software package (IBM, Armonk, NY, USA). To exclude unrealistic low and high concentration values, all data (except meteorological data averaged for the 1-h period) were truncated below the 1st percentile and above the 99th percentile [3]. A *p*-value lower than 0.05 was considered as statistically significant for all tests. Descriptive statistics were estimated for

$PM_{2.5}$ concentration outcomes from all instruments and for meteorological data for the single monitoring sessions, the two seasons, and the entire study period.

The evaluation of the AB by comparison with the reference method (as well as other direct-reading instruments) was carried out using different tests: (i) precision evaluation (evaluation of uncertainty between co-located MMs by means of uncertainty analysis and linear regression, according to the indications summarized by Watson et al. [42]); (ii) comparison with reference gravimetric method (Mann-Whitney test, Spearman's correlation (rho); regression analysis according to the indications that were summarized by Watson et al. [42]); (iii) evaluation of error trends (Bland-Altman plot method; absolute and relative errors); and, (iv) impact of meteorological variables on measurement errors (multiple linear regression analysis between AB absolute errors and meteorological parameters; only independent variables that were found to be statistically significant in the bivariate correlations were included in each multivariate model).

1-min averaged data were used for comparisons among direct-reading instruments (AB, Aerocet, OPC) while 8-h averaged values were used for comparisons between direct-reading instruments and the gravimetric reference method (EPA WINS). Because of the high strength of the relationships between co-located AB, as described in the Results and Discussion sections, for convenience, the mean of data for all the ABs was used as a new variable for the statistical analyses. Results regarding each AB device (AB1, AB2, and AB3) are reported in the supplementary material. The uncertainty between couple of ABs was calculated following the guidance that was reported by the EC Working Group [43]. AB data were averaged for 8-h instead of 24-h since the study design was based on a period of 8-h. The uncertainty of AB was calculated from the difference of measure according to Equation (1):

$$u_{bs}^2 = \frac{\sum_{i=1}^{n} (y_{i,1} - y_{i,2})^2}{2n}$$

Equation (1)

Equation (1) Uncertainty formula used in this study. u^2_{bs} represents the uncertainty; $y_{i,1}$ and $y_{i,2}$ represent AB measurements averaged for the entire monitoring session period (8-h); n represents the number of the total measurements considered in the analysis. Following the guidance report, the uncertainty was determined for the total dataset as well as for the two datasets that were obtained by splitting the entire dataset according to $PM_{2.5}$ concentrations: ≥18 μg/m^3 and <18 μg/m^3. Moreover, in this study, the uncertainty was also calculated separately for the summer and winter datasets. According to the guidance report, an uncertainty >2.5 μg/m^3 must be considered as an indication of unsuitable performance for one or both co-located instruments.

Linear regression was used to evaluate the level of agreement between the two methods and the reference method was considered as the independent variable while the method to be tested was the dependent variable. As reported by Watson et al. [42,44], equation parameters (R, slope, and intercept) can be used as indicators of the comparability and/or predictability between the two methods. In particular, the two methods can be classified as comparable and mutually predictable (i.e., the independent and dependent variables are considered interchangeable) if: (i) slope is equal to 1 ± 3 standard error (s.e.); (ii) intercept is equal to 0 ± 3 s.e.; and, (iii) R > 0.9. If R is >0.9 but the slope and intercept criteria are not met, the investigated methods can be considered as comparable but only the dependent variable is predictable from the independent variable. Finally, methods with R < 0.9 are classified as not comparable. Additionally, Bland-Altman plots were used to evaluate possible error trends [45,46]. In the present study, the plots were based on the entire dataset and reported absolute deviation between measurements and the upper and lower confidence intervals (calculated as the average difference ± 1.96 S.D. of the differences).

3.2.3. Results

3.2.3.1. Average PM2.5 Levels and Meteorological Parameters

Repeated 8-h monitoring sessions (N = 20 sessions; >150 h) were conducted at the urban background station during summer (July 2017–August 2017) and winter (January 2018–February 2018). A total of 20 filter-based samples (N = 19 valid) and N > 7000 were collected from gravimetric samplers and direct-reading instruments, respectively. Table 2 and Table 3 present the summary statistics of the $PM_{2.5}$ concentrations and the meteorological data that were acquired from all instruments during the two monitoring periods.

	$PM_{2.5}$ - total summer dataset (μg/m³)					
Data averaged for 1-min	N	Mean	Median	Min.	Max.	S.D.
AB 1	3816	7.1	7.2	0.7	17.8	4.7
AB 2	3862	6.5	6.1	0.7	15.6	4.2
AB 3	3259	6.8	6.4	0.6	18.0	4.8
Aerocet	4544	12.3	11.5	0.3	33.9	8.9
OPC	4530	6.6	6.2	0.2	17.3	4.7
	$PM_{2.5}$ - total winter dataset (μg/m³)					
	N	Mean	Median	Min.	Max.	S.D.
AB 1	3782	34.9	33.3	0.8	104.1	29.5
AB 2	3574	40.8	38.7	0.9	108.9	32.3
AB 3	3833	37.9	42.5	0.7	95.0	28.5
Aerocet	4645	50.8	43.7	0.8	202.6	46.5
OPC	4097	52	40.9	0.8	313.2	50.1
	$PM_{2.5}$ - total summer dataset (μg/m³)					
8-h data	N	Mean	Median	Min.	Max.	S.D.
AB 1	9	7.0	8.0	1.3	13.2	4.7
AB 2	9	7.2	8.0	1.3	13.0	4.6
AB 3	9	7.0	8.0	1.2	13.3	4.7
Aerocet	9	12.7	14.1	1.4	28.5	9.4
OPC	9	6.8	7.6	0.8	13.8	4.9
EPA WINS	9	12.5	14.8	2.3	21.7	7.2
	$PM_{2.5}$ - total winter dataset (μg/m³)					
	N	Mean	Median	Min.	Max.	S.D.
AB 1	10	38.1	39.8	5.3	98.1	31.0
AB 2	10	41.4	40.3	4.7	102.7	33.2
AB 3	10	36.1	36.1	5.0	88.0	27.1
Aerocet	10	50.3	47.9	7.0	147.8	41.9
OPC	10	47.8	47.1	0.0	133.9	41.7
EPA WINS	10	22.8	20.5	5.3	48.3	15.8

Table 2. $PM_{2.5}$ concentrations acquired with different monitoring devices. N: number of data point used for statistical analysis; Min: minimum; Max: maximum; S.D.: standard deviation.

Meteorological data - total summer dataset					
	Mean	Median	Min.	Max.	S.D.
ARPA cumulative rainfall (mm)	0.0	0.0	0.0	0.2	0.0
Temperature (°C)	29.2	29.8	17.1	38.7	5.1
RH (%)	40.7	34.9	16.1	82.6	17.1
Atmospheric pressure (hPa)	1002.6	1002.5	993.9	1009.0	5.0
Wind intensity (m/s)	0.9	0.9	0.1	1.7	0.3
Wind direction (°)	186.4	198.0	2.0	267.0	64.3
Meteorological data - total winter dataset					
	Mean	Median	Min.	Max.	S.D.
ARPA cumulative rainfall (mm)	0.0	0.0	0.0	0.0	0.0
Temperature (°C)	8.0	8.8	-0.9	14.0	3.2
RH (%)	67.8	72.4	23.9	99.9	21.1
Atmospheric pressure (hPa)	1005.4	1003.4	992.6	1022.3	8.6
Wind intensity (m/s)	39.5	0.5	0.0	229.0	75.4
Wind direction (°)	145.1	173.0	0.0	249.0	88.5

Table 3. Meteorological parameters at the sampling site during the two monitoring periods. N: number of data used in statistical analysis; Min: minimum; Max: maximum; S.D.: standard deviation.

During the warm period, the mean concentration values (mean ± S.D.) of ABs were similar (7.1 ± 4.7; 6.5 ± 4.2, and 6.8 ± 4.8 μg/m^3, respectively) and comparable to the average OPC concentration (6.6 ± 4.7 μg/m^3) (Table 2). On average, AB data tended to underestimate $PM_{2.5}$ levels when compared to Aerocet and the reference gravimetric method for $PM_{2.5}$ (12.3 ± 8.9 and 12.5 ± 7.2 μg/m^3, respectively) (Table 2). During the cold period, the average $PM_{2.5}$ concentrations were equal to 34.9 ± 29.5, 40.8 ± 32.2, and 37.9 ± 28.5 μg/m^3 for AB1, AB2, and AB3, respectively. Additionally, the AB values were lower than the Aerocet concentrations (50.8 ± 46.5 μg/m^3) but higher with respect to the average value for EPA WINS (22.8 ± 48.3 μg/m^3) (Table 2). When considering the entire dataset, maximum $PM_{2.5}$ concentrations were reached during the 18th monitoring session (EPA WINS: 48.3 μg/m^3; AB1: 98.1 μg/m^3; AB2: 102.7 μg/m^3; AB3: 88.0 μg/m^3), while the lowest values were registered during the first summer monitoring session (EPA WINS: 2.2 μg/m^3; AB1: 1.3 μg/m^3; AB2: 1.3 μg/m^3; AB3: 1.2 μg/m^3).

The warm period was characterized by low RH (mean: 40.7%) and by high temperature (mean: 29.2 °C; min.: 17.1 °C; max.: 39.7 °C). Typical winter meteorological parameters were found during the cold period. The average

RH was equal to 67.8%, while the temperature ranged from -0.9 °C to 14.0 °C (mean: 7.7 °C). The sampling site was characterized by generally low wind speeds (also reported in a previous study carried out in the same area [36]), mainly because of the sampling location (approximately 1.8 km from the banks of Lake Como) and the local topographic scenario (with moraine hills which surrounded the area). During the warm period, the wind intensity was <1.5 m/s in 96% of the cases (and <1 m/s in 62.7% of the cases), while during the cold period, the wind speed was <1.5 in 70.6% of the cases. Wind blew principally from S during summer and from SW during winter (Figures S2 and S3).

3.2.3.2. Precision Evaluation: Comparison among AB Copies

As previously stated, linear regression analyses were carried out on the total dataset with 1-min averaged values, and regression parameters were used as indicators of precision of co-located ABs (Table 4).

As reported in Table 4, R^2 values were always very high (>0.98). Nevertheless, the tested instruments can be classified as comparable but not mutually predictable, because of non-compliance with the slope and intercept criteria with regard to the Watson et al. approach [42,44]. Additionally, the absolute error (defined as the difference between tested and reference measurement) and relative error (absolute error divided by reference measurement) between the ABs were evaluated [47]. The mean absolute error between the three ABs was 5.7 μg/m^3, while the relative error was 9% (Table S1).

Instrument compared	Regression model				Slope			Intercept		
	N	R	R^2	*p*	m	SE	*p*	q	SE	*p*
AB1 vs AB2	6188	0.995	0.990	< 0.001	0.978	0.001	< 0.001	0.018	0.001	< 0.001
AB1 vs AB3	5862	0.994	0.988	< 0.001	1.004	0.001	< 0.001	0.004	0.002	0.037
AB2 vs AB3	5761	0.995	0.990	< 0.001	1.027	0.001	< 0.001	-0.011	0.002	< 0.001
AB1 vs AB2 AB1 vs AB3 AB2 vs AB3	Comparable and mutually predictable: NO Comparable but not mutually predictable: YES									

Table 4. Regression parameters between AB (data averaged on a 1-min basis). N: number of data; R: Pearson correlation coefficient; p: significance; m: slope; q: intercept; SE: standard error. Regression parameters that did not meet the Watson et al. criteria are marked in bold while values that met these criteria are underlined.

Subsequently, the uncertainty between pairs of co-located AB was calculated following the guidance for demonstration of equivalence [43] and it is presented in Table 5. Uncertainty was calculated for the total dataset as well as the four subsets (splitting the total dataset a function of $PM_{2.5}$ levels and seasons). 8-h averaged values were used for this analysis. As reported in Table 5, the uncertainty was higher than 2.5 $\mu g/m^3$ in the case of the total database and for winter and high-concentration (i.e., >18 $\mu g/m^3$) datasets, thus, indicating unsuitable performances of one or both the co-located instruments. Contrariwise, the uncertainty was lower than 2.5 $\mu g/m^3$ when considering the summer and low-concentration (i.e., <18 $\mu g/m^3$) datasets, thus, indicating better performance under these conditions. Therefore, this analysis outlined the potential presence of seasonal and proportional biases that must be verified.

	AB1-AB2 ($\mu g/m^3$)	AB1-AB3 ($\mu g/m^3$)	AB2-AB3 ($\mu g/m^3$)
Total database (N: 20)	2.58	2.80	4.25
High concentration (> 18 $\mu g/m^3$) (N = 6)	4.02	4.39	7.71
Low concentration (< 18 $\mu g/m^3$) (N = 14)	1.60	1.72	0.60
Summer (N = 10)	0.32	0.27	0.29
Winter (N = 10)	3.63	3.95	6.01

Table 5. Results of uncertainty analysis conducted between couple of co-located instruments. High-concentration database refers to particulate matter$_{2.5}$ ($PM_{2.5}$) concentrations ≥18 $\mu g/m^3$ while the low-concentration database refers to $PM_{2.5}$ concentrations <18 $\mu g/m^3$. N: number of sessions considered in the analysis. In bold and underline are marked results that are not in agreement with the criterion followed in this test (>2.5 $\mu g/m^3$).

For simplicity and considering the substantial level of agreement as outlined in the previous evaluations, all further statistical analyses were carried out with the variable ABx, i.e., the mean of the data for the three co-located ABs. Analysis for each AB is reported in the supplementary material.

3.2.3.3. Accuracy: Comparison with Reference Methods

Despite the low number of sampling sessions, the non-parametric Mann-Whitney test was performed as the first analysis to assess the differences between two independent groups of a continuous variable. A non-parametric test was chosen as it was verified that the AB concentration data (as well as

in the case of Aerocet and OPC) were not normally distributed (Kolmogorov-Smirnov test).
In this study, the concentration data obtained from all direct-reading instruments in each session were averaged on an 8-h basis and compared with the gravimetric $PM_{2.5}$ concentrations. As reported in Table S2, the obtained results clearly show statistically non-significant differences between the median concentrations of all direct-reading devices and the gravimetric method.

Table 6 (and Table S3) shows the correlation coefficients between the direct-reading monitors (ABx, Aerocet, and OPC–8-h averaged data) and the gravimetric method EPA WINS. The results revealed high correlation values between ABx and the gravimetric methods (rho = 0.916) and between ABx and the other direct-reading instruments (rho = 0.991 and 0.932 for Aerocet and OPC, respectively) (Table 6).

	ABx	Aerocet	OPC	EPA WINS
ABx	---	0.991	0.932	0.916
Aerocet	---	---	0.940	0.932
OPC	---	---	---	0.821
EPA WINS	---	---	---	---

Table 6. Correlations between all instruments (8-h averaged data). All the correlations are significant at 0.001 level and results are based on 19 monitoring sessions. Spearman's rank order correlation (rho) is reported in the table.

Correlations between direct-reading instruments were also performed on 1-min averaged data (Table 7 and Table S4), and, as expected, ABx was found to be highly correlated with the other direct-reading devices (ABx vs. Aerocet: 0.982 (rho); ABx vs. OPC: 0.987 (rho)).

	ABx	Aerocet	OPC
ABx	---	0.982 (N = 9009)	0.987 (N = 8467)
Aerocet	---	---	0.989 (N = 8429)
OPC	---	---	---

Table 7. Correlations between direct-reading instruments (1-min average). All correlations are significant at 0.001 level. Spearman's rank order correlation (rho) is reported in the table.

To assess the level of agreement between direct-reading instruments and the gravimetric method, a linear regression analysis was performed on the entire dataset, while considering ABx, Aerocet, and OPC concentrations as the dependent variable (y) and the reference gravimetric method concentrations as the independent variable (x). Table 8 reports the regression parameters between ABx, Aerocet, and OPC (averaged on 8-h basis) and the gravimetric method EPA WINS. Results concerning each AB are shown in the Supplementary Material (Table S5 and Figure S4).

As reported in Table 8, the highest R^2 value was reached between ABx and EPA WINS (R^2: 0.826), while R^2 for Aerocet and OPC were slightly lower (0.808 and 0.769, respectively). Additionally, to evaluate the comparability between the two methods, the indications that were summarized by Watson et al. [42] were followed. Evaluating these criteria, it is clear that Aerocet and OCP could not be considered mutually predictable and comparable with respect to the reference method, because slope and intercept criteria were not met, and R values were always <0.9. Contrariwise, ABx can be considered as comparable but not mutually predictable with respect to EPA WINS because R met the criteria reported above (which does not occur for slope and intercept parameters). The regression parameters between the direct-reading methods are reported in Table 9 and Table S6.

Instrument compared	Regression model				Slope			Intercept		
	N	R	R^2	*p*	m	SE	*p*	q	SE	*p*
ABx vs EPA WINS	9	0.909	0.826	<0.001	1.849	0.206	< 0.001	-9.522	4.543	0.051
Aerocet vs EPA WINS	9	0.899	0.808	<0.001	2.428	0.287	< 0.001	-11.042	6.336	0.099
OPC v EPA WINS	9	0.877	0.769	<0.001	2.397	0.319	< 0.001	-14.593	7.059	0.054

	Comparable and mutually predictable	Comparable but not mutually predictable
ABx vs EPA WINS	NO	YES
Aerocet vs EPA WINS	NO	NO
OPC vs EPA WINS	NO	NO

Table 8. Regression parameters between direct-reading instruments (8-h averaged data) and the gravimetric method. N: number of data; R: Pearson correlation coefficient; p: significance; m: slope; q: intercept; SE: standard error.

Instrument compared	Regression model			Slope			Intercept		
	R	R^2	*p*	m	SE	*p*	q	SE	*p*
Abx vs Aerocet	0.928	0.861	< 0.001	0.644	0.003	< 0.001	2.167	0.134	< 0.001
Abx vs OPC	0.876	0.767	< 0.001	0.575	0.003	< 0.001	6.632	0.170	< 0.001

	Comparable and mutually predictable	Comparable but not mutually predictable
ABx vs Aerocet	NO	YES
ABx vs OPC	NO	NO

Table 9. Regression parameters between direct-reading instruments (1-min averaged data). N: number of data; R: Pearson correlation coefficient; p: significance; m: slope; q: intercept; SE: standard error.

Despite the reduced sample size (9-10 samples per season), the linear regression analysis was also performed separately during summer and winter to evaluate the concordance between the direct-reading monitors and the gravimetric method across different climatic conditions and $PM_{2.5}$ concentrations. The results (Table 10 and Table S7) indicate that during summer and at lower concentrations, R^2 for all comparison analyses were higher than the R^2 outcomes for winter comparisons, thus, confirming the indication of a better performance under these conditions, as outlined by the uncertainty analysis (Table 5).

Summer database										
Instrument compared	Regression model				Slope			Intercept		
	N	R	R^2	*p*	m	SE	*p*	q	SE	*p*
ABx vs EPA WINS	9	0.984	0.968	< 0.001	0.629	0.043	< 0.001	-0.801	0.619	0.237
Aerocet vs EPA WINS	9	0.940	0.884	< 0.001	1.222	0.168	< 0.001	-2.582	2.395	0.317
OPC vs EPA WINS	9	0.969	0.939	< 0.001	0.660	0.063	< 0.001	-1.429	0.905	0.159

Winter database										
Instrument compared	Regression model				Slope			Intercept		
	N	R	R^2	*p*	m	SE	*p*	q	SE	*p*
Abx vs EPA WINS	10	0.943	0.889	< 0.001	1.808	0.225	< 0.001	-2.670	6.129	0.675
Aerocet vs EPA WINS	10	0.901	0.812	< 0.001	2.380	0.406	< 0.001	-3.975	11.094	0.729
OPC vs EPA WINS	10	0.900	0.810	< 0.001	2.369	0.405	< 0.001	-6.212	11.059	0.590

Table 10. Regression parameters between direct-reading instruments and EPA WINS (8-h averaged data). Regression parameters were calculated and reported for the summer and winter datasets. N: number of data; R: Pearson correlation coefficient; p: significance; m: slope; q: intercept; SE: standard error.

3.2.3.4. Accuracy: Measurement Error Trends

To better evaluate the possible errors and error trends, instruments were also analyzed by using the Bland-Altman plot method [45,46]. The single plots for each AB are reported in Figure S5. The results revealed good agreement between the two techniques, especially for lower concentrations (i.e., <20 $\mu g/m^3$); however, they also showed an error that tended to increase with increasing $PM_{2.5}$ concentrations.

Therefore, to evaluate whether the error increase was influenced by an increase in PM concentrations and not by an instrument drift over time, the Bland-Altman plot analysis was carried out while considering the differences between all direct-reading instruments (Figure 1). The Bland-Altman plot (Figure 1) clearly shows that all the direct-reading instruments were characterized by the same trend (increase in the absolute error with increase in $PM_{2.5}$ concentrations).

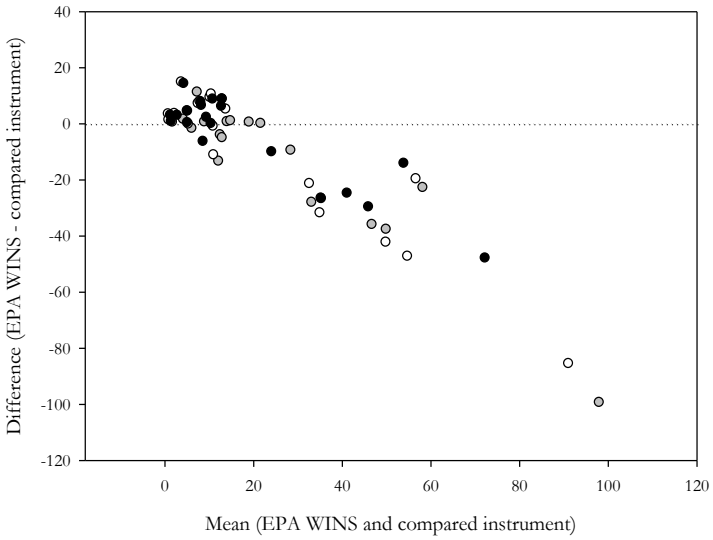


Figure 1. Bland-Altman plot for different instruments (grey: Aerocet; white: Optical Particle Counters (OPC); black: ABx).

The mean concentrations between the gravimetric reference method (EPA WINS) and the compared instrument are reported on the x-axis while on the y-axis the differences between methods are shown (8-h average). The dotted line represents the perfect agreement between the two instruments (absolute deviation: 0).

Regarding the relative error analysis between direct-reading instruments and the gravimetric method, as reported in Table 11, the ABx relative error for summer was very similar to the summer OPC relative error, but five times higher than relative error that was calculated between Aerocet and EPA WINS. Contrariwise, during winter, the average relative error calculated for AB was equal to half the relative error calculated for the other methods (OPC and Aerocet). When considering each single monitoring session (Table S8), the ABx relative error was lower than the OPC relative error in 66.6% of the cases and lower than the Aerocet relative error in 52.6% of the cases.

Similar results were obtained with the absolute error analysis (Table 11). Additionally, the absolute error for ABx during summer differed by less than 1 $\mu g/m^3$ from the OPC absolute error but was five times higher than the Aerocet error. During winter, the average AB absolute error was equal to half of the absolute errors for OPC and Aerocet. While considering each single session (Table S9), the ABx absolute error was lower than the OPC error in 68.4% of the cases and lower than Aerocet absolute error in 52.6% of the cases.

Relative and absolute errors (Table 11) were negative during summer and positive during the winter sessions, indicating an underestimation and overestimation of concentration data during summer and winter, respectively. To evaluate the relative error trend and to assess the relationship between the AB error and instrument drifts, the relative errors of all the selected direct-reading instruments were plotted vs. time (Figure 2). Figure 2 reports the ascending order of the monitoring sessions on the abscissa x and the relative error (%) between the direct-reading instrument and the gravimetric methods on the ordinate. The figure clearly indicates that summer data are characterized by a lower relative error and lower instrumental differences than the winter data. Further, the error trend was similar for all of the tested instruments, suggesting the lack of instrument calibration drifts. Finally, when considering the seasonal averaged ratio between the direct-reading instruments and the gravimetric method, different correction factors have been proposed for ABs, Aerocet, and OPC. In particular, the summer correction factors (calculated as the ratio between the reference PM concentrations and those measured by direct-reading instruments [20]) for

ABs, Aerocet, and OPC are 0.54, 0.90, and 0.49 for summer and 1.58, 2.13, and 2.11 for winter, respectively.

		ABx		Aerocet		OPC	
		Mean (± S.D.)	Median (Min.; Max.)	Mean (± S.D.)	Median (Min.; Max.)	Mean (± S.D.)	Median (Min.; Max.)
Relative error (%)	Total database	9 (± 64)	-27 (-70; 122)	55 (± 82)	38 (-67; 245)	23 (± 98)	-27 (-100; 204)
	Summer dataset	-46 (± 10)	-45 (-70; -32)	-10 (± 29)	-6 (-67; 50)	-51 (± 14)	-49 (-81; -27)
	Winter dataset	58 (± 51)	86 (-21; 122)	113 (± 69)	121 (32; 245)	90 (± 93)	122 (-100; 204)
Absolute error (µg/m³)	Total database	5.7 (± 15.5)	-0.8 (-8.8; 47.9)	14.6 (± 24.0)	4.0 (-2.9; 99.4)	10.5 (± 24.8)	-1.3 (-10.5; 85.6)
	Summer dataset	-5.5 (± 2.7)	-6.1 (-8.8; -0.8)	0.2 (± 3.4)	-0.6 (-2.8; 9.5)	-5.7 (± 2.6)	-5.2 (-9.3; -1.3)
	Winter dataset	15.7 (± 15.4)	12.1 (-2.2; 47.9)	27.5 (± 27.0)	24.7 (1.7; 99.4)	25.0 (± 26.8)	20.5 (-10.5; 85.6)

Table 11. Relative and absolute errors (mean ± S.D.; median, minimum, maximum) calculated between direct-reading instruments and the gravimetric method. The error is reported considering the mean values during summer and winter monitoring periods as well as the entire dataset.

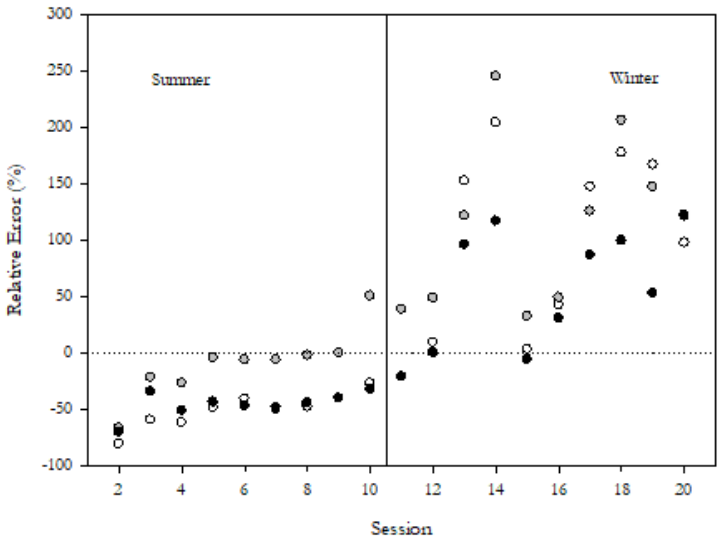


Figure 2. Relative error trend. The abscissa axis x reports the number of monitoring sessions while the ordinate axis y shows the relative error for the different instruments (grey: Aerocet; white: OPC; black: mean of ABx) as compared to the gold standard (gravimetric method).

3.2.3.5. Error and Meteorological Parameters

Finally, to evaluate whether meteorological parameters could affect the performances of ABs and other devices, a correlation analysis between errors (both absolute and relative errors) and meteorological variables (temperature, atmospheric pressure, wind intensity and direction) was performed. Rainfall has not been considered because it was absent during the entire monitoring period. As reported in Table 12, absolute errors between ABx (and also between the other direct-reading methods) and the gravimetric method were positively and highly correlated with RH and wind intensity and negatively correlated with wind direction. A moderate and negative correlation was also found with temperature. Contrariwise, the relative error was, in general, less correlated than the absolute error with the same meteorological parameters.

		Temperature (°C)	RH (%)	Atm.pressure (hPa)	Wind int. (m/s)	Wind dir. (°)
Absolute error						
ABx	Pearson correlation	-0.495*	0.690**	0.317	0.749**	-0.788**
Aerocet	Pearson correlation	-0.584*	0.685**	0.314	0.726**	-0.778**
OPC	Pearson correlation	-0.568*	0.734**	0.353	0.775**	-0.807**
Relative error						
ABx	Pearson correlation	-0.400	0.339	-0.231	0.431	-0.453
Aerocet	Pearson correlation	-0.710**	0.488*	-0.113	0.436	-0.492*
OPC	Pearson correlation	-0.639**	0.541*	-0.115	0.477*	-0.471*

*Table 12. Correlations between absolute and relative errors (direct-reading instruments vs. EPA WINS) and meteorological parameters (RH: relative humidity; Atm. pressure: atmospheric pressure; Wind int.: wind intensity; Wind dir.: wind direction). ** Correlation is significant at the 0.01 level (2-tailed); * Correlation is significant at the 0.05 level (2-tailed).*

ABx (μg/m³)						
Independent variable (predictors)	Unstandardized coefficient		Standardized coefficient	Sig.	95% C.I.	
	B	SE	Beta		Lower	Upper
(Constant)	4.406	19.285		0.823	-37.256	46.069
Temperature (°C)	0.052	0.225	0.046	0.820	-0.433	0.538
RH (%)	0.312	0.136	0.469*	0.039	0.018	0.607
Wind intensity (m/s)	0.056	0.075	0.255	0.466	-0.105	0.217
Wind direction (°)	-0.070	0.067	-0.365	0.311	-0.215	0.074
Regression model statistics						
R	R^2	Adj. R^2	Std. Error	*p*		
0.883	0.780	0.712	6.77141	< 0.001		

*Table 13. Summary of the multiple regression model results. Both unstandardized (B) and standardized (Beta) coefficients and the standard error (SE) for each independent variable, the model statistical significance (Sig.), and the upper and lower 95% confidence intervals (95% C.I.) for beta are reported. Other parameters are reported as indicators of the regression model: R, R^2, adjusted R^2 (Adj. R^2), standard error (Std. Error), and p value (p). * Variable is significant at the 0.05 level (2-tailed).*

Moreover, despite the low number of acquired samples and variables, a multiple linear regression analysis was performed between ABx absolute error (compared with the gravimetric method) and meteorological parameters that were measured at the sampling point (Table 13). In the model, the absolute error was included as the dependent variable and meteorological parameters (temperature, RH, atmospheric pressure, wind intensity, and wind direction) as predictors. Only meteorological variables that were found to be statistically significant in the bivariate correlation analysis (at a *p*-value <0.05) were considered in the multiple regression model. The results from this analysis must be carefully evaluated, mainly due to the low sample number and variables considered (N = 19). However, preliminary results, as reported in Table 13, indicate that RH exhibited the main influence on ABx absolute error.

3.2.4. Discussion

In this study, $PM_{2.5}$ MMs were tested at an urban background station to evaluate their performance against the reference gravimetric method for $PM_{2.5}$ (EPA WINS) and other common and widely used portable direct-reading instruments (Aerocet and OPC).

First, the tested ABs were mutually compared by linear regression analyses between the co-located instruments (Table 4). As reported in other studies, results in this study showed good precision among ABs throughout the entire monitoring period [31]. In particular, different AB copies can be classified as comparable to each other, even if not being characterized by mutual predictability. ABs were also comparable but not mutually predictable when compared to other traditionally used portable PM monitors (Aerocet). The uncertainty between couples of ABs was moderate during the entire study period (Table 5), even if not fully compliant with the uncertainty criterion proposed by the EC working group [43] (i.e., uncertainty <2.5 $\mu g/m^3$). Overall, these results show that ABs are characterized by good precision; however, some factors can interfere in defining measurement error that can potentially affect the precision and accuracy of the results (i.e., RH and $PM_{2.5}$ concentration).

It was observed that MMs tended to overestimate EPA WINS concentrations during winter and underestimate the reference concentrations during summer (Table 2, Figure 2). The regression analysis performed on the total dataset (Table 8) showed a regression slope significantly different from 1 with good R^2 values, indicating the presence of a proportional bias. Such bias could be related to differences in the PM that were monitored at the sampling point with respect to the standard particulate used for instrument calibration [21]. It is well known that the factory calibration factor of a photometer cannot be used to obtain accurate data when there are marked differences in terms of shape, morphologies, size-distribution, chemical composition, and reflectance properties between the analyzed particulate and the standard dust. As reported in different studies that were conducted in the study area [20,36,48], the local urban particulate is typically less dense than the standard dust, which could result in a significant overestimation of PM concentrations by optical particle counter and nephelometers. This can explain the

underestimation of average concentrations by a factor of about 0.5 in summer and an overestimation of mean concentrations by a factor of three during winter. These results are in accordance with those reported by Mukherjee [31] which showed that AB tended to underestimate or overestimate $PM_{2.5}$ concentrations depending on the aerodynamic diameters of the particles. Indeed, it was shown that, with larger particles, AB seemed to underestimate $PM_{2.5}$ concentrations whereas when the smallest fraction was predominant, PM concentrations tended to be overestimated. This is the case for the winter size-distribution at the sampling site, which is characterized by a sharp increase in the accumulation-mode peak during the cold season [36].

Further, it should be noted that all the instruments used in the field campaign (AB, OPC, and Aerocet) showed the same error trend over time (Figure 1 and Figure 2) and were characterized by a high overestimation error during winter and a slight underestimation error during summer when $PM_{2.5}$ concentrations were lower. Thus, it is reasonable to exclude the presence of an instruments drift over time and to assume the presence of a seasonal bias.

The regression analysis between EPA WINS and the mean of AB concentrations showed a high R^2 value ($R^2 > 0.80$), which is in agreement with the R^2 value calculated by manufacturers for regression between ABs and the gravimetric method and used as reference method [49] ($R^2 = 0.70$). However, as expected, ABs (like other instruments tested in this study (Aerocet and OPC) cannot be classified as mutually predictable with respect to the gravimetric method in the concentration range under investigation (2.3–48.3 $\mu g/m^3$). However, ABx (considered as the average of ABs) can be considered to be comparable to the gravimetric method (unlike the other direct-reading instruments tested).

Also, the Bland-Altman plot analysis showed a negative error trend that increased with increasing $PM_{2.5}$ concentrations (especially at concentrations >25 $\mu g/m^3$) for all instruments (Figure 1). The value of 25 $\mu g/m^3$ can be considered as a threshold above which the performance of instruments significantly decreases in accordance with the results that were reported by the manufacturers [49] and elsewhere [34]. However, it should be noted that

Johnson et al. [34]. evaluated the same sensor that was used in the ABs and indicated a suitability for PM concentrations <50 $\mu g/m^3$. Therefore, while the level of 25 $\mu g/m^3$ cannot be used as a clear demarcation value in terms of sensor performance, it should be remembered that the average annual concentrations of $PM_{2.5}$ across Europe are usually lower than this threshold [50] and can be overcome in particular microenvironments [51,52,53], especially during short-term periods [48].

The error associated with direct-reading methods could be reduced by using appropriate calibration factors. As reported in several studies, calibration factors can be calculated as the ratio between the reference PM concentrations and those that were measured by direct-reading instruments [20]. In this study, calibration factors were calculated separately for the two monitoring seasons (and as a function of $PM_{2.5}$ concentration), since the performance of ABs varied significantly with season. Once corrected based on EPA WINS $PM_{2.5}$ concentrations, AB performances were significantly improved (R^2 for comparison: AB1 vs. EPA WINS: 0.82; AB2 vs. EPA WINS: 0.82; AB3 vs. EPA WINS: 0.83) and all the ABs could be considered comparable to the gravimetric method. Therefore, correction factors should be used to obtain reliable concentrations by direct-reading instruments. As reported by Mukherjee et al. [31], the bias between ABs and the comparison instruments depended on the size distribution and chemical composition of the aerosol. It is important to note that the response of optical-based sensors is a function of aerosol properties at the specific sampling point (such as size distribution and chemical composition) [34] and the relationship between light scattered by the instrument and PM concentrations is set a priori by manufacturers using well characterized standard dust. The challenge with optical measurement techniques arises when the instruments measure PM that differs from the PM used for instrument calibration [21]. In this study, the correction factor was calculated for every comparison session and reported as a summer/winter mean correction factor. However, it is important to state that it must be calculated in a specific way (depending on the sampling period and location) for different monitoring sessions, and, for this reason, it should not be used in other contexts. Furthermore, in the case the correction factor is not calculated and not taken into account, it should

be considered that the introduced error may not be negligible (as in the case of direct-reading error reported in this study).

The influence of RH on the instrument performance and, in particular, on the light scattering methods, has already been analyzed in previous studies [20,54]. According to these investigations, a moderate high correlation (mean between AB: 0.589) between the (absolute) measurement error and RH was found and confirmed by multivariate analysis (Table 13). The results from the multivariate analysis confirmed the findings of the univariate analyses, namely, a significant relationship between absolute ABx error and RH, which was found to explain about 46% of the total variability in the multivariate model.

Some studies have reported the influence of RH on different particle properties, such as: (i) particle volume; (ii) shape; (iii) refractive index; and, consequently, (iv) light scattering properties [54,55]. Additionally, the AB manufacturer [49] indicates that the RH (>80%) has a negative effect on the accuracy of instrumental responses because aerosols take on water and become more reflective at high RH conditions. As reported in Figure S6–S10, the effects of RH on absolute and relative errors also seem to occur at lower RH values than those that were proposed by the manufacturer, especially in the presence of high PM concentrations (i.e., >25 $\mu g/m^3$). Lower errors seem to occur at RH values below 50% even when the PM concentrations are generally lower. Effects of RH on performance of low-cost PM sensors are reported in a recent study [56], and the results indicate that RH may also cause condensation on electrical components, leading to a resistive bridge across components. As reported above, the performance of AB was worst during winter when the average RH measured at the sampling point was 71.5% and better during the summer session which was characterized by lower RH (40.7% on average). The combined effect of RH and PM concentrations as a factor that focuses on the measurement error should be further explored in future studies to expand on case studies of data measured in the field under different conditions.

This study was specifically conducted during two different seasons that were characterized by different environmental conditions (PM concentrations,

temperature, RH, etc.) to evaluate instrument performance across several conditions. The error trend that was reported in this study could not be reasonably related to a single environmental factor but was related to the total contribution by different conditions, such as the increase in PM concentrations and an increase in RH. Therefore, it would be useful to perform laboratory tests in future studies to evaluate the effects of single potential error determinants on the error trend.

3.2.4.1. Practicability

The present study was conducted with the primary aim of evaluating the performance of ABs and their potential applicability in exposure assessment studies. It should be noted that despite these devices not being intended for use in techniques equivalent to gravimetric methods, these devices were compared to a reference filter-based method and to other direct-reading instruments that are widely used in the scientific literature and already evaluated elsewhere. For example, Spinazzè et al. [20] recently assessed the performance of different direct-reading methods (Aerocet and OPC) and gravimetric instruments at the same sampling point used in our study. As reported by Spinazzè et al. [20], portable direct-reading methods are easy to operate and are able to provide data at high temporal resolutions. Contrariwise, filter-based methods are generally not able to provide information at high spatial and temporal resolutions, which is an essential feature for monitoring environments characterized by high variability in terms of pollutant concentrations, such as urban environments [10]. The AB device tested in our investigation is smaller than the other widely used direct-reading instruments commercially available, cheaper than the other investigated devices, easy to transport and user-friendly, and able to provide additional data on temperature and RH. Moreover, it is associated with an Android application that affords an instant view of the concentration data and a facility of data-interpretation, even to the general population. Moreover, it is also possible to detect $PM_{2.5}$ maps and graphs in real-time directly from the smartphone. Finally, despite the fact that the AB cannot be considered to be mutually predictable, but only comparable with respect to the reference method and that its performance seems to be influenced by different variables (RH and PM concentrations), we found a similar

performance trend across different direct-reading instruments, such as Aerocet and OPCs, already widely used in human exposure assessment studies [53,56,57,58,59,60,61,62,63].

In addition to poor agreement with the reference method, another disadvantage that is related to the use of ABs is due to the data communication protocol. As mentioned above, data acquired by AB are sent to an Android application via Bluetooth and then stored. As can be seen in Table 2, the monitoring time (reported as the number of data points used during statistical analysis) is different for the three ABs because during the monitoring session the Bluetooth connection between AB and mobile phone could be lost.

To summarize, despite the disadvantages that are reported above and mainly related to the presence of a measure bias and to connection loss, AB could be used, with some precaution (i.e., application of a proper correction factor, management of potential outliers in the data series), across different and several applications. As reported by other authors [31], such sensors can be useful to assess the short-term changes in aerosol environment due to their acquisition rate and high response. Moreover, like other MMs, AB can potentially: (i) provide real-time data at high spatial and temporal resolutions; (ii) collect data across long or short-term campaigns and as stationary or mobile devices; (iii) collect data across different environments, both indoors and outdoors; (iv) be used for the evaluation of PM hot-spots; (v) be used as a support to fixed air quality monitoring stations; (vi) collect data at personal or individual levels, thus, enabling the subject to carry out the measurement themselves; and, (vii) provide pollutant data regarding community/individual exposure, or regarding a selected category of subjects (such as workers or susceptible subjects) [28,33].

Regarding the potential use in human exposure assessment studies, AB and MMs, in general, potentially can improve knowledge and become a novel way for human exposure assessment due to the advantages reported above, low costs, and their ability to measure pollutants across different environments, scenarios, and applications. One such application concerns the new paradigm of "citizen science" (the pros and cons of which should be carefully

evaluated) [28] being applied by the AirBeam-Aircasting application (http://aircasting.org).

3.2.4.2. Strengths and Limitations of The Study

The main limitation of this study is related to the low number of sampling sessions (N = 20) over the monitoring period, which are further reduced if the two different monitoring sub-periods (warm and cold period), specifically identified to evaluate the performance of MMs across different climatic conditions and at different $PM_{2.5}$ concentration levels, are considered.

Additionally, the portable instruments were evaluated only at a fixed site station and not under their normal use conditions, namely, as personal devices. A further development of this study will include the evaluation of AB performance as compared to other portable monitors for personal exposure measurement applications. Moreover, the monitoring sessions were carried out only at one urban background site, not allowing the assessment of possible spatial variations in the monitoring area. Further, despite reference methods and accepted standard practices were adopted for gravimetric sampling, the adoption of further precautions, and technical measures (i.e., field blanks, duplicated measurements, etc.) would have allowed for further control and reduction of the level of variability of the $PM_{2.5}$ gravimetric measurements. Finally, the changes in the AB performances were assessed only within a relatively restricted concentration range (2.3–48.3 $\mu g/m^3$), even though this is typical of a medium-sized provincial town, such as Como. In this context, the authors think that evaluations conducted at higher PM concentrations could be relevant because, as reported by the manufacturer [49], the relation between AB and the reference methods should become increasingly non-linear above 100 $\mu g/m^3$ [34]. Despite the results of different studies for PM sensors are quite difficult to compare among each other (as the responses of these sensors may be influenced by aerosol composition), it should be noted that a recent study that was performed in the framework of AQ-SPEC project by Feinberg et al., 2018 [64], concerning the long-term evaluation of air sensors, outlined that AB is one of the sensors with the highest correlation with reference measurements, despite they may have a certain level of measurement noise and a potential level of interference related to the presence of relative

humidity. Anyhow, further studies for PM miniaturized sensors are needed to in deep evaluate their performance for different air pollutant concentration ranges and aerosol characteristics, both in (i) long-term, in-field studies [64] and under controlled conditions [65].

Therefore, additional studies covering a wider range of $PM_{2.5}$ concentrations and assessing further influencing factors (e.g., particles size and shape, particles refractive index, etc.) on measurement errors are suggested and encouraged.

Despite the aforementioned limitations, one of the main advantages of the present study is that, to the knowledge of the authors, this is one of the first comparison studies on ABs conducted in real environmental conditions and not only through laboratory tests. The possibility to quantify the instrument performances under real-world conditions is indeed a key highlight of this study [31] because, in general, laboratory tests can hardly reproduce an aerosol mixture matching the complex composition and variability of particles in real environments [34]. However, field tests can provide a greater variation of conditions in contrast to the controlled conditions that were found in laboratory tests [66].

3.2.5. Conclusions

In conclusion, despite a moderate level of agreement between AB and the gravimetric method, especially at lower concentrations, relevant bias was found across the entire sampling period, indicating the necessity to develop standardized protocols and harmonize performance evaluation criteria for these devices. Moreover, it is important to interpret data outcomes from AB (and, in general, from optical particle counters and photometers) carefully, especially if appropriate calibration factors are not used. However, that very similar trends in performances were found to those of other widely used direct-reading instruments (Aerocet and OPC), should be underlined; although, all instruments that were compared are based on the same measurement technique.

Future developments should aim at evaluation of AB, and, in general, of MMs, across different environments that are characterized by different PM concentrations and chemical-physical characteristics. Furthermore, the

influences of meteorological and other environmental parameters should be better evaluated. Also, AB should be evaluated over a longer time-period and under the same conditions in which the instruments are actually used: as personal and mobile monitors. Evaluation of measurement instruments in real-word conditions and during real operation procedures can provide more information regarding the performance of instruments and their usability. In this regard, other tests should be performed under real use conditions to evaluate the response of subjects to the use of the instrument itself (in terms of portability, ease of use, interference with normal activities, etc.).

Figure S1. Setup of the sampling equipment and relative position (view from the above).

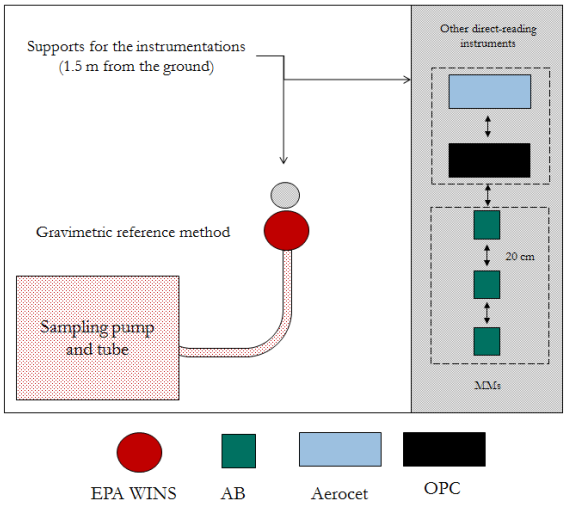


Figure S2. Wind direction (°) and intensity (m/s) during warm and cold periods.

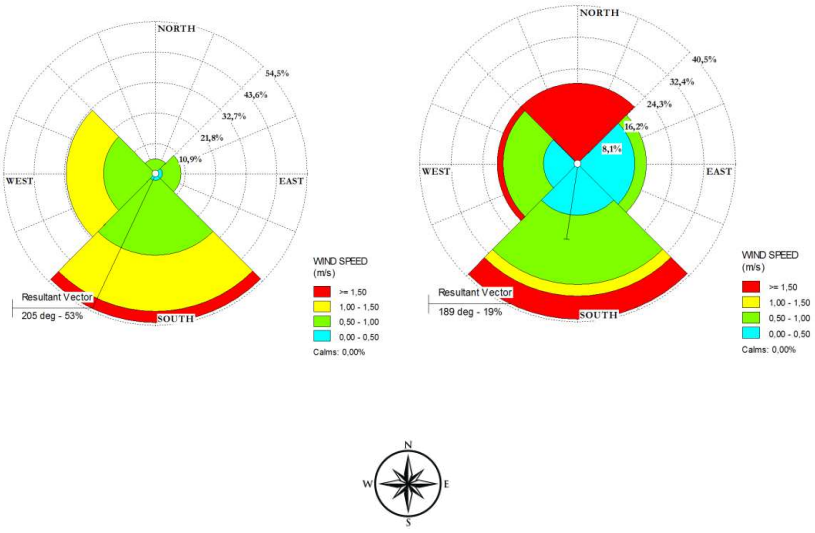


Figure S3. Maps of wind direction and intensity at the sampling point during cold and warm periods. Red areas correspond to wind intensity ≥ 1.50 m/s, yellow areas to wind intensity between 1 and 1.5 m/s, green areas between 0.5 and 1 m/s, and blue to wind intensity between 0 and 0.5 m/s.

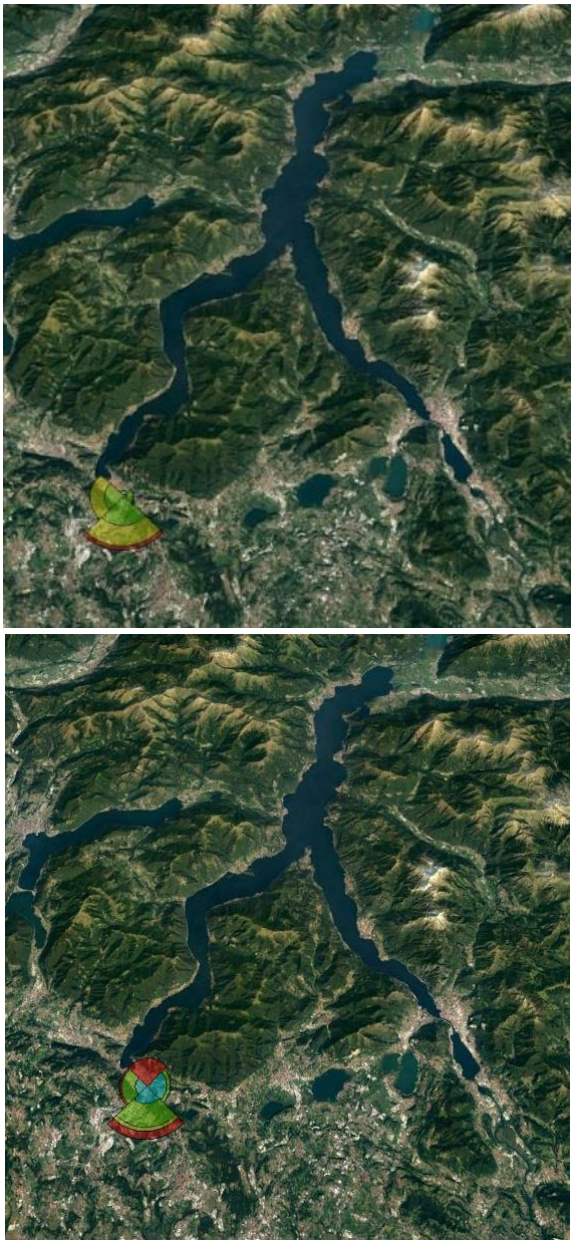


Table S1. Error between ABs - descriptive statistic. S.D.: standard deviation; Max.: maximum; Min.: minimum; C.I.: confidence interval.

	ABx (relative error %)	ABx (absolute error μg/m³)
Mean	9	5.7
S.D.	64	15.5
Max	122	47.9
Min.	-70	-8.8
Range	192	56.7
C.I. (95%)	31	7.5

Table S2. Mann-Whitney test statistics. Z: Mann-Whitney test statistics; Asymp. Sig: significance.

	Mann-Whitney U	Z	Asymp. Sig. (2-tailed)
AB1 vs EPA WINS	168	-0.365	0.715
AB2 vs EPA WINS	170	-0.307	0.759
AB3 vs EPA WINS	165	-0.453	0.651
Aerocet vs EPA WINS	154	-0.774	0.439
OPC vs EPA WINS	167	-0.394	0.693

Table S3. Correlations between all ABs (8-h averaged data). All correlations are significant at 0.001 level and results are based on 19 monitoring sessions. In the table is reported the Spearman's rank order correlation (rho).

	EPA WINS	AB1	AB2	AB3	Aerocet	OPC
AB1	0.954	---	0.939	0.947	0.979	0.884
AB2	0.889	0.939	---	0.988	0.981	0.963
AB3	0.881	0.947	0.988	---	0.982	0.935

Table S4. Correlations between direct-reading instruments (1-min averaged data). All correlations are significant at 0.001 level. In brackets are reported the number of data used for analysis. In the table is reported the Spearman's rank order correlation (rho).

	AB1	AB2	AB3	Aerocet	OPC
AB1	---	0.993 (N=6188)	0.989 (N=5862)	0.981 (N=7401)	0.986 (N=6813)
AB2	---	---	0.991 (N=5761)	0.983 (N=7241)	0.986 (N=6951)
AB3	---	---	---	0.978 (N=6851)	0.982 (N=6401)

Table S5. Regression parameters between direct-reading instruments (8-h average) and the gravimetric method. N: number of data; R: Pearson correlation coefficient; p: significance; m: slope; q: intercept; SE: standard error.

Instrument compared	Regression model				Slope			Intercept		
	N	R	R^2	*p*	m	SE	*p*	q	SE	*p*
AB1 vs EPA WINS	19	0.922	0.85	<0.001	1.375	0.14	<0.001	-0.473	0.17	0.013
AB2 vs EPA WINS	19	0.89	0.792	<0.001	1.346	0.168	<0.001	-0.416	0.203	0.056
AB3 vs EPA WINS	19	0.889	0.79	<0.001	1.272	0.159	<0.001	-0.347	0.193	0.09

	Comparable and mutually predictable	Comparable but ton mutually predictable
AB1 vs EPA WINS		YES
AB2 vs EPA WINS	NO	NO
AB3 vs EPA WINS		NO

Table S6. Regression parameters between direct-reading instruments (1-min averaged data). N: number of data; R: Pearson correlation coefficient; p: significance; m: slope; q: intercept; SE: standard error.

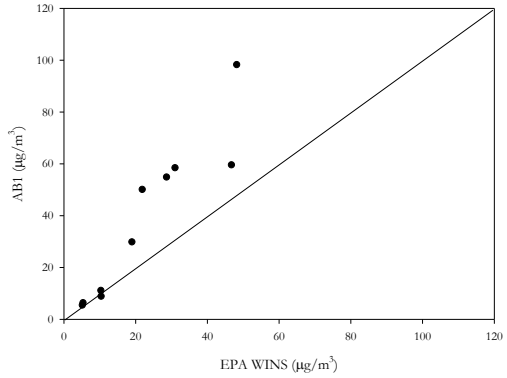
Instrument compared	Regression model				Slope			Intercept			Comparable and mutually predictable	Comparable but not mutually predictable
	N	R	R^2	*p*	m	SE	*p*	q	SE	*p*		
AB1 vs Aerocet	7401	0.969	0.939	<0.001	0.933	0.003	<0.001	-0.063	0.004	<0.001		
AB2 vs Aerocet	7241	0.968	0.937	<0.001	0.963	0.003	<0.001	-0.096	0.004	<0.001	NO	YES
AB3 vs Areocet	6851	0.969	0.939	<0.001	0.944	0.003	<0.001	-0.073	0.004	<0.001		
AB1 vs OPC	6813	0.981	0.962	<0.001	0.878	0.002	<0.001	0.123	0.003	<0.001		
AB2 vs OPC	6851	0.969	0.939	<0.001	0.944	0.003	<0.001	-0.073	0.004	<0.001	NO	YES
AB3 vs OPC	6401	0.979	0.958	<0.001	0.881	0.002	<0.001	0.124	0.003	<0.001		

Table S7. Regression parameters between AB and EPA WINS (8-h averaged data). N: number of data; R: Pearson correlation coefficient; p: significance; m: slope; q: intercept; SE: standard error. Regression parameters were calculated and reported for the summer and winter datasets.

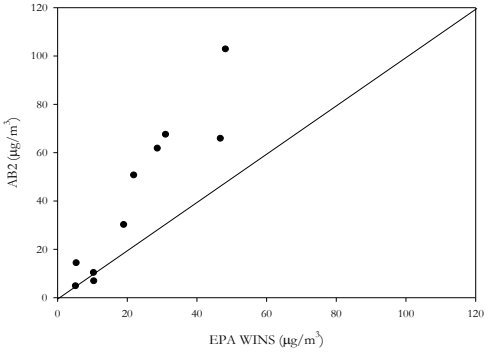
Summer Database										
Instrument compared	Regression model				Slope			Intercept		
	N	R	R^2	*p*	m	SE	*p*	q	SE	*p*
AB1 vs EPA WINS	9	0.980	0.960	<0.001	0.361	0.049	<0.001	-0.865	0.698	0.255
AB2 vs EPA WINS	9	0.982	0.964	<0.001	0.621	0.045	<0.001	-0.627	0.646	0.364
AB3 vs EPA WINS	9	0.986	0.972	<0.001	0.633	0.040	<0.001	-0.911	0.572	0.155

Winter Database										
Instrument compared	Regression model				Slope			Intercept		
	N	R	R^2	*p*	m	SE	*p*	q	SE	*p*
AB1 vs EPA WINS	10	0.940	0.884	<0.001	1.839	0.235	<0.001	-3.816	6.414	0.568
AB2 vs EPA WINS	10	0.940	0.884	<0.001	1.967	0.253	<0.001	-3.432	6.915	0.633
AB3 vs EPA WINS	10	0.944	0.891	<0.001	1.614	0.200	<0.001	-0.763	5.450	0.892

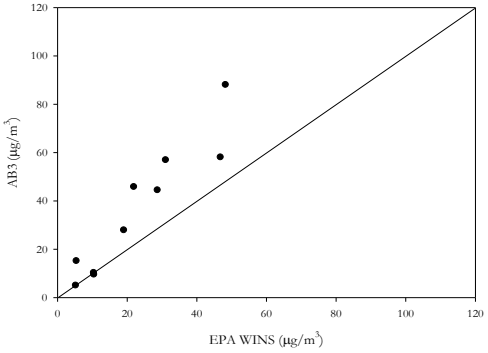
Figure S4. Regression between AB (a.: AB1; b.: AB2; c.: AB3) and the gravimetric method (EPA WINS).



(a)



(b)

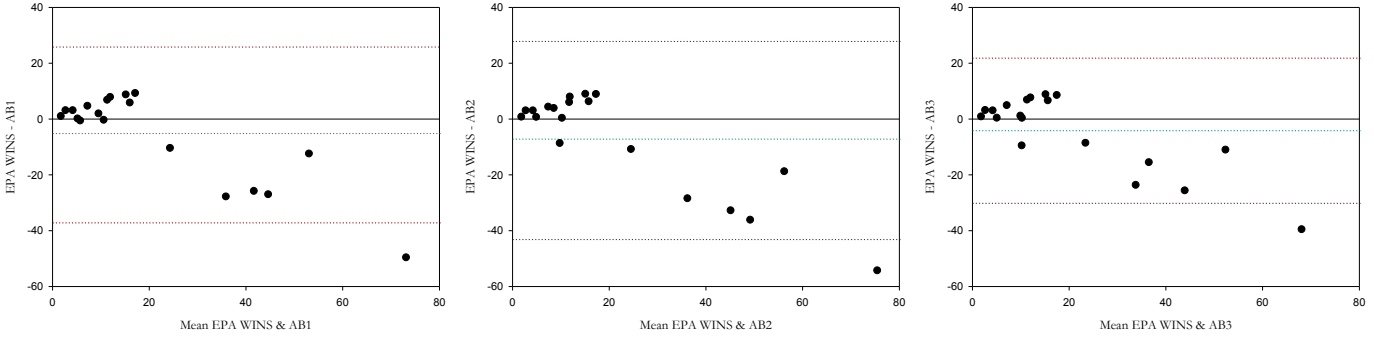


(c)

Table S8. Relative error (%) calculated during all monitoring sessions between direct-reading instruments and the gravimetric method.

		Relative Error					
Session	Season	ABx	AB1	AB2	AB3	OPC	Aerocet
2	Summer	-70.0%	-70.2%	-68.5%	-71.8%	-81.0%	-67.0%
3	Summer	-34.0%	-39.6%	-29.8%	-33.8%	-60.0%	-22.0%
4	Summer	-51.0%	-51.9%	-50.9%	-51.0%	-62.0%	-27.0%
5	Summer	-44.0%	-45.5%	-39.9%	-45.9%	-49.0%	-5.0%
6	Summer	-47.0%	-47.7%	-44.2%	-50.1%	-46.0%	-6.0%
7	Summer	-49.0%	-48.6%	-49.6 %	-47.6%	-50.0%	-6.0%
8	Summer	-45.0%	-44.1%	-45.2%	-44.5%	-48.0%	-3.0%
9	Summer	-40.0%	-42.0%	-40.4%	-38.8%	-40.0%	0.0%
10	Summer	-32.0%	-30.2%	-32.6%	-34.4%	-27.0%	50.0%
11	Winter	-21.0%	-17.4%	-35.8%	-9.8%	n.a	38.0%
12	Winter	0.0%	4.5%	-2.4%	-2.3%	9.0%	48.0%
13	Winter	95.0%	87.2%	116.5%	82.7%	152.0%	121.0%
14	Winter	117.0%	12.9%	160.8%	176.2%	204.0%	245.0%
15	Winter	-6.0%	-0.5%	-11.3%	-5.9%	3.0%	32.0%
16	Winter	30.0%	26.8%	40.3%	23.8%	42.0%	49.0%
17	Winter	86.0%	90.2%	114.4%	54.4%	147.0%	125.0%
18	Winter	99.0%	102.9%	112.5%	82.1%	177.0%	206.0%
19	Winter	53.0%	55.1%	57.2%	45.6%	166.0%	147.0%
20	Winter	122.0%	127.1%	130.0%	108.2%	97.0%	121.0%

Figure S5. Bland-Altman plot. Red dotted lines represent upper and lower confidence intervals (95%) while the green dotted line represents the average difference between instruments. The mean concentrations between EPA WINS and the compared instruments (a.: AB1; b.: AB2; c.: AB3) are reported on the x-axis while the differences between the methods are shown (8-h average) on the y-axis.



(a) *(b)* *(c)*

Table S9. Absolute error (µg/m³) calculated during all monitoring sessions between direct-reading instruments and the gravimetric method.

Session	Season	Absolute error					
		ABx	AB1	AB2	AB3	OPC	Aerocet
2	Summer	-2.99	-2.99	-2.92	-3.06	-3.45	-2.85
3	Summer	-0.77	-0.89	-0.67	-0.76	-1.34	-0.49
4	Summer	-2.95	-2.99	-2.93	-2.94	-3.57	-1.57
5	Summer	-6.46	-6.71	-5.89	-6.77	-7.20	-0.68
6	Summer	-4.54	-4.57	-4.24	-4.80	-4.42	-0.62
7	Summer	-7.72	-7.72	-7.87	-7.56	-7.93	-1.02
8	Summer	-8.72	-8.63	-8.84	-8.70	-9.35	-0.49
9	Summer	-8.78	-9.13	-8.79	-8.43	-8.75	-0.07
10	Summer	-6.14	-5.72	-6.18	-6.51	-5.17	9.53
11	Winter	-2.21	-1.83	-3.77	-1.03	-10.52	4.01
12	Winter	-0.01	0.47	-0.25	-0.24	0.96	5.06
13	Winter	29.71	27.14	36.26	25.74	47.33	37.72
14	Winter	6.37	0.70	8.79	9.63	11.14	13.39
15	Winter	-0.31	-0.03	-0.60	-0.31	0.16	1.70
16	Winter	14.19	12.54	18.88	11.15	19.68	22.80
17	Winter	24.82	25.93	32.90	15.63	42.30	36.00
18	Winter	47.93	49.73	54.39	39.67	85.57	99.43
19	Winter	10.06	10.53	10.94	8.71	31.83	28.09
20	Winter	26.76	27.92	28.58	23.78	21.38	26.60

Figure S6. Analysis of absolute error (absolute value - µg/m3) for ABs as a function of $PM_{2.5}$ concentrations (µg/m³) and RH (%).

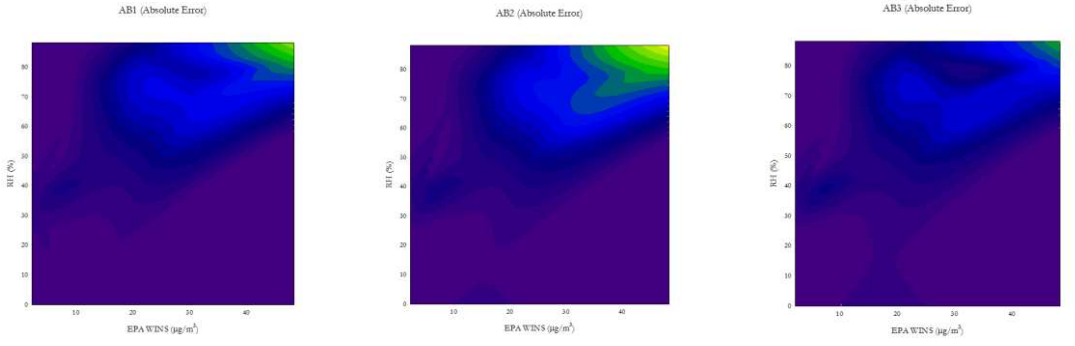


Figure S7. Analysis of relative error (absolute value - %) for ABs as a function of $PM_{2.5}$ concentrations (µg/m³) and RH (%).

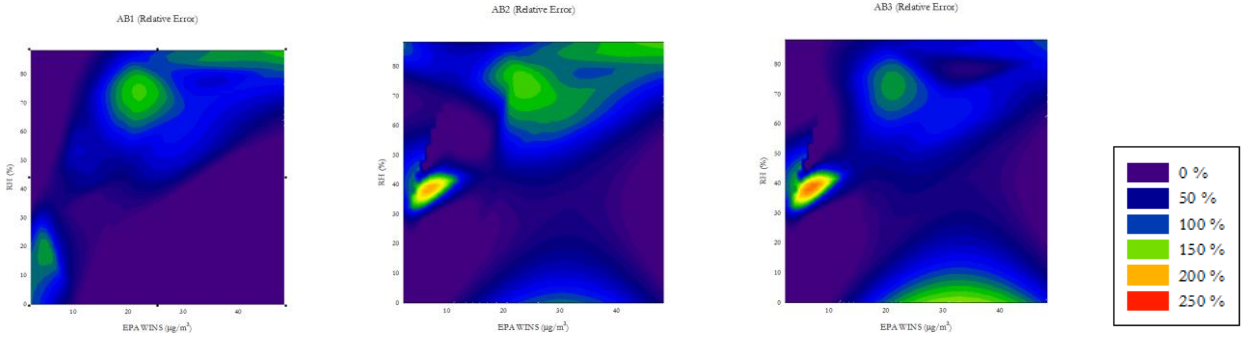


Figure S8. Analysis of absolute error (absolute value - µg/m3) for direct-reading instruments as a function of $PM_{2.5}$ concentrations (µg/m³) and RH (%).

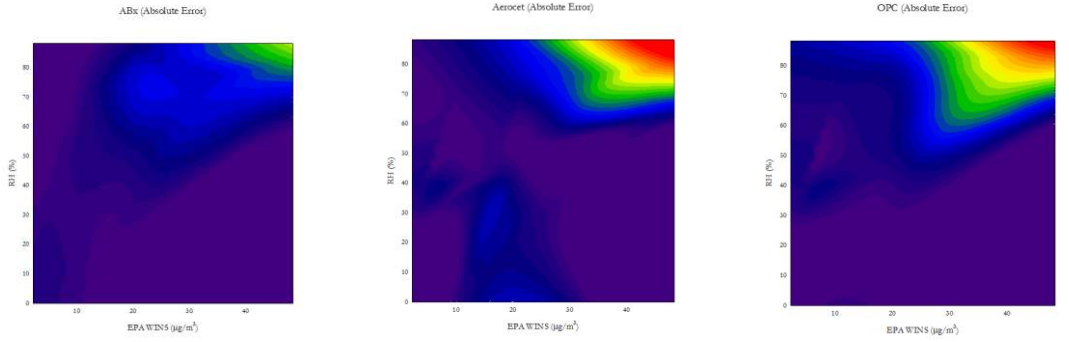


Figure S9. Analysis of relative error (absolute value - %) for direct-reading instruments as a function of $PM_{2.5}$ concentrations (µg/m³) and RH (%).

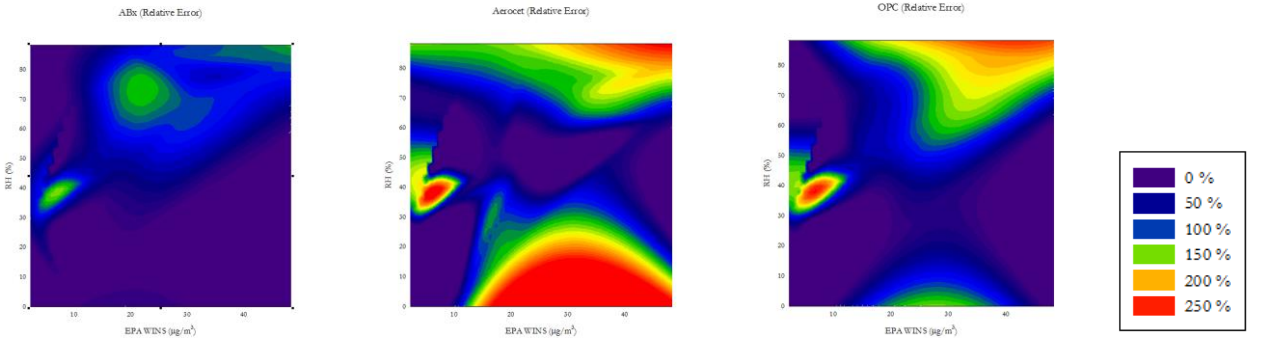
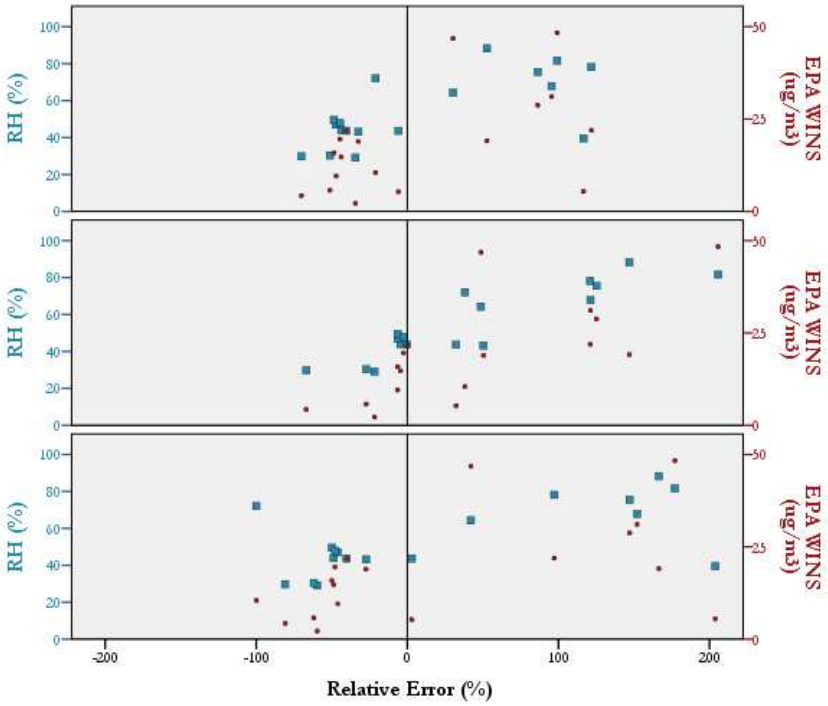


Figure S10. Analysis of relative error (%) for direct-reading instruments as a function of $PM_{2.5}$ concentrations ($\mu g/m^3$) and RH (%). a.: AB1; b.: AB2; c.: AB3.



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4. ASSESSING PERSONAL EXPOSURE OF SELECTED POPULATIONS TO AIR POLLUTANTS BY MEANS OF PORTABLE AND MINIATURIZED MONITORS

The following chapters are based on:

(4.1) Borghi et al. Commuter's personal exposure assessment and evaluation of inhaled dose to different atmospheric pollutants.
To be submitted

(4.2) Borghi et al. Exposure to Air Pollutants in Pregnancy: the INSIDE Project.
To be submitted

(4.3) Borghi et al. Evaluation of the inhaled dose across different Microenvironments.
IOP Conf. Series: Earth and Environmental Science 2019, 296.

PREFACE

As reported in the previous chapters, portable and miniaturized monitors could be used to provide a more representative characterization of exposure and to achieve a broader spatial coverage than those provided by fixed air quality monitoring stations. Moreover, and despite possible lacks in accuracy, MMs monitors can potentially be used across different applications such as community or individual exposure assessment [1].

Due to their reduced size and cost, to their ability to adapt to different experimental design, to the capability to measure pollutant concentrations at high spatial and temporal resolution and due to the fact that this kind of monitors can be usually integrated with other kind of devices (such as GPS and smartphone applications), MMs could become a new way for human exposure assessment. One of the main advantages related to the use of MMs in exposure science studies, other than the high spatial and temporal resolution of data acquired, is related to the fact that, due to advantages reported in Chapter 2, this kind of monitors can be used to assess the exposure to selected pollutants for selected populations. Some examples of exposure assessment of selected populations are therefore reported in the following chapters. In the first Chapter (4.1) the exposure assessment of a typical commuter

was performed: in this case the selected subject, for the request of the instrumental design,

had to wear and to carry around for an extended time different portable and MMs monitors. For this reason, reduced dimensions and low weight of the instrumentation were necessary to allow an easier monitoring session. In this case the enrolled subject was a trainer project researcher, expert in the exposure assessment field and in measurement campaign and the ease of use of the instrumentation was not a fundamental parameter to be taken into consideration for this study. Conversely, the ease of use, was considered a fundamental parameter for the other two studies (Chapter 4.2, 4.3 and 4.4) in which non-expert subjects (i.e., pregnant women, children) had to manage the instruments (from power-on to shut-down) independently. In addition, in all the reported studies, reduces dimensions of the different monitors used allowed to provide the enrolled subjects with more than one instrument, thus allowing to simultaneously measure the levels of exposure to different pollutants. Moreover, the possibility of associating a GPS with the instrumentation used has allowed, in all the studies reported below, the georeferencing of the subject's position, associating it with the measured exposure levels.

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4.1. COMMUTERS EXPOSURE ASSESSMENT

It is well known that time spent commuting may represent an important situation for exposure to different pollutants, despite the time spent traveling represent only a small fraction of the day. In fact, commuting is of great relevance both regarding exposure to pollutants and the dose of the same inhaled by commuters. Several studies are present in the scientific literature regarding the evaluation of exposure to different pollutants in (traffic and non-traffic) micro-environments (MEs), but only a few studies also deal with the evaluation of the inhaled dose of the pollutants, mainly due to technical-logistic problems that make the evaluation of physiological parameters (such as the pulmonary ventilation rate) necessary for the calculation of the inhaled dose difficult.

The main aim of this study is therefore to evaluate a commuter's the exposure to different pollutants (nitrogen dioxide - NO_2, and fractionated particulate matter - PM, including ultrafine particles – UFP), via miniaturized and portable real-time monitoring instruments in different and selected MEs; the inhaled doses of these pollutants were estimated in each of these MEs.

Measurements were performed along a typical commuter route defined a priori from subject's home (located in a medium-size city) to the workplace (an office located in a large city in the Northern part of Italy). In this framework different micro-environments were considered and evaluated (Walking in low traffic - lt -and high traffic - ht - conditions, Bike, Car, Underground, Train and Indoor). Experimental data were collected during four working weeks, in two different seasons (winter and summer). Different portable and miniaturized instruments were used to evaluate PM (direct-reading and filter-based instruments) and NO_2 (direct-reading instrument) exposure. More, the evaluation of physical effort (in terms of heart rate) was evaluated using a heart rate monitor.

Principal results show how higher exposures were measured in Underground (for all PM fractions and NO_2) and in Car (UFP), while lower exposure levels were measured in Car (PM and NO_2) and in Train (UFP). On the contrary, instead, higher values of inhaled cumulative dose were found in environments defined as Other, followed by Walking (ht) while lower values were found in Walking (lt) and in Car.

4.1.1. Introduction

It is well known that air pollution may cause health problems and it is also well known that the adverse effects of air pollution are particularly critical in urban areas, representing hotspots especially for traffic emissions [1]. Moreover, travel microenvironments may represent settings of high exposure to different air pollutants [2]. Despite the time spent commuting may be scarce compared to the whole day, this activity may lead to a great contribution to both exposure and inhalation of pollutants [2]. Different studies have been carried out to evaluate the exposure of commuters across Europe, considering different traffic (and non-traffic) microenvironments (MEs), as reported in literature reviews [3], [4], as well as to assess the variation between commuting modes. As reported in a recent paper [1] indeed, the number of studies based on personal monitoring during a simulated daily commute and carried out in different cities has increased in the last few years, considering different transport modes [5]–[18]. A recent paper for example reported that commuting via motorized modes leads to higher exposure to some pollutants (such as $PM_{2.5}$ and black carbon) than pedestrian or cyclists; contrariwise other studies identified higher exposure (for the same pollutants) during cycling [1]. Summing up, no consensus on the "cleanest" or "dirtiest" commuting route has been reached, even if authors agree on the fact that ambient or background air quality monitoring does not accurately reflect the variability of pollutant exposure concentrations [1].

In addition to this issue, and to the need for better understanding the determinants of exposure levels in traffic MEs, it is important to note that most of the literature only assess the commuters' exposures to airborne contaminants, but not the corresponding inhaled doses. The inhaled dose of airborne pollutants is determined based on the subject's pulmonary ventilation rate and physical activity (other than on the subject's exposure level to the airborne pollutant), but these parameters are often not considered in the experimental design of exposure assessment studies (generally due to technical issues associated with the measurement of some physiological parameters) [2]. However, the assessment of pollutants' inhaled dose can be of interest for risk assessment, especially in the case of commuters, because

higher dose can result owing to high exposure typically associated with urban transit/traffic environments [19], [20] and higher inhalation rates during active transport mode such as walking and cycling (i.e., increased physical effort leads to elevated inhalation rate and therefore higher inhaled dose and higher lung deposition of pollutants) [2].

The aims of this study are therefore: (i) to assess the exposure levels to different airborne pollutants, such as size fractionated particulate matter (PM_1, $PM_{2.5}$, PM_4, PM_{10}, Total suspended Particles - TSP), also including Ultrafine Particles (UFP) and nitrogen dioxide (NO_2) measured across a commuting route, from a provincial to a big city in the Northern part of Italy; (ii) to describe pollutants exposure levels across 8 different MEs; (iii) to evaluate the dose of the considered airborne pollutants inhaled during daily commuting and across different MEs, considering subject's physiological parameters; (iv) to check if different inhaled doses, compared to external exposure occur considering different MEs,.

4.1.2. Materials and methods

4.1.2.1. Study design and instrumentation

To simulate a typical home-to-work (and return) commuter's route, a fixed route (for a total of 90 km) was defined a priori, between a provincial city ("home" - Villa Guardia - 45° 47' N 9° 01' E) to an office placed in Milan (" Workplace" - 45° 27' N 9° 11' E), the largest city in the Lombardy region, Italy (Figure SM1).

The commuting route allowed to consider different MEs usually visited by commuters; a detailed report regarding MEs considered in this study is reported in Table SM1 but in general the MEs visited by the commuter are the following: Walking (lt- Low Traffic condition); Walking (ht - High Traffic condition); Bike; Car; Underground; Train; Indoor and Other (defined as the transition period (2 min) between an environment to another). Experimental data were collected over two working weeks (Monday-Friday) in two different seasons (winter campaign: 11/03/19-15/03/19 and 18/03/19-22/03/19; summer campaign: 08/07/19 - 12/07/19*, 15/07/2019 - 19/07/19; *the monitoring of the Thursday 11/07/2019 was canceled due to a public-transport strike and re-scheduled on the following available Thursday –

25/07/2019), to characterize the weekly and seasonal pollutants concentration variability.

Portable and miniaturized monitors were used to assess the exposure levels to different airborne pollutants. All the instruments were worn by one of the authors (F.G.) using a backpack. All instruments inlets were placed in the breathing zone of the operator, or rather the hemisphere of 30 cm radius extending in front of the face (Figure SM2). All instruments were daily checked, and all guidelines provided by the manufacturer were followed to ensure quality controlled data. Instruments were also constantly checked during the monitoring phase to prevent instruments failure. All instruments were set up with an acquisition rate equal to 60s.

Different portable instruments, both direct-reading and filter-based, were used to evaluate size-fractionated PM exposure. UFP exposure levels were measured via a portable diffusion size classifier (DiSCmini, Matter Aerosol AG, Wohlen AG, Swiss - DSC). The DSC used in this study can measure the number concentration and the average size of particles in the range of $10 < Dp < 700$ nm. The continuous determination of size fractionated PM concentration was also carried out by means of a second portable direct-reading monitor (Aerocet 831-MetOne Instrument Inc., Grant Pass, Oregon, USA - Aerocet), that provide concentration data of different PM fraction (PM_1, $PM_{2.5}$, PM_4, PM_{10} and TSP). Finally, a complementary miniaturized monitor was used for the evaluation of $PM_{2.5}$ concentration (AirBeam, HabitatMap Inc., Brooklyn, New York, USA - AB). This monitor is based on an Arduino board and it can detect particles in a range from 0.5 to 2.5 μm and a $PM_{2.5}$ concentration up to 400 $\mu g/m^3$. $PM_{2.5}$ samples were collected by means of a GK2.05 sampler (BGI Inc., Waltham, MA, USA), operating with a sampling pump with a flow rate equal to 4 L/min; particles were collected on PTFE filters. Mass concentration were determined via gravimetric analysis following a standard reference method [21], [22]. The weighing procedure [23]–[25] contemplates the conditioning of filters in a controlled environment (temperature: 20±1 °C; relative humidity: 50±5%) for a minimum of 24h, following which filters were weighted, before and after the sampling, with a microbalance (Gibertini Micro 1000, Novate, Milan, Italy). Gravimetric data

were used to correct PM data outcomes from direct reading instruments, providing a daily correction factor, applied *a posteriori* to the whole PM dataset.

The measurement of NO_2 concentration was performed by means of a miniaturized electrochemical monitor (CairClip NO_2, Cairpol; La Roche Blanche - France - CC). The evaluation of physical effort, in terms of heart rate, was evaluated using a heart rate monitor (SUUNTO 9). This instrument was also used to acquire GPS data, with the same acquisition rate of other used instruments (60 s).

4.1.2.2. Statistical analysis and inhaled dose calculation

Following well-established practices in statistics and the literature, data obtained via direct-reading instruments were examined and handled in order to exclude zero and unreliable data: for this reason, concentration distributions were truncated above the 99th percentile and below the 1st percentile [26]. Moreover, following the literature [27] on the validation and evaluation of micro-sensors, NO2 value found below the calculated limit of detection ("LOD" = 1.692 μg/m3) have been replaced with LOD/2 (somewhat justified [28]. Furthermore, following the technical references of direct-reading instruments, PM data acquired in extreme microclimatic conditions (RH > 80%; T > 50 °C) have been eliminated, to exclude data afflicted by recognized environmental interference. As mentioned before, the error associated to the PM direct-reading instruments was managed using a calculated correction factor. The correction factor, calculated dividing daily PM concentration measured gravimetrically for the daily average PM concentration measured simultaneously via direct-reading instruments, was applied to data measured from direct-reading instruments monitoring [24], [29]. UFP mass concentrations were calculated based on number concentrations, particle diameter and mean mass density factors [20].

In this paper, a descriptive statistic (reporting number of observations, mean, minimum, maximum and standard deviation) was performed on the total dataset and for each kind of MEs considered in this study to provide an overview of data acquired during the two different monitoring periods. Moreover, in order to deeply evaluate the exposure concentration in each MEs, the average values (as the total and for different season) measured in

different environments are reported.

Descriptive statistics regarding the heart beat (bpm) measured in each MEs and the calculated ventilation rate (l/min) are also reported. As reported in the literature [1], the pollutant inhaled dose can be calculated as the product of the measured exposure concentration, the inhalation rate and the time spent in each particular MEs. In this regard, the subject's ventilation rate was calculated following the literature [30], where the ventilation (l/min) rate was calculated as reported in Equation 1. The descriptive statistic of the inhaled dose is reported in this study as the average dose calculated in each MEs.

$$VE = 0.00071 \times HR^{2.17}$$

Equation 1. Calculation of the ventilation rate [30]. *VE: Ventilation rate (l/min); HR: heart rate (bpm).*

To assess distribution of exposure data, the Kolmogorov-Smirnov test was performed. Once verified that the distributions were not normally (and neither log-normally) distributed, a non-parametric test (Mann-Whitney test) was performed to evaluate differences of pollutant exposure levels among MEs. Data were analyzed using SPSS Statistic 20.0 (IBM, Armonk, NY, USA) and a significance level of 0.05 was used in all statistical tests.

4.1.3. Results and Discussions

4.1.3.1. Descriptive analysis: pollutants exposure levels and physiological parameters

During the two monitoring periods the evaluation of pollutant exposure levels was performed across different MEs considered. Table 1 reports a descriptive statistic regarding total and seasonal (winter and summer) levels of exposure while Figure 1 represents the average contribution of differential PM fractions to the total (for the whole period and for the two considered seasons).

Parameter	N	Min.	Max.	Mean	S.D.	Monitoring Period
*UFP number**	*8179*	*212*	*74436*	*9640*	*7027*	
*UFP diameter***	*8228*	*<LOD*	*300.0*	*49.2*	*15.2*	
*UFP ldsa****	*8228*	*0.6*	*203.9*	*24.4*	*15.9*	
UFP mass	8239	*<LOD*	197.3	3.7	4.1	
PM_1	8365	0.1	174.8	10.2	12.5	
$PM_{1\text{-}2.5}$	8026	*<LOD*	106.4	3.2	5.8	
$PM_{2.5}$	8342	0.2	160.8	13.1	15.4	
$PM_{2.5\text{-}4}$	8046	*<LOD*	139.9	3.4	5.9	Total
$PM_{2.5}$ (AB)	7394	1.4	134.9	35.5	22.6	
PM_4	8348	0.3	189.0	16.2	18.9	
$PM_{4\text{-}10}$	8023	*<LOD*	303.5	8.3	13.2	
PM_{10}	8345	0.6	378.5	24.0	28.4	
$PM_{>10}$	8033	*<LOD*	399.6	4.5	9.1	
TSP	8340	0.6	480.6	28.2	33.0	
NO_2	8690	0.9	478.5	30.5	52.7	
*UFP number**	*4014*	*477*	*63678*	*10133*	*7449*	
*UFP diameter***	*4063*	*<LOD*	*130.3*	*44.5*	*11.0*	
*UFP ldsa****	*4063*	*0.6*	*203.9*	*24.3*	*17.6*	
UFP mass	4074	*<LOD*	197.3	3.2	4.5	
PM_1	4164	0.3	174.8	11.1	13.8	
$PM_{1\text{-}2.5}$	3744	*<LOD*	76.5	4.4	7.1	
$PM_{2.5}$	4162	0.7	160.8	14.8	17.0	
$PM_{2.5\text{-}4}$	3747	*<LOD*	92.2	4.5	6.7	Winter
$PM_{2.5}$ (AB)	3763	26.5	116.5	50.6	14.7	
PM_4	4162	1.1	189.0	18.7	21.0	
$PM_{4\text{-}10}$	3747	*<LOD*	303.5	11.3	16.6	
PM_{10}	4162	1.1	378.5	28.6	33.0	
$PM_{>10}$	3747	*<LOD*	399.6	5.7	11.0	
TSP	4162	1.5	480.6	33.5	38.6	
NO_2	4389	0.9	478.5	29.0	50.6	
*UFP number**	*4165*	*212*	*74436*	*9164*	*6560*	
*UFP diameter***	*4165*	*18.7*	*300.0*	*53.8*	*17.2*	
*UFP ldsa****	*4165*	*1.8*	*168.0*	*24.4*	*14.0*	
UFP mass	4165	0.1	73.9	4.2	3.5	
PM_1	4201	0.1	70.2	9.2	11.0	
$PM_{1\text{-}2.5}$	4282	*<LOD*	106.4	2.2	4.2	
$PM_{2.5}$	4180	0.2	106.4	11.4	13.5	
$PM_{2.5\text{-}4}$	4299	*<LOD*	139.9	2.4	4.8	Summer
$PM_{2.5}$ (AB)	3631	1.4	134.9	19.9	18.3	
PM_4	4186	0.3	139.9	13.7	16.3	
$PM_{4\text{-}10}$	4276	*<LOD*	183.1	5.8	8.4	
PM_{10}	4183	0.6	190.6	19.5	22.1	
$PM_{>10}$	4286	*<LOD*	214.9	3.5	7.0	
TSP	4178	0.6	223.8	22.9	25.1	
NO_2	4301	0.9	478.5	32.0	54.7	

*Table 1. Descriptive statistic performed on the total dataset and for winter and summer campaign (N: number of data; Min.: minimum; Max.: maximum; S.D: standard deviation; ldsa: lung-deposited surface area; $PM_{2.5}$ (AB): $PM_{2.5}$ measured via AirBeam). Data are reported as $\mu g/m^3$ (*particle/cm^3; **nm; ***$\mu m^2/cm^3$). Data in italics refers to those used for the calculation of UFP mass.*

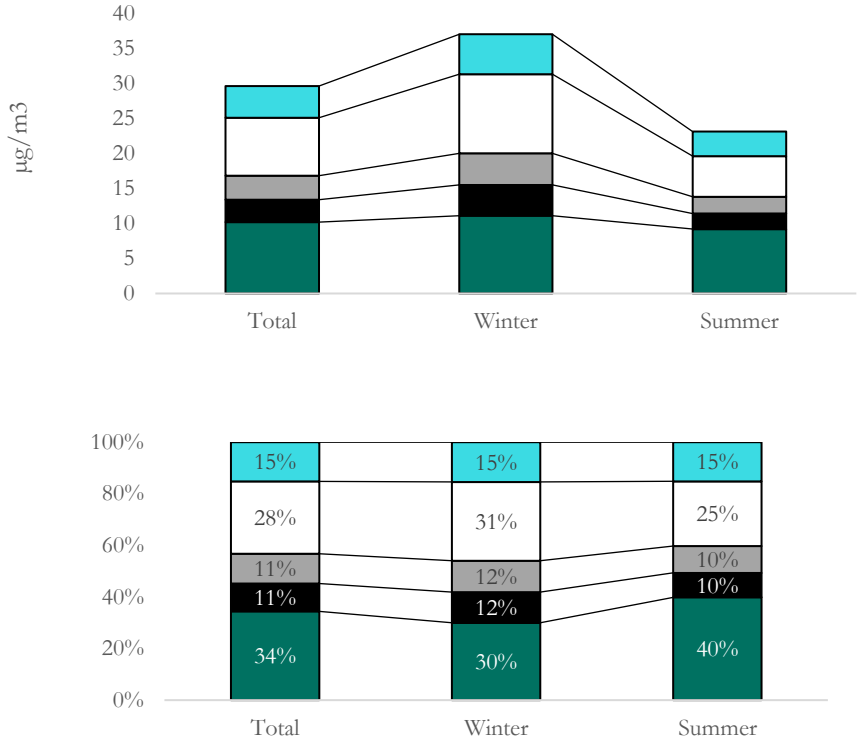

Figure 1 Descriptive statistic of differential concentration calculated for the total dataset and for season dataset (summer and winter). Green: PM_1; black: $PM_{1\text{-}2.5}$; grey: $PM_{2.5\text{-}4}$; white: $PM_{4\text{-}10}$; Light blue: $PM_{>10}$.

As expected, during the summer period, average exposures to airborne pollutants were lower than the exposures measured during the winter, except for UFP and NO_2 exposure levels.

Figure 1 shows the contribution of the different fractions on the total: PM_1 represent 40% of the total during the summer period and 30% during the winter period. $PM_{1\text{-}2.5}$ and $PM_{2.5\text{-}4}$ are very similar during the two periods considered (12% and 10% respectively), as well as for $PM_{>10}$ (equal to 15%).

The PM_{4-10} fraction has a major contribution during the winter period (31% of the total) than in the summer period (25% of the total).

In order to evaluate changes and variation of exposure levels as a function of the considered MEs, a descriptive statistic of average exposure levels found across MEs is reported in Table 2. In particular, MEs considered in this study refer to: Walking (lt), Walking (ht), Bike, Car, Underground, Train, Indoor and Other. Higher exposure concentration was measured in Underground (for all PM fractions and NO_2) and in Car (UFP), while lower exposure levels were measured in Car (PM and NO_2) and in Train (UFP). This trend is present in the total database, as well as in the seasonal datasets (summer and winter). Higher summer exposure concentrations were found in particular MEs: exposure to UFP was higher in summer than in winter in Walking (lt), Car, Train, Indoor and Other environments while PM_1 summer exposure was found higher in Walking (lt) and in the Indoor MEs. NO_2 exposure were also found higher in the warm season in Walking (lt), Bike, Car, and Other environments. Finally, higher concentration during the summer were measured in Walking (lt) for $PM_{2.5}$, PM_4 and PM_{10}. In general, higher differences between summer and winter exposure concentrations were measured in the Underground environment (ranging from 0.5 $\mu g/m^3$ - UFP, to 80.5 $\mu g/m^3$ TSP) while lower differences were found in Train environment (ranging from 0.7 $\mu g/m^3$ UFP, to 5.6 $\mu g/m^3$ TSP).

From Figure 2 it is possible to observe the trend of the differential concentrations calculated in the different ME (calculated for total and seasonal database). PM_1 shows an important contribution to the total in the Car ME, during the winter period (59%) while it has similar percentages to those found in other MEs during the summer period (51%). In fact, during winter the percentages of PM_1 found in the other MEs range from 29% (Walking (lt)) to 37% (Train) while it varies from 30% (Underground) to 46% (Train) during summer. Regarding the $PM_{1-2.5}$ fraction, this appears to have a percentage contribution on the total very similar in the different ME considered and during both seasons considered. The percentages vary from 7% (Train) to 15% (Underground) during the winter and from 5% (Train) to 15% (Underground) during the summer. The same trend was found in the $PM_{2.5-4}$ fraction, which varies from 8% (Train and Walking (lt)) to 14%

(Underground) in winter and from 6% (Train) to 13% (Underground) during the summer. The PM_{4-10} fraction appears to have a scarce influence on the total in the Car environment during the summer (16%) and during the winter period (14%), compared to the other MEs considered. In fact, the percentages of this fraction in the other MEs range from 25% (Train) to 40% (Walking (lt)) in winter and from 21% (Train) to 32% (Walking (lt)) in summer. Finally, the $PM_{>10}$ fraction is very similar in the different MEs and in the different seasons considered, except for the Train environment (winter: 24%, summer: 22%) and for the Indoor environment during the winter period (19%). In fact, during the winter period the percentages range from 9% (Car) to 16% (Walking (lt)) in winter and from 10% (Walking (lt), Walking (ht), Bike) to 15% (Underground and Other) in summer.

	Walking (lt)			Walking (ht)		
	Total (mean)	Winter (mean)	Summer (mean)	Total (mean)	Winter (mean)	Summer (mean)
*UFP number**	*9218*	*9384*	*9053*	*13735*	*16432*	*11484*
*UFP diameter***	*46.7*	*45.1*	*48.3*	*46.9*	*42.9*	*50.5*
*UFP ldsa****	*22.9*	*22.6*	*23.2*	*34.0*	*38.2*	*30.2*
UFP mass	*3.3*	*3.3*	*3.3*	*4.5*	*4.3*	*4.8*
PM_1	12.8	11.3	14.4	12.3	13.1	11.5
$PM_{1-2.5}$	2.7	3.2	2.3	2.9	3.8	2.1
$PM_{2.5}$	15.5	14.5	16.7	15.2	16.9	13.6
$PM_{2.5-4}$	3.1	3.0	3.2	3.8	4.9	2.7
$PM_{2.5}$ (AB)	38.5	49.8	25.5	37.5	51.5	24.3
PM_4	18.6	17.5	19.9	19.0	21.8	16.3
PM_{4-10}	13.5	15.7	10.9	10.2	13.7	7.0
PM_{10}	32.1	33.2	30.8	29.2	35.5	23.3
$PM_{>10}$	5.0	6.2	3.6	3.5	4.3	2.7
TSP	37.1	39.4	34.4	32.7	39.8	26.0
NO_2	32.3	25.5	39.9	38.5	39.5	37.5

	Bike			Car		
	Total (mean)	Winter (mean)	Summer (mean)	Total (mean)	Winter (mean)	Summer (mean)
*UFP number**	*15655*	*17824*	*13700*	*13843*	*14161*	*13447*
*UFP diameter***	*44.4*	*44.2*	*44.6*	*51.5*	*47.2*	*57.0*
*UFP ldsa****	*37.1*	*42.6*	*32.2*	*37.1*	*36.8*	*37.6*
UFP mass	*4.6*	*5.4*	*3.9*	*6.3*	*5.6*	*7.3*
PM_1	15.0	16.4	13.8	5.8	6.8	4.4
$PM_{1\text{-}2.5}$	4.1	5.1	3.1	1.0	1.2	0.9
$PM_{2.5}$	19.1	21.5	16.9	6.8	8.0	5.3
$PM_{2.5\text{-}4}$	5.5	7.2	4.0	0.9	1.0	0.8
$PM_{2.5}$ (AB)	37.5	50.7	25.5	31.1	46.1	11.3
PM_4	24.6	28.7	20.9	7.7	9.0	6.1
$PM_{4\text{-}10}$	14.3	19.7	9.5	1.6	1.6	1.4
PM_{10}	38.9	48.4	30.4	9.3	10.6	7.5
$PM_{>10}$	4.4	5.5	3.3	1.1	1.0	1.1
TSP	43.3	53.9	33.7	10.4	11.6	8.6
NO_2	44.6	30.6	57.5	10.8	5.9	17.0

	Underground			Train		
	Total (mean)	Winter (mean)	Summer (mean)	Total (mean)	Winter (mean)	Summer (mean)
*UFP number**	*11195*	*12638*	*9932*	*5925*	*5518*	*6291*
*UFP diameter***	*49.8*	*48.2*	*51.2*	*51.4*	*43.2*	*58.8*
*UFP ldsa****	*30.1*	*33.1*	*27.5*	*14.9*	*12.4*	*17.1*
UFP mass	*4.5*	*4.8*	*4.3*	*2.6*	*1.5*	*3.5*
PM_1	27.9	42.7	17.5	7.1	7.5	6.8
$PM_{1\text{-}2.5}$	14.2	21.4	8.7	1.1	1.4	0.7
$PM_{2.5}$	42.1	64.1	26.2	8.2	8.9	7.5
$PM_{2.5\text{-}4}$	12.7	19.8	7.7	1.2	1.6	0.9
$PM_{2.5}$ (AB)	54.4	66.3	46.7	32	50.9	14.2
PM_4	54.8	83.9	33.9	9.4	10.5	8.4
$PM_{4\text{-}10}$	26.1	40.7	15.9	4.0	5.0	3.1
PM_{10}	80.9	124.6	49.8	13.4	15.5	11.5
$PM_{>10}$	11.2	14.5	8.8	4.1	4.9	3.3
TSP	92.1	139.1	58.6	17.5	20.4	14.8
NO_2	66.3	69.4	63.4	11.9	12.1	11.7

	Indoor			Other		
	Total (mean)	Winter (mean)	Summer (mean)	Total (mean)	Winter (mean)	Summer (mean)
*UFP number**	*8531*	*7712*	*9229*	*10038*	*11559*	*8802*
*UFP diameter***	*49.1*	*47.1*	*50.8*	*50.7*	*45.8*	*54.7*
*UFP ldsa****	*22.2*	*20.0*	*24.0*	*25.6*	*28.0*	*23.7*
UFP mass	*3.4*	*3.0*	*3.8*	*3.9*	*3.7*	*4.1*
PM_1	7.5	7.2	7.7	12.5	15.4	10.1
$PM_{1\text{-}2.5}$	1.7	2.2	1.4	3.8	4.8	3.0
$PM_{2.5}$	9.2	9.4	9.1	16.3	20.2	13.1
$PM_{2.5\text{-}4}$	2.1	2.3	1.7	3.9	4.9	3.0
$PM_{2.5}$ (AB)	32.1	49.7	14.0	35.6	50.9	22.8
PM_4	11.3	11.7	10.8	20.2	25.1	16.1
$PM_{4\text{-}10}$	5.0	6.2	4.1	9.4	12.5	7.0
PM_{10}	16.3	17.9	14.9	29.6	37.6	23.1
$PM_{>10}$	3.2	4.2	2.2	4.5	5.2	4.0
TSP	19.5	22.1	17.1	34.1	42.8	27.1
NO_2	29.1	33.4	2.2	41.1	36.5	45.1

*Table 2. MEs descriptive statistic (mean) performed on the total dataset and for winter and summer campaign, Data are reported as $\mu g/m^3$ (*particle/cm^3; **nm; *** LDSA: lung-deposited surface area, $\mu m^2/cm^3$; $PM_{2.5}$ (AB): $PM_{2.5}$ measured via AirBeam)). Data in italics refers to those used for the calculation of UFP mass.*

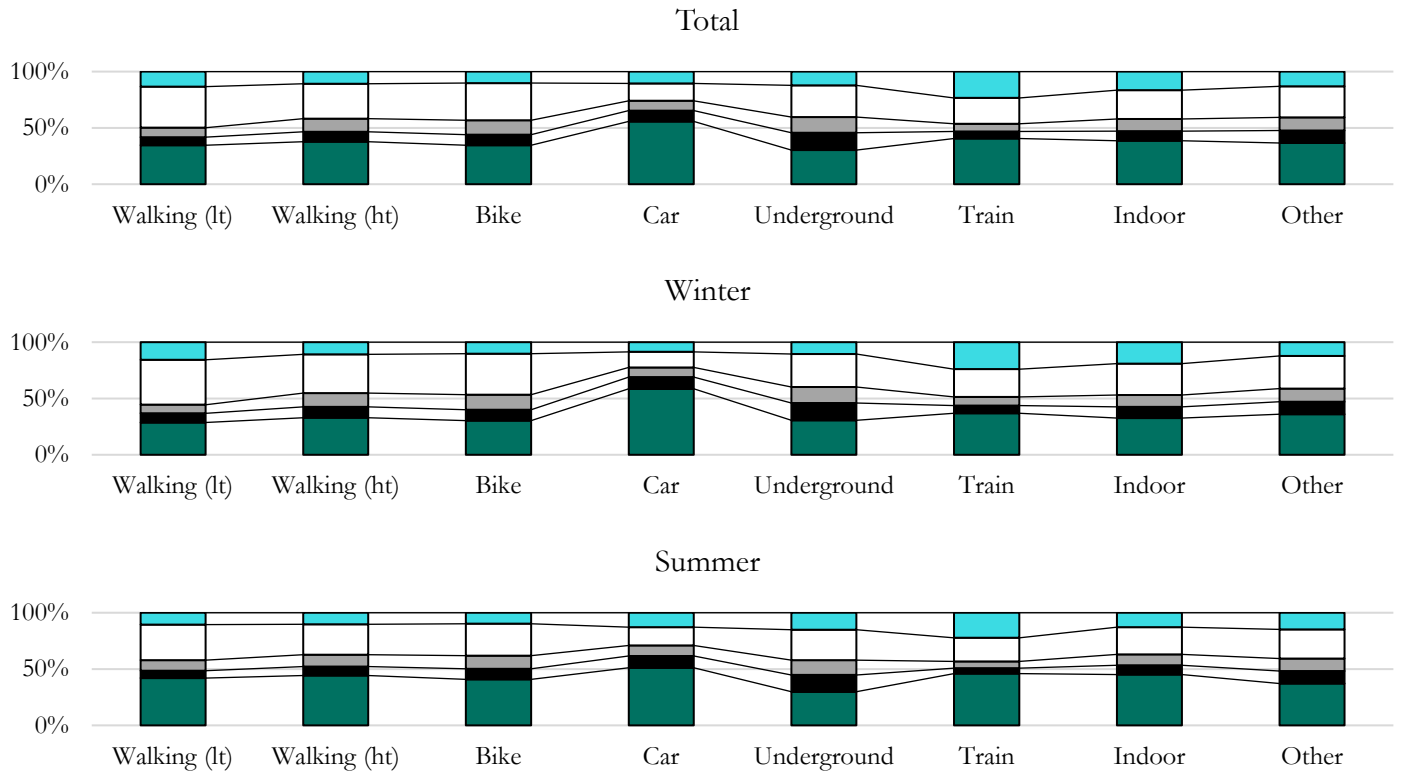

Figure 2 Differential concentration (%) calculated for different ME (total and seasonal dataset). Green: PM_1; black: $PM_{1\text{-}2.5}$; grey: $PM_{2.5\text{-}4}$; white: $PM_{4\text{-}10}$; Light blue: $PM_{>10}$.

In addition to exposure data, subject's physiological parameters (heartbeat) were acquired during the whole monitoring campaign and used to calculate the ventilation rate [1]. In Table 3 a descriptive statistic regarding the heartbeat and ventilation rate calculated for each MEs is reported. As expected, higher values were found in active commuting (101-104 bpm for walking and cycling) while lower values, equal to 66 and 69 bpm, were measured in car and train MEs. As consequences and as expected, ventilation rate was found higher in active transport modes.

Physiological parameters					
Environment	Min.	Max.	Mean	S.D.	
Total	46	209	81	26	Heartbeat (bpm)
	3	77	11	9	Ventilation rate (l/min)
Walking (lt)	52	187	101	35	Heartbeat (bpm)
	4	60	18	14	Ventilation rate (l/min)
Waking (ht)	49	194	104	35	Heartbeat (bpm)
	3	65	19	14	Ventilation rate (l/min)
Bike	53	161	104	19	Heartbeat (bpm)
	4	44	18	6	Ventilation rate (l/min)
Car	52	97	69	8	Heartbeat (bpm)
	4	15	7	2	Ventilation rate (l/min)
Underground	47	190	88	25	Heartbeat (bpm)
	3	63	13	10	Ventilation rate (l/min)
Train	46	191	66	11	Heartbeat (bpm)
	3	63	7	4	Ventilation rate (l/min)
Indoor	46	165	77	17	Heartbeat (bpm)
	3	46	9	5	Ventilation rate (l/min)
Other	48	209	85	27	Heartbeat (bpm)
	3	77	12	10	Ventilation rate (l/min)

Table 3. Physiological parameters (Heartbeat and calculated Ventilation rate) reported for the total and for MEs dataset (bpm: beats per minute).

4.1.3.2. Inhaled dose across different micro-environments and differences in exposure levels across MEs

A descriptive statistic of the inhaled dose calculated for each pollutant following Equation 2 is reported in Table 4.

$$Inhaled\ Dose: Conc. \times T \times VE$$

Equation 2. Inhaled Dose (μg) calculation. Conc: exposure concentration (μg/m³); T: time (min); VE: pulmonary ventilation rate (m³/min)

Pollutant	Walking (lt)	Walking (ht)	Bike	Car	Underground	Train	Indoor	Other	Total
UFP	0.6	3.8	1.3	1.5	1.4	1.7	2.2	4.9	17.4
PM_1	2.3	10.5	4.3	1.3	8.7	4.5	4.8	15.6	52
$PM_{1\text{-}2.5}$	0.5	2.5	1.2	0.3	4.4	0.7	1.1	4.7	15.4
$PM_{2.5}$	2.8	13	5.5	1.6	13.1	5.2	5.9	20.3	67.4
$AB_{2.5}$	6.9	32.1	10.8	7.2	17	20.4	20.7	44.4	159.5
$PM_{2.5\text{-}4}$	0.5	3.2	1.6	0.2	4	0.8	1.4	4.9	16.6
PM_4	3.3	16.2	7.1	1.8	17.1	6	7.3	25.2	84
$PM_{4\text{-}10}$	2.5	8.8	4.1	0.3	8.1	2.5	3.2	11.7	41.2
PM_{10}	5.8	25	11.2	2.1	25.2	8.5	10.5	36.9	125.2
$PM_{>10}$	0.9	3	1.3	0.3	3.5	2.6	2.1	5.7	19.4
TSP	6.7	28	12.5	2.4	28.7	11.1	12.6	42.6	144.6
NO_2	5.8	32.9	12.8	2.5	20.7	7.6	18.7	51.3	152.3

Table 4. Descriptive of the inhaled dose (μg) or airborne pollutants, reported as an average for each MEs and as total.

In general, higher values of inhaled dose were found in environments defined as Other, followed by Walking (ht) while lower values were found in Walking (lt) and in Car.

The trend reported above indicates the general trend of the inhaled dose according to the MEs, but it is important to underline that it may vary according to the fraction of particulate and to the pollutant considered. For this reason, in Table 5 the inhaled dose values are reported according to the ME considered.

UFP	PM_1	$PM_{1-2.5}$	$PM_{2.5}$	$PM_{2.5-4}$	PM_4	PM_{4-10}	PM_{10}	$PM_{>10}$	TSP	NO_2
Lt	Car	Car	Car	Car	Car	Car	Car	Car	Car	Car
0.6	1.3	0.3	1.6	0.2	1.8	0.3	2.1	0.3	2.4	2.5
Bike	Lt	Lt	Lt	Lt	Lt	Lt	Lt	Lt	Lt	Lt
1.3	2.3	0.5	2.8	0.5	3.3	2.5	5.8	0.9	6.7	5.8
Under.	Bike	Train	Train	Train	Train	Train	Train	Bike	Train	Train
1.4	4.3	0.7	5.2	0.8	6.0	2.5	8.5	1.3	11.1	7.6
Car	Train	Indoor	Bike	Indoor	Bike	Indoor	Indoor	Indoor	Bike	Bike
1.5	4.5	1.1	5.5	1.4	7.1	3.2	10.5	2.1	12.5	12.8
Train	Indoor	Bike	Indoor	Bike	Indoor	Bike	Bike	Train	Indoor	Indoor
1.7	4.8	1.2	5.9	1.6	7.3	4.1	11.2	2.6	12.6	18.7
Indoor	Under,	Ht	Ht	Ht	Ht	Under.	Ht	Ht	Ht	Under.
2.2	8.7	2.5	13.0	3.2	16.2	8.1	25.0	3	28.0	20.7
Ht	Ht	Under.	Under.	Under.	Under	Ht	Under.	Under.	Under.	Ht
3.8	10.5	4.4	13.1	4	17.1	8.8	25.2	3.5	28.7	32.0
Other	Other	Other	Other	Other	Other	Other	Other	Other	Other	Other
4.9	15.6	4.7	20.3	4.9	25.2	11.7	36.9	5.7	42.6	51.3

Table 5. Inhaled dose values (μg) reported from the lowest to the higher for different pollutants. Under.: Underground; lt: Walking lt; ht: Walking ht.

The average inhaled dose values are always found higher in the environment defined as 'Other', probably since this ME is considered as a moment of transition from one environment to another, influenced therefore by a high variability (in terms of exposure concentration and of VE). Moreover, during this period, the subject had to move quickly, in most cases changing transport modes: for this reason, it is likely to think that the concentrations of exposure could have been staggered by these sudden movements of the subject. High inhaled dose values were also found in the Walking (ht) and Underground (and Indoor, only for UFP). It should be noted that, despite the exposures measured in the Walking (ht) environment were about a third compared to those measured in the Underground, and the time spent within that environment was about a half (Walking (ht): 10 min. on average; Underground: 24 min.), inhaled dose values calculated for these two MEs are in the same order of magnitude for all the pollutants (with the exception of UFPs). Further, pulmonary ventilation rate measured in the Walking (ht) ME was among the highest observed during the whole monitoring period (18 l/min): this can therefore explain the high inhaled doses measured in this environment. Doses in the same order of magnitude were measured in the following environments: Bike, Train and Indoor (except for UFP). Lower doses were calculated in Walking (lt) and in Car (for all pollutants except UFP). Low values found in the Car environment can be explained by the fact that in this ME the lowest concentrations and the pulmonary ventilation rate

(7 l/min) of the entire route were observed, as was. The difference between doses calculate for the two Walking environments (lt and ht) can be explained by the fact that in the Walking (lt) environment, the average time spent in that environment was about a quarter of that spent in the Walking (ht) environment (10 and 45 min respectively). The other two parameters indeed appear to be very similar: the ventilation was in fact equal to 18 and 19 l/min for Walking (lt) and Walking (ht), respectively. The measured concentrations of exposure were instead found to be very similar for all pollutants considered (average differences between the two environments: 0.2 $\mu g/m^3$; ranging from -6.2 to 4.4 $\mu g/m^3$).

The obtained $PM_{2.5}$ inhaled dose are different than those observed by Tan and collaborators [1]: in their study, authors indeed found that the highest mean inhaled dose was obtained for the walking mode (23.1 μg), followed by taxi (2.4 μg), bus (3.0 μg) and underground (2.6 μg). Regarding the ratios calculated between inhaled dose values and exposure levels, lower ratios, close to 0 were found in Walking (lt) and Car environments (ratio: 0.2), followed by Bike and Underground (ratio: 0.3), Train (ratio: 0.6), Indoor (ratio: 0.8) and Walking (ht) (ratio: 0.9). The only ratio found >1 was found in Other environments (ratio: 1.2).

Moreover, once verified that exposure data were not normally, and neither not log-normally distributed (via Kolmogorov-Smirnov test, $p < 0.001$ for all pollutants), a non-parametric test (Mann-Whitney test) was performed to evaluate the presence of statistically significant differences of pollutant exposure levels among different MEs. A summary of results is reported in Table 6.

Compared MEs		UFP	PM_1	$PM_{1-2.5}$	$PM_{2.5}$	$PM_{2.5-4}$	$PM_{2.5}$ (AB)	PM_4	PM_{4-10}	PM_{10}	$PM_{>10}$	TSP	NO_2
Lt	Ht	*<0.001*	0.129	0.211	0.171	0.203	0.663	0.182	0.115	0.440	0.211	0.270	0.393
Lt	Bike	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	0.735	*<0.001*	*<0.001*	*<0.001*	*0.017*	*<0.001*	0.126
Lt	Car	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Lt	Under.	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Lt	Train	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	0.847	*<0.001*	*<0.001*
Lt	Indoor	0.402	*<0.001*	*0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Lt	Other	*0.002*	0.381	0.236	0.313	0.826	*0.030*	0.429	*0.015*	0.221	0.118	0.419	*0.037*
Lt	Bike	0.577	*0.001*	*<0.001*	*<0.001*	*<0.001*	0.965	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*0.001*
Ht	Car	.154	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Ht	Under.	*0.011*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Ht	Train	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*0.048*	*<0.001*	*<0.001*
Ht	Indoor	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Ht	Other	*<0.001*	0.251	0.998	0.671	0.075	*0.003*	0.389	0.121	0.347	*<0.001*	0.538	0.053
Bike	Car	0.690	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Bike	Under.	0.085	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Bike	Train	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Bike	Indoor	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Bike	Other	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*0.021*	*<0.001*	*<0.001*	*<0.001*	0.124	*<0.001*	*<0.001*
Car	Under.	0.307	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Car	Train	*<0.001*	*0.002*	0.197	*0.005*	*0.001*	*0.008*	*0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Car	Indoor	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*0.027*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Car	Other	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Under.	Train	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Under.	Indoor	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Under.	Other	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Train	Indoor	*<0.001*	0.410	*<0.001*	*<0.001*	*<0.001*	0.250	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Train	Other	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Indoor	Other	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*<0.001*	*0.001*

Table 6. Summary of the Mann-Whitney test. Values represent the level of significance (p). Pair comparisons with p<0.05 are reported in italics. Under.: Underground; lt: Walking lt; ht: Walking ht.

In general, as reported in Table 6, measured exposure levels were found to be statistically different in different MEs, with some exceptions. For example, no statistically significant differences in exposure levels were also found for UFP exposure levels for the comparison Walking (lt) vs Indoor, Walking (ht) vs Bike and Walking (ht) vs Car, Bike vs Car, Bike vs Underground and Car vs Underground. No statistically significant differences in exposure levels were also found for PM_1 and $PM_{2.5}$ (measured via AB) for the comparison Indoor vs Train. Interestingly, no differences were found for exposures to NO_2 and to all PM fraction (from PM_1 to TSP) for the comparison between Walking (ht) and Walking (lt), Walking (lt) vs Other and Walking (ht) vs Other.

4.1.4. Conclusions

The first aim of this study was to evaluate the exposure to different pollutants (NO_2 and size-fractionated PM) in environments (traffic and non-traffic related) typically visited by commuters. This was possible thanks to the simultaneous use of different portable and miniaturized direct-reading instruments for the measurement of airborne pollutants exposure, able to provide data characterized by a high temporal resolution (1-minute acquisition rate).

The study's design also included the use of a heart rate monitor: the instrumentation allowed the real-time acquisition of physiological data (heart rate). This last were then used to calculate pulmonary ventilation data, needed to estimate the inhaled dose of pollutants in each investigated ME. To date, probably due to technical-logistical problems related to the real-time measurement of physiological parameters (heart beat or ventilation rate), studies reporting data on the inhaled dose of pollutants - especially across different traffic MEs - are still limited: this study can therefore contribute to broaden knowledge about this topic in the scientific literature.

Both for the exposure assessment and for the inhaled dose estimation in traffic environments, the results deriving from available studies do not agree with each other and indeed, very often disagree with each other. This is probably caused by the different conditions occurred in different commuting ME considered, which make it difficult to obtain a concordance between the

different studies. Furthermore, as regards to the calculation of the inhaled dose, other parameters are taken into consideration, in addition to the pollutant exposure concentrations: pulmonary ventilation rate and time spent in a given ME can in fact vary significantly from study to study, as well as (especially as regards to the pulmonary ventilation rate) from subject to subject. Studies regarding the evaluation of the inhaled dose of pollutants should in any case be conducted, trying to standardize the conditions that lead to the determination of the inhaled dose in a certain ME, in order to assess which environment (and the boundary conditions - pollutant exposure concentrations, pulmonary ventilation rate and time spent in a given MEs) is more or less impactful on the pollutant inhaled dose.

4.1.4.1. Advantages and limitations

Main advantages related to this study concern the fact that several instruments were used simultaneously for the personal exposure assessment. Moreover, due to the design of the study, it was possible to identify and assess the levels of exposure (and consequently the values of the subject's inhaled dose) in particular (traffic and non-traffic) micro-environments. More, the route chosen for this study was defined a priori and always traveled by the same operator: in this way a certain level of reproducibility of data was ensured. Again, due to the experimental design, (i) different replicas of the same route, even if during (ii) different days and (iii) seasons (summer and winter), have been evaluated. Finally, regarding the calculation of the inhaled dose of pollutants, the major advantage refers to the fact that, unlike most of the studies in the scientific literature, subject's physiological parameter (heart beat that allow to calculate the pulmonary ventilation rate) were acquired at a personal level and no tabular standard data were used.

Principal disadvantage of this study is indeed related to the fact that the study was conducted in one single route (towards Milan).

4.1.4.2. Further developments

Some future development should be assessed and deeply evaluated. First, in this study the pulmonary ventilation rate was derived starting from the value (per minute) of the subject's heart rate, calculating the corresponding

pulmonary ventilation rate. For this reason, it would be useful to evaluate whether the equation used for this calculation is applicable to larger populations and if other equation present in the scientific literature may provide different results. More, since the calculation of the inhaled dose of pollutants was carried out relying on a simple equation (that relates the pollutant exposure concentration with the subject's pulmonary ventilation rate and to the time spent by the subject in a particular environment), it would be interesting to re-analyze the data related to the inhaled dose with a more detailed model. The mathematical MPPD model (Multiple-Path Particle Dosimetry Model) can be useful for this purpose, as it is able to process data referring to the deposition of a determined PM fraction within the respiratory tract.

Finally, although already developed in another study [31], a sensitivity analysis will be performed using the data obtained from this study, in order to evaluate which of the parameters included in the calculation of the inhaled dose (exposure concentration, pulmonary ventilation and time spent in a particular environment) have the greater influence on the inhaled dose itself.

Supplementary material

Figure SM1. Lombardy region (Italy). In red is reported the commuters' route chose for this study.

*Table SM1. Summary of the ME considered in this study. Hour and time of stay refers to those a priori planned, even if small variations should be considered. (LT: low traffic condition; HT: high traffic condition; n.a.: not available). * Return trip – these MEs refer to the same MEs frequented during the first part of the journey.*

ME	Hour (from–to; min)	Time of stay (min)	Route length (km)
Car	7:50-8:10	20	10
Walking - LT	8:25-8:35	10	0.7
Train	8:45-9:35	50	45
Walking - LT	9:35-9:55	20	1.5
Walking - HT	9:55-10:05	10	0.5
Underground	10:05-10:15	10	2.5
Walking - HT	10:20-10:30	10	0.6
Cycling	10:30-10:50	20	3
Indoor	10:50-12:00	70	n.a
Walking - HT*	12:00-12:10	10	0.6
Underground*	12:10-12:20	10	2.5
Walking - HT*	12:20-12:30	10	0.5
Walking - LT*	12:30-12:50	20	1.5
Train*	13:20-14:10	50	45
Walking - LT*	14:10-14:20	10	0.7
Car*	14:20-14:40	20	10

Figure SM2. Setup of the instruments placed in a backpack. Inlets were placed in the breathing zone of the operator.

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4.2. SUSCEPTIBLE SUBJECTS (PREGNANTS)

This chapter is based on: Borghi et al. Exposure to Air Pollutants in Pregnancy: the INSIDE Project.
To be submitted

The principal aim of this study is to evaluate the personal exposure to airborne pollutants (size-fractionated particulate matter - PM - and nitrogen dioxide - NO_2) of a selected population of susceptible subjects (84 pregnant women), in one of the most urbanized metropolitan area in Europe (Milan, Italy), via personal and miniaturized instruments. Exposure levels were measured in common microenvironments, with a particular detail on transport microenvironments: Home, Hospital, Walking, Car, Bus, Underground, Tram, Train, Bike, Scooter, Other Indoor and Other Outdoor.

Summarizing the results, the most critical environments (in terms of exposure assessment), turned out to be: Scooter, Underground, Bus and Train while those characterized by generally lower exposure levels were: Bike, Train, Home, Hospital and Other Outdoor. The non-parametric test (Kruskal-Wallis) was used to evaluate exposure differences among MEs: the level of significance was found lower than <0.001: to deeply evaluating this issue, the Mann-Whitney test was performed for median exposure levels measured in each pair of MEs. Generally, statistically differences in exposure levels ($p < 0.05$) occurred, even if no statically significant differences were found for particular pairs of MEs and for selected PM fractions and NO_2. Results outcomes from this study indicate that the transport mode can affect the exposure levels and that the exposure levels may vary across MEs, and especially across transport MEs, even if some trend and no-statistically differences were found in particular environments.

4.2.1. Introduction

Milan is the second largest city in Italy, with about 1.4 million inhabitants and, as well as many other large cities worldwide, suffers from high levels of air pollution [1]. Such large cities could be of particular interest to evaluate human exposure to airborne pollutants in transport microenvironments (MEs), since many residents and commuters spend a substantial portion of their outdoor time commuting. In fact, even if a small portion of daily time (87.4 min, equal to 6% of the day) is spent commuting [2], it is recognized that this activity may lead to a substantial contribution to daily exposure to air pollutants [3]. However, the evaluation of human exposure to airborne pollutants in urban environments is usually carried out via fixed monitoring stations or modeling, it should be noted that these kind of methods are generally not able to accurately characterize (with proper temporal and spatial resolution) the exposure of individual subjects or subpopulations in movement through complex environments such as urban environments and transport MEs [4]. Previous studies also show that this approach tends to underestimate the exposure to airborne pollutants of specific population subgroups, for which personal and direct measurement techniques would be better suited to characterize the exposure to airborne pollutants. Moreover, because the fact that people spend most of their time indoors and commuting, the personal exposure is determined by the pollutant concentration in these kinds of MEs, that can be substantially different from outdoor concentration measured via ordinary urban networks of fixed monitoring stations [5,6]. Finally, it is important to underline that high levels and peaks in exposure may occur in commuting MEs, because the proximity of emission sources [7]. Probably due to these reasons, the exposure assessment to air pollutants (and in particular to airborne particulate matter - PM) during commuting is getting increasingly interesting in the last years. Particularly, MEs usually investigated refer to: subway, bus, taxi, private car, bicycle and walking [8].

Recent studies evaluated indeed the exposure assessment in subways [9,10,19,20,11–18], during bus trips [9,10,25,11,13,19–24], in private or public (i.e., taxi) [9,11,25–29,13,18–24]. Studies regarding exposure assessment during bicycle rides [9,13,19–24,30] and during walking activities [10,11,13,22,30–32] are also present in literature.

The aim of this study was therefore to evaluate the personal exposure to airborne pollutants of a selected population of susceptible subjects (pregnant woman) living in one of the most urbanized and air-polluted metropolitan areas in Europe (Milan, Italy) by personal monitoring. The subjects were recruited in the framework of the INSIDE project (INdividual air pollution exposure, extracellular vesicle SIgnaling and hypertensive disorder DEvelopment in pregnancy), which aims to assess the biological mechanisms of effects from environmental exposure to airborne particulate matter (PM) in susceptible subject. The present study refers only to short-term exposures to the selected pollutants (size-fractionated PM and NO2) of the enrolled subjects.

The environmental monitoring was focused on nitrogen dioxide (NO_2) and size-fractionated PM (i.e. airborne particles with aerodynamic diameters below 1 μm (PM_1), 2.5 μm ($PM_{2.5}$), 4 μm (PM_4), 10 μm (PM_{10}) and the Total Suspended Particulate (TSP)), other than differential PM fractions (i.e. $PM_{1-2.5}$, $PM_{2.5-4}$, PM_{4-10}, $PM_{>10}$) of people living in an urban area, while performing their usual activities. Exposure levels associated with 12 MEs (*Home*, *Hospital*, *Other Indoor*, *Other Outdoor*, *Walking*, *Car*, *Bus*, *Underground*, *Tram*, *Train*, *Bike* and *Scooter*) was performed via miniaturized or portable direct-reading instruments.

4.2.2. Materials and Methods

4.2.2.1. Study design

84 different pregnant women, attending the Fetal Medicine Unit (FMU) of Fondazione IRCCS Ca' Granda - Ospedale Maggiore Policlinico (Milan, Italy) were recruited during 2 consecutive winter periods (October 2017 - April 2018 and October 2018 - April 2019): it is important to underline that, due to the study design, it has not been possible to obtain replicas on single subjects.

After signing a detailed informed consent form, each subject was asked to wear a miniaturized or portable personal sampling device (described in paragraph 2.2) for the measurement of the exposure to different airborne pollutant during a limited period of time, before a clinical evaluation. Subjects

were trained to turn on instruments and start the personal monitoring when waking up in the morning of Monday and move to the Ospedale Maggiore Policlinico later the same day (between 9:00 and 14:00) to undergo blood drawing and specialist medical visits, and to return the sampling device to the study team. During the monitoring period, subjects were asked to perform their routine activities and continue their voluntary habits. Subjects also completed a questionnaire collecting detailed personal data, including area of residence, time spent commuting in traffic, mode of commuting and smoking habits.

Due to the need to perform some clinical evaluations on an homogeneous sample, volunteers were screened before the recruitment according to the following exclusion criteria: (i) non-Caucasian women; (ii) BMI>30 kg/mw; (iii) over 40 years old; (iv) having suffered previous pregnancy at risk and/or severe uterine contractions during the current pregnancy; (v) having twin pregnancy or pregnancy with assisted fertilization; (vi) with not health problems (such as arterial hypertension, diabetes, anemia and kidney failure), (vii) resident in the Lombardy region, Italy. As expected, the major part of the recruited subject lived in the metropolitan area of Milan, located in the Po valley, in the northern part of Italy (Figure 1).

Figure 1 Area of the study (province of Milan), within the Lombardy region, located in the northern part of Italy.

4.2.2.2. Instrumentation

Measurement instrumentation consisted of monitors for PM and NO_2 (Figure 2). The Aerocet 831 monitor (MetOne Instrument Inc., Grant Pass, Oregon, USA) provide real-time concentrations of size-segregated PM (PM_1, $PM_{2.5}$, PM_4, PM_{10} and TSP). To improve data quality, comparative sessions between the PM monitor and a gravimetric gold standard for $PM_{2.5}$ (Harvard Impactor MS&T Area Sampler Diagnostic and Engineering, Inc., Harrison, ME, USA, named here as "HI") were carried out. Inter-comparison tests consisted in weekly outdoor comparison (lasting 4h per session) between direct reading monitor and the gravimetric method and their goal was to provide a weekly correction factor, applied *a posteriori* on PM data. HI worked at a flow rate of 10 L/min for the collection of PM onto 37 mm PTFE filters. Mass concentrations were determined via gravimetric analysis following a standardized procedure (UNI EN 1234, 2014 and UNI EN 14907, 2005). Briefly, the filter was conditioned in a controlled environment (temperature: 20±1 °C; relative humidity; 50±5%) for a minimum of 24h and then weighted, before and after the sampling, with a microbalance (Gibertini Micro 1000, Novate, Milan, Italy) QA/QC details can be found in Spinazzè *et al.*, 2017; Rovelli *et al.*, 2017; Borghi *et al.*, 2018. The measurement of NO_2 was performed using an electrochemical miniaturized monitors (Cairclip NO_2, Cairpol; La Roche Blanche – France) recently purchased and calibrated by the manufacturer (March 2017). Both Cairclip and Aerocet were set with an acquisition rate of 1 min. Finally, in order to track and record the position of subjects during the monitoring sessions, a mobile phone (LG K4 2017) provided with an Android application (GEO TRACKER – GPS TRACKER; Version 3.3.0) was used, set with an acquisition rate of 30s and a precision of 50m. As a support for the reconstruction of the routes carried out and environments frequented, volunteers were asked to complete a Time Activity Diary (TAD – reported in Figure SM1).

(a) (b) (c) (d)

Figure 2 Measurement instruments used in this study (a: overview of the instruments as worn by a subject; b: Aerocet; c: Cairclip; d: smartphone).

4.2.2.3. Data treatment and analysis

Data measured via direct-reading instruments were first examined and handled to exclude zero and unreliable data. For this reason, concentration distributions were truncated above the 99th percentile and below the 1st percentile [36]. Following a report on the validation and evaluation of micro-sensors [37], NO_2 value found below the calculated limit of detection (LOD: 1.692 μg/m^3) have been replaced with LOD/2 (NO_2 data <LOD were found to be 12% of the total: for this reason the substitution of data <LOD with LOD/2 is somewhat justified [38]). Concerning PM data, as told, the error associated to the direct-reading measurement was managed and minimized by using custom calibration factors to correct real-time PM measurements. These custom calibrations factors were calculated by dividing the PM concentration obtained by means of a standard gravimetrical sampling technique using the mean PM concentration measured simultaneously with the direct-reading instrument and applied for an a-posteriori correction of data [39,40].

Descriptive statistic was performed on the total dataset and for each MEs, to provide an overview of the central tendency and variability of data. To assess the normality of the distribution, Kolmogorov-Smirnov tests were

performed. As data were not normally and neither log-normally distributed, non-parametric tests have been carried out to evaluate differences in pollutant exposure levels across MEs. In particular, the Kruskal-Wallis test was used to compare scores between groups while Mann-Whitney statistic was performed to test pair of independent groups (MEs) on pollutant concentration, in terms of their medians. Finally, ratios between average exposure levels measured among selected MEs was performed and reported in terms of macro and micro-environments. Data were analysed using SPSS Statistics 20.0 (IBM, Armonk, NY, USA) and a significance level of 0.05 was used for all statistical tests.

4.2.3. Results and Discussions

4.2.3.1. *Exposure levels across different MEs*

In order to evaluate possible changes and variation of exposure levels as a function of the environment considered, a descriptive statistic of average exposure levels found across different MEs is reported in Figure 3 (graphical representation of differential and cumulative concentration calculated in different MEs), while box-plots for each kind of transport mode considered are reported in supplementary materials (Figure SM2). As reported previously, pollutant exposure levels refer to the following MEs: *Home*, *Hospital*, *Other indoor* (i.e. office, restaurant or nursery), *Other outdoor* (i.e. public park), *Walking*, *Car*, *Bus*, *Underground*, *Tram*, *Train*, *Bike* and *Scooter*.

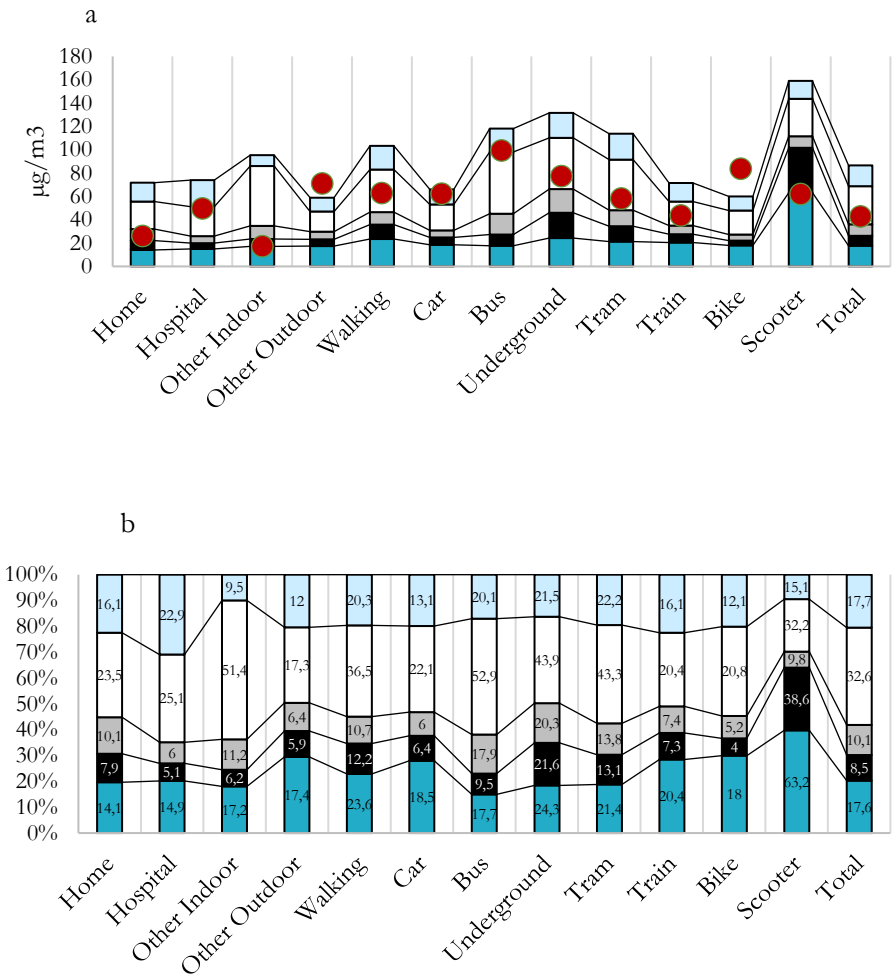


Figure 3 Descriptive statistic of differential concentration calculated in different MEs and for the total dataset. Dark blue: PM_1; black: $PM_{1-2.5}$; grey: $PM_{2.5-4}$; white: PM_{4-10}; Light blue: $PM_{>10}$. Red dots (Figure a) represent NO_2 exposure concentrations.

Regarding **walking** MEs in this study, average exposure levels were 23.6, 35.8 and 83.0 $\mu g/m^3$ for PM_1, $PM_{2.5}$ and PM_{10}, slighter higher than walking exposure levels found in the city of Milan by Ozgen and collaborators [6], equal to 10.7, 20.2 and to 79.3 (for PM_1, $PM_{2.5}$ and PM_{10}). As reported by Karanasiou and collaborators in their review [41], the average $PM_{2.5}$ exposure concentration during **cycling** across Europe, was found in a range 29-72 $\mu g/m^3$, while for PM_{10}, the range was 37-62 $\mu g/m^3$. Results outcomes from this study shows lower average values for $PM_{2.5}$ (22.0 $\mu g/m^3$) and PM_{10} values in the same range of European concentration (47.9 $\mu g/m^3$). In a previous study [6], PM_{10} exposure (84.8 $\mu g/m^3$) was almost twice than that measured in this study (48.0 $\mu g/m^3$) while $PM_{2.5}$ exposure levels were similar (21.1 $\mu g/m^3$). As regards PM_1, higher values were found in the present study (18.0 vs 12 $\mu g/m^3$) but it is important to note that the exposure levels for cyclists depend on the trip and may vary depending on the route (i.e. on the distance to the traffic sources). Typical exposure levels for European commuters in **cars** were found in the range of 36-76 $\mu g/m^3$ for PM_{10} and in a range of 22-85 $\mu g/m^3$ for $PM_{2.5}$ [41], in accordance with average results from this study (24.9 and 53.0 $\mu g/m^3$ respectively for $PM_{2.5}$ and for PM_{10}), even if in Milan PM exposure levels were fond much lower (2.7, 3.9 and to 13.4 respectively for PM_1, $PM_{2.5}$ and PM_{10}) [6]. Karanasiou and collaborators [41] reported that the exposure of car's commuters seemed to be mainly influenced by the traffic intensity and by the kind of ventilation used inside the car, as well as the leading vehicle emissions [42]. Average exposure levels for PM in **buses** environments were found, in this study, equal to 27.2 and to 98.0 $\mu g/m^3$ respectively for $PM_{2.5}$ and for PM_{10}. Typical $PM_{2.5}$ exposure concentrations in Europe were higher and in the range 36-69 $\mu g/m^3$ [41]. Average levels of PM_{10} exposure concentration in European **underground** environments ranged from 103 to 1030 $\mu g/m^3$ while $PM_{2.5}$ exposure concentration ranged from 59 to 375 $\mu g/m^3$. In this study, average exposure concentration varied from 45.9 to 110.1 $\mu g/m^3$ (respectively for $PM_{2.5}$ and for PM_{10}), lower than exposure levels reported elsewhere [6] (147.7, 91.1 and 36.7 $\mu g/m^3$ for PM_{10}, $PM_{2.5}$ and for PM_1 respectively). As reported in the literature [41], the variations in the exposure levels among this kind of MEs could be explained by different factors, such as the abrasion of railways, catenary metal and braking systems, in addition to the age of construction and the type of ventilation systems used

inside the trains. It is worth notify that, as reported in several studies, results regarding the exposure levels in different transport MEs are often not in agreement, which can be explained by the dependency of exposure concentration on a large number of variables [6], such as road characteristics, meteorological conditions, vehicle ventilation/conditioning and vehicle fuel [43]. Finally, due to high variability of PM concentration in indoor environments, we decided to not report here a comparison with other European measurements, as well as outdoor concentrations (named here as "*Other outdoor*"), even if in a study conducted in the northern part of Italy [44] shows higher indoor winter concentrations (equal to 31.1, 36.0 and to 42.0 $\mu g/m^3$ respectively for PM_1, $PM_{2.5}$ and PM_{10}) with respect to this study. Summarizing, the highest PM mean exposure concentration measured in this study refers to *Scooter* ME, followed by *Underground*, *Walking, Bus* and *Tram*. Lower exposure concentrations were measured in the indoor environments (*Home* and *Hospital*) and in the *Bike* ME. Higher exposure concentration of NO_2 was indeed measured in *Bus*, *Bike* and *Underground* MEs (99.6, 83.9 and 77.6 $\mu g/m^3$ respectively) while the lowest values were measured in *Other indoor* (17.4 $\mu g/m^3$) and *Home* MEs (26.3 $\mu g/m^3$). Graphs in Figure 3 show that the finer fractions of PM (up to $PM_{2.5}$) had greater influence in outdoor environments (*Other outdoor, Walking, Bike, Scooter*), in the *Train* and in the *Car* environments. On the contrary, the coarser particles (from PM_4 to TSP) mainly contribute to the total concentration in the indoor environments (*Hospital, Indoor*) and in the other means of transport (*Underground, Bus, Tram*).

Regarding NO_2, exposure levels were found lower than those found in Lille, France in *Other indoor* and *Other outdoor* environments (56 and 115 $\mu g/m^3$ respectively, in respect to exposure levels reported here equal to 17 and 71 $\mu g/m^3$) and similar to those found in *Home* (22 $\mu g/m^3$) [45].

4.2.3.2. Differences among MEs

Since exposure data are not normally (and neither not log-normally) distributed (verified via Kolmogorov-Smirnov test, $p < 0.001$) a non-parametric test (i.e., Kruskal-Wallis test) for the evaluation of exposure differences among MEs was used. Results, obtained for each pollutant, showed a significance level <0.001; to further evaluate this issue, an evaluation of the differences between median exposure concentration foe each possible pair of MEs was performed, via Mann-Whitney test. The results of the non-parametric test are reported in supplementary material (Table SM1). In general, for all pollutants (differential PM concentration and NO_2) and for the majority of comparison among MEs, statistically significant different exposures ($p < 0.05$) occurred, as similarly reported in another study performed in the city of Milan [6].

In general, regarding the PM_1, the main differences were found in the *Train* environment, if compared with the other means of transport and for the *Bike* environment. Great differences were also found considering the $PM_{1\text{-}2.5}$ (for comparisons between the environments *Train* and *Bike* vs the other ME). Differences between the *Bike* environment and the indoor MEs were found for the $PM_{2.5\text{-}4}$. Differences between several ME were finally found for the $PM_{4\text{-}10}$ and $PM_{>10}$. P values related to the evaluations carried out on NO_2 data were generally found > 0.05 for comparisons between *Bike* and *Scooter* environments vs other MEs, as reported in Table SM1. Overall, results indicate that the exposure levels may vary across MEs, and especially across transport MEs, thus that the transport mode can affect the personal exposure levels.

4.2.3.3. Exposure levels ratio

In order to check if exposure levels were generally higher or lower in a particular environment (if compared with *Indoor* and *Walking* environments) the ratios between exposure concentrations found across macro environments and across micro-environments are reported in Table 1 and in Table 2.

For the calculation of exposure ratios in macro-environments, the average exposure concentration has been calculated for the following re-named environments:

- IndoorMACRO: average exposure levels in *Home*, *Hospital*, *Other Indoor*;
- OutdoorMACRO: same exposure levels for *Other outdoor*;
- WalkingMACRO: same exposure levels for *Walking*;
- CommutingMACRO: average exposure levels in *Car*, *Bus*, *Underground*, *Tram*, *Train*, *Bike*, *Scooter*.

As reported in Table 1, ratios between OutdoorMACRO and IndoorMACRO are, in most comparisons, lower than 1 (Table 1a), as well as the comparison IndoorMACRO/WalkingMACRO and OutdoorMACRO/WalkingMACRO (Table 1b).

a.

	PM_1	$PM_{1-2.5}$	$PM_{2.5}$	$PM_{2.5-4}$	PM_4	PM_{4-10}	PM_{10}	$PM_{>10}$	TSP	NO_2
	Indoor Denominator									
Outdoor	1,1	0,9	1,1	0,7	1	0,5	0,7	0,7	0,7	2,3
Walking	1,5	1,9	1,6	1,2	1,5	1,1	1,3	1,3	1,3	2
Commuting	1,7	2,2	1,9	1,3	1,7	1	1,3	1,1	1,3	2,2

b.

	PM_1	$PM_{1-2.5}$	$PM_{2.5}$	$PM_{2.5-4}$	PM_4	PM_{4-10}	PM_{10}	$PM_{>10}$	TSP	NO_2
	Walking Denominator									
Indoor	0,7	0,5	0,6	0,9	0,7	0,9	0,8	0,8	0,8	0,5
Outdoor	0,7	0,5	0,7	0,6	0,6	0,5	0,6	0,6	0,6	1,1
Commuting	1,1	1,2	1,1	1,1	1,1	0,9	1	0,8	1	1,1

Table 1 Fractionated and differential PM and NO_2 ratios calculated in different Macro-Environments (in particular between a. IndoorMACRO and b. WalkingMACRO vs other macro-environments). Ratios >1 (reported in grey and in italics) indicate lower exposure in indoor (a) or walking (b) macro-environments with respect to other macro-environments.

Detailed information regarding ratio calculated between *Home* and *Walking* (chosen as terms of comparison as MEs always represented in each monitoring session) and the other MEs are reported in Table 2. Regarding comparison between *Home* and other MEs (Table 2a), ratios (in regard to PM and PM differential fractions) were found lower than 1 for the comparison with *Hospital*, *Other Outdoor*, *Car*, *Train* and *Bike*. NO_2 exposure levels were always found higher in *Home* environments (ratios ranging from 1.7 to 3.8) except in *Other Indoor* environments. The ratio between *Walking* (Table 2b) and other MEs was found lower than 1 (or very close to 1) for the majority of comparisons (*Hospital*, *Other Indoor*, *Other Outdoor*, *Car*, *Bus*, *Train* and *Bike* MEs).

		PM_1	$PM_{1-2.5}$	$PM_{2.5}$	$PM_{2.5-4}$	PM_4	PM_{4-10}	PM_{10}	$PM_{>10}$	TSP	NO_2
		Home									
		Denominator									
a.	Hospital	1.1	0.6	0.9	0.6	0.8	1.1	0.9	1.4	1	1.9
	Other Indoor	1.2	0.8	1.1	1.1	1.1	2.2	1.5	0.6	1.3	0.7
	Other Outdoor	1.2	0.7	1.1	0.6	0.9	0.7	0.8	0.7	0.8	2.7
	Walking	1.7	1.5	1.6	1.1	1.4	1.6	1.5	1.3	1.4	2.4
	Car	1.3	0.8	1.1	0.6	1	0.9	1	0.8	0.9	2.4
	Bus	1.3	1.2	1.2	1.8	1.4	2.3	1.8	1.2	1.6	3.8
	Underground	1.7	2.7	2.1	2	2.1	1.9	2	1.3	1.8	3
	Tram	1.5	1.7	1.6	1.4	1.5	1.8	1.6	1.4	1.6	2.2
	Train	1.4	0.9	1.3	0.7	1.1	0.9	1	1	1	1.7
	Bike	1.3	0.5	1	0.5	0.8	0.9	0.9	0.8	0.8	3.2
	Scooter	4.5	4.9	4.6	1	3.5	1.4	2.6	0.9	2.2	2.4

		PM_1	$PM_{1-2.5}$	$PM_{2.5}$	$PM_{2.5-4}$	PM_4	PM_{4-10}	PM_{10}	$PM_{>10}$	TSP	NO_2
		Walking									
		Denominator									
	Home	0.6	0.6	0.6	0.9	0.7	0.6	0.7	0.8	0.7	0.4
	Hospital	0.6	0.4	0.6	0.6	0.6	0.7	0.6	*1.1*	0.7	0.8
	Other Indoor	0.7	0.5	0.7	*1*	0.7	*1.4*	*1*	0.5	0.9	0.3
b.	Other Outdoor	0.7	0.5	0.7	0.6	0.6	0.5	0.6	0.6	0.6	*1.1*
	Car	0.8	0.5	0.7	0.6	0.7	0.6	0.6	0.7	0.6	*1*
	Bus	0.7	0.8	0.8	*1.7*	*1*	*1.4*	*1.2*	*1*	*1.1*	*1.6*
	Underground	*1*	*1.8*	*1.3*	*1.9*	*1.4*	*1.2*	*1.3*	*1.1*	*1.3*	*1.2*
	Tram	0.9	*1.1*	*1*	*1.3*	*1*	*1.2*	*1.1*	*1.1*	*1.1*	0.9
	Train	0.9	0.6	0.8	0.7	0.8	0.6	0.7	0.8	0.7	0.7
	Bike	0.8	0.3	0.6	0.5	0.6	0.6	0.6	0.6	0.6	*1.3*
	Scooter	*2.7*	*3.2*	*2.8*	0.9	*2.4*	0.9	*1.7*	0.7	*1.5*	*1*

Table 2 Fractionated and differential PM and NO_2 ratios calculated in different Micro-Environments (in particular between a. Home and b. Walking vs other micro-environments). Ratios >1 (reported in grey and in italics) indicate lower exposure in indoor (a) or walking (b) environments with respect to other micro-environments.

4.2.4. Conclusions

Exposure levels of fractionated PM and NO_2 were characterized in this study across 12 different MEs in the city of Milan, Italy. Summarizing the results, in the first part of this work, concerning the evaluation of exposure levels measured across different MEs, graphical description of exposure levels measured in different MEs have been reported (Figure 3). However, it is important to underline that a comparison with the scientific literature is difficult because the exposure levels measured in different studies are conditioned by numerous and different variables (such as road characteristics and meteorological conditions). Leaving aside the *Scooter* environment (where the highest concentrations were found for most of the pollutants considered

in this study), as it is characterized by a low number of data (n = 31), the highest exposure levels (in general for all the pollutants) were measured in the *Underground*, *Bus* and *Tram* environments. On the contrary, lowest exposure levels were found in the *Bike*, *Hospital* and in the *Other Outdoor* environments, as well as in *Train* and *Home* environments. Regarding differential PM concentrations measured in different ME, finer fraction seem to have a greater influence on the subjects' exposure in outdoor (commuting and non-commuting) environments, as well as in *Train* and *Car*. Coarser fractions indeed mainly contribute to the total exposure in indoor environments.

The non-parametric test (Kruskal-Wallis) was used to evaluate exposure differences among MEs: the level of significance was lower than 0.001: to further evaluate this and to check statistically differences among MEs, the Mann-Whitney test was performed for each environment and pollutant considered. Results outcomes from this analysis shows how, in general, statistically significant different exposure ($p<0.05$) occurs in the major of comparison ME-ME and for the majority of pollutants considered even if some non-difference have been found in some case, especially for comparisons between *Bike-Scooter-Train* and the other considered MEs.

Finally, in order to understand if exposure levels were higher or lower in a particular environment, the ratio between exposure concentration found across macro and micro-environments was performed. Ratios between OutdoorMACRO and IndoorMACRO and are generally lower than 1, as well as the comparison IndoorMACRO/WalkingMACRO and OutdoorMACRO/WalkingMACRO.

This study evaluated the personal exposure of a subset of the general population (a selected population of susceptible subjects; (i.e., pregnant woman) living in one of the most urbanized and air-polluted metropolitan areas in Europe (Milan, Italy) by means of personal monitoring. Outcomes from this study indicate that the transport mode can affect the exposure levels and that the exposure levels may vary across MEs, and especially across transport MEs. In this regard, obtained evidences allowed to define the modes of transport (and the MEs) that involve a potential minor exposure, which would therefore be preferable to choose, especially by the subjects.

A major strength of this study consists in the fact that several instruments were used simultaneously for personal exposure assessment. Furthermore, due to the design of the study, it was possible to identify and assess the exposure levels in specific MEs (traffic and non-traffic). Moreover, in this study the route was not defined a priori, which contributed to the collection of data characterized by a high variability. Disadvantages are indeed related to the fact that (i) the daily monitoring period lasted only for few hours and that (ii) the study was conducted in one single city (Milan). Further research should check if some personal parameters, strictly related to the transport mode (i.e. subject's pulmonary ventilation rate and the time spent in a particular ME) may have an impact on the inhaled dose of pollutants.

Supplementary materials

Figure SM1: TAD (Time Activity Diary) used in this study, as given to the subjects (in Italian).

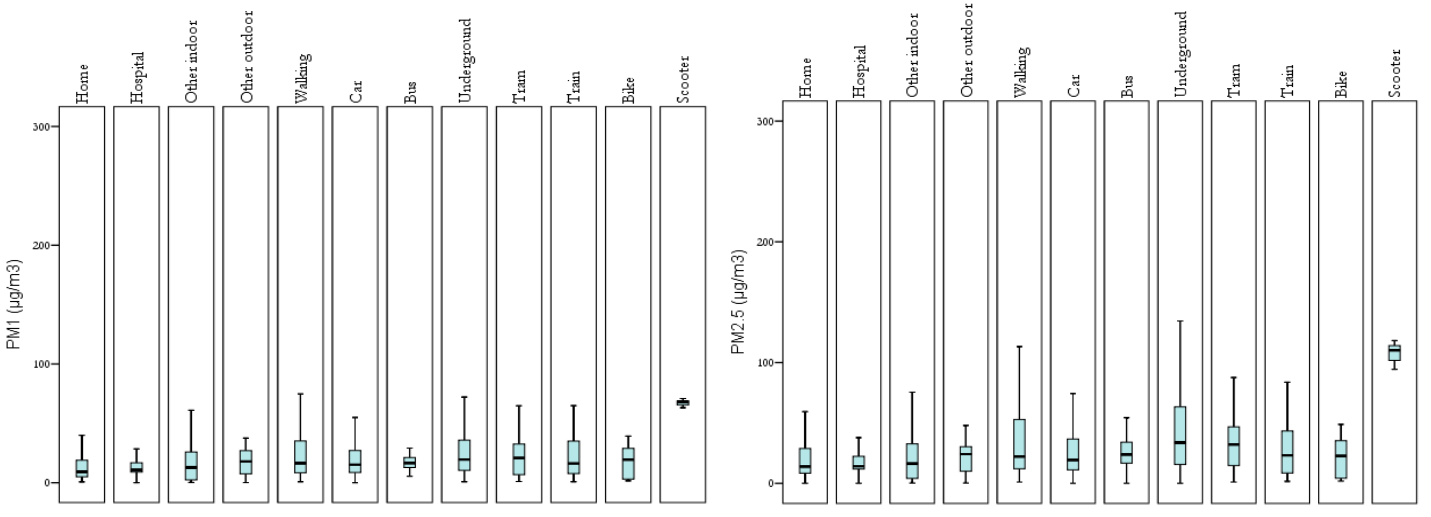
Luoghi frequentati

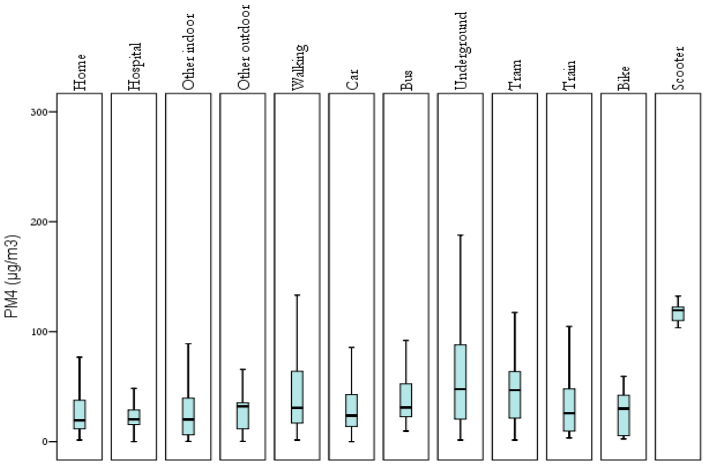
Ora inizio-fine	Ambiente	Fumo di sigaretta	Uso di fiamme	Tipo di ventila-zione
7:00-7:10	*Casa*		*Uso gas*	*Naturale*
7:00-8:30	*Casa*			*Naturale*
__:__ __:__				
__:__ __:__				
__:__ __:__				
__:__ __:__				
__:__ __:__				
__:__ __:__				
__:__ __:__				

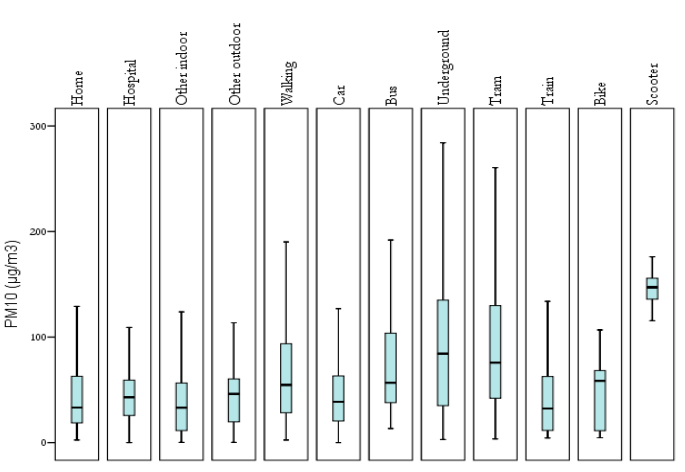
Spostamenti

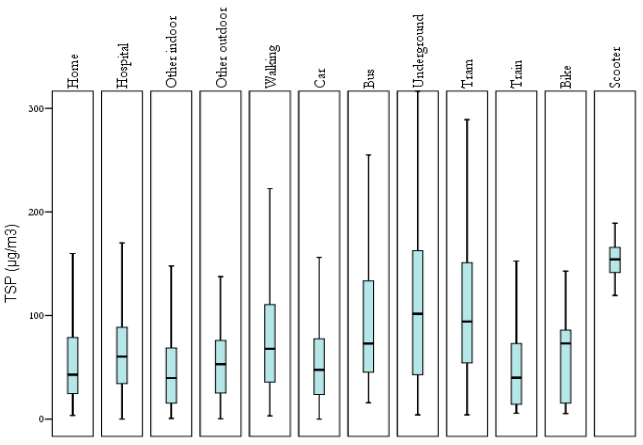
Ora inizio-fine	A piedi	Mezzi pubblici	Mezzi privati
8:30-8:35	*X*		
7:00-8:30		Tram 4	
__:__ __:__			
__:__ __:__			
__:__ __:__			
__:__ __:__			
__:__ __:__			
__:__ __:__			
__:__ __:__			

Figure SM2: Box-plots for PM_1, $PM_{2.5}$, PM_4, PM_{10}, TSP and NO_2 exposure levels for different environments considered in this study.




PM4 (µg/m3)
0
100
200
300
Home
Hospital
Other indoor
Other outdoor
Walking
Car
Bus
Underground
Tram
Train
Bike
Scooter


PM10 (µg/m3)
0
100
200
300
Home
Hospital
Other indoor
Other outdoor
Walking
Car
Bus
Underground
Tram
Train
Bike
Scooter


TSP (µg/m3)
300
200
100
0
Home
Hospital
Other indoor
Other outdoor
Walking
Car
Bus
Underground
Tram
Train
Bike
Scooter

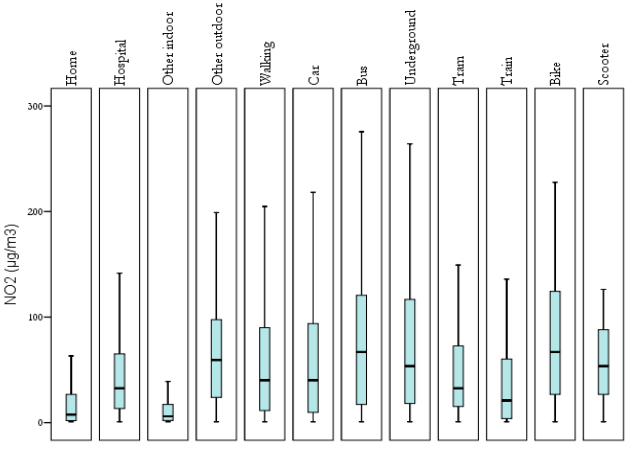

NO2 (µg/m3)
300
200
100
0
Home
Hospital
Other indoor
Other outdoor
Walking
Car
Bus
Underground
Tram
Train
Bike
Scooter

Table SM1: Mann-Whitney test – significance values (Other In.: Other Indoor; Other Out.: Other Outdoor). p values > 0.05 are highlighted in grey and in italics.

	Home	Hospital	Other In.	Other Out.	Walking	Car	Bus	Underground	Tram	Train	Bike	Scooter	
Home	---	<0.001	0.02	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*0.13*	<0.001	
Hospital	---	---	0.01	0.02	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.03	<0.001	
Other Indoor	---	---	---	0.03	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.02	<0.001	
Other Outdoor	---	---	---	---	0.01	*0.75*	*0.81*	<0.001	0.01	*0.08*	*0.88*	<0.001	
Walking	---	---	---	---	---	<0.001	*0.60*	0.02	*0.91*	*0.07*	0.01	<0.001	
Car	---	---	---	---	---	---	*0.05*	<0.001	<0.001	*0.16*	*0.95*	<0.001	PM_1
Bus	---	---	---	---	---	---	---	0.01	0.02	*0.69*	*0.73*	<0.001	
Underground	---	---	---	---	---	---	---	---	*0.24*	<0.001	<0.001	<0.001	
Tram	---	---	---	---	---	---	---	---	---	*0.49*	0.01	<0.001	
Train	---	---	---	---	---	---	---	---	---	---	0.04	<0.001	
Bike	---	---	---	---	---	---	---	---	---	---	---	<0.001	
Scooter	---	---	---	---	---	---	---	---	---	---	---	---	

	Home	Hospital	Other In.	Other Out.	Walking	Car	Bus	Underground	Tram	Train	Bike	Scooter	
Home	---	<0.001	<0.001	0.013	<0.001	*0.263*	0.003	<0.001	<0.001	<0.001	0.010	<0.001	
Hospital	---	---	<0.001	*0.317*	<0.001	0.004	<0.001	<0.001	<0.001	<0.001	*0.989*	<0.001	
Other Indoor	---	---	---	*0.357*	<0.001	<0.001	<0.001	<0.001	<0.001	*0.400*	*0.767*	<0.001	
Other Outdoor	---	---	---	---	<0.001	0.046	<0.001	<0.001	<0.001	*0.125*	*0.886*	<0.001	
Walking	---	---	---	---	---	<0.001	*0.390*	<0.001	<0.001	<0.001	<0.001	<0.001	
Car	---	---	---	---	---	---	0.003	<0.001	<0.001	<0.001	0.006	<0.001	$PM_{1\text{-}2.5}$
Bus	---	---	---	---	---	---	---	<0.001	0.001	<0.001	<0.001	<0.001	
Underground	---	---	---	---	---	---	---	---	0.003	<0.001	<0.001	<0.001	
Tram	---	---	---	---	---	---	---	---	---	<0.001	<0.001	<0.001	
Train	---	---	---	---	---	---	---	---	---	---	*0.830*	<0.001	
Bike	---	---	---	---	---	---	---	---	---	---	---	<0.001	
Scooter	---	---	---	---	---	---	---	---	---	---	---	---	

	Home	Hospital	Other In.	Other Out.	Walking	Car	Bus	Underground	Tram	Train	Bike	Scooter	
Home	---	0.003	<0.001	*0.074*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*0.552*	<0.001	
Hospital	---	---	<0.001	0.009	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*0.681*	<0.001	
Other Indoor	---	---	---	0.029	<0.001	*0.358*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
Other Outdoor	---	---	---	---	<0.001	*0.092*	<0.001	<0.001	<0.001	<0.001	*0.248*	<0.001	
Walking	---	---	---	---	---	<0.001	0.025	<0.001	<0.001	<0.001	0.002	<0.001	
Car	---	---	---	---	---	---	<0.001	<0.001	<0.001	<0.001	0.016	<0.001	$PM_{2.5-4}$
Bus	---	---	---	---	---	---	---	<0.001	*0.052*	<0.001	<0.001	0.047	
Underground	---	---	---	---	---	---	---	---	0.021	<0.001	<0.001	*0.234*	
Tram	---	---	---	---	---	---	---	---	---	<0.001	<0.001	*0.748*	
Train	---	---	---	---	---	---	---	---	---	---	<0.001	<0.001	
Bike	---	---	---	---	---	---	---	---	---	---	---	<0.001	
Scooter	---	---	---	---	---	---	---	---	---	---	---	---	

	Home	Hospital	Other In.	Other Out.	Walking	Car	Bus	Underground	Tram	Train	Bike	Scooter	
Home	---	<0.001	<0.001	*0.975*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	
Hospital	---	---	<0.001	<0.001	*0.942*	<0.001	<0.001	<0.001	<0.001	<0.001	*0.816*	<0.001	
Other Indoor	---	---	---	0.005	<0.001	*0.110*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
Other Outdoor	---	---	---	---	<0.001	*0.065*	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	
Walking	---	---	---	---	---	<0.001	<0.001	<0.001	<0.001	<0.001	*0.831*	<0.001	
Car	---	---	---	---	---	---	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	PM_{4-10}
Bus	---	---	---	---	---	---	---	*0.270*	*0.284*	<0.001	0.009	*0.133*	
Underground	---	---	---	---	---	---	---	---	*0.802*	<0.001	<0.001	*0.895*	
Tram	---	---	---	---	---	---	---	---	---	<0.001	<0.001	*0.961*	
Train	---	---	---	---	---	---	---	---	---	---	<0.001	<0.001	
Bike	---	---	---	---	---	---	---	---	---	---	---	<0.001	
Scooter	---	---	---	---	---	---	---	---	---	---	---	---	

	Home	Hospital	Other In.	Other Out.	Walking	Car	Bus	Underground	Tram	Train	Bike	Scooter	
Home	---	<0.001	<0.001	0.008	*0.858*	<0.001	<0.001	<0.001	<0.001	<0.001	*0.384*	*0.549*	
Hospital	---	---	<0.001	<0.001	<0.001	<0.001	*0.203*	0.004	0.037	<0.001	<0.001	0.024	
Other Indoor	---	---	---	0.047	<0.001	*0.802*	<0.001	<0.001	<0.001	*0.073*	<0.001	0.003	
Other Outdoor	---	---	---	---	0.006	*0.090*	<0.001	<0.001	<0.001	*0.428*	*0.158*	*0.076*	
Walking	---	---	---	---	---	<0.001	<0.001	<0.001	<0.001	<0.001	*0.333*	*0.687*	
Car	---	---	---	---	---	---	<0.001	<0.001	<0.001	*0.068*	0.004	0.005	$PM_{>10}$
Bus	---	---	---	---	---	---	---	*0.725*	*0.650*	<0.001	<0.001	*0.146*	
Underground	---	---	---	---	---	---	---	---	*0.745*	<0.001	<0.001	*0.149*	
Tram	---	---	---	---	---	---	---	---	---	<0.001	0.001	*0.173*	
Train	---	---	---	---	---	---	---	---	---	---	0.036	0.010	
Bike	---	---	---	---	---	---	---	---	---	---	---	*0.463*	
Scooter	---	---	---	---	---	---	---	---	---	---	---	---	

	Home	Hospital	Other In.	Other Out.	Walking	Car	Bus	Underground	Tram	Train	Bike	Scooter	
Home	---	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
Hospital	---	---	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*0.43*	<0.001	<0.001	*0.06*	
Other Indoor	---	---	---	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
Other Outdoor	---	---	---	---	0.01	0.01	*0.41*	*0.91*	0.01	<0.001	*0.18*	*0.48*	
Walking	---	---	---	---	---	*1.00*	<0.001	<0.001	<0.001	*0.61*	<0.001	*0.43*	
Car	---	---	---	---	---	---	<0.001	<0.001	*0.57*	<0.001	<0.001	*0.47*	NO_2
Bus	---	---	---	---	---	---	---	*0.15*	<0.001	<0.001	*0.78*	*0.23*	
Underground	---	---	---	---	---	---	---	---	<0.001	<0.001	*0.12*	*0.63*	
Tram	---	---	---	---	---	---	---	---	---	<0.001	<0.001	*0.19*	
Train	---	---	---	---	---	---	---	---	---	---	<0.001	<0.001	
Bike	---	---	---	---	---	---	---	---	---	---	---	*0.14*	
Scooter	---	---	---	---	---	---	---	---	---	---	---	---	

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4.3. SUSCEPTIBLE SUBJECTS (PREGNANTS) – INHALED DOSE

This chapter is based and published on: Borghi et al. Evaluation of the inhaled dose across different microenvironments.
IOP Conf. Series: Earth and Environmental Science 2019, 296.

The principal aim of the INSIDE project (INdividual air pollution exposure, extracellular vesicles SIgnaling and hypertensive disorder DEvelopment in pregnancy) is to assess the molecular effects of environmental exposure to airborne particulate matter (PM) of susceptible subject. Different approaches are considered to evaluate these effects, including an exposure-effect study performed on a selected population. The short-term exposure to different pollutants (PM and NO_2) was evaluated considering 51 subjects recruited from October 2017 to April 2018. Each subject was asked to carry personal instruments for few hours before a clinical evaluation (blood and cardiological examination) during their journey from home to the hospital. Instruments used in the study were: (I) CairClip - CairPol (NO_2) and (II) Aerocet 831 - Aerosol Mass Monitor, Met One Instruments (size-fractionated PM). Moreover, a (III) smartphone with a GPS application and a (IV) Time Activity Diary (TAD) were used in this study to acquire information about the microenvironments (MEs) visited by subjects during the monitoring sessions. The experimental design of the project allowed to further investigate issues related to the mode of exposure: through the analysis of TADs and GPS data, it was possible to document the time spent by each subject in the different MEs and characterize the average exposure and inhaled dose associated to different MEs. The microenvironmental inhaled dose of pollutants was estimated considering the average exposure to PM and NO_2, the time spent across these MEs and the specific ventilation rate of each subject. Moreover, to understand which of these parameters has the major impact of the dose model, a sensitivity analysis was performed, on the total and on the MEs dataset.

4.3.1 Introduction

Travel microenvironments may represent sets of high exposure to air pollutants [1]. Despite the time spent commuting constitutes a small fraction of the whole day, it can be a significant contributor to total daily exposure. Several studies have been carried out to assess the microenvironmental exposure of commuters across Europe [2-11], but most of these studies do not consider the dose inhaled by exposed subjects. As reported by Dons and

collaborators [1], the inhaled dose is influenced by subject ventilation rate and by physical activity but, despite this, these parameters are often not considered and, as results, few studies are based on the evaluation of inhaled dose, especially during commuting.
In general, as reported by Betancourt et al. [12], most studies indicate that concentrations found in different means of transport are higher than those measured along pedestrian or cycling routes. It is recognized [13] that the factors that affect pollutant concentrations across different transportation modes are principally related to: (i) the travel mode (transport system, technology, energy source) and (ii) route characteristics (street configuration, micrometeorology, traffic). However, an additional aspect to consider is the possible difference between air pollution exposure and inhalation dose. As reported in [14], commuters that use passive transport, such as cars, train and subways are much exposed to air pollutants than commuters that use active transport (pedestrians or cyclists). Contrariwise, due to higher inhalation rate and higher time spent on road by active commuters, inhaled and deposited doses of pollutants are higher for active commuters.

The principal aim of this study is to evaluate the inhaled dose of pollutants across different MEs and the relative influence of input parameters on the dose estimates. The data used in this work were collected in the framework of the INSIDE project (INdividual air pollution exposure, extracellular vesicles SIgnaling and hypertensive disorders DEvelopment in pregnancy).

4.3.2. Materials and Methods

The principal aim of the INSIDE project is to assess the molecular effects of environmental exposure to airborne particulate matter (PM) in susceptible subjects (pregnant women). To achieve this purpose, different approaches are considered including an exposure-effect study performed on a human population. The exposure assessment to different pollutants (PM and NO_2) was carried out on 51 pregnant women recruited the first phase of the project (October 2017 - April 2018).
The enrolled subjects were asked to carry some portable instruments for the measurement of air concentrations in the breathing zone while moving to the hospital for the clinical evaluation on routes not fixed a priori. The

monitoring period and route length was not fixed a priori but was variable according to the habits of enrolled subjects and to the clinical evaluation time. Personal measurements were performed once for each subject enrolled. The measurement of NO_2 concentration were performed using an electrochemical miniaturized monitor (CairClip NO_2, Cairpol; La Roche Blanche – France – named "CC") and the continuous monitoring of PM concentrations was achieved via a portable direct reading monitor (Aerocet 831-MetOne Instrument Inc., Grant Pass, Oregon, USA – named "Aerocet") that provided concentration data of size-fractionated PM (PM_1, $PM_{2.5}$, PM_4, PM_{10} and TSP). To improve the data quality, comparative sessions between a freshly calibrated Aerocet and a gravimetric gold standard for $PM_{2.5}$ (Harvard Impactor MS&T Area Sampler Diagnostic and Engineering, Inc., Harrison, ME, USA, named here as "HI") were carried out. Both CC and Aerocet were set with an acquisition rate equal to 1 minute. In order to track and record the position of subjects during the monitoring sessions, a mobile phone (LG K4 2017), provided with an Android application (GEO TRACKER – GPS TRACKER; Version 3.3.0) was used and set with an acquisition rate of 30s and a precision of 200m. As a support for the reconstruction of the routes and frequented microenvironments, volunteers were asked to complete a Time Activity Diary (TAD).

The inhaled dose was estimated using 3 parameters: personal exposure, time fraction spent across different MEs and individual ventilation rate (VE). In this study individual VE has been measured during the clinical evaluation and reported as resting or warm-up ventilation. Values referred to the resting ventilation has been considered as VE during passive activities (indoor environments and passive commuting) while warm-up values were used to estimate the inhaled dose during active transport (walking or cycling). To assess how much VE, time spent in MEs and exposure concentrations affect the inhaled dose, a sensitivity analysis was performed.

4.3.3. Results

Average time spent across different MEs is reported in Figure 1. On average, 69% of time has been spent in indoor environments, while only 1% in an outdoor environment. 30% of time has been spent commuting and in detail

the major part of the travel has been spent on private transport (i.e., car - 34%) and moving by foot (30%). The time spent concerning the use of underground was equal to 17%, while time spent in train, tram, bike and bus was respectively equal to 6%, 6%, 4% and 3%.

In Table 1, the average exposure concentrations and individual inhaled dose are reported for $PM_{2.5}$ and NO_2, considering different MEs. Concentration data were combined with the time spent by subject across MEs and pulmonary ventilation rate (VE), calculated or measured for each subject, to estimate the inhaled dose of pollutants for each subject in each ME visited. Results of sensitivity analysis are reported in Figure 2. The sensitivity analysis was performed changing single variables (concentration, ventilation rate and time spent across different microenvironment) and considering minimum, maximum and mean value for the calculation of estimated inhaled dose. From the graph is clear that the time spent in a ME is an influent parameter for the dose, followed by personal exposure and by personal ventilation rate.

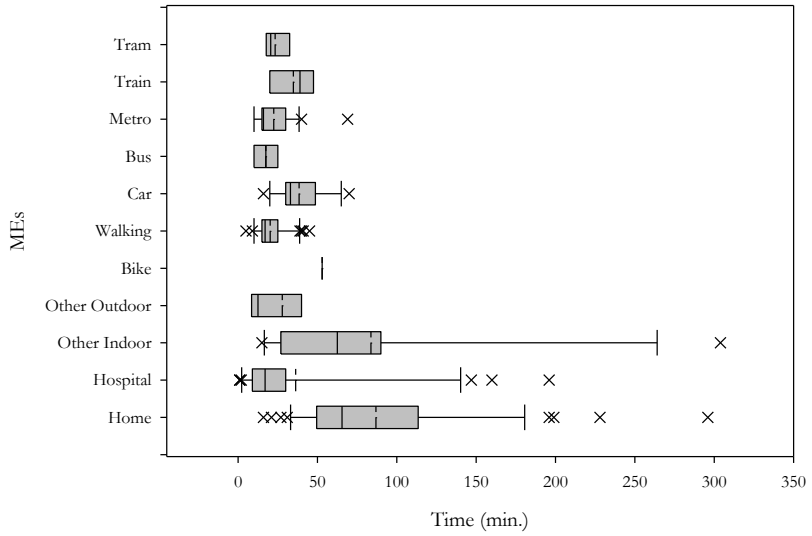

Figure 1. Time spent across different MEs.

	Tram	Train	Metro	Bus	Car	Walking	Bike	Outdoor	Indoor	Hospital	Home
$PM_{2.5}$	42.3	15.2	36.8	23.8	23.7	26.3	18.5	28.4	19.5	14.8	19.40
	*7.5	*11.0	*9.2	*5.6	*10.1	*8.2	*18.5	*5.9	*23.8	*7.3	*17.8
NO_2	65.7	47.6	42.2	69.7	69.9	64.9	65.9	61.5	46.0	62.4	54.1
	*24.9	*13.8	*22.4	*17.6	*30.7	*21.9	*65.3	*14.1	*30.0	*27.3	*22.4

Table 1. Mean concentration and subject inhaled dose (*) for $PM_{2.5}$ and NO_2 across different ME ($\mu g/m^3$).

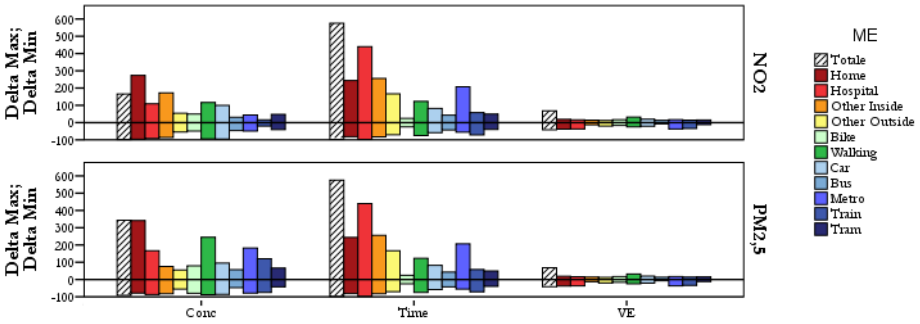

Figure 2. Sensitivity analysis performed considering personal exposure ($\mu g/m^3$), time spent across different MEs (minutes) and the ventilation rate of subjects (m^3/min).

As reported in Figure 3, the parameters having the major impact on the inhaled dose are the time spent in a ME and personal exposure. VE seems to have a low impact on the inhaled dose, both for MEs and kind of pollutant. Personal exposure has the major impact during active commuting (walking and cycling), even if these results are not in agreement with Zuurbier and collaborators [11]. In their work is reported how VE is the parameter that influence more the inhaled dose, since with the physical effort the VE increase. Also, regarding the passive transport considered in this study (car, bus, metro, train and tram), it is possible to identify that personal exposure most influences the inhaled dose.

4.3.4. Conclusions

The aim of this study was to evaluate the inhaled dose of $PM_{2.5}$ and NO_2 across different MEs and in particular during commuting, since most literature usually report only the exposure assessment to different pollutant and not results regarding the inhaled dose. The inhaled dose was calculated based on the measured exposure to airborne pollutants, time fraction spent across different MEs and the subject VE. Moreover, via sensitivity analysis, it has been observed that the most influence parameter on the dose value is the time spent in a ME, followed by personal exposure.

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4.4. SUSCEPTIBLE SUBJECTS (CHILDREN)

As mentioned before, although not directly related to the project reported here, the selected MMs, evaluated and used in this project were also used to assess the exposure concentration for a selected population of children, in the framework of the MAPS MI Project (Mapping Air Pollution in a School catchment area of Milan). In brief, the MAPS MI project has the principal aim to assess personal exposure to air pollution of schoolchildren and to identify the "ideal home-school paths", or rather the least polluted route from home to school, in particular in one sub-area (about 25 km^2) of Milan, located in the Northern part of Italy. More details of this study are reported by Boniardi and collaborators [1, 2].

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5. MODELLING PERSONAL EXPOSURE OF SELECTED AIRBORNE POLLUTANTS

This chapter is based on: Borghi et al. Development of a LUR model for the exposure assessment to air pollutants in the city of Milan (Italy), using miniaturized and portable monitors (in preparation).

PREFACE

It is well known that the improvement of estimates of personal exposure may prove an asset for different kind of study, such as epidemiological studies, which are usually based on limited ambient monitoring data as input [1,2]. Moreover, in a recent paper, the authors [3] reported that transferring the participatory sensing information (eventually obtained by means of MMs) to a specific population could be considered as a basic requirement for epidemiological studies in the future. Other authors [4] also reports how the recent improvements of low-cost MMs has the potential to provide high-resolution mapping of air quality in urban environments, despite the worst performances of these monitors in respect to traditional monitoring stations. In this paper [4], authors, trying to overcome the issue related to the performances of MMs, presented a data fusion method based on geostatistics, merging observation from a network of low-cost sensors and spatial information from an urban-scale air quality model, with the aim to provide highly detailed maps of urban air quality. Moreover, as the use of MMs is relatively recent, only few studies have been carried out using data acquired via MMs for mapping urban-scale air quality. Some studies investigated the use of mobile air sensors for generating long-term average maps (i.e. along street networks or for urban area as a whole) [5-8], using a network of passive samplers [9] or applying land-use regression techniques [10].

The aim of the work presented in the following chapter is indeed to develop a land use regression model using data based on personal monitoring campaign, that could lead to greater detail and resolution in pollutant estimates (Borghi et al., in preparation).

The use of this kind of data, derived from MMs, could be useful in improving the precision and the accuracy of the procedure for assessing exposure value to a selected population or subject, and therefore potentially useful in epidemiological studies.

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5.1. Introduction and Background

It is well known that air pollution can causes adverse effects on human health and on the environment [1, 2]: for this reason, and as mentioned before, one of the main objectives of the health impact studies is to accurately assess the human exposure to selected pollutants, for each subject/population taken into account in different studies (such as epidemiological studies), in order to quantify the impact of pollutant concentration on the health risks. Usually, this evaluation is performed using statistical models, based on environmental concentration data acquired via fixed monitoring stations. The instrumentation used for these kinds of assessments is characterized by numerous advantages: (i) excellent quality of the data; (ii) a historically used monitoring system; (iii) ability to monitor several pollutants simultaneously; (iv) extensive monitoring system on the territory and (v) integrated in the national area. The main disadvantage deriving from the use of these monitoring systems refers to the poor spatial resolution of the data, which, due to technical-logistic reasons, must be acquired in specific and selected locations [3], failing, in some cases, to provide a density of monitoring stations able to deeply describe pollutants concentration variation [4-6]. In addition to this kind of instrumentation, portable (to miniaturized) sensors have been developed in the last years: due to some advantages related to their use (such as reduced cost/size and ease of use), these tools are increasingly used in different applications [7] especially based on the high spatial and temporal resolution provided by these kind of instruments. These tools, even if not yet fully validated, could be useful as support to fixed measurement stations, providing a support for the modeling issue and implementing the spatial resolution of the acquired data [3, 8]. One of these aforementioned applications could be related to the development of LUR (Land Use Regression Model) models, used to explain the spatial variability of atmospheric pollutant concentrations in specific sites [4, 9-15]. The aim of this study is therefore to develop and to evaluate a LUR model for the city of Milan, comparing the results with the LUR model for the city of Turin [16]. The model will be developed using a different approach from the traditional one: environmental concentration data deriving from stationary monitoring

stations will not be used and instead of them, concentration data obtained from personal monitoring campaigns, acquired during the movement of moving subjects. In particular, data outcomes also from the INSIDE project (Chapter 4.2) will be used.

5.2. Methods

As described in the previous paragraph, for the development of a LUR model, 2 different kinds of data are necessary, which can be summarized in (i) pollutant concentration data and (ii) data that can be defined as "land use". At present, both types of information for the development of the LUR model are available. Briefly, the LUR models are based on computer systems (GIS) and on statistical techniques that, extrapolating geographical information, explain the spatial variation of the environmental concentrations measured at specific and well-characterized sites. The variables usually used for the development of these models, and associated with concentration data in a specific site, refer to: (i) traffic, (ii) land use, (iii) population density and (iv) altitude, which can be acquired from online datasets.

In the period 2015-2019, different monitoring campaigns were performed in order to evaluate the exposure assessment of selected population (evaluate subjects > 100) in the Milan metropolitan area. The exposure concentrations to atmospheric pollutants (different fractions of PM and NO_2) were acquired during the commuting of the subjects in different micro-environments. For this reason, for the development of the LUR model only the concentration data relating to the moments spent by the subjects in the outdoor environment will be considered. Briefly, the instrumentation used consisted of portable and miniaturized monitors for the measurement of atmospheric particulate matter and NO_2. In particular, the continuous measurement of PM concentrations (PM_1, $PM_{2.5}$, PM_4, PM_{10} and TSP) was carried out using direct reading portable monitors (Aerocet 831-MetOne Instrument Inc., Grant Pass, Oregon, USA and AirBeam, HabitatMap Inc., Brooklyn, NY, USA) while NO_2 concentrations (carried out only for part of the subjects under examination) were acquired through a miniaturized monitor (CairClip, Cairpol; La Roche Blanche, France). Monitored subjects were also provided with a GPS, in order to associate the pollutant concentration to a specific position in the space.

Regarding the land use data, the following information was acquired from online database and analyzed using GIS software: (i) land use - DUSAF 5 (populated areas, industrial areas, areas dedicated to mobility, green areas, agricultural/rural/forest areas); (ii) population density - Eurostat; (iii) road network - Geoportal (distance from major roads, length of roads); (iv) altitude - EU-DEM 1.1 and (v) vehicular traffic (traffic on major and minor roads). The data (exposure concentration and land use data) will be used as input variables for the development of the model and, as anticipated, only the concentration data acquired in the outdoor environment will be taken into account. The model will finally be developed and validated following what reported by Beelen and collaborators [16] and therefore, briefly: (i) choice of independent variables to be included in the model and evaluation of the expected effect on pollutant concentrations (positive or negative); (ii) choice of buffer sizes to be used for each geographical variable, based on scientific literature; (iii) analysis and development of new geographical variables based on previously identified buffers; (iv) development of the LUR model; (v) evaluation of the model (through multicollinearity, heteroscedasticity, normality and autocorrelation tests - Moran's I - residues); (vi) validation of the model.

Regarding the development of the model, a linear regression analysis will first be carried out between all the independent geographical variables and the dependent variables (exposure levels), in order to obtain a basic first model (higher R^2), the starting point for the inclusion of the subsequent independent variables. Each variable will then be added to the model only if the following conditions are met: (i) increase in the value of $R^2 > 1\%$; (ii) model coefficients conform to the direction of the effect, identified *a priori*; (iii) non change in the direction of the coefficients already present in the model.

5.3. Expected results and limits of the study

Unlike the models developed on the basis of data obtained from traditional fixed monitoring networks, the LUR model developed with this methodology will be based on personal monitoring campaigns performed with an acquisition rate equal to 1 minute, that could lead to greater detail and resolution of pollutant concentration estimates in a large and heterogeneous

area such as the urban area of Milan. This issue would be of fundamental importance for the purpose of improving the precision and accuracy of the procedure for assigning exposure values to selected subjects/populations, also for the purpose of assessing the potential impact on health resulting from exposure to air pollutants.
The limits of the project refer mainly to the kind of data to be used for the development of the model: the data acquired are indeed characterized by high variability. Furthermore, the data collected is not repeatable: the subjects (and the route taken by them) were in fact evaluated only on one occasion in which replicas or multiple measurements conducted on the same route by the same subject are not available; these aspects could introduce a certain level of uncertainty in the model. Furthermore, it is important to underline that portable instruments for measuring concentrations of airborne pollutants have limitations regarding their use as predictors of long-term exposure [13, 17]. The limitations in question refer to the choice of the path taken by the subjects, to the intrinsic temporal variability of some factors present during the monitoring and to the "short-term" nature of these types of assessments [13, 18]. Trying to overcome these limitations, it may be possible to integrate the data acquired at the level of personal monitoring with concentration data relating to fixed control units in the Milan area. Despite the limitations reported, the main objective of the project is to verify whether portable (and miniaturized) sensors can also be used in the field of modeling, thus making them useful for larger studies (epidemiological studies).

A first preliminary model has already been developed in the framework of this Ph.D. project, using the geographical variables previously described. In the final model, the most significant variables are those related to the population (in a 1000 m buffer), the land use (in a 500 m buffer) and the distance from the main roads. The model is unsatisfactory (in terms of the explained variability), probably due to problems regarding vehicular traffic, it is not possible to include these variables within the basic model. This data is now available and will be used for model development. This second model will also be integrated by adding personal exposure data relating to the second measurement campaign of the INSIDE project.

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6. DISCUSSIONS AND FURTHER RESEARCH

6.1. Overall discussions

The principal aims of this Ph.D. project were to report the state-of-the-art about the use of portable and miniaturized monitors and evaluate advantages and disadvantages related to their in-field uses and in exposure science studies. Since some issues related to the measurement performances of these monitors emerged from the literature review, two studies concerning the evaluation of the performance of portable and miniaturized monitors have been conducted. Once the instruments were evaluated and their instrumental limits were considered, two exposure assessment studies on selected subjects were conducted. Finally, the use of data acquired via portable and miniaturized monitors for the development of exposure models was evaluated. The principal results and discussions outcomes from these issues are briefly reported in the following paragraphs.

6.1.1. The literature review

As reported before, the main aim of this very first part of the project was to evaluate and report the state of the art about the in-field use of miniaturized monitors (for measurement of exposure both to airborne PM and gaseous pollutants). In general, available studies outlined that, because their characteristics (reduced cost/dimensions/weight and capability to acquire data at high and adequate spatial and temporal resolution) miniaturized monitors could provide a significant enhancement in exposure assessment studies. Available studies reported that miniaturized (as well as portable) monitors are characterized by worse performances with respect to the traditional air quality stations, commonly used also to roughly assess the human exposure to pollutants by static sampling. Anyhow, despite the limitation in accuracy and precision of measurement, this kind of monitors are particularly versatile (especially due to the reduced dimensions and weight), therefore usable in study with different experimental designs. Another key finding from the literature review regards the accessibility of data: in particular, some studies outlined that the way to communicate and share scientific data is changing, probably due to some advances in exposure science, such as: (i) the integration of personal monitoring systems with GPS; (ii) communication and data transfer via wireless and (iii) data transfer via

web or smartphone applications. As reported in Chapter 2, the simultaneous use of these implementations could be useful in citizen-science with the aim of creating awareness about atmospheric pollution and to support innovative studies (e.g. novel approaches for environmental epidemiology). In short, available papers show the potential of miniaturized monitors to support human toxicology and epidemiology or become a new way to assess human exposure.

6.1.2. The instrumental performance

This research (Chapter 3) showed that the intercomparison between different portable PM monitors (based on the light-scattering phenomenon) tend to over-estimate the actual PM concentrations measured by a reference technique. Further, portable light-scattering devices show over or under-estimation of PM concentrations with respect to the gold standard (i.e. a filter-based method). The evaluation of miniaturized monitors showed on the whole that, despite a moderate level of agreement between the tested instrument and the filter-based method (especially at low concentrations), a relevant bias was found across the whole comparison period: the development of standardized performance evaluation criteria and calibration protocols are therefore necessary before using these instruments on the field. In general, the main experimental findings indicate that, data collected by portable and miniaturized monitors should be carefully interpreted, especially if appropriate calibration or correction factors are not used. Further, the relative humidity seems to play a major role in determining the measurement error, which should be carefully taken into account to achieve the most accurate results in exposure assessment studies.

6.1.3. Exposure assessment studies and modeling

The exposure assessment studies were carried out to develop a protocol that could potentially be used for larger populations, with the intention of producing further analysis (i.e., the development of a novel land-use regression model based on mobile monitoring for health impact assessments. Owing to the fact that portable and miniaturized monitors allow an evaluation of personal exposure at temporal resolution, they were used for the exposure assessment of two selected populations: (i) commuters and (ii)

pregnant women. Thus, exposure levels were not analyzed as an average for each subject but allow to split the monitoring period into different micro-environments (traffic and non-traffic). This can be very useful in urban environments because of the heterogeneity of micro-environments (especially during commuting) and the high number and variety of emission sources. Moreover, the analysis of exposure concentrations as a function of individual physiological parameters and the time spent across each micro-environment has made it possible to calculate the dose of inhaled pollutants for each micro-environment.

6.2. Further research

As reported in Chapter 3, the issue of the evaluation of measurement performance, especially with regard to miniaturized sensors, should be better assessed. In particular, MMs should be evaluated in different real environments (not only at an urban-background station), at different pollutant concentrations and in different physical-chemical and meteorological conditions. In addition, these instruments should be evaluated for a prolonged period, to evaluate the performance trend in a long-term basis and to evaluate the zero instrumental drift.

Other exposure assessment studies via the estimated of the inhaled dose are already planned and should be performed taking into account the following issues:

(i) In the commuter exposure study, the pulmonary ventilation rate was derived starting from the value (per minute) of the subject's heartbeat and calculating the corresponding pulmonary ventilation rate. For this reason, it should be useful (i) to evaluate whether the equation used for this calculation is applicable to larger populations and (ii) if other equations presented in the literature may provide different (and best) results.

(ii) The calculation of the inhaled dose of pollutants was carried out through a simple equation that relates the pollutant exposure concentration with the subject's pulmonary ventilation rate and to the time spent by the subject in the various micro-environments. Finer elaborations about the deposition of a single PM fraction within the respiratory tract can be calculated using a mathematical model (MPPD model - Multiple-Path Particle Dosimetry Model). Further

developments will therefore need the reprocessing of the whole dataset to comply to the model specifications.

Finally, the project mentioned in Chapter 5 regarding the development of the land-use regression model for the city of Milan still needs to be refined and evaluated, due to the fact that in the first pilot study no vehicular traffic data have been used as predictor variable.

6.3. Pro e Cons of the study

Advantages and disadvantages related to each study phase have already been presented within different chapters and are summarized below.

Comparison of portable and miniaturized monitors

The major strengths are that the instrumental performance of different analyzers has been evaluated at the same time. Thanks to this, it was therefore possible to evaluate the instrumental performances in relation to the size distribution of airborne particles. In addition, it was possible to compare the instruments (i) with respect to a reference gravimetric method and (ii) between them, to identify the best instrument to be used for further studies. Furthermore, MMs portable monitors have been evaluated in different seasons, which allowed the evaluation of the monitors' performances in different environmental conditions (such as different air pollutant concentrations, temperature and relative humidity). Finally, it is worth noting that both studies were conducted at a well-known (urban background) site, where direct and near field sources of pollution were not present. On the contrary, the use of a single monitoring point could be considered a disadvantage in terms of data variability and representativeness of real exposure conditions. Furthermore, no long-term studies were carried out to assess the instrumental performances over a long period of time.

Exposure assessment studies

The major strengths of both the exposure assessment studies consist in the fact that several instruments were used simultaneously for personal exposure assessment. Furthermore, due to the design of the study, it was possible to identify and assess the exposure levels (and consequently the subjects' inhaled dose) in specific micro-environments (traffic and non-traffic environments). In

addition, the study of commuters was characterized by additional strengths: (i) the route, defined a *priori*, was always traveled by the same operator (in this way a certain level of reproducibility of the data was ensured); (ii) different replicas of the same route have been evaluated (iii) in different seasons (summer and winter). Regarding the evaluation study of the exposure during pregnancy to the contrary, a strength can be referred to the fact that the route has not been defined a *priori*: this has contributed to the collection of data characterized by a high variability. Moreover, in this study, due to the experimental design, the monitoring lasted for a short period of time (few hours). Finally, the main disadvantage of the two exposure assessment studies is related to the fact that the studies were conducted only in one single city (Milan).

Calculation of the inhaled dose

Regarding the calculation of the inhaled dose of pollutants, the major advantage refers to the fact that, unlike most of the studies in the scientific literature, subject's physiological parameters (pulmonary ventilation rate acquired across different stress conditions in one case and calculation of the pulmonary ventilation rate starting from the heartbeat of the subject in the other case) were collected at a personal level so that standardized tabular data were not used.

Development of the land-use regression model

A strength point in the development of the LUR model, was that input data were characterized by a high spatial variability. The development of a LUR model using exposure data collected by personal monitoring and by means of MMs could lead to greater detail and resolution in pollutant estimates with respect to traditional LUR approaches. Further, the use personal exposure data could be useful in improving the precision and the accuracy of the exposure estimates to be used in epidemiological studies. The major limitation refers to the fact that input data are not exactly those traditionally required for the development of these models, because some intrinsic limitations.