UNIVERSITÀ DEGLI STUDI DI MILANO

PhD course in Environmental Sciences
XXXII Cycle

Clinical Sciences and Community Health department,
and Environmental Sciences and Politics department

A participatory approach to assess children personal exposure to black carbon in an urban environment: spatial analysis, personal measurements, and possible mitigation actions.

Scientific disciplinary sector:
L-32

Ph. D. candidate: Dr. Luca Boniardi

Tutor
Prof. Silvia Fustinoni

Head of the doctoral course
Prof. Francesco Ficetola

Academic year 2019/2020

SUMMARY

Introduction: According to the World Health Organization (WHO), ambient and household air pollution are currently a major cause of death and disease globally. However, air pollution does not affect the whole population in the same way. In particular, a larger impact is reported being linked to the most susceptible subgroups of the population, such as children. To effectively tackle this public health threat, strengthen actions to protect the most vulnerable ones are needed, as well as environmental education interventions aiming to effectively raise awareness among the public. This is especially true for the city of Milan, which is located in one of the most polluted areas in Europe.

Moreover, since a multitude of new evidences shows up on the relation between air pollution and health outcomes, reducing exposure misclassification in epidemiological studies remains an important challenge in the framework of exposure science.

The aim of this dissertation is to present a novel participatory approach to assess schoolchildren exposure to air pollution with different approaches and to find possible exposure-mitigation actions. The common thread of the whole research process is black carbon (BC), an important component of particulate matter, a well-known indicator of traffic-related air pollution, linked with both long- and short-term health outcomes. In this process, some of the newest approaches in the framework of the exposure science are experienced.

Methods: A four-step research project was set up. In the first part, BC was monitored on fixed sites during two seasons in a school catchment area. The monitoring sites were identified by involving the school, schoolchildren parents and the residents of the neighborhood. The spatial distribution of the contaminant was studied and modelled as well, focusing in particular on the morning rush hour. In the second part, a two-module environmental education intervention was carried out with a participatory and experienced-based approach. In the third part, more than 100 schoolchildren were involved in a two-season personal monitoring campaign to identify the weight of different microenvironments (MEs) on the overall daily personal exposure to BC. Finally, a validation of the previously developed spatial model focused on morning rush hour was conducted

by using personal BC concentration, measured during home-to-school paths in order to assess the effectiveness of the tool in the identification of the cleanest routes.

Results and conclusions: The two seasonal fixed-sites monitoring campaigns showed that the cold season is the most critical period for BC concentrations, while the morning rush hour is the most critical daily time-window. In general, according to our data, increasing concentrations are linked to the period during which people move, whether they go to work or to school (weekly morning rush hour), or spend time in the city for leisure activities (weekend nighttime). These findings especially highlight the need for actions to mitigate personal exposure during weekly morning rush hours, the time during which children go to school. The six developed spatial models show that traffic variables are the main factors that explain BC distribution inside the school catchment area, suggesting that traffic mitigation actions can be useful to lower BC concentrations.

In the second part of the project, 128 schoolchildren were involved in a multitude of ludical activities on air pollution, raising their awareness and their level of engagement in the research process. This participatory approach helped to recruit volunteers for the following step: the two-season personal monitoring campaigns. The measured personal concentrations of BC, matched with time-activity diaries and GPS data, showed that indoor MEs are the most relevant source of personal exposure. Moreover, although it accounts only for 5-10% of the overall daily personal exposure, transportation-related exposure is actually the most intense, i.e. it exposes schoolchildren to the highest peaks of concentration in a very short period. Among the others, home-to-school commuting period is confirmed as the highest critical time-window for personal exposure for both warm- and cold-season.

Furthermore, the comparison between spatial model estimates and personal exposure data collected during the home-to-school routes shows moderate to good agreement, suggesting that a modelling approach is a valuable choice to identify and predict the cleanest routes to school. Moreover, although the model tends to a systematic underestimation of personal measured concentrations, this can be a valuable starting point toward more refined tools for lowering exposure misclassification bias in the framework of environmental epidemiology studies.

In summary, starting from the analysis and the spatial modelling of a selected air pollutant, passing by the personal exposure assessment, to the validation of the model with personal exposure data, this dissertation confirms that a participatory approach is a valuable choice that can add social value to the research project without losing in scientific quality.

1. GENERAL INTRODUCTION

1.1. PROBLEM STATEMENT

Ambient and household air pollution is currently estimated to cause 5.6 million deaths related to non communicable diseases and 1.5 million pneumonia deaths all over the world. Moreover, year after year, increasing evidence and new research link exposure to air pollution at all the stages of life and negative health outcomes, ranging from respiratory to neurological effects.

However, air pollution does not affect the whole population in the same way, and in fact a larger impact is reported being linked to the most susceptible subgroups of the population. In particular, according to the World Health Organization (WHO) estimates, more than 98% of Italian children in 2016 were exposed to fine particulate matter (PM2.5) concentrations higher than 10 $\mu g/m^3$, the recommended limit value to protect general population health *(WHO, 2018a)*.

To effectively answer to this public health threat, the first global conference on air pollution took place in November 2018, in Genève, Switzerland. Among the others, the conference outcomes highlighted the need:

a) to “strengthen action to protect the most vulnerable populations, especially children. […] These actions need to be taken in the home, streets, parks, clinics and schools”;
b) to “enhance education on air pollution as a key factor for improving health and quality of life, within a lifelong learning approach. Target audiences include children, educators, doctors, health and environment workers, patients and the general population […]” *(WHO, 2018b)*.

According to the U.S. Research Council, Committee on Human and Environmental Exposure Science, the engagement of communities and citizens in the research process is one of the key aspects to achieve the exposure science vision of 21th Century *(Lioy and Smith, 2013)*. Furthermore, as reported by the United Nations (UN) “since the adoption of the UN Convention on the Rights of the Child in 1989, Article 12 – the provision that children have a right to express their views and have them taken seriously in accordance with their age and maturity – has proved one of the most challenging to implement” *(UN, 2011)*.

Finally, from year to year, a multitude of new evidences shows up on the relation between air pollution and both long- and short-term health outcomes. Therefore, with the aim to reduce possible misclassifications, another fundamental challenge in environmental epidemiology is to refine exposure attribution process. In particular, even if personal exposure during transportation has become an important field of study due to its relevance in everyday life, it seems that epidemiological studies still prefer indicators of personal exposure such as concentration at home, school or other fixed addresses.

Given all this, an even greater commitment is request to professionals of exposure science to raise awareness among public opinion, refine methods, and enhance the impact of their research, focusing especially on the most vulnerable segments of the population.

1.2. RESEARCH OBJECTIVES

The overall aim of the dissertation is to present an innovative research design focused on participatory approach in the framework of the exposure science. The starting hypothesis is that using a participatory approach in a research project on air pollution could add social value by raising awareness among the engaged population, without lowering the quality of the scientific process.

To reach the goal, some of the newest available technologies and state-of-the art approaches are used in a multi-step process that consisted in:

a) modelling spatial distribution of air pollution in a school catchment area focusing especially on morning rush hour;
b) engaging teachers, schoolchildren and their families in the research process;
c) assessing personal exposure to air pollution of the engaged schoolchildren;
d) validating the morning rush hour model by using personal exposure data to test the effectiveness of this approach in the estimate of personal exposure during transportation.

In this framework, methodologies are applied to the air pollutant black carbon (BC), a fraction of fine particulate matter (PM2.5), a well-known indicator of traffic related air pollution, the main source of exposure in the outdoor urban environment.

This contribution is part of the MAPS MI project, "Mapping Air Pollution in a School catchment area of Milan with a participatory approach", supported by Fondazione Cariplo [grant numbers 2017-1731]. The project aims at:

a) raising awareness of schoolchildren, parents and teachers about air pollution;
b) assessing ambient personal exposure to air pollution of schoolchildren with different techniques (i.e. personal air sampling, biomarker of exposure analysis, epigenetic analysis, microbiota analysis, exposure modelling etc.);
c) developing a model framework to identify the least polluted routes to reach school.

The chosen approach included different stages and requires the use of different techniques that are reported in Figure 1.

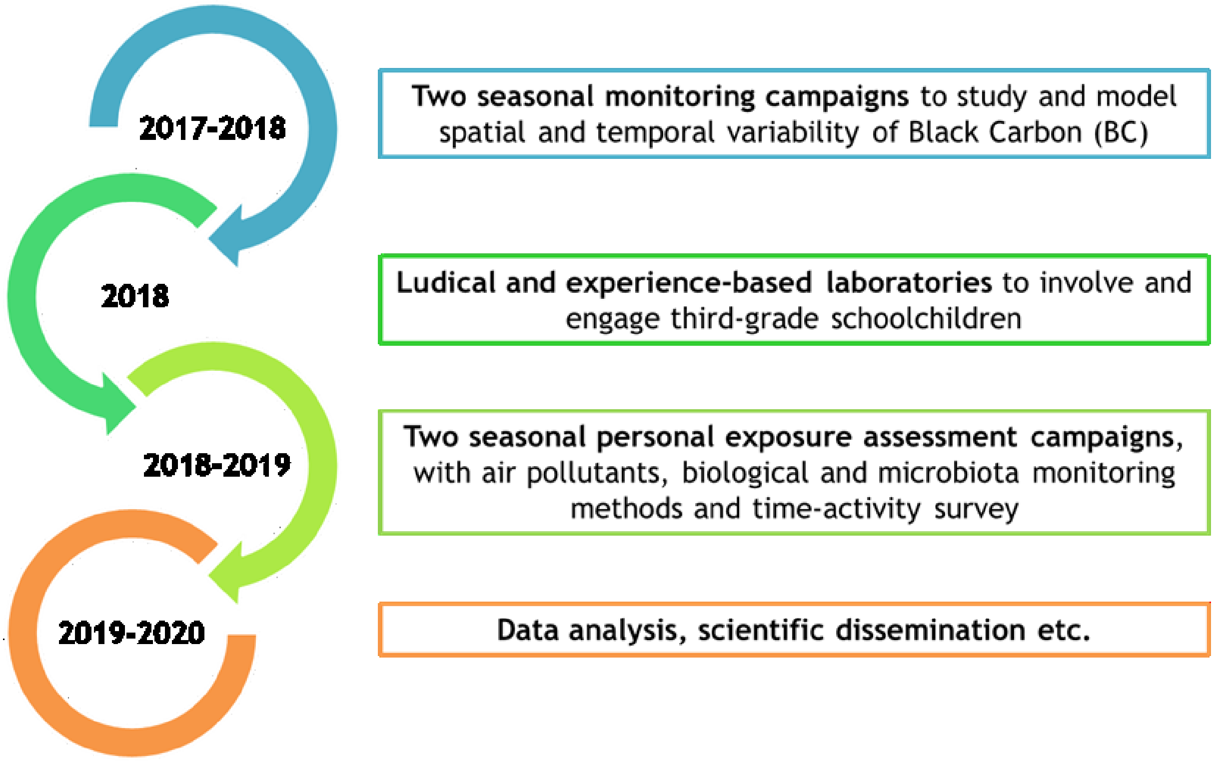


Figure 1. The four stages of the MAPS MI project "Mapping Air Pollution in a School catchment area of Milan with a participatory approach"

1.3. OUTLINE OF THE THESIS

In Table 1 the structure of the thesis is given, as well as the main research questions. The dissertation starts with a presentation of the state of the art linked with the main topics and methodologies covered by the thesis. The third chapter focuses on spatial distribution of BC in an elementary school catchment area of the city of Milan, and on its modelling using a Land Use Regression (LUR) technique and a participatory approach to select monitoring sites. Then, the fourth chapter focuses on schoolchildren engagement and the personal exposure assessment. The fifth chapter describes the validation of a Land Use Regression model for BC using personal exposure data and focusing especially on home-to-school trips. Finally, a conclusive chapter highlights the main contributions of this dissertation to the state of the art.

Table 1. Chapters of the dissertation and main research questions

CHAPTER 1	GENERAL INTRODUCTION
CHAPTER 2	STATE OF THE ART
CHAPTER 3	ANALYSING AND MODELLING THE SPATIAL DISTRIBUTION OF BLACK CARBON IN A SCHOOL CATCHMENT AREA
- **Q1**	Is the participatory approach suitable to identify monitoring sites to develop a LUR model?
- **Q2**	Is it possible to develop performant LUR model using BC data collected on a neighborhood-scale environment, such as a school catchment area?
- **Q3**	Is it possible to develop LUR models focusing on MRH, by increasing the frequency of measurement and using only collected data between 7 am and 9 am?
- **Q4**	Are there different spatial patterns in the distribution of BC during different seasons and time of the day?
CHAPTER 4	A PARTICIPATORY APPROACH TO INVOLVE TEACHERS, SCHOOLCHILDREN AND THEIR PARENTS IN THE RESEARCH PROCESS
- **Q5**	Is the used participatory approach to involve directly the school (i.e. teachers and children) in the research project a valuable approach to raise awareness on air pollution topic?
- **Q6**	Is this a suitable approach to recruit volunteers in the research process?
CHAPTER 5	MEASURING PERSONAL EXPOSURE OF SCHOOLCHILDREN TO BLACK CARBON
- **Q7**	Is transportation period an important factor to consider when analysing schoolchildren personal exposure in everyday life?
CHAPTER 6	VALIDATION OF A LUR MODEL BY USING PERSONAL EXSPOSURE DATA AND IDENTIFICATION OF THE CLEANEST HOME-TO-SCHOOL ROUTES
- **Q8**	Is it possible to apply a LUR model to mitigate the risk of exposure to air pollution, and in particular to identify the least expositive home-to-school paths?
- **Q9**	Can a LUR model developed on fixed monitoring sites help to reduce misclassification of exposure during transportation?
CHAPTER 7	CONCLUSION AND NEXT STEPS

2. STATE OF THE ART

2.1. AIR POLLUTION: AN OVERVIEW

As proposed by Seinfeld JH and Pandis S. (2016), ambient air pollution is defined as the presence in the atmosphere of substances in higher concentration and in longer duration than expected in natural circumstances(Seinfeld and Pandis, 2016). Moreover, to talk about air pollution, these contaminants should be capable to generate adverse effects on environment, human health or other targets (such as buildings, infrastructure etc.). According to the World Health Organization (WHO), nowadays air pollution is one of the major global public health concern (WHO, 2016).

2.1.1. Classification of air pollutants

Air pollutants are usually classified according to their physical state, sources, type of emission etc. In Table 2 the main families of air pollutants are reported according to their classification. In particular:

a) if we focus on physical state it is possible to distinguish between gaseous/vapour pollutants at normal temperatures and suspended droplets and/or solid particles;
b) we usually identify primary or secondary class of pollutants depending on whether contaminants are originated directly from the sources or are the results of atmospheric chemical reactions;
c) we can also distinguish between air pollutants in indoor and outdoor environments;
d) more in general, it is possible to classify contaminants by sources and in particular using the two natural and anthropogenic sources categories: among the first, it is possible to include such sources as sand and dust winds, pollen grains, wild fires etc.; while transportation, heating systems, agriculture, industries etc. are few of the sources among the latest class.

Table 2. Air pollutants classified by physical state, origin and environment (dapted from(Bernstein et al., 2004).

Physical state	Gaseous/ vapours	Carbon oxides (CO, CO_2), nitrogen oxides (NO_x), sulphur dioxides (SO_2), ozone (O_3), semi-volatile and volatile organic compounds (SVOC and VOC, aldehydes, alcohols, benzene, polycyclic aromatic hydrocarbons (PAHs) etc.)
	Particulate	Particulate matter (aerodynamic diameter ≤10 μm, PM10), coarse particulate (<10μm and >2,5 μm, PM10-2.5), PM fine (≤2,5 μm, PM2.5), PM ultrafine (≤0,1 μm, PM0.1, UFP).
Origin	Primary	PM, SO_2, NO_x, CO, organic carbon (OC), elemental carbon (EC), black carbon (BC)
	Secondary	O_3, NO_2, PM, OC etc.
Environment	Indoor	CO, CO2, radon, biologic agents, SVOC
	Outdoor	Particulate matter, SO_2, ozone, NO_x, CO, PM, SVOC

Among the others, in the last decades, atmospheric particulate matter and in particular its fine fraction (PM2.5) has shown to represent a major player in atmospheric pollution by leading to a broad spectrum of negative effects including health-related effects, ecosystems degradation, climate change, a decrease in visibility etc.

In particular, among other pollutants, PM2.5 is the major contributor of premature death for both all-causes and in particular for cardiovascular disease (Hoek et al., 2013). Moreover, the global burden of disease project attributes to outdoor fine particulate matter exposure 4.2 million deaths and 103.1 million disability-adjusted life-years (DALY) in 2015 (Cohen et al., 2017). These estimates make exposure to PM2.5 the fifth leading risk factor for death worldwide.

2.1.2. Air quality in Europe

In a recent scientific contribution, Ciarelli G et al (2019) using different datasets found a substantial decrease in the concentration of PM2.5 during the 1990-2015 period (Figure 2).

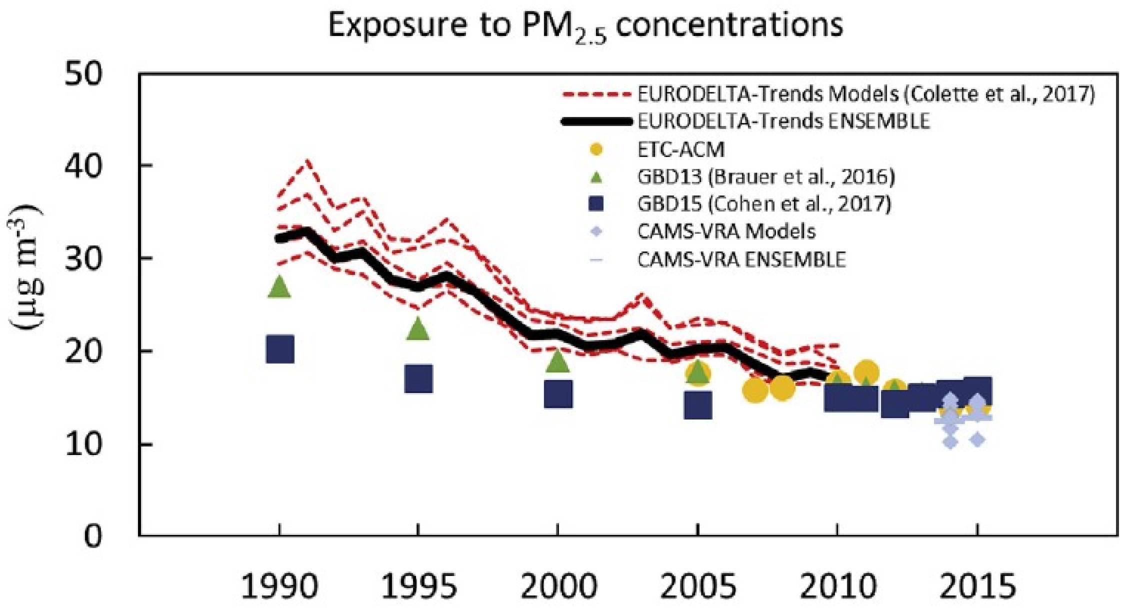


Figure 2. Trend in PM2.5 concentration for 1990-2015 years in Europe according to different models 3 (Ciarelli et al., 2019)

This reduction in overall concentration of particulate matter has been supported for Italy and, in particular, for the Po valley by Manara et al (2019) who, among others, compared long time series of visibility measures with PM2.5 data finding a general improvement in visibility and a negative correlation with PM2.5 concentrations (Manara et al., 2019).
Despite this positive trend, the European Environment Agency estimates that about 8% of the European population still experience an exposure to PM2.5 over the European Union (EU) limit values (Figure 3). However, all this contribution shows a strong decreasing trend

that tends to a plateau in the last few years pointing out the need of further and new interventions to bring air pollutants concentration below health-based limit values.

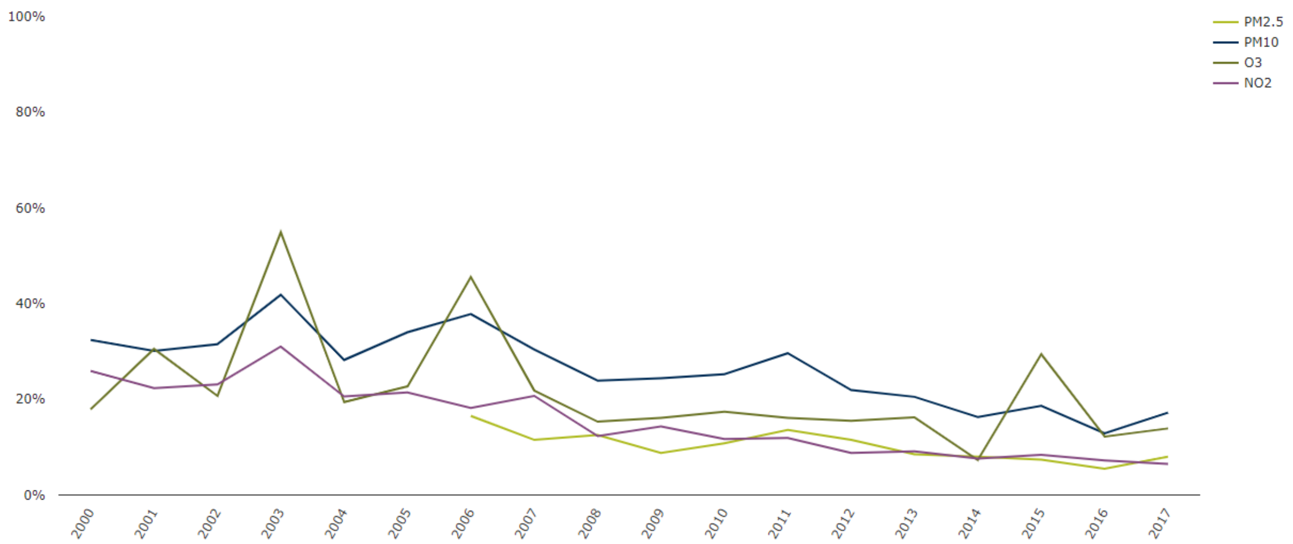


Figure 3. Fraction of urban population exposed to air pollutant concentrations above selected limit and target values (EEA, 2018)

This estimate dramatically increase to about 81% if we consider the more stringent World Health Organization threshold (Table 3).

Table 3. Air quality standards in EU and WHO guideline thresholds

	EU	WHO
NO_2	200 µg/m^3 (1h mean, 18 times/year) 40 µg/m^3 (annual mean)	200 µg/m^3 (1h mean) 40 µg/m^3 (annual mean)
PM10	50 µg/m^3 (1day mean, 35 days/year)	20 µg/m^3 (1day mean)
PM2.5	25 µg/m^3 (annual mean)	25 µg/m^3 (1day mean) 10 µg/m^3 (annual mean)
SO_2	350 µg/m^3 (1h mean, 24 days/year)	20 µg/m^3 (1day mean)
O_3	120 µg/m^3 (8h mean, 25 days/year)	100 µg/m^3 (8h mean)

These two set of limit values appear very different because of their different nature. In particular, WHO thresholds are identified after a massive work in reviewing the body of scientific evidence that in literature links exposure to health outcomes. For instance, PM2.5 10 μg/m^3 limit value was the lowest (by 2005) level at which total, cardiopulmonary and lung cancer mortality have been shown to increase the long-term exposure significantly (WHO, 2005). On the contrary, European limit values and, more in general, national standards, are the result of a complex balance among health risks, technological feasibility, economic considerations and various other political and social factors (EU, 2008).

2.1.3. Air quality in the Po Valley

In the EU framework, Northern Italy is one of the most polluted areas (Figure 4).

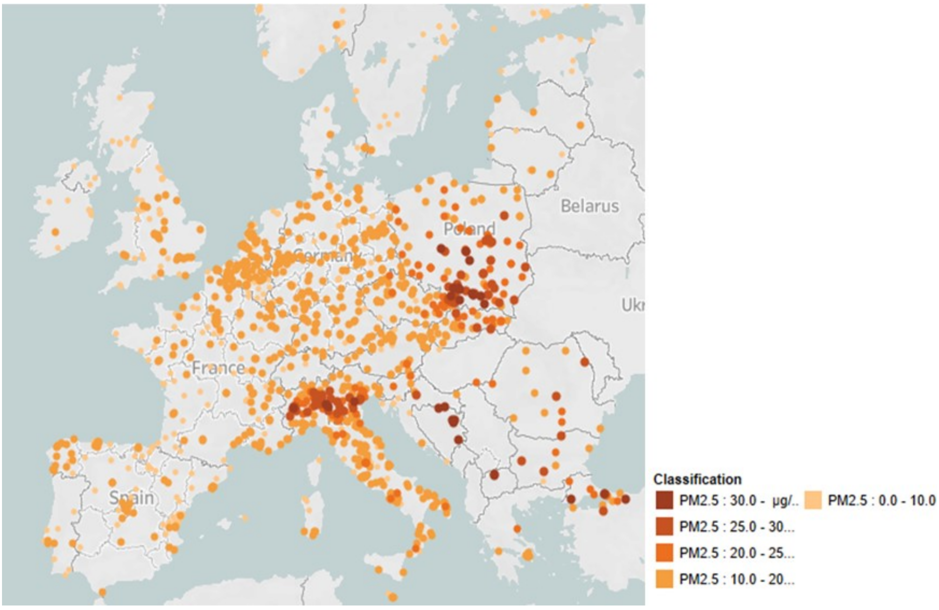


Figure 4. 2017 average concentration of PM2.5 in Europe (EEA, 2019)

The Po valley region is a highly populated, industrialized area with one of the highest motorization rate in Europe (EUROSTAT, 2019). This picture is further complicated by extremely adverse meteorological conditions: Caserini et al (2017) studied a 20-year time series of temperature vertical profile measured at Milano Linate station, a monitoring site representative of the so called higher Po valley (Caserini et al., 2017). Sounding data revealed a minimum of about 105 days/year of temperature inversion and a maximum of about 150 days/year. Moreover, because of climate change, temperature inversion and stagnation events (i.e. days of light low- and high-level winds and lack of precipitation) are projected to increase in the future. Afterwards, the presence of high mountain chains on three sides of the valley influence the stagnation of air in the lower layers of the atmosphere resulting in a very low annual wind speed average (Figure 5).

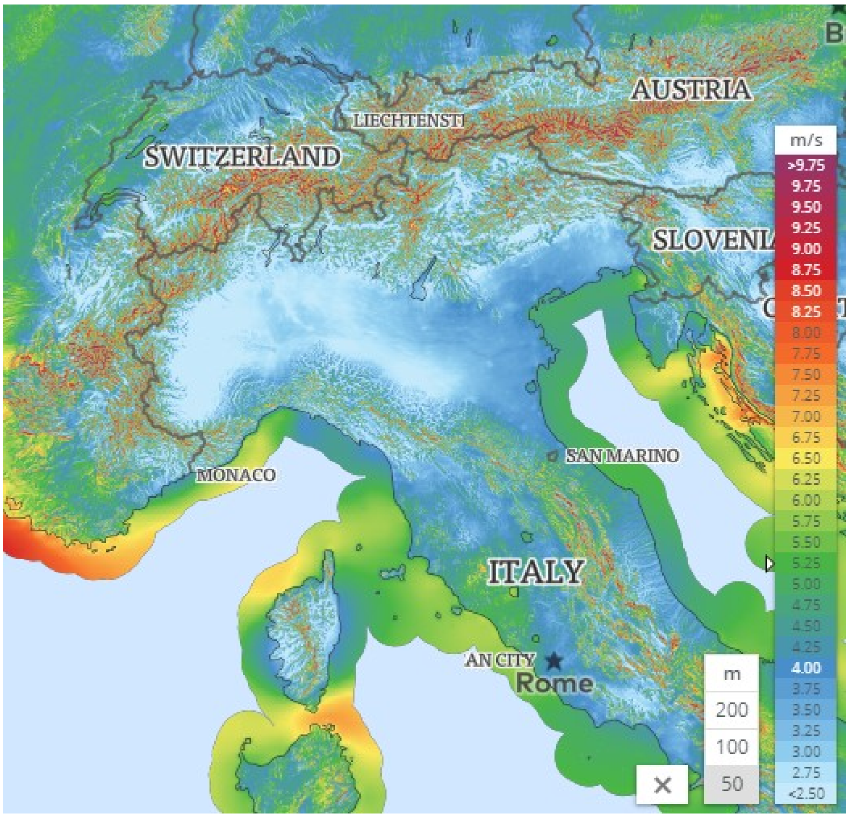


Figure 5. Annual wind speed average in the Northern part of Italy and the surrounding areas (DTU, 2019)

The combination of these factors reduces the potential of dispersion of the atmosphere and influence the chemical reactions that underlie the formation of secondary class of pollutants.

2.1.4. Conclusion

Air pollution is currently one of the most important health-related challenges at a both global and European scale. Among others, the Po valley is one of the most polluted areas in Europe due to many reasons, included meteorological and geomorphological characteristics. In the attempt to tackle this issue, a particular focus on fine particulate matter is needed given its relative important impact on health when compared to other air pollutants.

2.2. PARTICULATE MATTER

2.2.1. Definition and characteristics

Particulate matter is a mixture of solid contaminants and liquid droplets that it is possible to find in nature at different scales of dimension, from nanoscale (<0.1 μm in at least one dimension) to a maximum of 100 μm. Generally speaking, the mass of PM2.5, the portion that has an aerodynamic diameter ≤2.5 μm, account for a significant fraction of PM total mass; while, for its part, ultra-fine particles (UFP) accounts for about 5% of PM2.5 mass (Cabada et al., 2004)(Figure 6). However, this proportion proved to be both location- and time-dependent; for example, Brauer et al. (2012) estimated a range of PM2.5/PM10 ratio from 0.13 to 0.94 in 21 different regions of the world (Brauer et al., 2012).

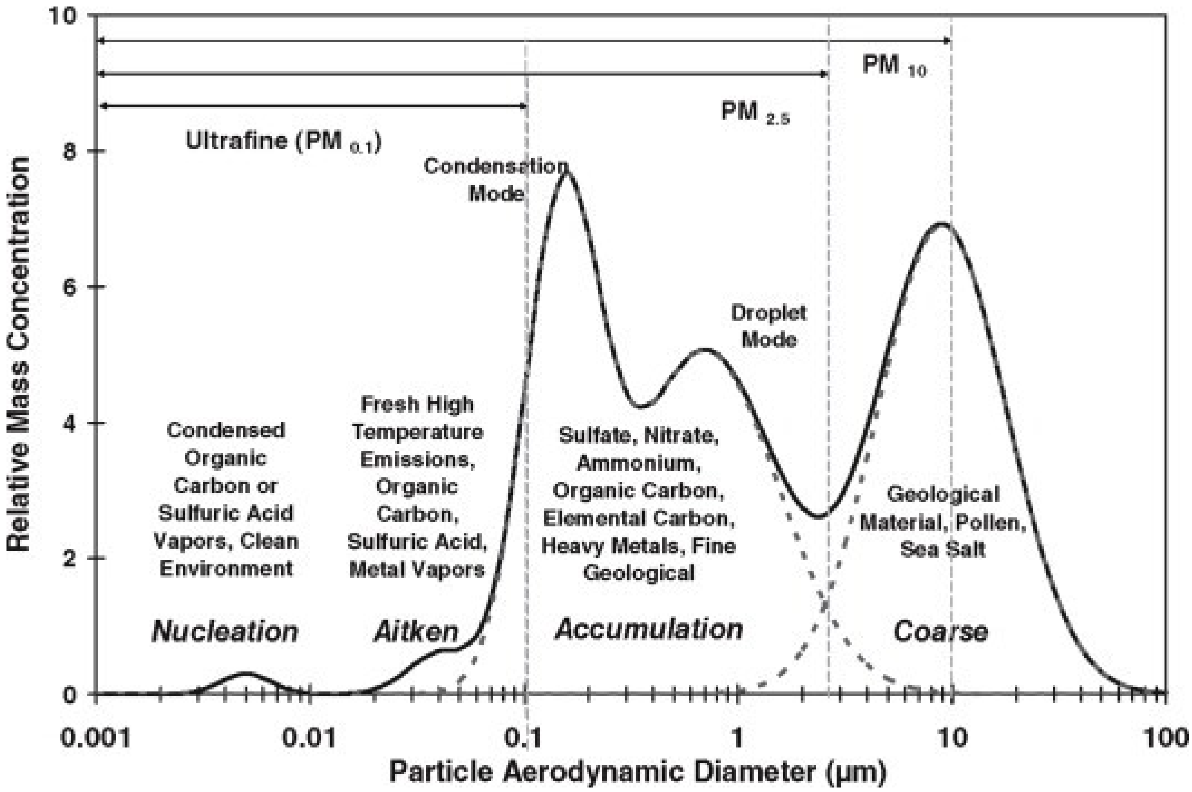


***Figure 6**. Major features of the mass distribution of atmospheric particles by particle size (John G. Watson and Judith C. Chow. 2014)*

Anthropogenic processes are a major source of particulate matter. In those area in which combustion of fossil fuels and biomasses are prevailing, the fine fraction of PM is usually predominant. Moreover, natural processes are to be taken in account, particularly in Italy where wildfire (both natural and human related) are common during summer (Faustini et al., 2015), as well as Sahran-Sahel dust blown by winds (Mallone et al., 2011).

2.2.2. Chemical composition of PM in Milan

Particulate matter is a complex mixture of different contaminants and its chemical composition may vary from location to location. This is due to the influence of different variables, such as the presence of heavy industries, population density, the presence of natural sources, the proximity to traffic and biomass heating. This variability in composition is present also at local scale. For example, by comparing four sets of paired roadside and urban background locations, Harrison et al (2004) found that the increment in PM10 and PM2.5 concentration at roadside sites is comprised very largely of elemental carbon, organic compounds and iron-rich dusts (Harrison et al., 2004).

Because of different seasonal sampling campaigns carried out in Milan between 2006 and 2009, Perrone MG et al (2012) characterized PM2.5 composition at a traffic site (Perrone et al., 2012). Among other results, as reported in Figure 7, they found that:

a) elemental carbon accounted for a significant fraction in the mixture with a seasonal trend;
b) organic material (carbonaceous plus other) was the major contributor in both the seasons;
c) the three inorganic ions nitrate (NO_3^-), sulphate ($SO_4^=$) and ammonium (NH_4^+) accounted for a large fraction of the PM2.5 mass in both winter and summer.

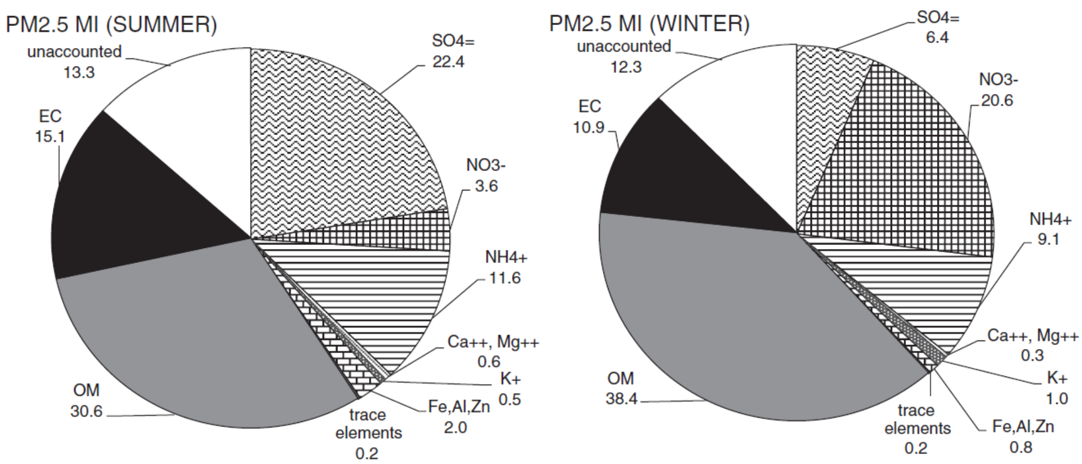


Figure 7*. Average seasonal PM2.5 composition in Milan measured in a urban traffic site (adapted from(Perrone et al., 2012)*

Moreover, the Environment Agency of Lombardy recently characterized PM collected in a urban background site in Milan for the 2017-2018 period (ARPA, 2018b). The average fractions in the chemical composition of PM2.5 were: (1) 6% of elemental carbon; (2) 30% of organic carbon; (3) 28% of ammonium sulphate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3). The different composition of PM suggest a different influence of primary and secondary sources.
Among the organic materials, polycyclic aromatic hydrocarbons (PAHs) are a major health concern for the general population. PAH are normed by the EU Directive 2008/50/CE (EU, 2008). In particular, benzo(a)pyrene (BaP) is classified as a carcinogen, group 1, by the International Agency for Research on Cancer (IARC, 2016b).

2.2.3. Source apportionment of PM2.5 in Milan

The air quality inside the city is usually affected by a complex panel of primary and secondary sources that contribute in different percentage according to time and location. Perrone MG et al (2012) accounted for the source apportionment of PM2.5 in the traffic site of Torre Sarca (45°31′19″N, 9°12′46″E) founding that traffic emissions were the primary contributor to PM2.5 total mass with a relative weight of 17%, 24%, 23% and 23% during spring, summer, fall and winter respectively. However, also biomass burning was found to contribute significantly with 8%, 1%, 30% and 25% of relative weight during spring, summer, fall and winter respectively. As part of the AIRUSE LIFE+ European project, ARPA Lombardy apportioned the source of PM2.5 in a urban background site from January 2013 to January 2014 (ARPA, 2016). The low impact of traffic exhaust is likely to be linked to the different location and classification of the monitoring site (Figure 8).

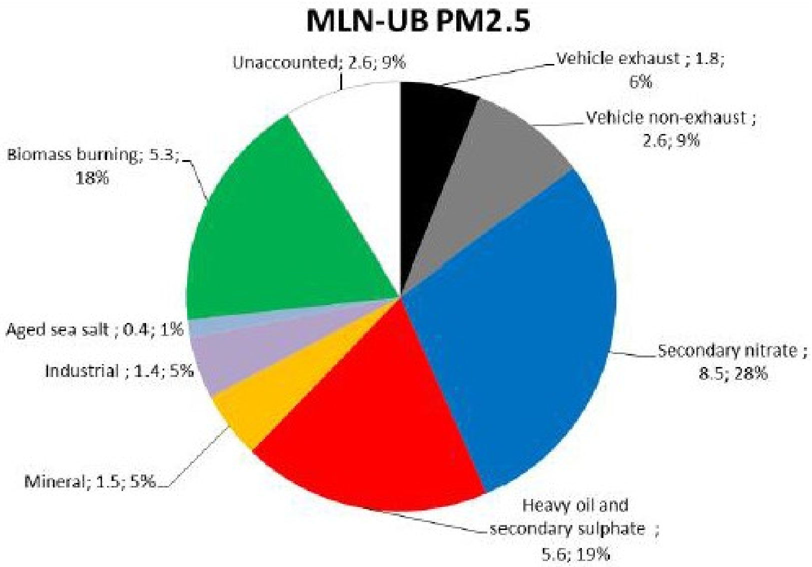


Figure 8. Pie chart of the identified source contributions in Milan urban background site (ARPA, 2016)

Moreover, since also part of the secondary inorganic material (i.e. secondary nitrate, secondary sulphate) can be attributed to specific sources, the final average annual impact of traffic was estimated to be about 29%, while for the biomass burning was 21%.

2.2.4. Inventory of Emissions of PM2.5 in Milan, greater municipality

As regarded the emission in the territory of Milan greater municipality, as reported by the Inventory of Emission in the Air of ARPA (ARPA, 2018a)(Figure 9), the largest part of the total emitted PM2.5, as well as PM10, Elemental Carbon (EC) and Black Carbon (BC), can be attributed to traffic sources. On the contrary, organic carbon (OC) is mostly attributable to non-industrial combustion such as heating systems.

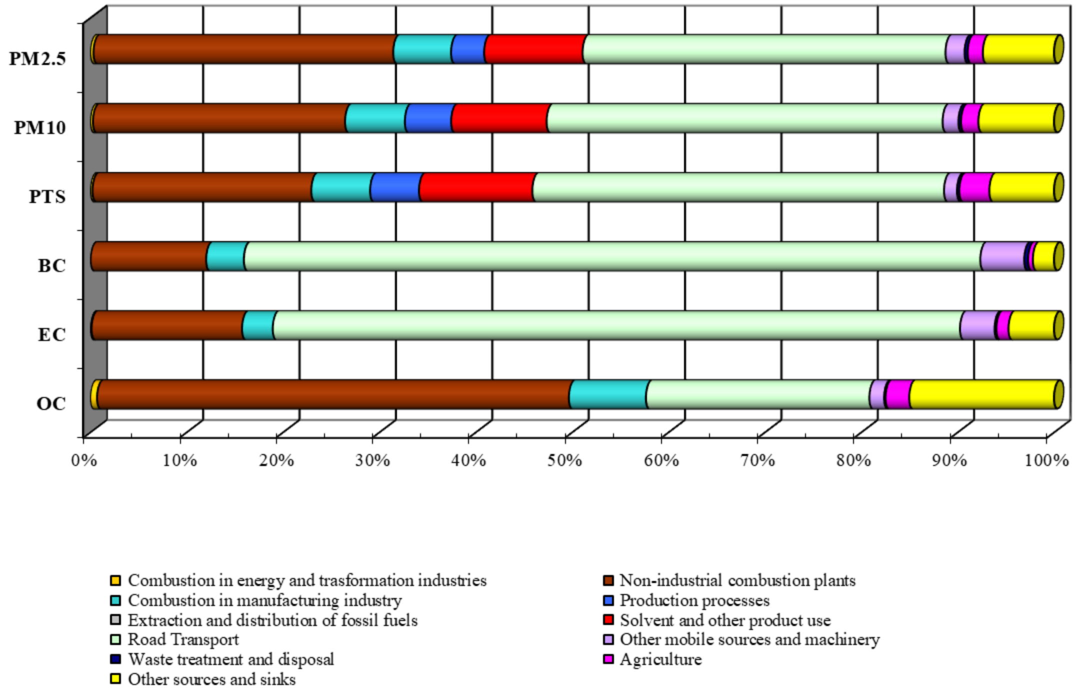


Figure 9. Emission sources per atmospheric pollutant in the Milan greater municipality (ARPA, 2018a)

2.2.5. Conclusions

In the territory of Milan, particulate matter, and especially its fine fraction (PM2.5), is mainly emitted by traffic sources. However, at a local scale source apportionment experiences show different gradient of contribution related to different seasons and location. Nevertheless, traffic remains a very important source as well as biomass burning. This fact represents an important variable when addressing personal exposure since people, especially if we consider people living in urban environment, usually spend a significant portion of their life in transport or at a close distance from these kind of sources (Dons et al., 2012). Given this picture, addressing personal exposure to traffic related air pollutants is fundamental in the area of Milan. Finally, Elemental Carbon (EC) and Black Carbon (BC) are among the best tracers of traffic related air pollution (EPA, 2012).

2.3. BLACK CARBON

2.3.1. Definition, characteristics and dispersion

In atmospheric science, BC is a term that is often used interchangeably with EC. However, the definitions of these two contaminants refers to different characteristics (Figure 10). In particular:

a) EC is usually defined with is thermal property as the carbon fraction inert in atmosphere up to 3500 °C;
b) BC is defined with is optical property as the mixture of carbonaceous elements, mostly pure, that strongly absorbs solar radiation at all the wavelengths, the most effective form of PM, by mass, at absorbing solar energy, and the major component of “soot”, a complex light-absorbing mixture that also contains OC (EPA, 2012).
c) BC is operationally defined as an aerosol species based on measurement of light absorption and chemical reactivity and/or thermal stability (UNEP and WMO, 2011).

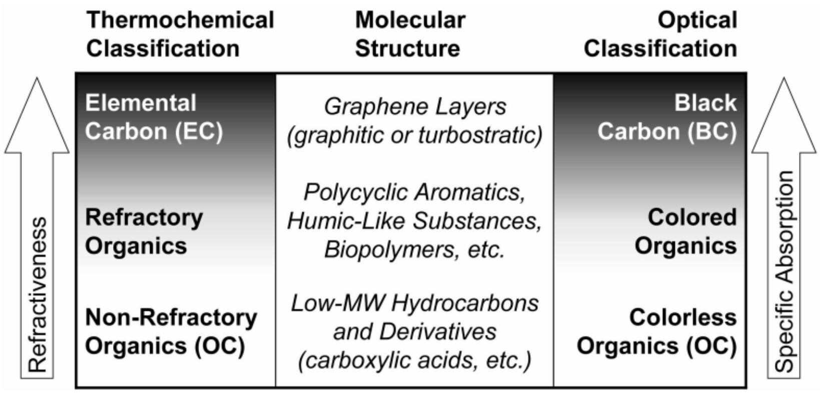


Figure 10 – Comparison of EC, BC, OC by optical and thermochemical properties (Poschl, 2003)

Actually, EC and BC cover about the same fraction of carbonaceous elements: a mixture of natural carbon and graphite-like structures included entirely in the fine fraction of particulate matter. BC is a primary pollutant entirely linked to the partial combustion of fossil fuels and biomasses that in Europe account for 5-10% of total PM2.5 mass and possibly up to 20-25% at kerbside sites (Putaud et al., 2004; Viidanoja et al., 2002). BC is considered as a good tracer of PAHs: in fact, its high surface-to-volume ratio and affinity to non-polar substances are linked to a high capacity for adsorbing this class of contaminants (Dachs and Eisenreich, 2000). Moreover, even though BC is defined as a short-life pollutant, with an estimated lifetime of 4-12 days (Cape et al., 2012), it has been classified as the second climate forcers after CO_2 (Bond et al., 2013)(Figure 11).

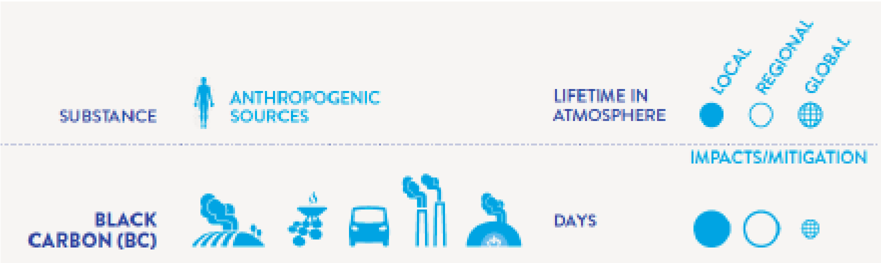


Figure 11. - sources and impact of Black Carbon (adapted from Fultescu et al., 2018)

Due to the uncertainty that currently affects global inventories of BC, it is not simple to define clearly the total amount of emissions and the influence of sources (Dong et al., 2019). By using the GAINS integrated assessment model, an already used tool by the European Commission for the EU Thematic Strategy on Air Pollution, Klimont z et al (2017) found that anthropogenic emission of BC were about 7.2 Tg (75% of the global total) in 2010 with an increasing trend in emission at a global scale from 2005, mainly driven by Asia. BC was considered to account for the 15% of global PM2.5, but up to 50% focusing on transportation sector (Cofala et al., 2010; Klimont et al., 2017). Residential combustion is the main global source of BC, while transport sector was found to account for about the 25% of global BC emission, however this pattern follows a strong regional variability. In Europe they observed a decline in BC emission, and a different contribution of sources: transport sector was found to weight about 50% on the total emission in 2010 with a decreasing trend from 2000. BC in Europe remains mostly driven by transport sector and, consequently, at a very local scale by traffic congestion.

Concluding, BC is an important air pollutant that threat human health and contribute significantly to the radiative forcing, by affecting environment at local, regional and global scales.

2.3.2. Measurement techniques and artefacts

As previously reported, BC is defined through its optical properties as the fraction of PM2.5 capable to efficiently absorb the solar radiation from short to long wavelengths in the visible spectrum up to infrared (IR) (EPA, 2012). Several techniques take advantage of this optical property, but no standardization has been proposed so far. Therefore, the use of terms in literature is not consistent and lends to incomprehension. Moreover, the complex nature of Light Absorbing Carbon (LAC) and, in particular, the highly variable presence in aerosols of organic-coated absorbing carbon particles, or Brown Carbon, further complicates the setting, pointing out all the limitations of optical-based measurement techniques (Andreae and Gelencser, 2006). In this dissertation, we will refer to Black Carbon (BC) as the result of the measurement performed by a filter-based optical technique at a wavelength of 880 nm.

Among the other, the most used filter-based measurement methods consist in:

a) the transmittance of a beam of light through a filter, used by the aethalometer (Hansen et al., 1984) and the Particle Soot Absorption Photometer (PSAP; Radiance Research, Seattle, WA);
b) both the reflectance and transmittance: these methods are combined by the Multi Angle Absorption Photometer (MAAP; (Petzold et al., 2002)).

In literature, all these techniques appear well correlated with high R^2 but significant variability in absolute values (Hitzenberger et al., 2006; Park et al., 2006; Snyder and Schauer, 2007).

Moreover, filter-based optical instruments that take advantage only of transmittance, show some peculiar artefacts, which are:

a) the so-called shadowing effect (Weingartner et al., 2003);
b) the multiple light scattering.

These two analytical issues are linked to the fact that the attenuation of light through the filter is not only related to the absorption of the same light, but it is also influenced by the scattering, caused by both aerosols' particles and filter fibres (Ran et al., 2016). In particular, the shadowing effect reduces the optical path in the filter: the increasing amount of absorbing material on the filter, contrasts the overall multiple scatter induced by the filter fibres leading to an underestimate of the BC concentration (LaRosa et al., 2002). However this issue only proved to be a critical one in those environments dominated by aerosols composed by fresh-highly absorbing-particles, conversely aged aerosols dominated by organic-externally coated-BC show higher scattering behaviour that is inversely proportional to the magnitude of the shadowing effect (Weingartner et al., 2003). This effect is correlated to the single scattering albedo (ω_0) of the sampled aerosols, by definition the ratio between scattering to extinction, a parameter that gives information on the composition of the aerosol and can be estimated by combining absorption and scattering measurement. The second artefact consists in the multiple scattering of light due to the filter material and the aerosol and leads to an enhancement of the optical path in the filter and a consequent overestimate of BC concentration. The MAAP account for this analytical issue and for this reason is often used as a gold standard in comparison with the aethalometer. All the measurements included in this dissertation were performed by using micro-aethalometer devices.

2.3.3. The Aethalometer device

Aethalometer derived from the greek word aethaloun that means blacken with soot. The device provides an estimate of optically absorbing material concentration in the sampled aerosol. The calculation starts from the measure of the rate of change in optical transmission through a filter onto which the aerosol is continuously collected at a constant airstream velocity. The transmitted light intensity is collected by a photodetector and amplified proportionally to the optical attenuation (ATN). The rate of increase of this signal is therefore related to the rate of deposition of BC on the filter. Finally, the rate of attenuation of the light through the loaded spot is compared to a reference unloaded filter to correct for any variations in incident light intensity and drift in electronics (Figure 12).

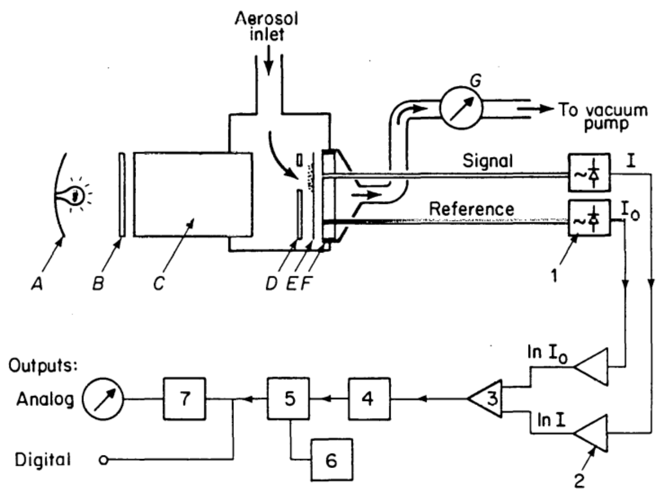


Figure 12 - Sampling scheme of the original aethalometer ((Hansen et al., 1984)) instrument. Optical and aerosol collection components: A, light source; B, 530-nm band pass filter; C, quartz light guide; D,transparent mask; E, filter with particles collected on portion underneath hole in mask; F, filter support with optical fibres set in; G, flowmeter. Electronic system components: 1, silicon photodetectors; 2, logarithmic amplifiers; 3, difference amplifier giving output proportional to ln(I/I_o); 4, A/0 converter; 5, storage and subtraction; 6, variable time base; 7, 0/A converter.

This technique is based on the Beer-Lambert law that explain the relation between the intensity of a beam of light incident on a filter (I_0) and the remaining light intensity after passing the material (I):

$$\frac{I}{I_0} = e^{-b_{abs} \cdot x}$$

Where b_{abs} is the absorption coefficient of the medium with thickness x.
Another way to write the above-mentioned equation is reported below:

$$b_{abs} = \frac{A}{Q} \cdot \frac{\Delta ATN}{\Delta t}$$

Where A is the area of the filter spot, Q the flow rate, ΔATN the change in attenuation and Δt is the time interval in which the change happens.
Finally, absorption coefficient is related to a concentration by dividing b_{abs} by the mass absorption cross section of BC (MAC). MAC is dependant from the mixing state of BC, i.e. the degree of coating of BC particles that is linked to the age of the aerosol and to the source of combustion (Bond and Bergstrom, 2006; Knox et al., 2009).
In the last few years, new devices have been developed giving an answer to the need of portability expressed by exposure sciences' researchers. It is the case of the micro-aethalometer AE51 and MA200, the two optical instruments used to perform the measurements included in this dissertation (Figure 13).

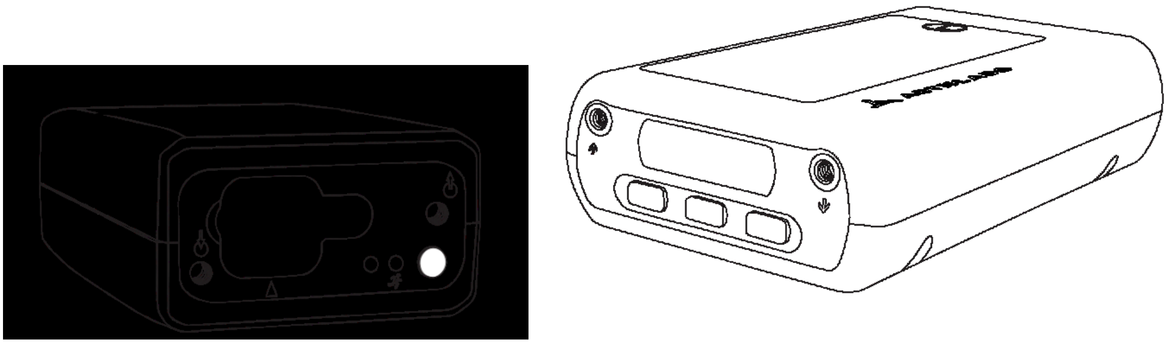


Figure 13. microaethalometer AE51 and MA200 (AethLabs, San Francisco, California, US)

The AE51 device measure BC at only one wavelength (880 nm, the most representative of highly absorbing particulate) combining high portability (weight: 280 g, dimension 117 mm x 66 mm x 38 mm) with long battery life, built-in memory and adaptability to different conditions (with the possibility to set up temporal resolution and flowrates). The MA200 (weight: 420 g, dimension: 137 mm x 85 mm x 36 mm) add a multi-wavelength measurement (from 375 nm, UVPM, to 880 nm interpreted as BC) and a new technology capable to account for shadowing effect (Dualspot©)(Drinovec et al., 2015). In particular, by performing a double-parallel-measurement at different flowrates on the same filter, the device is able to compare the different rate of loading and then calculating a compensating factor that allow to overcome the shadowing effect (Figure 14).

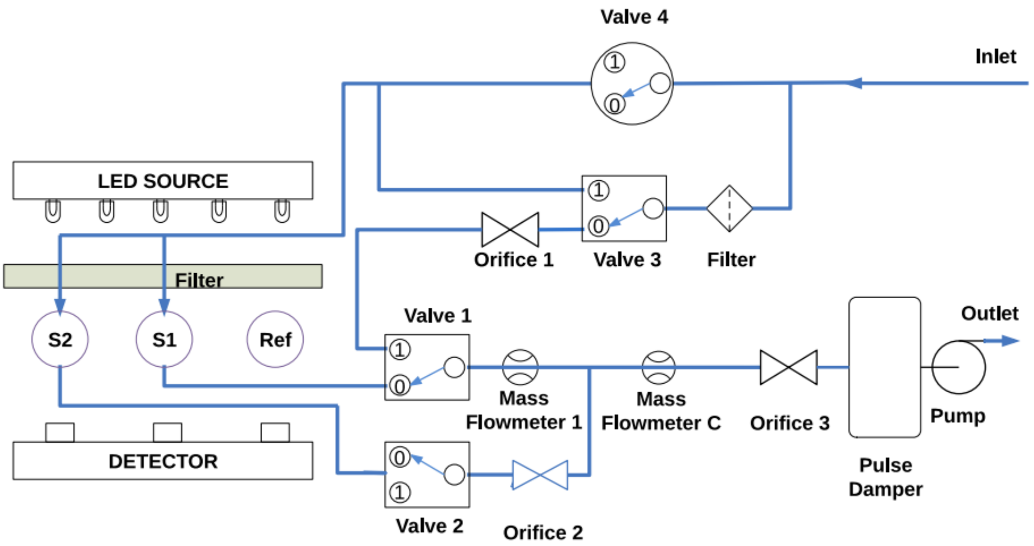


Figure 14. Aethalometer equipped by Dualspot © technology diagram. The air passes through filter spots S1 and S2, each with a different flow rate. Flowmeter 1 measure airflow speed from S1, while flowmeter C measure the total speed. Airflow speed from S2 is calculated by difference. The valves allow to choose different settings.

Moreover, the multi-wavelength modality allows to catch the spectral dependence of aerosol absorption and to speculate about the mixing state of the aerosol and, consequently, about different sources.

2.3.4. Conclusions

Black Carbon is an important primary pollutant, a fraction of PM2.5 defined and measured thanks to its optical properties. It is possible to measure this contaminant by filter-based optical portable device that allows designing personal monitoring campaign. The optical artefacts related to filter-based measurement are important issues, partially overcome by the devices of new generation. For this reasons and because BC is emitted directly from the combustion of fossil fuels and biomasses, it is a valuable pollutant for assessing air pollution exposure in the urban environment.

2.4. HEALTH EFFECTS OF PARTICULATE MATTER AND BLACK CARBON

2.4.1. Overview

Particulate matter is linked with a broad spectrum of different short- and long-term adverse health outcomes and recently it was included in the IARC Group 1 list of carcinogen agents to humans (IARC, 2016b). In literature a special focus is provided for the fine fraction of particulate matter (PM2.5) that appear to be the most dangerous (Cohen et al., 2017; Hoek et al., 2013). This is due to the small dimension of this particles that can enter in depth the airways up to the alveoli, can promote inflammation responses and oxidative stress near the membranes; moreover, ultrafine particles (UFP, <0.1 um) can even pass membranes entering in the circulatory system and provoking systematic inflammation (Figure 14)(Stone et al., 2017). Dockery et al. (1993) were the first to discover a relation between ambient PM2.5 and all-cause mortality, cardiovascular and lung-cancer mortality in a prospective cohort of 8111 adults from 6 United States cities (Dockery et al., 1993). Starting from the same cohort Lepeule et al. (2012) have stressed the non-threshold linearity of the relationship between chronic exposure and all-causes, cardiovascular and lung-cancer mortality with PM2.5 concentration below 8 $\mu g/m^3$ (Lepeule et al., 2012). Furthermore, particulate matter and especially traffic related air pollution can act as a trigger for acute events like myocardial infarction, ischemic and thrombotic effects (Mills et al., 2007; Nawrot et al., 2011).

More recently, PM2.5 and UFP were suspected to be neurodevelopmental toxicant by inducing inflammation cascade and oxidative stress condition once overcome the olfactory epithelium and reached the brain trough the axons or the blood brain barrier (Brockmeyer and D'Angiulli, 2016). The principal inhalation pathways for the penetration of particulate matter into the human body are reported in Figure 15.

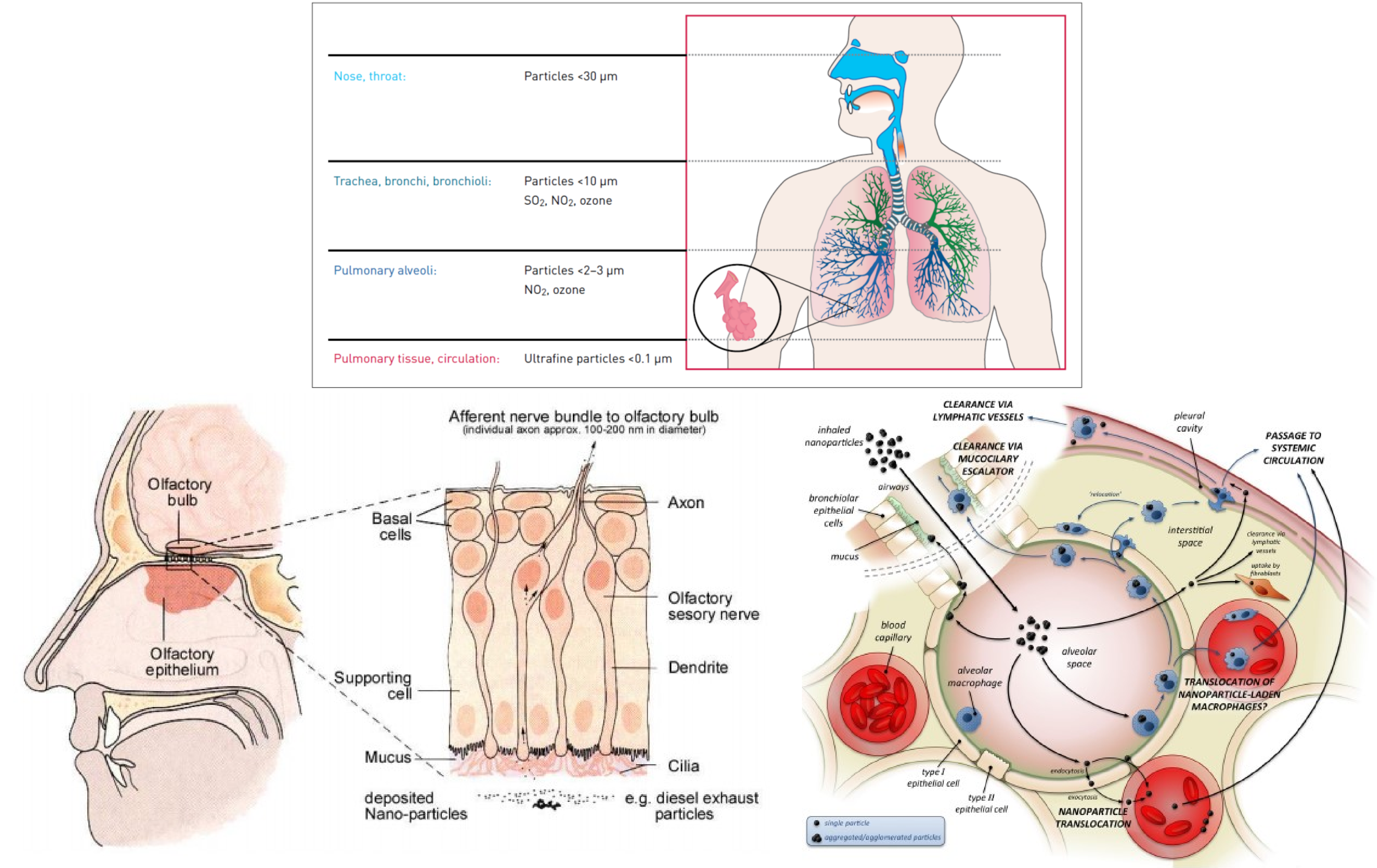


Figure 15. Different pathways of exposure to fine, ultrafine particles and nanomaterial (adapted from(Stone et al., 2017);(ERS, 2010; Madl, 2012))

As reported in chapter 1.3.1., Black Carbon is the constituent of fine particulate matter that can weight up to 20-25% of its mass. As a function of type of sources and location, in particular if close to traffic sources, BC can even be smaller than µm and tends to be included in ultrafine class (Costabile et al., 2015). Together with NO_2, BC is one of the best tracer of fossil fuel combustion, particularly of diesel engine vehicles (U.S.EPA, 2012). In 2014, the International Agency for Research on Cancer (IARC) classified diesel engine exhaust as carcinogenic to humans (IARC, 2014). Moreover, Janssen NA et al. (2011) identified BC as a valuable additional air quality indicator to evaluate the health risks of aerosols dominated by primary combustion particles (Janssen et al., 2011). More recently, Tobias A et al. (2014) looking at respiratory mortality and asthma hospital admissions in Barcelona estimated greater effects for BC than PM2.5 and PM10. They also found that the developed BC models were more robust (Tobias et al., 2014).

2.4.2. Exposure to air pollution and vulnerability: focus on school age children

Health effects related to particulate matter exposure does not affect the population homogeneously. In the past, concentration-response relationship has been related to type of exposure, vulnerability and genetic susceptibility (Makri and Stilianakis, 2008). Among other factors, life stage is one of the most important population characteristic that influence this relation. In particular, children have higher exposure, due to higher respiratory rate, and to both higher activity level and higher resting metabolic rate than adults. Moreover, they live and breathe close to the ground and air pollution sources (i.e. tailpipes), and tends to stay more outside during the day, resulting exposed to higher level of air pollution (Bateson and Schwartz, 2008; Vanos, 2015; WHO, 2018). Consequently, the inhalation of air per body weight combined with the still evolving lung structure and immune system determine a condition of vulnerability. Moreover, natural barriers against exogenous malignant factors such as the blood-brain barrier and nasal epitheliums have been shown to be compromised in children living in urban environment and exposed to air pollution (Calderon-Garciduenas et al., 2015). From prenatal to the second decade of life, if the development process is interrupted or impaired by environmental pollutants the health consequences for the child may last for a lifetime (Dratva et al., 2016).
The WHO estimates that more than 98% of children in Italy are exposed to PM2.5 level above 10 µg/m3 (Figure 16).

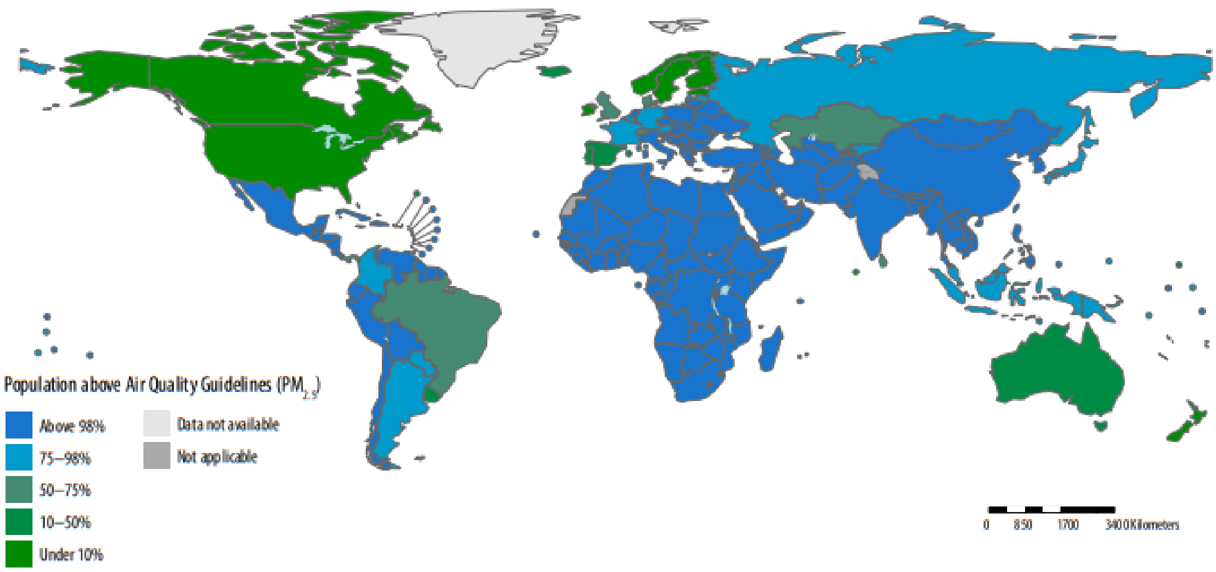


Figure 16. Proportions of children under 5 years living in areas in which the WHO air quality guidelines (PM2.5) are exceeded, by country, 2016 (WHO, 2018)

2.4.3. Children long term health effect

In the last decade, numerous studies have shown significant associations between exposure to ambient air pollution and long term adverse health effect on children. For instance, the relation between exposure to PM and TRAP and the risk of developing asthma is more and more evident. Khreis et al. (2017) in a systematic review and meta-analysis found statistically significant associations for BC, NO2, PM2.5, PM10 exposures and risk of asthma development; in particular the relation with BC appeared the strongest with a random-effects risk estimates (95% CI) of 1.08 (1.03, 1.14) per $0.5\times10^{-5}m^{-1}$ PM2.5 absorbance, as a marker for BC (Khreis et al., 2017a). Gehring et al. (2013) linked with a consistent relationship PM2.5 concentrations and PM2.5 absorbance to a decrease in lung function in children aged 6–8 years (Gehring et al., 2013). Long term effect of particulate matter and black carbon exposure can be also associated with neurological outcomes (Suades-González et al., 2015). For instance, in a prospective study of birth cohort, Suglia et al. (2008) measured intelligence, memory and learning tests of more than 200 children (mean±sd age = 9.7 ± 1.7 y) finding that increasing levels of long term exposure to BC were associated with lower performances (Suglia et al., 2008). Lower performances and an increased number of errors in a specific performance task were also found by Chiu et al. (2013) linked to children in the 2^{nd} and 3^{rd} tertile of BC exposure (Chiu et al., 2013).

Moreover, there is an increasing growing evidence of an association between exposure to ambient air pollution in prenatal and early postnatal periods and long-term health effects.

Bowatte et al. (2015) linked early childhood exposure to TRAP and a higher risk of developing asthma in later childhood (Bowatte et al., 2015). Exposure to PM2.5 during prenatal period was found to be positively linked with the incidence of recurrent pulmonary infections in 214 children with seven-year follow up (Jedrychowski et al., 2013).

Chiu et al. (2016) found associations between PM2.5 levels at different weeks of gestational age and outcomes such as reduced IQ and general memory in 267 children (age 6.5 ± 0.98 y)(Chiu et al., 2016). Rundle et al. (2012) measured higher BMI in 341 children (age 7 y) whose mother resulted exposed to higher level of PAHs with a relative risks of obesity of 2.26 (Rundle et al., 2012).

Finally, the incidence of cancer in children is increasing worldwide and leukaemia and lymphoma account for almost half of all childhood cancers (IARC, 2016a). In particular, a significant relation between exposure to TRAP and acute lymphoblastic leukaemia was found in a case-control study that involved 3,590 children (age < 6 y) with various types of cancer (Heck et al., 2013). Filippini T et al. (2019) in a recent meta-analysis found an association between exposure to benzene and childhood acute myeloid leukaemia, with no indication of any threshold effect (Filippini et al., 2019). They suggested also that other measured and unmeasured pollutants from motorized traffic could have a possible role in the relationship.

2.4.4. Children short term health effect

Ambient air pollution exposure can determines short-term health effects on children. There is broad consensus that breathing pollutants exacerbates asthma in children. A meta-analysis covering Australia, Canada, China, Denmark, Finland, Turkey and the USA, Lim H et al. (2016) found an increase of 4.8% in risk of asthma-associated hospital admissions related to a 10 µg/m^3 short-term increase in PM2.5 concentrations.

Furthermore, short-term exposure events exacerbates acute respiratory infections. Nhung et al. proposed a meta-analysis of 17 studies for children up to 18 years of age and found that short-term increases of many pollutants including PM2.5 were associated with increased hospital admissions for pneumonia (Nhung et al., 2017). Carugno et. al (2018) linked short- and mid-term PM10 concentrations and increased risk of hospitalization due to respiratory syncytial virus bronchiolitis in infants in Lombardy, Italy (Carugno et al., 2018).

Short- and mid-term exposure to traffic related air pollutants, including BC, were also associated with an increased concentration of airway oxidative stress and airway inflammation markers in a cohort of 130 Belgian children (6-12 y)(De Prins et al., 2014). Paunescu et al. (2019) found a positive association between increasing short-term (24 h) BC levels and increasing fractional exhaled nitric Oxyde (FENO) and lung function parameter (FEV_1, FVC) in 147 children (9-11 y) with persistent respiratory symptoms (Paunescu et al., 2019). Finally, recent exposure to increasing level of particulate matter including fine fraction, was also related to reduced neurobehavioral performances as well as to reduced blood vessel diameter of retinal microcirculation, a possible underlying mechanism through which fine PM contributes to age-related disease development, in a cohort of Belgian children (age 8-12) (Provost et al., 2017; Saenen et al., 2016).

2.4.5. The epigenetic pathway

Many pathways have been studied through which air pollution may influence our health, the most known of which are inflammation and oxidative stress. In the last two decades, research have shown another important mechanism of action in the relationship between ambient air pollution and health: epigenetic pathway. With epigenetics we usually refer to those processes that alter genome expression without changes in DNA sequence (Wolffe and Guschin, 2000). These mechanisms may be trigged by exogenous factors, such as air pollutants, and can even become stable alteration of gene activity with a propagation from the original altered cell to the next generation (Bollati and Baccarelli, 2010).
In a recent literary review on altered methylation and exposure to particulate matter, Ferrari et al. (2019) showed that selected scientific works covered the entire lifespan (Ferrari et al., 2019). However, not all the life stages are impacted at the same level (Figure 17).

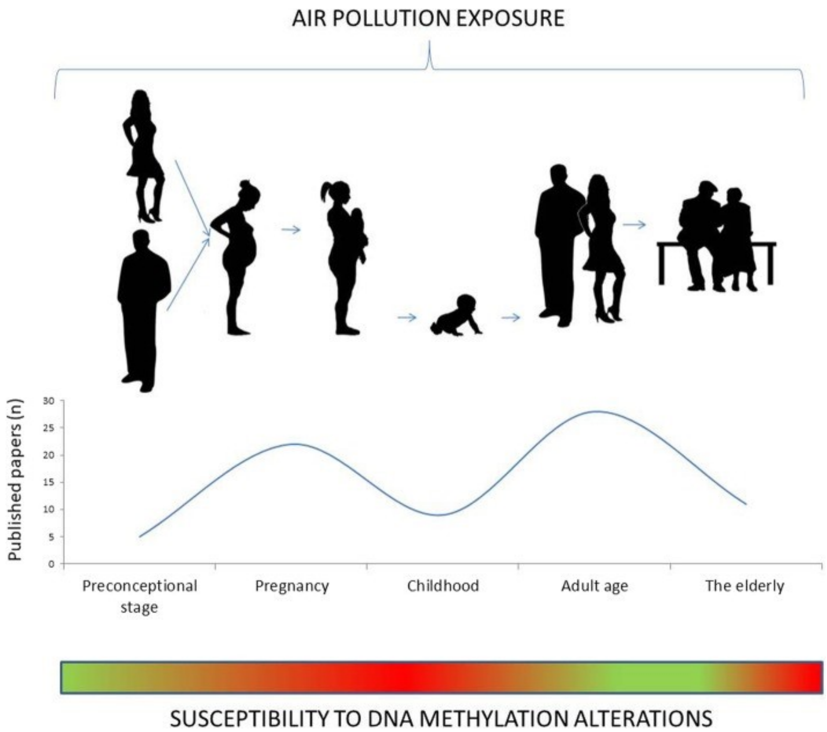


Figure 17. Susceptibility to DNA methylation at different life stages. In red the most concerning life windows (adapted from Ferrari et al. 2019)

For instance, Gruzieva et al. (2019) identified the epigenetic mechanisms through which PM exposure during pregnancy possibly contributes to several respiratory system dysfunctions in children (Gruzieva et al., 2019). Furthermore, in asthmatic children, high level of BC exposure was found to favour DNA methylation of pro-inflammatory genes (Jung et al., 2017).

2.4.6. Particulate matter and microbiota

Another relatively new topic of research that regards exposure to particulate matter is human microbiota. With this word we usually refer to the human bacterial community that acts as a barrier against exogenous stressors and influences the host immune response (Turnbaugh et al., 2007).

In particular, changes in the composition of internal microbiome can alter the anti-oxidant and pro-inflammatory balance and play a role in the development of asthma in childhood (Sbihi et al., 2019). It is likely that ambient air pollution plays a major role in this process (Muñoz et al., 2019). So far, there is no scientific publications that investigated the relation between children, particulate matter and microbiome, however some evidences have been shown for healthy adults. For instance, Mariani et al. (2018) have linked short-term (3 days) effect of PM2.5 and PM10 to microbiota characteristics and structure highlighting a positive association with Moraxella taxa (Mariani et al., 2018). Anyway, they concluded stressing the opportunity of further researches on the role that these alterations have in the development of diseases.

2.4.7. Conclusions

The fine and ultrafine are considered as the most health-threatening fractions of PM because of their small dimension and their capability to carry other pollutants. The PM-related exposure health consequences are more evident on vulnerable population group, such as children, than on healthy adults. In general, traffic related air pollution have been linked to a broad range of health effects in children. Moreover, the effect of this kind of exposure on both long and short term health suggest the need to implement integrated personal exposure assessment that include both measures at a high time resolution and modelling approach to estimate longer term exposure.

2.5. EXPOSURE ASSESSMENT TO AMBIENT AIR POLLUTION

2.5.1. The exposure framework

Exposure in general is defined as the contact between a chemical, physical, or biological agent and a target. In particular, referring to air pollution, inhalation exposure can be defined as the contact between an air pollutant and a human physical boundary (Ott, 1982). Generally, exposure scientists and occupational and environmental hygienists are particularly interested in temporally-averaged exposure and peak exposure (Figure 18) that are normed in both occupational and general environment as threshold limit values, occupational limit values (TLVs, OLVs) or air quality standards.

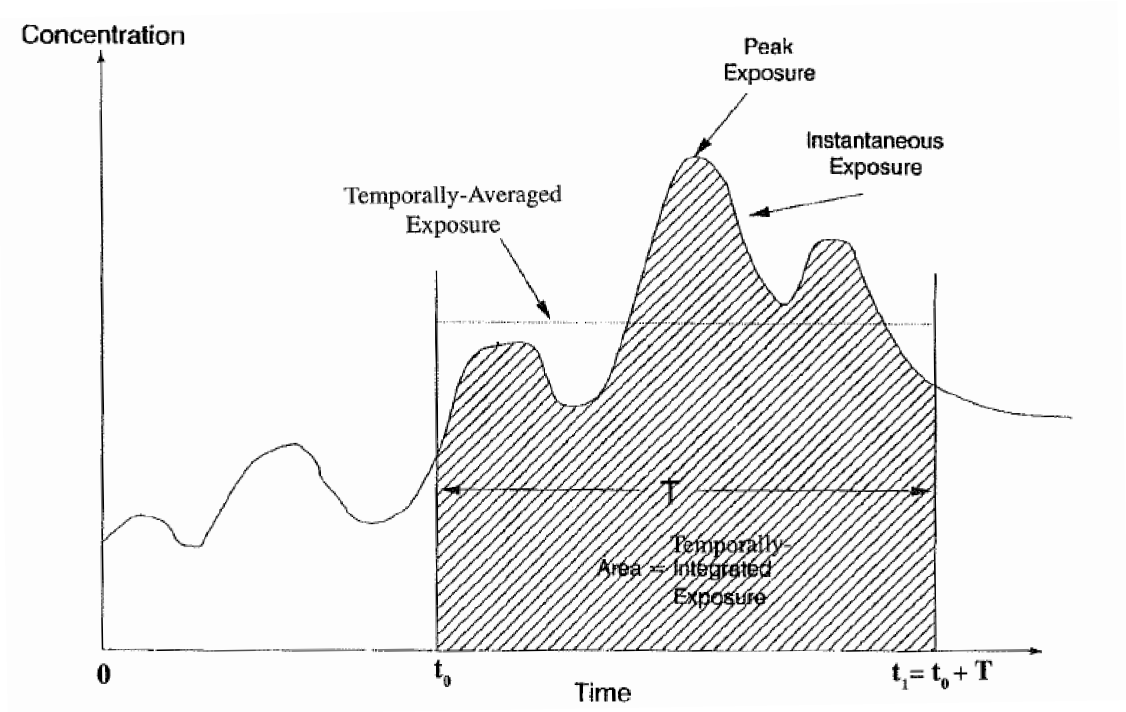


Figure 18. Hypothetical exposure time profile: temporally averaged exposure, peak exposure, instantaneous exposure and temporally integrated exposure are reported as a function of time (Adapted from Zartarian, Ott and Duan 1997).

Exposure can be even defined in a quantitative way. For instance, averaged temporally-averaged exposure (ξ_{ta}) to a certain concentration (C) at a certain position (x,y,z) can be defined as the integral of instantaneous contact between the target and the agent over the time (t) divided by the duration of the selected time window (Zartarian et al., 1997), according to the formula:

$$\xi_{ta}(x,y,z) = \frac{\int_{t_1}^{t_2} C\,(x,y,z,t)\,dt}{t_2 - t_1}$$

Another important framework in the exposure sciences is the so-called temporal-integrated spatially-integrated exposure (ξ_{tisi}), i.e. the attempt to divided a complete continuous-exposure time profile (m) in discrete time-windows related to each microenvironment (j) in which a target experience a certain contact at time t over the selected time window:

$$\xi_{tisi} = \sum_{j=1}^{m} \int_{t_{j1}}^{t_{j2}} C_{i,j}\,(t)\,dt$$

This last approach allows to focus on the relative weight of each microenvironment in a certain exposure time profile (Klepeis, 1999). To reach such level of detail, the most effectiveness method is to measure directly the personal exposure with a portable device at high time resolution.

Moreover, another important concept is included in the exposure framework: the notion of dose. If the definition of exposure restricts its range to the contact between a stressor and a human surface, the definition of dose involves the overcoming of this boundary and a consequent double way of action: 1) the non-diffusing dose defined as intake dose; 2) the diffusing dose defined as absorbed dose (EPA, 1992). In the particular case of inhalation dose, the final amount of pollutants that enter airways depends on both the concentration of pollutants in the air and the breathing rate and volume of the target. These last two variables are influenced by multiple factors such as gender, age, weight and current status (inactive or active)(Oravisjärvi et al., 2011). Given this, in the attempt to accurately study exposure and link it to adverse health outcomes, it seems important accounting for the volume of air inhaled per minute in order to reduce misclassifications (Greenwald et al., 2019). For instance, Int Panis et al. (2010) have already shown how different can be the intake of air pollutants by different city users and in different environments (Dons et al., 2017; Int Panis et al., 2010).

2.5.2. Time-activity pattern

The place in which we live, if we are running or walking, if we are studying or sleeping: personal exposure to air pollutants is closely related to environment and habits, ultimately to our daily agenda. As successfully geo-visualized by Kwan M. (2000) with the space-time density plot and the space-time aquarium plot (Kwan, 2000)(Figure 19), daily movements performed by a selected population can result in extremely complex trajectories. Afterwards, multiple dimensions such as location, duration, type of activity etc, can characterize each trajectory.

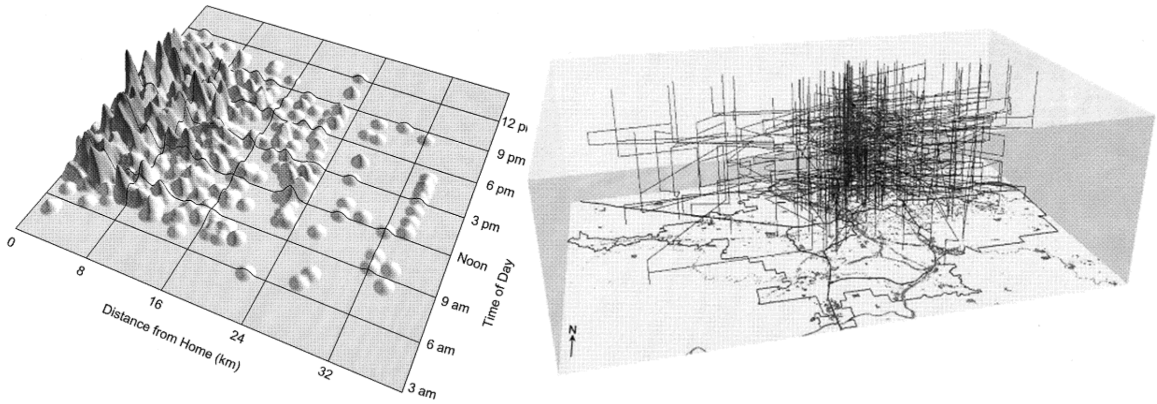


Figure 19. Space-time activity density plot (on the left) and space-time aquarium with the space-time paths (on the right)(Kwan, 2000)

The framework results in an even more complex figure if we consider different population subgroups. In fact, the individual time-budget within this groups appears composed by different life-paths given peculiar physiological and physical necessities (Hägerstrand, 1970). For instance, an office worker has a large portion of her/his routine occupied by work shifts, while a school-age child by school hours (Figure 20)

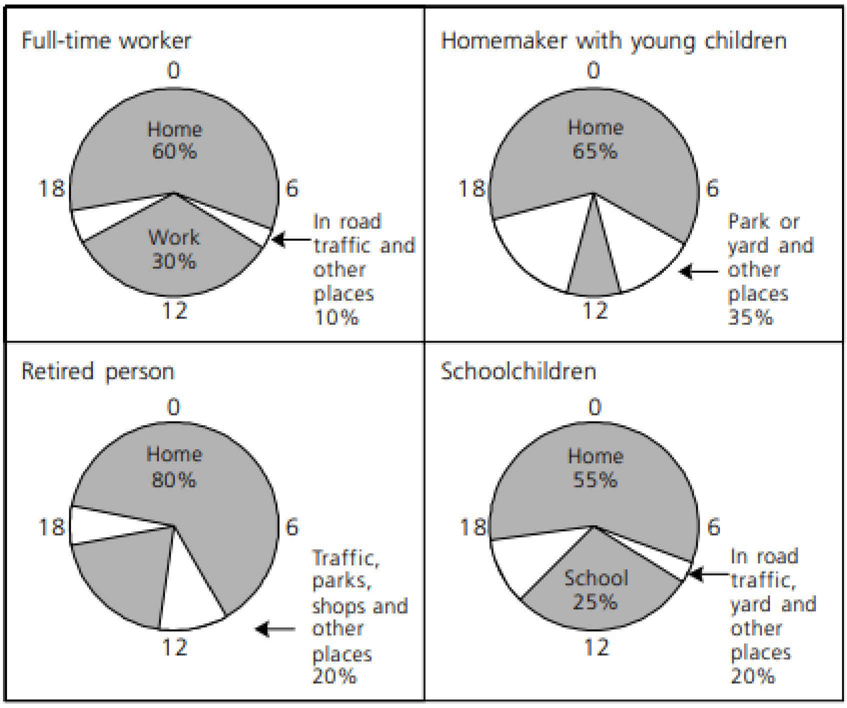


Figure 20. Examples of time-activity pie charts for typical 24-hour days (Bower et al., 1999)

Since personal exposure can be seen as a function of air pollution and the position of affected people, understanding better time-activity patterns of the general population seems to be a crucial task for exposure scientists (Dons et al., 2011; Klepeis et al., 2001).

Nowadays, with the rise of geographical information system (GIS) and global positioning system (GPS), time-activity surveys are usually conducted with the complementary use of classical techniques, such as paper-based or electronic diaries, and GPS logger (Dons et al., 2011; Gerharz et al., 2013).
However, many issues remain. In particular, not always GPS loggers prove to be accurate, especially in urban environment, but even more important, collecting information consistently and at high time resolution, means to ask the people involved in the project to spend time and efforts to keep the diary updated, with a consequent high risk of dropout and low data quality. This kind of issues could be reduced by enhancing the level of engagement of the participants.

2.5.3. The role of urban environment

Urban environment has always had a central role in the health of citizens. One of the first epidemiological surveys reported in literature is the famous John Snow's "Mode of communication of Cholera" in which the physician studied the spatial patterns of the 1854 London Cholera epidemic. Still today, even if the determinants have changed, cities remain an important source of health risks that affect an increasing and diversified crowd of people (Khreis et al., 2017b; Nieuwenhuijsen et al., 2018). In fact, urbanization is a peculiar social process that from the first industrial revolution has proved to characterize our societies: if in the early 20th century just 10–15 % of the global population lived in urban areas, now the percentage is projected to reach 67% by 2050 (UN, 2018). Given this picture, the United Nations in 2015 included sustainable cities and communities among the sustainable development goals. As it is possible to read in SDG 11 "Cities are hubs for ideas, commerce, culture, science, productivity, social development and much more. At their best, cities have enabled people to advance socially and economically", however, the increasing urbanization trend gives important challenges ahead: "Common urban challenges include congestion, lack of funds to provide basic services, a shortage of adequate housing, declining infrastructure and rising air pollution within cities."(UN, 2015).
Among many risk factors, one of the most worrying is urban air pollution. This phenomenon is strictly linked with the energy consume driven by transportation and heating systems. In particular, if we focus on individuals, living in an urban environment means to be exposed to a certain background of air pollution concentration and a variable number of

peaks, which are mainly influenced by individual time-activity patterns and due to the time spent in transport (Dons et al., 2019)(Figure 21).

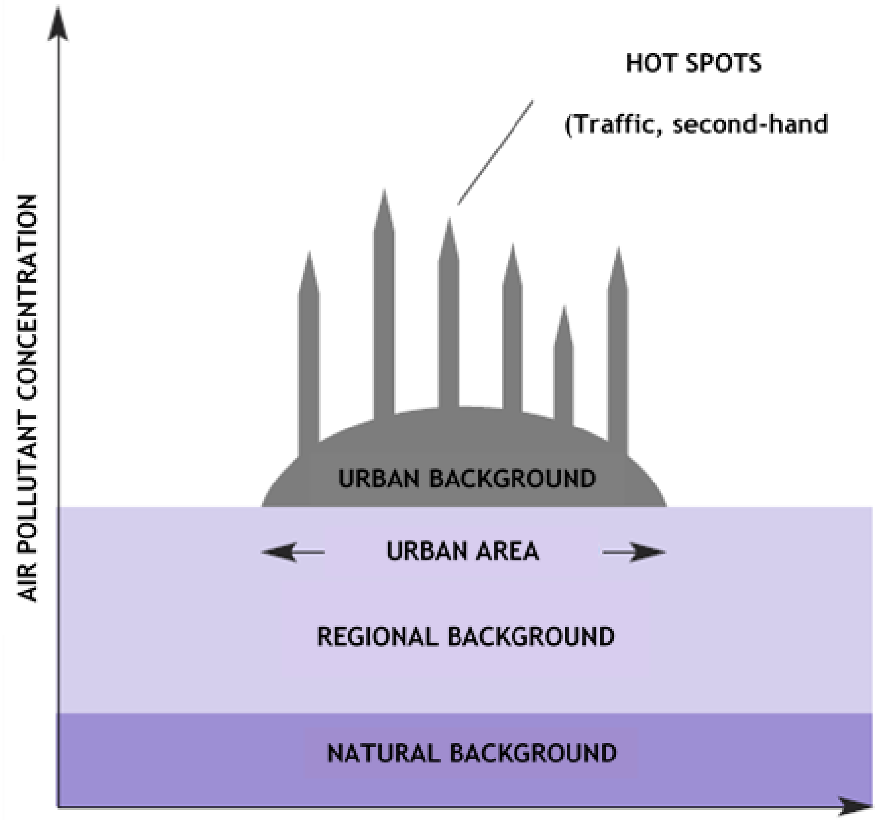


Figure 21. Individual exposure pattern in urban environment (Ranzi, 2012)

In 2018 the European Environmental Agency estimated that for certain pollutants like PM2.5, benzo[a]pyrene or ozone, more than 80% of people living in European cities are exposed at concentrations above the WHO guideline thresholds (EEA, 2018).

In a review on urban, transport planning environmental exposure and health topics, Nieuwenhuijsen MJ (2016) stressed that environmental interventions at a community scale are generally more cost-effective than at individual scale. In particular, variables such as road networks, distance to major roads, traffic density, household density, presence of green areas etc. proved to influence the variability that it is usually measured among personal exposure to urban risk factors, and in particular to air pollution (Nieuwenhuijsen, 2016). Related to this, urban and transport planners seem to have key role in achieving the UN sustainable goals related to cities. However, another important player in this game is the community that can represent either a driver or a brake of innovation. A participatory approach in environmental research and planning can work to make the first prevail on the second one (Nieuwenhuijsen et al., 2017).

2.5.4. Participatory approach in exposure science

In the attempt to pursue a healthier and more sustainable development for our cities, a fundamental factor is the level of awareness and engagement of citizens.
Moreover, if we focus on exposure sciences, Lioy and Smith (2013) identified in the engagement of communities and citizens in the research process one of the key aspects to achieve the exposure science vision of 21th Century (Lioy and Smith, 2013). In their proposal, this approach is fundamental to broader the view of exposure sciences from the point of contact between stressor and receptor, inward into the organism and outward to the general environment and society (i.e. the so-called endo- and eco-exposome). In the last decades, the scientific literature has seen a constantly increasing multitude of citizen science projects. Many of them are framed in the Community-Based Participatory Research (CBPR) definition that include different approaches to science with some common denominators, i.e. participation, research and action (Minkler, 2005)(Figure 22).

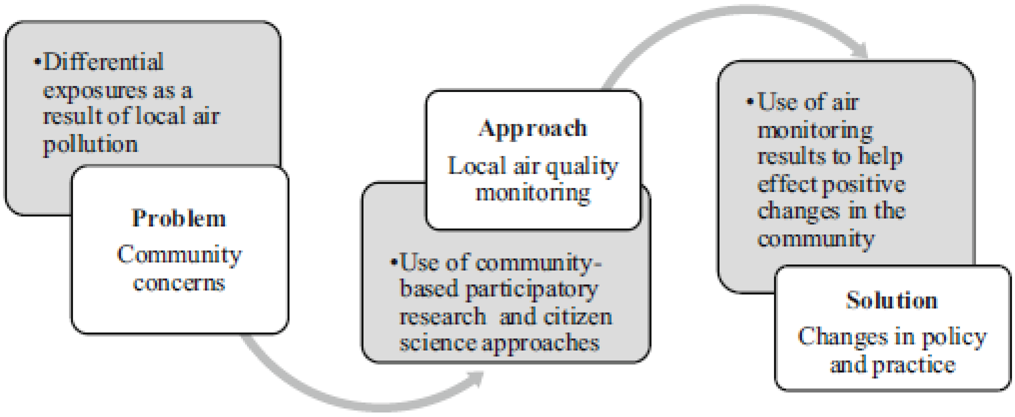


Figure 22. Flowchart of Community-based participatory research for exposure science (Commodore et al., 2017)

Research projects that have embraced this philosophy proved in many occasion to be valuable contributions to exposure science. For instance, Commodore A. et al (2017) in a review of 36 CBPR and citizen science studies found that from the action-oriented aspect of such approaches can result important achievements, such as:

a) long-lasting partnerships between different and multidisciplinary players (universities, no-profit organizations, municipalities and regulatory authorities etc.);
b) enhanced capacity for both researchers and citizens;
c) air quality awareness even on issues at a local scale;
d) new health protective practices and policies;

e) increasing level of trust between researchers and community; 6) Increased quantity and quality of data collection;
f) increased dissemination;
g) translation of research into policy (Commodore et al., 2017; Minkler, 2010; O'Fallon and Dearry, 2002).

Even if participatory research is generally recognised as a great opportunity, such an approach presents many challenges. For instance, from an academic perspective finding time and resources to maintain at the same time research activities, local presence, and participatory activities is not trivial (Cargo M et al, 2008). Moreover, different actors can have different expectations and objectives, i.e. academic part could be more interested in a publishable work, while other could be more interest in near-term results. Finally, bias in selection of sample and data collection may affects the overall interpretation and generalizability of the results. However, new technologies such as GIS mapping and real-time air monitoring seem to be useful tools to both reach high quality level of data collection and enhance the understandability of technical and complex phenomenon, even if the accessibility of this kind of devices could lead to a selection bias, by excluding certain segments of population (English PB et al, 2018).

2.5.5. Measuring personal exposure

Personal exposure to air pollution can be measured directly using passive or active portable devices. The first are generally low-cost, are usually based on diffusion mechanism through a barrier or permeation through a membrane, and have been introduced in the field since 1970 (Kot-Wasik et al., 2007). The concentration measured by a passive sampler is a time-weighted concentration over the sampling time with possibly high spatial resolution, but low time resolution. On the other hand, active samplers can measure pollutant concentration at high time resolution enabling researchers to explore the time-space dimension of exposure and causality of the relation between air pollution sources and adverse health effects. Active air samplers are equipped with a pump that drives the air internally where a detector measures or estimates the concentration of the pollutant in the sample. Different devices can insist on different chemical or physical characteristics of the pollutant. For instance, optical devices take advantage by optical properties, photoacoustic by the capacity of pollutants to absorb light energy and release a certain acoustic signal. These techniques allow to measure concentrations in real time even detecting exposure peaks.

However, since the cost in both a sufficient number of instruments and the time consuming of massive quantity of data collected, this approach remains too expansive, especially if the aim is to characterize a broad population focusing not only on short- but also mid- and long-term exposure (Klepeis, 1999). This seems to remain true also after the last decade of market-growth in low-cost sensors: in a recent review, analysing 17 large projects Moraskwa L et al (2018) found that not so many advances seems to be made in wide-scale monitoring of personal exposures. This is probably linked to the level of engagement and commitment that requires such an approach (Morawska et al., 2018). The way weather these instruments represents a valuable alternative of classic and more expansive devices is still a matter of debate, in particular remains high the level of concern about data quality, especially related to air quality legislative compliance applications (Castell et al., 2017; Kumar et al., 2015). However, the availability of low-cost sensors and the growing awareness and level of engagement of the general population still represents an opportunity for exposure researchers. Snyder et al. (2013) stressed that this change of paradigm in exposure science can represents a great opportunity to enhance and expand application such as personal exposure, source compliance, conversation with the community and integrating official air quality monitoring networks (Snyder et al., 2013).

2.5.6. Modelling personal exposure

In the last two decades satellite-based new technologies like GIS, GPS allowed exposure science taking steps further (Briggs, 2005; Croner et al., 1996; Hoek, 2017; Kistemann et al., 2002; Wang and Christopher, 2003). In the new scenario, the opportunity to link position, time-activity information, characteristic of the surrounding environment and spatial distribution of air pollutants represents still today an effective approach to avoid misclassification of exposure (Panis, 2010). Indeed, the spatial distribution analysis of air pollutants can resolve in high spatial resolution concentration grids valuable for exposure assignment. This approach can be followed by applying different techniques, such as dispersion models, land use regression (LUR) models or a combination of the two (HEI, 2010; Jerrett et al., 2005; Jerrett et al., 2010). In addition, statistical rescaling methods to derive hourly or daily trend can even improve the temporal resolution of the model allowing professionals to investigate health effects in relation to different exposure time windows (Dons et al., 2014).

Land use regression (LUR) modelling is a widely used technique that consists in the implementation of a multiple regression model using as response variable a pool of measurements of the air pollutant under investigation, and, as independent variables, a pool of potential predictors such as traffic intensity, population density land use parameters etc. Once developed, the model is used to predict concentration at unsampled sites. The published reviews on the topic identified works that measured from 20 to more than 100 sites (Hoek et al., 2008; Ryan and LeMasters, 2007). There is no published guideline to perform such analysis, so in the literature it is possible to find different ways to choose the number and the type of monitoring sites. Ultimately, the aim is to stress the spatial contrast inside the study area regardless of the fact that you choose a more formal or a more experienced-based way to set up the monitoring campaign and different ways to build up the model (Kanaroglou et al., 2005; Poplawski et al., 2009).

Afterwards, GIS software, such as QuantumGIS or ArcGIS, allow to georeference each of the monitoring sites on a map and then to measure possible predictors. In particular, different layers incorporating data on roads, traffic, population, land use etc. are usually overlapped and used to intersect the previously drawn buffers for each monitoring site. Buffers can be drawn in different shapes and with different radius in order to cover the behaviours of sources and variables (Figure 23).

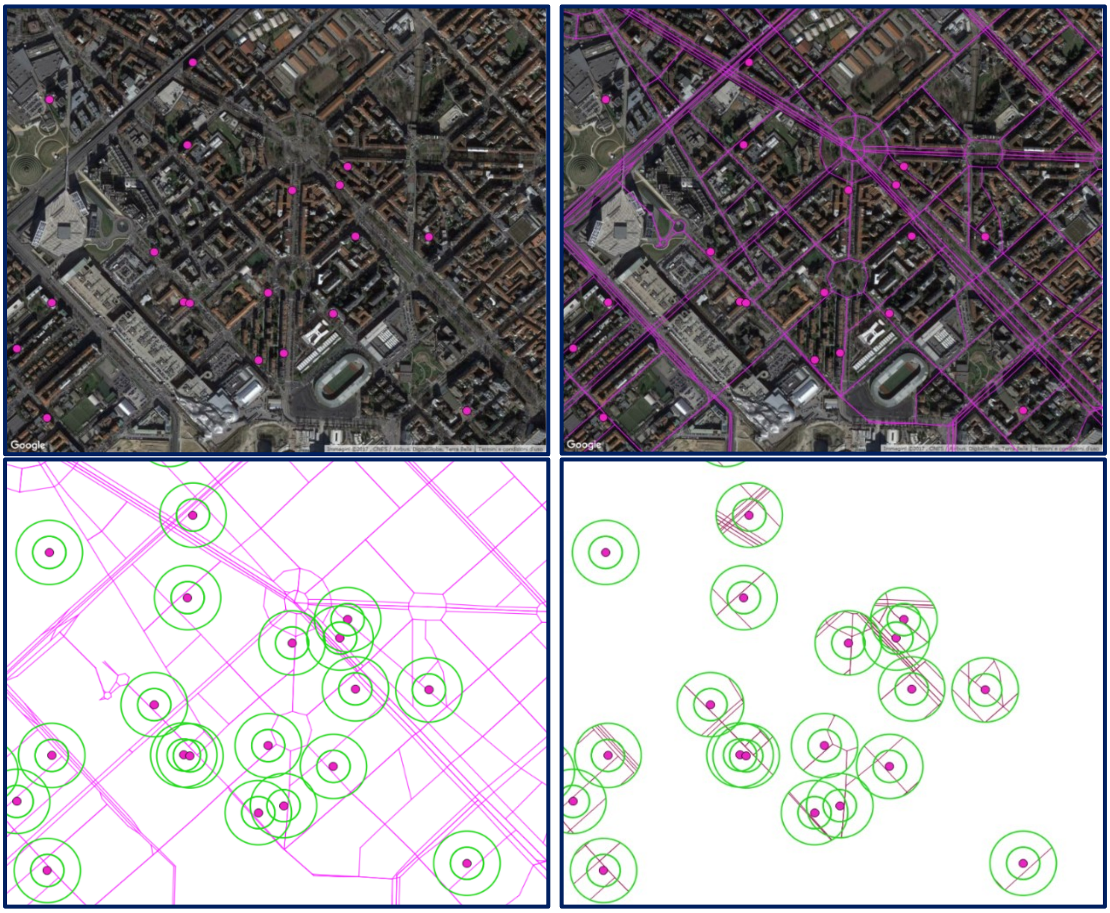


Figure 23. GIS visualization of the intersection procedure between buffers and road layer used in the LUR selection process of explanatory variables

Just as for the monitoring sites choice, also for the model development process there is not a gold standard. However, a well-known procedure is the one proposed by Henderson et al. (2007)(Henderson et al., 2007), that consists in:

a) ranking variables by the level of correlation with the pollutant;
b) identifying subgroups of variables, and eliminate the variables correlated with the highest-ranking one;
c) entering all the remaining variables in a stepwise linear regression and supervise the influence of the variables on the model parameters;
d) removing not significant variables and those that result inconsistent with a priori assumption (for instance, the coefficient of traffic intensity variable can't be negative);
e) removing variables that contribute less than 1% to the R^2 for a final, parsimonious model.

The validation of the model can be conducted by multiple approaches. If the number of monitoring sites is enough, the most effective way to test the model is to split the sample in two: a) the training set, b) the validation set. Afterwards, this technique, named hold-out validation, requires to compare the estimates performed by the model developed using the training set with the validation set(Briggs et al., 1997). If the sample size does not allow performing such analysis, the leave one out cross validation (LOOcV) is another valuable option. In this case, the model developed on n-1 monitoring sites is used to estimate concentration at n^{th} monitoring site. Thereafter, n^{th} estimate is compared to n^{th} measurement and the procedure repeated for n times (Brauer et al., 2003). However, Wang et al (2012) found that LUR models based on small training sets seemed to perform worse when evaluated against independent sets of measures if compared to a LOOcV validation technique (Wang et al., 2012).

Linking the life-paths of each individual with his or her exposure is the final aim of the modelling approach. So, ultimately, LUR models are used in combination with time-activity diaries to attribute a concentration at selected locations or during time-windows in the attempt to better profile personal exposure (Ryan et al., 2008). The same result can be obtained by using different techniques. However, even if LUR modelling proved to be one of the most reliable approach in the field, it is not the only way to estimate concentration (Gulliver et al., 2011).

Moreover, in the last few years, the rise of machine learning techniques, the satellite-based optical measurement and the massive use of low-cost sensors have brought new life to the field allowing to refine the process of exposure modelling and paving the way for new studies (Brokamp et al., 2019).

2.5.7. Conclusion

According to the classical definition, an individual is exposed when a pollutant comes in contact to his/her physical boundary. In the study of exposure determinants, time-activity patterns play a major role. Moreover, urbanization and urban variables, such as urban planning and transportation, give important health-related challenges ahead. Generally, to profile individual exposure to air pollutants direct personal measurements are the best way allowing considering the influence of different sources and of time-activity patterns. However, this technique is still highly demanding in term of both time and costs. The rise of GPS system linked with indirect exposure assessment techniques and time-activity diaries help to achieve a high level of accuracy in exposure attribution. In particular, Land

Use Regression modelling seems to be a valuable technique to estimate personal exposure. Finally, to achieve better results and move toward healthier and sustainable cities, participatory approach involving citizens is considered one of the key aspects of exposure science vision of 21th century.

3. ANALYSING AND MODELLING THE SPATIAL DISTRIBUTION OF BLACK CARBON IN A SCHOOL CATCHMENT AREA

This chapter is based on:

Boniardi, L; Dons, E; Campo, L; Van Poppel, M; Int Panis, L; Fustinoni, S; 2019. *Annual, seasonal, and morning rush hour Land Use Regression models for black carbon in a school catchment area of Milan, Italy*. Environmental Research 176.

DOI: 10.1016/j.envres.2019.06.001

RESEARCH QUESTIONS AND ANSWERS

Q1: Is the participatory approach suitable to identify monitoring sites to develop a LUR model?

A1: Even if the eligibility criteria were quite rigid, the participatory approach helped to collect a relevant quantity of valuable monitoring sites among those it was possible to find the final set. Furthermore, this process allowed engaging the school and the parents in the first stage of the research project

Q2: Is it possible to develop performant LUR model using BC data collected on a neighborhood-scale environment, such as a school catchment area?

A2: Even if the spatial extent of the study area was very small (~20 km^2), the set of chosen monitoring sites showed heterogeneity in BC concentrations. Furthermore, the developed LUR models proved to perform very well without spatial autocorrelation issues. This confirms that BC is a valuable pollutant to study spatial heterogeneity of air pollution inside urban environment.

Q3: Is it possible to develop LUR models focusing on MRH, by increasing the frequency of measurement and using only collected data between 7 am and 9 am?

A3: Two seasonal LUR models focused on MRH were developed using data collected between 7 am and 9 am. These models proved to perform very well, outperforming in two cases (cold-season and annual models) the models developed on the overall collected data.

Q4: Are there different spatial patterns in the distribution of BC during different seasons and time of the day?

A4: Even if the overall BC concentration was higher in cold- than in warm-season, the spatial contrast among Street (S), Urban Traffic (UT) and Urban Background (UB) sites was found to be larger during the warm season. Moreover, for both of the seasons, a similar increase in absolute BC concentrations was found during the Morning Rush Hour (MRH) period. This increment seems to follow different spatial patterns, being of greater magnitude near S and UT sites. However, the only seasonal spatial pattern seems to be related to the relative increment of BC concentrations that affects more the S than the UB sites during cold season, while is the opposite during the warm season. This is mostly due to the overall higher level of BC concentration during the cold season that smooths the relative increment of concentration of UB sites during the MRH.

ABSTRACT

Introduction: The European Environment Agency has identified Northern Italy as one of the most polluted areas in Europe. Among air contaminants, black carbon (BC) has been identified as a sensitive marker of traffic related air pollution. This study aims to investigate the spatial distribution of BC in the catchment area of an elementary school of Milan, the biggest city in Northern Italy, using Land Use Regression (LUR) models and focusing especially on Morning Rush Hour (MRH).

Methods: Two recruitment campaigns were performed asking schoolchildren's parents and residents of the study area to host a monitoring site in their own dwellings. Finally, 34 monitoring sites and 1 reference site were sampled. BC was measured in two seasonal campaigns using eight micro-aethalometers. Six seasonal and annual LUR models were developed, 3 focused on MRH.

Results: Overall, median BC was 3247 and 1309 ng/m^3 in the cold and warm season, respectively. In both seasons, there was a significant spatial variation between the monitoring sites. MRH values were higher than the daily values with median concentrations of 4227 and 2331 ng/m^3, respectively. Developed LUR models showed that BC variability is well explained only by traffic variables; R^2 ranged from 0.52 to 0.79 and from 0.65 to 0.81, for seasonal/annual and MRH LUR models respectively.

Discussion: LUR models based on traffic variables explain most of the measured BC distribution variability for both warm and cold season. MRH represents a critical moment for BC during all the year, with an increase of 1000 ng/m^3 respective to the daily median value and differences in magnitude according to location. Our results highlight that the mobility issue is one of the most important challenges to reduce air pollution in the city of Milan and this is of particular concern for elementary schoolchildren that commute to school during MRH.

3.1. INTRODUCTION

According to the World Health Organization (WHO) air pollution is currently one of the major global public health concerns *(WHO, 2016)*. Recently the European Environment Agency (EEA) has identified Northern Italy as one of the most polluted areas in Europe for both gaseous pollutants and particulate matter (EEA, 2018). In the greater Municipality of Milan, the biggest city in the Northern Italy basin with an estimated population of about 3.2 million residents *(ISTAT, 2018)*, urban motorized traffic is an important source of local air pollution (ARPA, 2018a; Perrone et al., 2012). In 2014, the International Agency for Research on Cancer (IARC) classified diesel engine exhaust as carcinogenic to humans (IARC, 2014).

Currently, one of the most investigated air pollutants related to traffic is black carbon (BC), a fraction of particulate matter (PM) emitted during the incomplete combustion of fossil fuels, in particular diesel exhaust and biomass (U.S.EPA, 2012). BC is also an important climate-forcing agent, second only to carbon dioxide (Bond et al., 2013). This pollutant has been proposed by WHO as a valuable indicator for the evaluation of local traffic control policies and as an additional indicator of the health effects of air particulate matter (Janssen et al., 2011).

The health impact of exposure to traffic related air pollutants seems to be greater for the weaker population groups, such as children; for instance, many studies have suggested relationships between air pollution and lung development and airway disorders like inflammation, wheezing, asthma, sensitization and allergies *(Bateson and Schwartz, 2008; Bowatte et al., 2015; Khreis et al., 2017a)*. In particular, in *De Prins S et al. (2014)* a significant increase in Fractional exhaled Nitric Oxyde (FeNO), a marker of airway inflammation, was linked with a BC Inter Quartile Range (IQR) increase in the last 24 hours (4.50 $\mu g/m^3$) and last week (1.73 $\mu g/m^3$) of exposure(De Prins et al., 2014). The sample was a Belgian cohort of 130 children (aged 6-12 y) and the exposure was measured and estimated at a central station, at home and at school respectively. More recent studies have investigated the link between children's exposure to BC and their cognitive skills (Saenen et al., 2016; Sunyer et al., 2015). In particular, *Alvarez Pedrerol M et al. (2017)* found a significant reduction in the growth of working memory in a Spanish cohort of 1,234 children (aged 7-10 y) related to an IQR increase of BC concentration estimated for the walking commute schools (Alvarez-Pedrerol et al., 2017). More recently, BC was found to act through different pathways: in particular, as well as representing a carrier for the main harmful compounds such as metals and polycyclic aromatic hydrocarbons, it also acts directly inducing immune response at the site of exposure, activating different mediators (Niranjan and Thakur, 2017)

If we focus on urban environment, the activity space of children is reasonably limited to their school catchment area and, on a typical weekday, home-school routes are one of the most critical windows of exposure. This is true especially in Milan in which (a) more than 190.000 people enter the city with their own private motorized vehicles every working day for work or study reasons (*Milan*, 2011), (b) parents still prefer private motorized vehicles to reach school. The sustainable mobility plan of Milan estimates that currently about 20% of the traffic during morning rush hour (MRH) is due to the so-called school run (AMAT, 2015).

In the past, most of the studies carried out in the environmental epidemiology field have limited their exposure assessment to measuring or estimating concentrations of pollutants in pre-defined places such as home, workplace and school. This approach biases the real exposure of subjects since it does not account for the spatial distribution of pollutants and peoples' movement between areas, not considering that during these activities subjects are in direct contact with traffic pollutants(Dons et al., 2012; Int Panis et al., 2010).

To overcome this issue, it is possible to use a personal exposure assessment approach that links spatial and temporal variability of air pollutants and GPS data. One of the most used models in this field is the so-called Land Use Regression (LUR) model that consists of a multiple regression that uses sampling data of the chosen air pollutant as the response variable, and information on the territory, such as land use, population density, traffic data, as explanatory variables. LUR allows drawing high spatial resolution maps of air pollutant concentrations (Hoek et al., 2008; Ryan and LeMasters, 2007).

The aim of the MAPS MI project, "Mapping Air Pollution in a School catchment area of Milan", is to study exposure to air pollution of schoolchildren in Milan, using LUR models, air pollutants personal monitoring and biological monitoring techniques with a participatory approach. The aim of the present report is to study the spatial distribution of BC in the catchment area of an elementary school in Milan focusing especially on MRH.

3.2. MATERIALS AND METHODS

3.2.1. Reference area, monitoring sites and the participatory approach

The study area is located in the northwest part of the city of Milan (Figure 24), one of the most important gateways into the city, with intense motorized traffic. This area represents the catchment area of an elementary school, which is attended by more than 700 children, aged 6 to 11.

In order to study the spatial variation of BC in the area, 34 monitoring sites and one reference site were a priori selected. Monitoring sites were made available from parents of the schoolchildren and from area residents, following their involvement in the study. A reference site was placed inside the courtyard of the school.

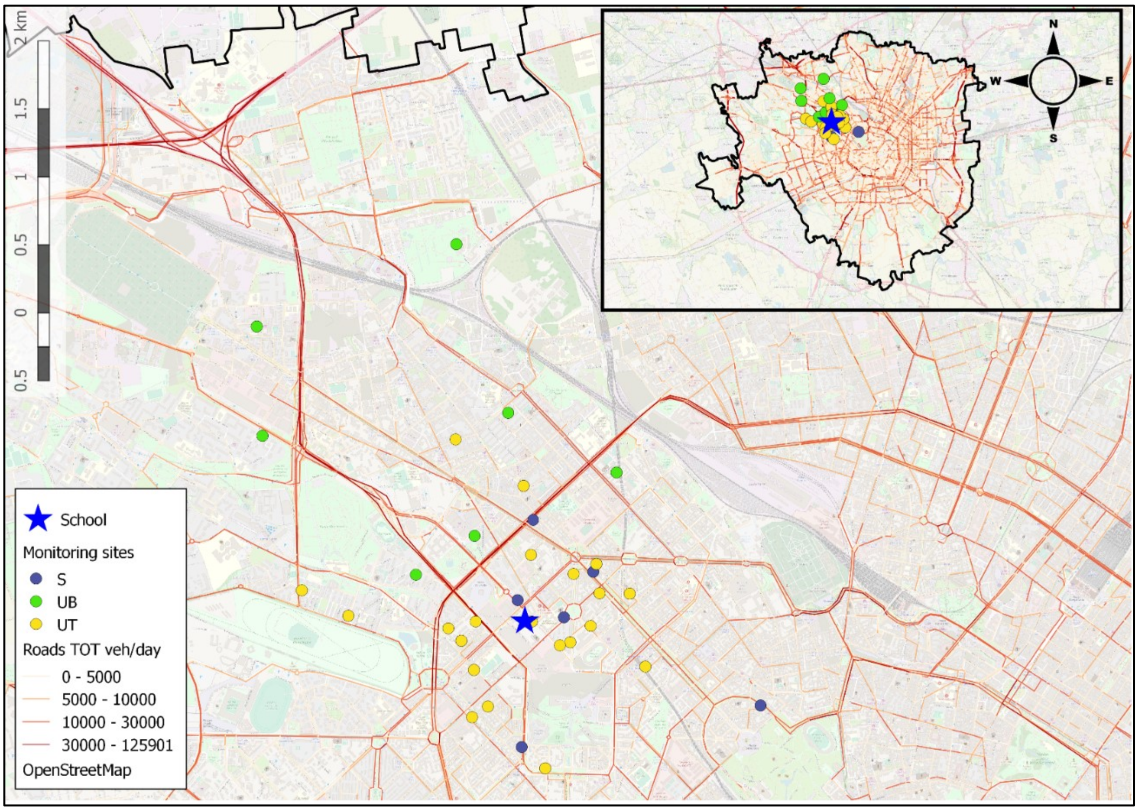


Figure 24. Study area with roads(line line thickness proportional to traffic intensity), monitoring sites and reference site (School). In the small frame the map location within the city of Milan is reported.

Firstly, the project was submitted to and approved by the school board. Parents were asked to join the study by hosting a monitoring site in their own dwellings. Only dwellings located at the ground or first floor and with a window facing the street were eligible. Additionally, area residents were asked to join the study to increase the number of potential monitoring sites; their involvement was sought through social media, creating and spreading a project focus event for the principal community groups.

Table 4. Summary of main characteristics of the 34 monitoring sites.

	Monitoring Sites		
	S	**UT**	**UB**
Definition	Street site, site with very important traffic influence	Urban Traffic, site with traffic influence	Urban Background, site without important traffic influence
Classification variables	Adjacent road > 10000 veh/day, no obstacles in between	Adjacent road < 10000 veh/day, no obstacles in between	Nearest road with > 1000 veh/day at a distance > 50 m AND nearest road with > 10000 veh/day at a distance > 75 m
N	6 (18%)	21 (62%)	7 (20%)
Distance to the nearest road (m)	9-23	3-36	50-201
Tot vehicles per day on the nearest road (veh/day)	3379-20284	47-18224	89-324
Number of addresses in a circular buffer with radius = 50 m (N)	6-27	3-72	1-30

To focus on the variation of BC in the study area, monitoring sites were selected based on the proximity to/intensity of traffic sources, and grouped in three classes: street sites (S), urban traffic sites (UT) and urban background sites (UB) (Figure 24). Characteristics of the monitoring sites, including definitions, are summarised in Table 4. The reference site was chosen to be not directly influenced by traffic sources; therefore, it was placed in the school courtyard. The courtyard is closed on three sides by a three floor building (height > 20 m) and on the fourth side by a garden.

Monitoring devices for sampling BC were placed on windowsills, on balconies and in gardens, at a maximum height of 5 meter from the ground.

3.2.2. BC monitoring campaigns and meteorological data

BC was monitored during the warm season (from May 7 to June 12, 2017) and the cold season (from January 7 to February 12, 2018). These periods were chosen as representative of different meteorological conditions and reflecting a different use of the heating system, one of the major sources of PM. In particular, according to the Mayor's order, private and public buildings' heating systems in Milan are switched on at mid-October and switched off at mid-April. In this paper these two monitoring periods are defined as warm and cold seasons, respectively. The reference site was sampled by a micro-aethalometer, type MA200 (AethLabs, USA),for the whole period of both seasonal monitoring campaigns, allowing to measure both BC_{ref}, the seasonal BC averages,, and BC_{ref-i}, i.e. the BC weekly averages The 34 monitoring sites were sampled using seven micro-aethalometers, type AE51 (AethLabs, USA); each of those sites were sampled for a single week, allowing the determination of BC_i. Seven to 8 devices simultaneously collected air samples for approximately an entire week at each site. It means that every new week a new set of 7-8 monitoring sites was measured.

For both the monitoring campaigns, a seasonal estimate of *BC* (BC_{season}) for each monitoring site was inferred by comparison with the BC concentration measured at the reference site during the complete monitoring campaign by season (BC_{ref}), and in the specific week of monitoring (BC_{ref-i}), by applying the formula [1].

$$BC_{season} = BC_i \frac{BC_{ref}}{BC_{ref-i}} \qquad [1]$$

From May 26, 2017 to June 1, 2017, some failures of the sampling device at the reference site occurred. To deal with this issue, we extrapolated both MRH and daily BC concentrations at the reference site based on the urban background station operated by the air quality network (AQN) of Milan (ID station 10283, via Ponzio 34/6 – Pascal Città Studi). The correction factors for MRH and daily periods were similar to the regression slopes between the reference site and the AQN site computed for the entire monitoring period (S6-S7).

BC annual estimate (BC_{annual}) at each site was obtained as a mean value of the warm and the cold BC_{season}, assuming that both the monitoring campaigns represented a period of six months.

Meteorological data were collected from the nearest Milan AQN station (piazza Zavattari, ~ 1 km from the school reference site).

R (Team, 2014) was used to perform statistical analysis. Kruskal-Wallis and Bonferroni post-hoc tests, with significance set at $\alpha = 0.05$ and rejected H_o if $p <= \alpha /2$, were used to check differences among classes of monitoring sites.

3.2.3. Micro-aethalometer devices and BC data handling

BC was estimated as equivalent black carbon using seven micro-aethalometers AE51 and one micro-aethalometer MA200. The AE51 and the MA200 were run at a 5 minute temporal resolution and the 100 ml/min flowrate was calibrated before each measurement campaign with a portable flow calibrator (Alicat scientific, USA). The AE51 measures BC at 880 nm wavelength, while the MA200 supports a multi-wavelength setup that includes 375 nm, 625 nm, 528 nm, 470 nm and 880 nm. The micro-aethalometers are optical portable devices that link the attenuation rate (ΔATN) of a beam of light that passes through a filter spot to the concentration of black carbon. This relation was found to be non-linear due to some artefacts, the most important of which are the so-called shadowing effect linked with the increasing filter load and the multiple scattering of the filter fibres (Weingartner et al., 2003). The shadowing effect is of concern for the AE51 devices, while for the MA200 device, it is automatically corrected by the Dualspot© technology. This technology was available only for the cold season campaign, while during the warm season, the attenuation threshold of the MA200 was set at a low value (40 ATN), to minimize the filter loading. For the AE51 no processing algorithm has been applied to the raw data but, to avoid the shadowing effect artefact, filters were regularly changed, once or even twice a day, during highly polluted days.

BC raw data were post-processed by removing reported errors, by smoothing with the Optimized Noise-reduction Algorithm *(ONA)(Hagler et al., 2011)* and by applying correction factors to account for differences between devices. Indeed, to evaluate the comparability between AE51s and the MA200, inter-comparison exercises were conducted pre- and post-monitoring for each campaign; these were performed running all devices simultaneously and next to each other for 24 hours. The MA200 was the most recent device calibrated by the manufacturer, so we decided to consider it as the gold standard. By comparing the MA200 with the AE51s, we calculated correction factors for each device that were applied to the raw data to obtain the final BC estimates. These values ranged from 0.53 to 1.06, and representing the regression slopes between MA200 and AE51s. The applied factors were calculated as the mean value between the pre- and post-monitoring inter-comparisons.

Finally, the BC obtained by the MA200 device was also used to calculate the Absorption Ångström Exponent (AAE) of the two seasonal monitoring campaigns. In fact, this device measures black carbon at five different wavelengths allowing studying the absorption coefficient of the measured aerosol. In particular, the AAE gives information about the type of aerosol and contribution of different sources (Kirchstetter et al., 2004). In this study the AAE was derived from the aerosol absorption coefficient (b_{abs}) measured at the UV channel (λ = 375 nm) and the IR channel (λ =880 nm), using the following equation:

$$AAE = -\frac{ln\left(\frac{b_{abs}(375)}{b_{abs}(880}\right)}{ln\left(\frac{375}{880}\right)} \qquad [2]$$

Higher AAE values were reported for aerosols with higher concentrations of organic compounds components, typically derived from the combustion of biomass; for traffic related aerosols lower AAE values were reported (Martinsson et al., 2017; Sandradewi et al., 2008)

3.2.4. LUR models and independent variables

LUR models to estimate BC distribution in the study area were developed using BC_{season} as the dependant variable. Six seasonal and annual LUR models were developed, three focused on MRH. In particular, MRH models were developed using data from 7 am to 9 am on working days, while seasonal models used all available data.

As independent variables, GIS based covariates were calculated using QGIS software(*Team*, 2016). Overall, more than 100 variables (S1) were obtained and grouped in three different classes: a) road and traffic variables, b) population variables, c) land use variables. Shapefiles and metadata were obtained from different institutions and in particular:

- road and traffic data from the Mobility and Environmental Agency of the Municipality of Milan (AMAT, 2017);
- population data from the Statistic National Institute of Italy (ISTAT, 2011) and the open data site of the Municipality of Milan (2018);
- land use data from the Urban Atlas project of the EEA (2011).

When necessary, different reference systems were converted in the local projected coordinate system (Monte Mario, EPSG:3003). For all variables, circular buffers of different size around monitoring sites, were tested. In particular, for traffic variables we tested circular buffers of radius 50, 100, 300, 500 and 1000 m, while for land use and population variables we tested circular buffers of radius 50, 100, 300, 500, 1000 and 3000 m. Traffic variables were estimated by the Mobility and Environment Agency of the Municipality of Milan using a four-step travel demand model (Citilabs, USA), representing daily mean values or MRH mean values. Elevation variables were not collected because there are no substantial differences in altitude in the city, while a Sky View Factor (SVF) was estimated for each monitoring site by the DEMtools QGIS experimental plugin (K, 2014), to consider possible urban canyon effect (Eeftens et al., 2013). No microclimate data were included into the model; nevertheless, the study design, measuring BC over five weeks and two different seasons, allowed to partially take into account meteorological variability.

Each model was developed by using the ESCAPE methodology (Eeftens et al., 2012): a supervised forward stepwise procedure was performed using the above-mentioned variables. Multicollinearity was checked before entering the variables in the model. The collinearity cut-off was set at Pearson's $|r| \geq 0.6$. The final models were those with a higher coefficient of determination (adjusted R^2) and lower Root Mean Square Error (RMSE). Spatial autocorrelation was checked on model residuals by calculating the Moran's I index with the free GeoDa software *(Anselin L et al., 2006)*. The leave one out cross validation (LOOcV) procedure was used to test the performance of the models focusing on R^2 and RMSE.

Six BC concentration maps were developed in QGIS by 1) applying the models to a set of more than 70,000 points on a regular grid inside the study area 2) applying a Natural Neighbour interpolation algorithm *(Sibson R, 1981)* to obtain six 1x1 meter spatial resolution maps. Finally, three maps were developed to show the relative increment of BC during the MRH periods. The percentage value of each 1x1 meter pixel is the increment of BC concentration during the MRH compared to the daily period, computed using the same regular grid, data and interpolation algorithm previously mentioned.

3.3. RESULTS

3.3.1. Monitoring sites and the participatory approach

Seven hundred and forty letters and brochures were sent to parents of schoolchildren (S9-S10), 40 of which expressed their availability to host the sampling device; among them 14 dwellings met the requested characteristics and were selected as monitoring sites. The recruitment campaign on social media allowed to identify 19 additional monitoring sites. A monitoring site was then placed at the main entrance of the school (via Gattamelata, 33, Milano), for a total of 34 monitoring sites.

3.3.2. BC monitoring data, Absorption Ångström Exponent (AAE) and meteorological data

In Figure 25 the measured concentrations of weekly BC on the different monitoring sites are reported, for the warm and cold season as median, 25th and 75th percentiles. Differences in BC concentrations were observed during the monitoring campaigns, especially in the warm season. For this reason, it was necessary to integrate the observed temporal variability estimating the seasonal BC concentration for each monitoring site.

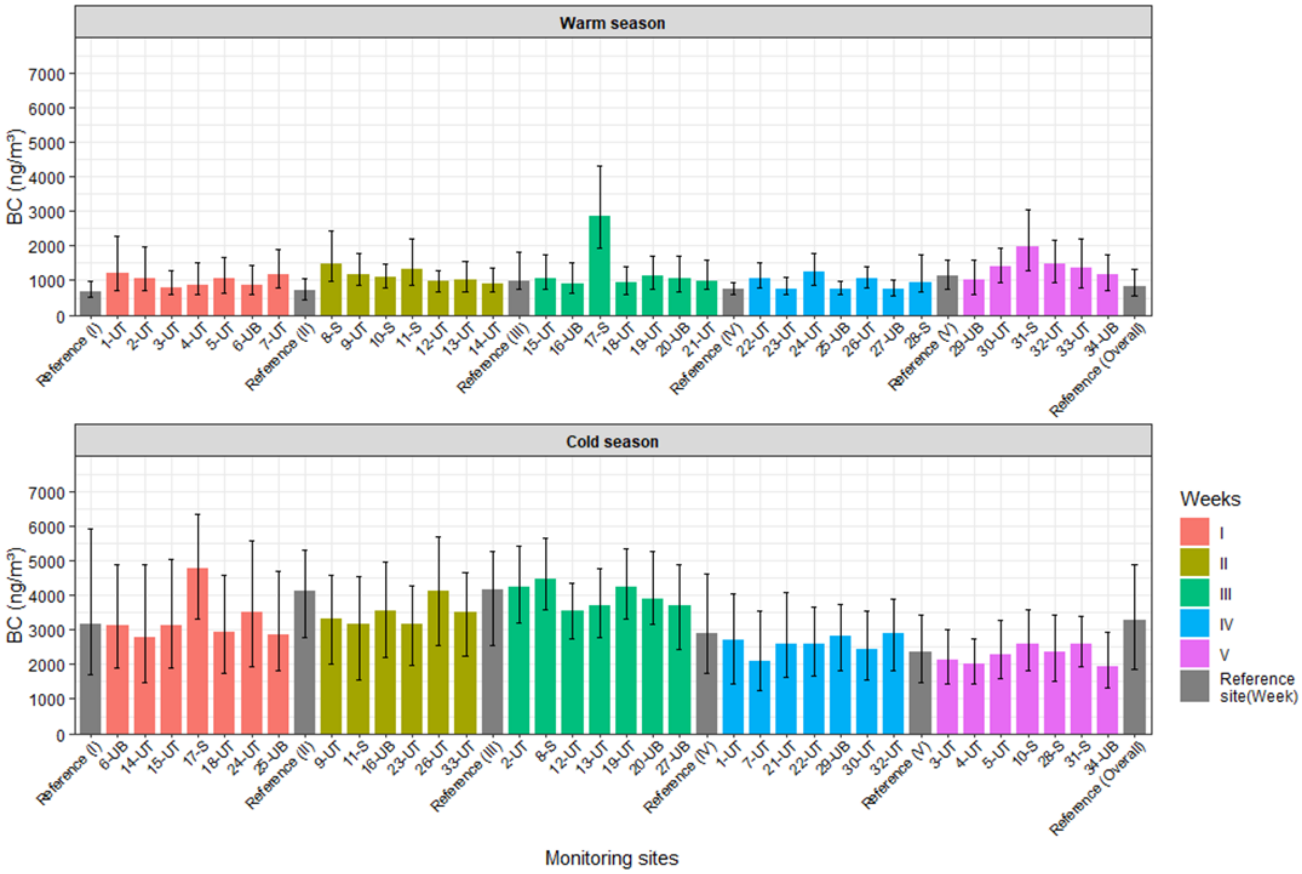


Figure 25. Weekly median (25th-75th percentile) BC concentrations at the 34 monitoring sites and the reference site in the two investigated seasons.

In Table 2 estimated seasonal and annual BC concentrations, divided in seasonal and MRH values, are reported. Highest concentrations of BC were observed in the cold season with an overall median (IQR) of 3247 (455) ng/m^3, while in the warm season the overall median (IQR) was 1309 (639) ng/m^3 (Table 5). The comparison between different types of monitoring sites showed concentrations that ranged from 906 ng/m^3 on an UB site, to 2584 ng/m^3 on a S site in the warm season, and from 2684 ng/m^3 on an UT site to 5111 ng/m^3 on a S site in the cold one. The same comparison but focusing on MRH showed values ranging from 1536 ng/m^3 to 4264 ng/m^3 during the warm season, and from 3298 ng/m^3 to

6764 ng/m^3 during the cold season. In Figure 26, the same data reported in Table 2, are presented as box plots. The figure shows that the differences between classes were more pronounced in the warm season, with BC at the S sites about 1.5 fold-higher than UT, and UT 1.2 fold-higher than UB, according to both BC and MRH BC. In the cold season the picture was similar, but with a smaller contrast between sites. Kruskal-Wallis and Bonferroni post-hoc test (S8) showed that: a) UB and S sites were always significantly different; b) UB and UT sites were significantly different only according to the annual non-MRH estimates; b) UT and S sites were always significantly different, with the exception of cold season data.

Table 5. Statistics of estimated seasonal, annual and MRH BC at different monitoring sites

BC (ng/m^3)		**S***	**UT***	**UB***	**All**
Warm season	Median	1922	1322	1039	1309
	IQR	588	308	125	639
	Min-Max	1768-2584	922-1846	906-1177	906-2584
Cold season	Median	3684	3286	3005	3247
	IQR	290	375	215	455
	Min-Max	3128-5111	2684-4227	2901-3239	2684-5111
Annual	Median	2735	2335	2039	2331
	IQR	373	228	64	446
	Min-Max	2519-3847	1894-2774	1962-2149	1894-3847
Warm season MRH	Median	3888	2394	2102	2357
	IQR	552	637	232	1018
	Min-Max	3412-4264	1769-3167	1536-2320	1536-4264
Cold season MRH	Median	5042	4104	3857	4227
	IQR	1100	489	727	726
	Min-Max	4642-6764	3298-5560	3374-4308	3298-6764
Annual MRH	Median	4441	3282	2882	3299
	IQR	596	485	340	739
	Min-Max	4029-5382	2678-3948	2645-3314	2645-5382
	N	6	7	21	34

**the differences between different classes of monitoring sites were tested by a Kruskal-Wallis test. Mostly of the monitoring sites were significantly different from each other according to Bonferroni post hoc (a = 0.05, reject H_o if p <= a /2). UB and UT sites were not different during both cold and warm season. Moreover, during the cold season also S and UT sites were not significantly different.*

In Figure 27, seasonal hourly median and IQR BC trends during working days and weekend are presented; highest peaks were found corresponding to the time with the highest traffic, i.e. morning rush hour period during working days (7-9 am), and leisure night time during the weekend. During the weekend the MRH peak was still present but with a much lower concentration. MRH peak during working days was found in both seasons, although in the warm season it was slightly earlier in the morning. On working days, an evening peak was observed only during the cold season. Wind speed data are presented in the same figure with opposite trends when compared to BC. Highest values took place during the afternoon and, in particular, in the warm season during which it was also measured a more intense and prolonged daily solar radiation (S3). Meteorological parameters during the monitoring campaigns, as measured at the nearest Milan air quality network station (piazza Zavattari, ~ 1 km), are summarised in Supplemental Table S2 together with the solar radiation daily trend plot (S3), accumulated rain plot (S4) and wind rose diagram (S5). At the reference site located in the school courtyard the averaged Angstrom exponent during the cold season was 1.9 (± 0.19) and during the warm season was 1.5 (± 0.25).

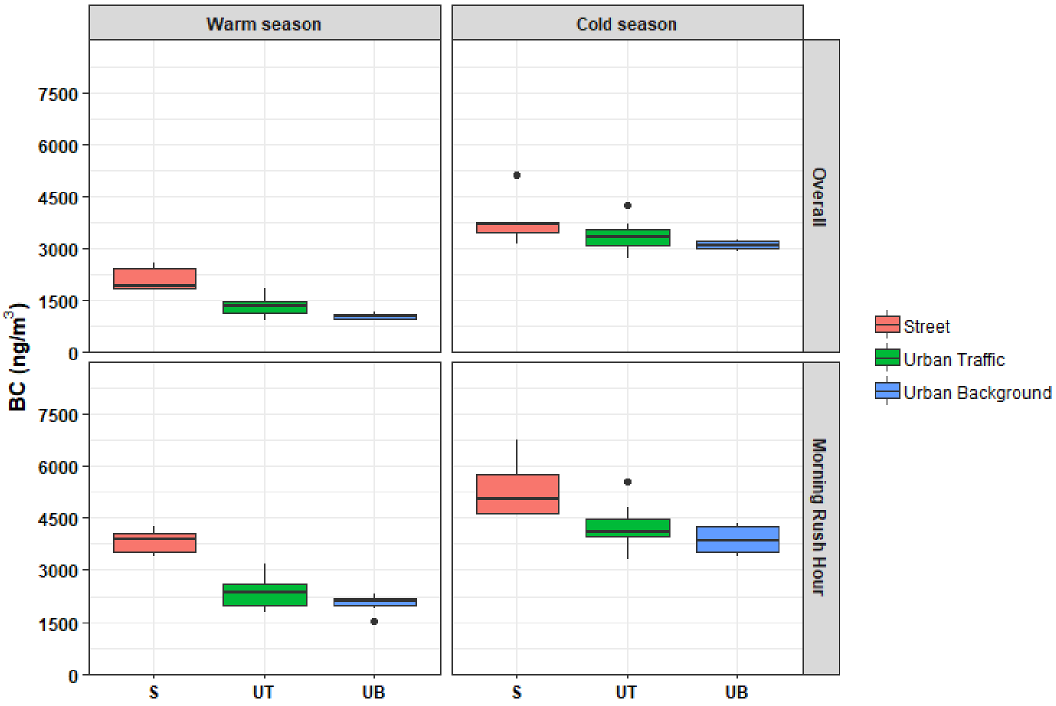


*Figure 26. Boxplots of seasonal and MRH BC at different type of monitoring sites. Black dots are outliers: x<Q1-(1.5*IQR), x>Q3+(1.5*IQR). Inferior and superior whiskers represent: (Q1-1.5*IQR)<x<Q1, Q3<x<(Q3+1.5*IQR). Where x=data, Q=quartile and IQR is interquartile range.*

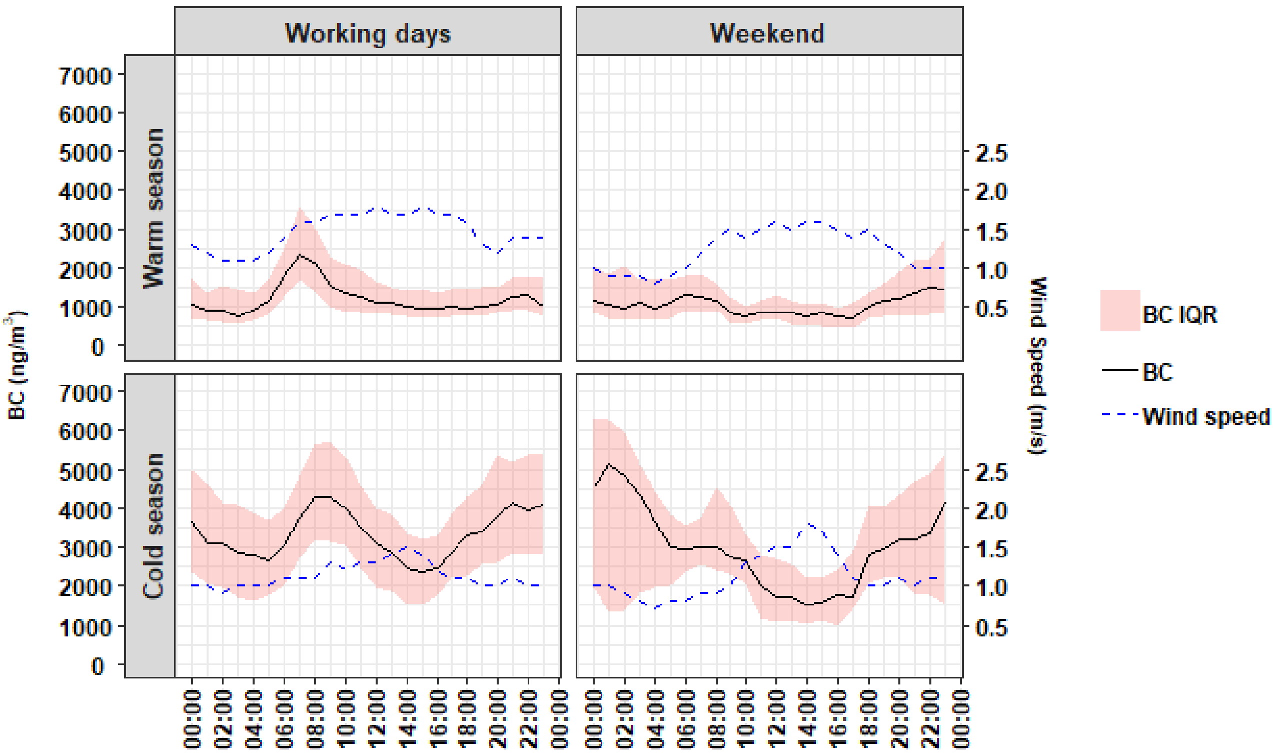


Figure 27. BC concentrations and wind speed hourly trends during the warm and the cold season, by working days and the weekend. Data are presented as median value for both BC concentrations and wind speed, and IQR only for BC concentrations.

3.3.3. Annual and seasonal LUR models for BC

Table 5 shows a summary of relevant parameters of the annual and seasonal LUR models. Models explain from 52 to 79 % of BC variability. Among the investigated covariates (traffic variables, population variables and land use variables), the most explanatory ones were those related to traffic. In particular, the most significant for the annual and warm season models were DAILY_TOTINVDist, that is the ratio between total vehicle/day and the distance to the nearest road and TRAFLOAD_100, which is the product of total vehicle/day and the length of the roads in a circular buffer of 100 m radius. The Variance Inflation Factor (VIF) showed no collinearity between these covariates. For the cold season model only TRAFLOAD_50, i.e. the product of total vehicle/day and length of the roads in a circular buffer of 50 m radius, significantly contributed to the model. Intercepts ranged between 1013 ng/m^3, in the warm season model, to 3095 ng/m^3, in the cold season model, showing the different seasonal background of BC.

The root mean square errors (RMSE) for the daily annual, warm and cold season models were 173.68 ng/m^3, 203.99 ng/m^3, 304.32 ng/m^3 (Table 6). These values were lower than the standard deviations of the estimated data (380 ng/m^3, 426 ng/m^3, 443 ng/m^3, Table 2). The LOOcV technique confirmed positive results for the daily annual and warm season model, with high R^2 LOOcV RMSE (0.67 and 0.73), that were similar to the model RMSE. For the cold season model, the cross validation resulted in a lower value of LOOcV R^2 (0.35). Overall, there was only one influential observation (Cook's D value >2) that affects both the annual and the cold season models. No spatial autocorrelation was highlighted according to the Moran's I test applied on residuals.

3.3.4. MRH annual and seasonal LUR models

Table 7 shows a summary of relevant parameters of the MRH annual and seasonal LUR models. Models explain from 65 to 81 % of BC variability. Once again, only traffic variables with small buffers significantly contributed to models. In particular, TRAFLOAD_100_MRH and TOTINVDist_MRH have the same meaning of the daily variable explained above, but were obtained using data MRH-focused. Variance Inflation Factor (VIF) showed no collinearity between these covariates.

The RMSE (300.04 ng/m^3, 456.98 ng/m^3, 508.63 ng/m^3) of the models were lower than the standard deviation of the estimated data (639 ng/m^3, 709 ng/m^3, 731 ng/m^3, Table 5). The LOOcV technique confirmed positive results for all the models (R^2 = 0.78, 0.59, 0.51) and LOOcV RMSE were similar to the model RMSE. Overall there was only one influential observation (Cook’s D value >1) that affected the cold seasonal MRH model. No spatial autocorrelation was found according to the Moran’s I test applied on residuals.

3.3.5. BC concentration maps and spatial patterns

In Figure 28 the concentration maps of BC derived by the six LUR models (Table 6 and 7) are shown. In dark red, the highest values were estimated according to the LUR cold MRH model, while in green the lowest concentrations were estimated according to the LUR warm season model. For each couple of seasonal/annual and MRH models, the latter showed higher BC concentrations. Furthermore, to better explain spatial differences between seasonal/annual and MRH models, Figure 29 presents the relative incremental percentage of BC concentration that occurred during MRH, according to the estimates given by LUR models. All the pictures show a general increment in BC concentrations that go from +33% to +233%, while spatial patterns seem to be different in the two seasons.

.

Table 6. Summary of parameters of the daily annual and seasonal LUR models for BC (ng/m^3).

	Variables[a]	Units	Estimate	Std err	T Value	P	VIF[b]	Variable range	R^2	Adj R^2	LOOcV R^2	RMSE	LOOcV RMSE	highest Cook's D	Moran's I
Annual	Intercept	ng m^{-3}	2007	45.57	44.040	.00*	-	-	.79	.78	.67	173.68	217.27	2.23	.0507
	TOT_INVDist	veh·day^{-1}·m^{-1}	4.044×10^{-1}	8.144×10^{-2}	4.966	.00*	1.196	4.386-1.893×10^{3}							
	TRAFLOAD_100	veh·day^{-1}·m	5.278×10^{-5}	7.744×10^{-6}	6.816	.00*	1.196	0-2.207×10^{7}							
Warm season	Intercept	ng m^{-3}	1013	53.51	18.921	.00*	-	-	.77	.75	.73	203.99	219.41	.065	.0278
	TOT_INVDist	veh·day^{-1}·m^{-1})	5.783×10^{-1}	9.565×10^{-2}	6.046	.00*	1.196	4.386-1.893×10^{3}							
	TRAFLOAD_100	veh·day^{-1}·m	4.497×10^{-5}	9.094×10^{-6}	4.945	.00*	1.196	0-2.207×10^{7}							
Cold season	Intercept	ng m^{-3}	3095	66.770	46.355	.00*	-	-	.52	.51	.35	304.32	354.58	2.58	.0381
	TRAFLOAD_50	veh·day^{-1}·m	1.928×10^{-4}	3.258×10^{-5}	5.916	.00*	-	0-7.645×10^{6}							

[a] TOT_INVDist = the ratio between total vehicle/day and the distance to the nearest road; TRAFLOAD_100 = that is the product of total vehicle/day and the length of the roads in a circular buffer of 100 m radius; TRAFLOAD_50 = that is the product of total vehicle/day and the length of the roads in a circular buffer of 50 m radius

[b] Variance Inflation Factor for multicollinearity

*p < .001

Table 7. Summary of parameters of the MRH-focused annual and seasonal LUR models for BC (ng/m³).

	Variables[a]	Units	Estimate	Std err	T Value	P	VIF[b]	Variable range	R^2	Adj R^2	LOOcV R^2	RMSE	LOOcV RMSE	highest Cook's D	Moran's I
Annual	Intercept	ng m^{-3}	2842	73.1	38.883	.00*	-	-	.81	.80	.78	300.04	278.74	.17	-.16
	TOT_INVDist_MRH	veh·day^{-1}·m^{-1}	11.71	1.796	6.521	.00*	1.197	0.318-1.367×10^2							
	TRAFLOAD_100_MRH	veh·day^{-1}·m	1.020×10^{-3}	1.700×10^{-4}	5.999	.00*	1.197	0-1.616×10^6							
Warm season	Intercept	ng m^{-3}	1979	109.2	18.120	.00*	-	-	.65	.62	.59	456.98	416.51	.61	-.07
	TOT_INVDist_MRH	veh·day^{-1}·m^{-1}	11.18	2.683	4.166	.00*	1.197	0.318-1.367×10^2							
	TRAFLOAD_100_MRH	veh·day^{-1}·m	1.032×10^{-3}	2.540×10^{-4}	4.063	.00*	1.197	0-1.616 e×10^6							
Cold season	Intercept	ng m^{-3}	3706	113.8	32.574	.00*	-	-	.65	.62	.51	508.63	433.73	1.51	-.29
	TOT_INVDist_MRH	veh·day^{-1}·m^{-1}	12.24	2.795	4.380	.00*	1.197	0.318-1.367×10^2							
	TRAFLOAD_100_MRH	veh·day^{-1}·m	1.007×10^{-3}	2.646×10^{-4}	3.806	.00*	1.197	0-1.616×10^6							

[a] TOT_INVDist_MRH = the ratio between total vehicle/MRH and the distance to the nearest road; TRAFLOAD_100_MRH = that is the product of total vehicle/MRH and the length of the roads in a circular buffer of 100 m radius; TRAFLOAD_50 = that is the product of total vehicle/MRH and the length of the roads in a circular buffer of 50 m radius

[b] Variance Inflation Factor for multicollinearity

*p < .001

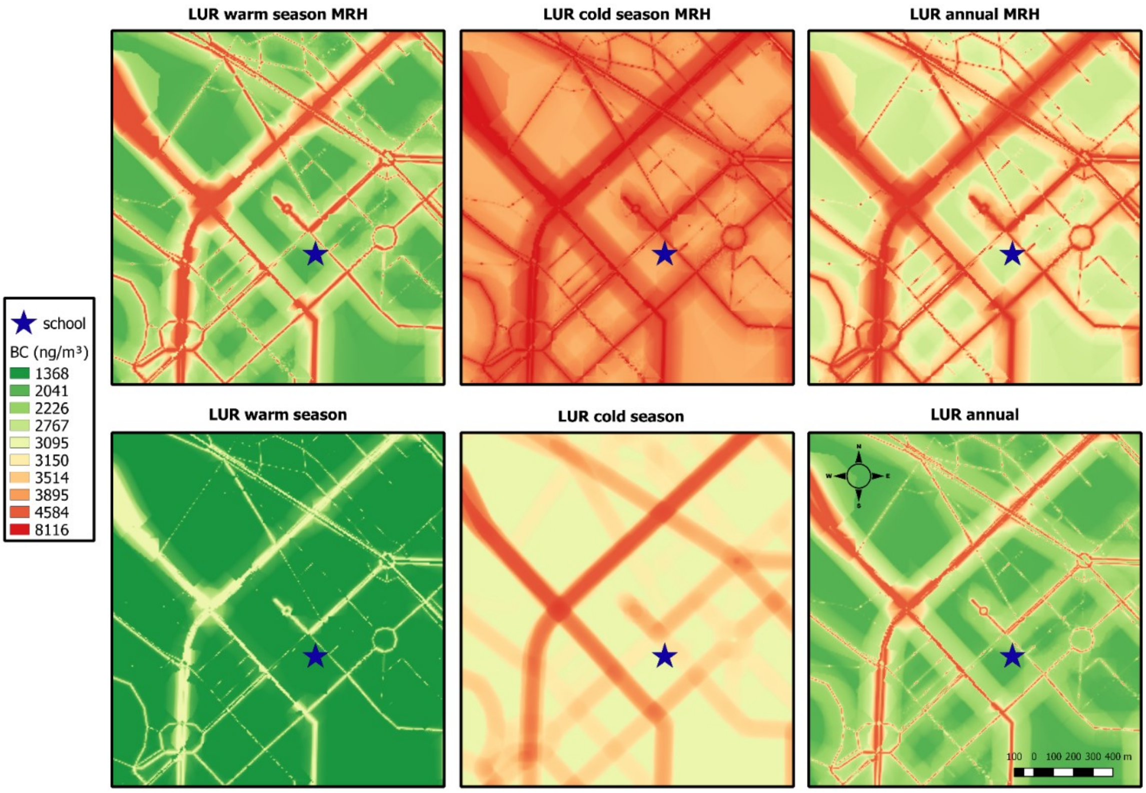


Figure 28. BC concentration maps (ng/m^3). The BC concentration value of each pixel (1x1 meters resolution) was estimated using the LUR models (Table 3 and 4) on a set of more than 70,000 points, and applying a Natural Neighbour interpolation algorithm. The colour classification is based on the total distribution's deciles, i.e. the distribution of all the seasonal and MRH-seasonal estimates merged together. The blue star indicates the school.

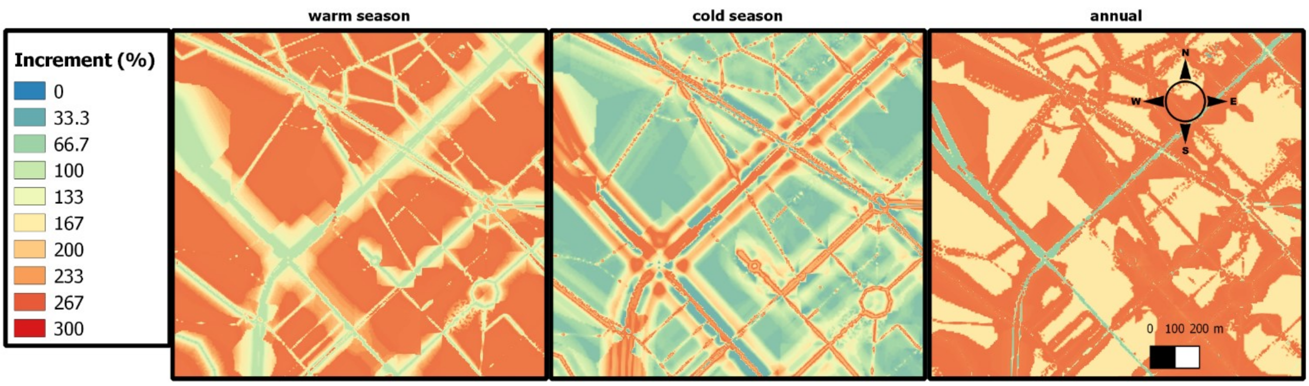


Figure 29. Increment BC maps of MRH according to the warm season, cold season and annual models. The percentage value of each point is the increment of BC concentration measured during the MRH compared to the daily period, using the 70,000 points and data from Figure 5. A Natural Neighbour interpolation algorithm was applied to obtain the spatial resolution of 1x1 meters.

3.4. DISCUSSION

Two seasonal BC monitoring campaigns were carried out in the catchment area of an elementary school in the city of Milan using optical devices. The spatial distribution of BC measured at different monitoring sites allowed us to develop annual, seasonal, and MRH Land Use Regression models.

Weekly median concentrations of BC at 34 monitoring sites and the reference site (Figure 2) show that street sites (S) were those with the highest values. Particularly, the highest BC concentration was measured at site 17-S: this site is facing the outer ring road of the city, that in this particular section doubles the carriageways from four to eight, by an additional elevated road (Cavalcavia della Ghisolfa). During the warm season, BC concentration at the reference site was comparable to or lower than BC concentration at all the other monitoring sites. This was expected, given that the reference site was located inside the courtyard of the study school, protected from direct traffic sources. Conversely, in the cold season BC concentration at the reference site was higher than the other monitoring sites. This may be due to the use of the MA200 device equipped with the Dualspot© technology, that was not available for the AE51s devices used at the 34 monitoring sites; this technology automatically corrects for the shadowing effect, avoiding the underestimation of BC usually observed in the presence of high values of ATN that occur more often during the cold season. Another possible explanation is the contribution of the school heating system exhaust to BC at the reference site.

Overall, BC values were lower in the warm season (median 1309 ng/m^3) than in the cold season (median 3247 ng/m^3) (Table 5). This is attributable mainly to the contribution of heating systems, operating in Milan from mid-October to mid-April. MRH (7 am-9 am) represents a very critical window for exposure to BC, with median (IQR) concentrations of 2331 (446) and 4227 (726) ng/m^3 in the warm and cold season, respectively, and an overall increase of 1000 ng/m^3 in comparison with the daily median value, due to the vehicular traffic of commuters.

Annual BC concentrations in our study are consistent with those reported in other studies. In Antwerp in 2010-2011 *Dons et al. (2013)* found BC average (± SD) values of 2654 (± 766), 2417 (± 660) and 2224 (± 297) ng/m^3 for S, UT and UB sites, respectively . In 2009 *Reche C et al. (2011)* found BC average (± SD) values of 1900 (± 700), 7800 (± 2700) and 3500 (± 1300) ng/m^3 at a UB and a S site in London, and in a S site in Bern, respectively . In these last two S sites BC values were greater probably because they were particularly affected by traffic: both located in street canyons, and close to highly congested roads (80,000 veh/day, London; 30,000 veh/day, Bern)(Dons et al., 2013; Reche et al., 2011). Moreover, on the monitoring site located in Bern, BC was measured with a multiangle absorption photometer that is not affected by the shadowing effect. In 2011 a 3-day BC monitoring campaign was performed in Milan during the warm season, measuring daily average (± SD) BC concentration of 1600 (± 400), 2000 (± 500) and 1500 (± 500) ng/m^3 at a UB site, 3100 (1700), 2800 (1400) and 2600 (1900) ng/m^3 at a UT site and 6300 (2900), 5200 (2300) and 3300 (1900) ng/m^3 at a S site (Invernizzi et al., 2011). These values appear to be higher than those we measured during the warm season monitoring campaign because they did not consider night-time, but also probably due to the stricter vehicle emission standards introduced over the years.

The chosen set of monitoring sites allowed us to catch the spatial contrast inside the study area (Figure 26). The differences in median BC among sites (Table 5) were more pronounced during the warm season with an increase of about 85% (883 ng/m^3) from UB to S sites, 45% (600 ng/m^3) from UT to S, 27% (283 ng/m^3) from UB to UT, while during the cold season, the increase was 23% (679 ng/m^3) from UB to S, 12% (398 ng/m^3) from UT to S, 9% (281 ng/m^3) from UB to UT. The above mentioned differences suggest that BC distributes more homogeneously in the study area during the cold season than during the warm season, probably due to the impact of heating system source and meteorological condition. In particular, very low wind speed values (S2-S5) and the frequent thermal inversions that usually characterize the cold season in the study area, favour the stagnation of particulate matter (Caserini et al., 2017; Vecchi et al., 2004) A similar pattern was observed in the comparison between seasonal MRH BC data. Although these considerations were broadly supported by the significance tests applied to the data set, concentrations measured at the UB sites and UT sites were not found to be significantly different, with the exception of the annual estimates. This is probably due to the used a priori selection criteria (Table 3) that did not allow to clearly distinguishing these two classes.

The BC hourly trends (Figure 27) show the highest peaks in connection to the commuting to work periods, i.e. MRH in working days. Elevated levels of BC were also measured during night time in working days in the cold season; this peak and the consequent accumulation of BC is probably due to the commuting from work, the use of biomass heating systems and finally favoured by the decrease of wind speed observed starting from 4 pm. During

the weekend, a different hourly trend was found: MRH peak was always less pronounced, while highest BC levels were observed during night-time, probably in connection with people entering the city for leisure activities.
Six LUR models, three of which focused on MRH, were developed (Table 5 and 6). The variability of BC explained by our annual and warm season models (R^2 = 0.79 and 0.77), as well as RMSE values (217 and 219 ng/m^3) are comparable to those reported in Dons et al. (2014) (R^2 = 0.73 and 0.70, RMSE = 384 and 343 ng/m^3); conversely, the performance of our cold season model (R^2 = 0.52, RMSE = 304 ng/m^3) is worse than the one developed in the just mentioned study (R^2 = 0.69, RMSE = 403 ng/m^3); this is probably linked to the ADDRESS_50 explanatory variable, i.e. the number of addresses in a 50 meter circular buffer, that was able to partly catch the portion of variability caused by heating systems. Moreover, the other explanatory variables appear very similar, especially focusing on the warm season model in which traffic variable with small buffers played an important role. Finally, intercept values appear lower in *Dons et al. (2014)* probably due to both the lower background BC concentration in Antwerp and the presence of rural sites in the pool of monitoring sites used to develop the models (Dons et al., 2014). Similar to LUR season models developed in Pittsburgh by *Tunno BJ et al.(2018)* and, once again, in Antwerp (Dons E et al., 2014), our models better explained the variability of BC in the warm than in the cold season(Tunno et al., 2018). This is probably connected with both the different contribution of sources to BC concentrations and our ability to explain the variability of BC caused by these non-traffic sources. The higher average Absorption Ångström Exponent value found for the cold season (mean ± SD, 1.9 ± 0.19) than the warm season (mean ± SD, 1.5 ± 0.25), reinforces this hypothesis, possibly indicating a major role played by combustion for heating, and especially biomass heating (Martinsson et al., 2017).
Moreover, in our study, the high time resolution of BC acquisition (every 5 min) and the availability of dynamic traffic variables, allowed us to focus on MRH. In particular, for the cold season and the annual models, MRH models better explained BC variability, with adj R^2 that increased from0.51 to 0.62 and from 0.78 to 0.80, respectively. In general, better performances of LUR models focused on MRH are expected due to the higher contribution of traffic source; however, for the warm season our models show an opposite behaviour with adj R^2 that worsened from 0.78 to 0.62. One of the possible reasons could be the effect of wind, not included in the models, which behaved differently in the two seasons: as showed in Figure 4, during the warm season wind speed morning increment take place

simultaneously to the MRH, probably influencing BC spatial distribution. Despite BC is strongly related to traffic source, there are only a few LUR models that focus on rush hours; this is probably due to expensive equipment, and logistic and technical issues that are required for BC monitoring. In particular, *Tunno et al. (2018)* developed two seasonal rush hour models in Pittsburgh, USA, that explained the 75% and the 61% of BC variability for summer and winter periods respectively (Tunno et al., 2018). These two models used only traffic variables with 200 meters circular buffers. Besides, *Dons et al (2013)* developed for Flanders hourly annual LUR models explained the 59% and 58% of the BC variability measured at 7 am and 8 am during weekdays; these LUR models used traffic, land use and population dynamic explanatory variables(Dons et al., 2013). However, both these two examples are not comparable to our study: models by *Dons et al. (2013)* used a pool of regional-scale BC data; while *Tunno et al. (2018)* used BC data that represents an average concentration of both morning and evening rush hours.

Furthermore, the spatial patterns shown by the application of our LUR models (Figures 5 and 6) suggest an overall increase in BC concentrations during MRH, with differences in magnitude according to location. In particular, during the warm season, while the highest concentrations are linked to the major roads (Figure 28), the main relative increase seems to affect the background and the local roads network (Figure 29). Conversely, during the cold season both highest BC concentration and main relative increase are linked to the major roads. The different behaviour observed according to the relative increase of BC concentration during MRH period is probably due to the very high background concentration of BC linked to the presence of residential heating. This source is active only during the cold season and probably affects especially the concentration in urban background sites, lowering the relative impact of traffic sources. Nevertheless, the annual model showed similar pattern to the warm season model suggesting that traffic remains a major issue during MRH. Our work has some limitations. Raw BC data were not post-processed to account for optical related artefacts *(Good et al., 2017)*. This might have caused, especially during cold season, an underestimation of BC concentrations and it might have contributed to the lower performance of the cold season LUR models. However, to partially deal with this issue, we increased the frequency of filter replacement, up to twice a day during highly polluted periods; moreover, by applying a correction factor resulting from two 24-hours intercomparison between AE51s and the MA200, we took advantage of the correction of BC introduced by the Dualspot©

technology. This correction factor should have partially corrected the systematic underestimation of BC concentrations caused by the filter loading effect. However, due to technical reasons, we were able to use the Dualspot© technology only during the cold season monitoring campaign. Therefore, it is likely that warm season campaign measurements are more biased than the cold one, even if during this season the underestimation is usually lower. Another limitation is that LUR models were developed using a pool of data collected in two seasonal 5-weeks monitoring campaigns, during which each site was monitored only for one week; this may have introduced some temporal variability bias, that we tried to address by applying equation [1]. Furthermore, some LUR models suffer high Cook's D values (max 2.58), pointing out the presence of an influential observation. In particular, it was found that there was one street site characterized by an extremely high flux of traffic, site 17-S (Figure 25). We decided not to exclude this site because in a very congested city like Milan we expect to find other locations like this, and because this issue was not consistently seen in all models. Finally, a part of the unexplained variability in our LUR models could be attributed to the use of land use variables from 2011 that could not properly take into account the urban transformations, which happened in the last few years. Moreover, for the cold season LUR models there is a lack of explanatory variables that properly account for the contribution of heating systems. These systems may differently contribute to BC concentrations at the ground level, due to the different fuels burnt and the variable heights of surrounding buildings. Ultimately, more studies are needed to better understand the spatial variability of BC during the cold season, especially referring to the portion of variability caused by heating systems.

3.5. CONCLUSION

In conclusion, BC spatial variability was analysed for the first time in Italy by a multisite and high time resolution approach, with the aim to characterize a very specific portion of the urban environment and focusing on the most critical daily time window for exposure, i.e. a school catchment area and MRH. Furthermore, to increase awareness among citizens and in particular schoolchildren's parents, we used a participatory approach by involving all the actors of the selected school from the very first part of the project.

This study confirms that traffic is a major source of BC in Milan, and MRH is the part of the day in which the highest concentrations occur. Transport policy should aim to reduce air pollution exposure in the city of Milan and limit its impact on health, in particular during the cold season when a high background concentration is added to the daily peaks of exposure. Children are especially susceptible to the effects of air pollution and when they commute to school concentrations tend to be the highest, partly because many parents drive their children to school. Our spatial analysis could help policy makers to identify hot spots and reduce emission inside the study area, for example through the promotion of less polluted school streets. Finally, reducing the emissions of BC has the important co-benefit of reducing global warming and achieving the United Nations Intergovernmental Panel on Climate Change goal *(ONU, 2018)*.

4. A PARTICIPATORY APPROACH TO INVOLVE TEACHERS, SCHOOLCHILDREN AND THEIR PARENTS IN THE RESEARCH PROCESS

RESEARCH QUESTIONS AND ANSWERS

Q5: Is the used participatory approach to involve directly the school (i.e. teachers and children) in the research project a valuable approach to raise awareness on air pollution topic?

A1: Inspired by the IVAC methodology and consisting in a) the gamification of the topic, and b) the experience-based and participatory approach, the environmental education intervention proposed in the framework of the MAPS MI project proved to be a valuable way to engage the stakeholders and raise awareness among schoolchildren.

Q6: Is this a suitable approach to recruit volunteers in the research process?

A2: the two educational modules were planned to take place just before the two seasonal personal monitoring campaigns in order to help to recruit volunteers. The relatively high response rate (63%) and the increase in number of participants (+22%) of the first and of the second monitoring campaign respectively, could be seen as an indicator of the effectiveness of such an approach.

ABSTRACT

Introduction:

The engagement of communities and citizens in the research process is one of the key aspects to achieve the exposure science vision of 21th Century. Moreover, enhancing education on air pollution is considered a key factor for improving health and quality of life, especially for children. This chapter discuss an environmental education intervention focused on air pollution and carried out with a participatory approach aiming to raise awareness and involve children and their parents in a two-seasonal personal monitoring campaign.

Methods: The environmental education intervention consisted in a double series of ludical and experience-based laboratories set according to the Investigation, Vision, Action, Change (IVAC) methodology. The design of the intervention was firstly shared with the Teaching Committee of the school, and then planned according to the collected suggestions. To assess children awareness on air pollution topic, the data collected during a personal monitoring campaign performed during home-to-school commuting were compared to their according perceptions.

Results:

With the environmental education intervention 128 children (9-10 yrs.) were involved in the research process. Children were involved in a multitude of ludical activities on air pollution topic starting from their perceptions and experiences in the neighborhood. Moreover, the overall response rate to the personal monitoring recruitment was 63% according to the first, with a 22% increment in the number of participants according to the second one. Finally, a first attempt to compare children perceptions to the personal exposure measurements of Black Carbon shows that Children overestimated BC concentration in the 42% of the cases, while underestimated in 33%.

Discussion:

This experience showed the potential of a participatory approach in the framework of exposure science to both raising awareness among stakeholders and help researchers to involve volunteers in the research process.

4.1. INTRODUCTION

Northern Italy is one of the most polluted areas in Europe according to the European Environment Agency (EEA). Among those located in this territory, Milan is the biggest city with an estimated population of about 3.2 million residents. If we focus on this urban environment, air pollution is mainly caused by motorized traffic and, among air contaminants, Black Carbon (BC) has been identified as a sensitive marker of traffic-related air pollution (TRAP). The health impact of TRAP exposure is reported to be heavier for the weaker population groups, such as children; for instance, many studies have suggested relationships between TRAP exposure, airways disorders and cognitive skills. In particular, Morning Rush Hour (MRH) is the most congested period of a common urban working day and it is also the time during which schoolchildren commute to school and are directly exposed to traffic pollution. The United Convention on the Rights of the Child states the rights for all children to live in a healthy and safe environment, to express their opinion, to be informed and listened to about what affects them. Moreover, as reported by the United Nations (UN) "since the adoption of the UN Convention on the Rights of the Child in 1989, Article 12 – the provision that children have a right to express their views and have them taken seriously in accordance with their age and maturity – has proved one of the most challenging to implement" (UN, 2011). Moreover, the 2030 Agenda for Sustainable Development puts at the top of its concerns the most vulnerable people, including children.

This part of the dissertation will focus on the development of an environmental education intervention to raise awareness among teachers, schoolchildren and their parents and to favour an active and informed participation to a two-season personal monitoring campaign.

4.2. MATERIALS AND METHODS

Firstly, the project was submitted to and approved by the school board of the elementary school IC Pietro Micca, via Gattamelata 35, Milano (MI). Then, a preliminary document of the contents of the ludical laboratories as well as the proposed activities were shared with the schoolteachers' commission, asking for comments. Finally, according to the different curricula and the teachers' opinions, six third grade-classes were chosen to be involved in the project. The intervention took place in spring and autumn 2018, and consisted in a double-serie of ludical and experience-based laboratories set according to the Investigation, Vision, Action, Change (IVAC) methodology.

4.2.1. The IVAC model of pedagogy

According to Jensen and Schnack (1997), "[…] the aim of environmental education is to make students capable of envisioning alternative ways of development and to be able to participate in acting according to these objectives", and the better way to achieve the goal is through a multi-step process that include as key components: Knowledge, Commitment, Visions and Action experiences. This framework is better known as "action competence" approach *(Jensen et Shnack, 1997)*. Given this, the IVAC model represents a practical declination of the theory that uses questions to define the process by which reaching the original goals. In particular, starting from a first introductive part focused on the common definition of the problem (A), the group of students should deal with the construction of a vision on the future related to the issue of concern, and how it could be according to their hopes (B). Finally, a discussion and an implementation of actions should take place by looking at both positive and negative consequences and by choosing the ones to be carried out (C) *(Jensen, 1997)*. In Table 8 the questions related to the IVAC approach are given.

Table 8. The Investigations, Visions, Actions and Changes (IVAC) approach

A: Investigation of a theme	- why is this important to us? - its significance to us/others?—now/in the future? - what influence do lifestyle and living conditions have? - what influence are we exposed to and why? - how were things before and why have they changed?
B: Development of visions	- what alternatives are imaginable? - how are the conditions in other countries and cultures? - what alternatives do we prefer and why?
C: Action and change	- what changes will bring us closer to the visions? - what changes within ourselves, in the classroom, in the society? - what action possibilities exist for realising the changes? - what barriers might prevent carrying out these actions? - what barriers might prevent actions from resulting in change? - what actions will we initiate? - how will we choose to evaluate these actions?

4.2.2. General approach and ludical laboratories in the MAPS MI framework

The environmental educational intervention proposed in the framework of the MAPS MI project consisted in seven meetings divided in two modules co-designed with ABCittà cooperativa ONLUS, a non-profit organization historically focused on participatory processes: the first took place in March and April 2018, while the second during October and November of the same year. The first module cover the first two contents of the IVAC approach, i.e. investigation and the development of a vision, while the second was more focused on action and change. Common threads of the whole experience were both a participatory and a gamification approach to raise the level of engagement of both children and teachers, and an experience-based approach. Such an approach was achieved by setting all the activities on the neighbourhood of the school, a well-known environment to children, and by asking them to act starting from their own experience and perception in that environment. In Table 9, the original IVAC sheet proposed to the schoolteachers commission is given. Among the other, the proposed activities included:

a) a story-telling on air pollutants to make children familiar with the topic;
b) a series of ludical activities to make children comfortable with the topic, starting from their own experiences, focusing especially on home-to-school commuting;

c) six BC monitoring campaigns around the school area;
d) a presentation and discussion of measured data, by playing with charts and maps;
e) a focus on Sustainable Development Goals (SDGs) with the aim to develop an awareness-raising campaign.

Finally, Figure 30 and 31 give a schematic overview of the first module, with key moments, while Figure 32 gives four of the posters designed by schoolchildren for the awareness-raising campaign.

Table 9. IVAC scheet of the MAPS MI project

IVAC	*Goals*	*Specific goals*	*Example of activities*
INVESTIGATION	Turning the classroom into a laboratory, getting comfortable, organizing collaborative relationships, presenting a different way of working, making the most of listening to oneself and others as tools for getting to know the territory, be funny and having fun, broadening participation, reflecting on collected data.	> To contextualize, identify and share the general objectives of the project (environment, sociality, health); > To define together the role of children in the project (from the neighborhood mapping, to research, to action); > To start the first reflections on the home-to-school commuting and on the perception and memory of the key-places in the neighborhood; > To experience the learned things in the neighborhood > To describe and analyze the home-to-school paths putting it in a system together with the other children' paths and the different perceptions of places; > To use drawing, maps and interactive games to visualize the learned concepts;	☺ Drawing the map of the neighborhood together; ☺ Visualizing ugly and beautiful places of the area on the map; ☺ Drawing and systemitize home-to-school paths; ☺ Presenting the identikit of Black Carbon and other air pollutants; ☺ Identifying where Black Carbon is hiding on the map of the neighborhood; ☺ Acting as a researcher, by monitoring Black Carbon in the neighborhood.
VISION	Collecting and reading data, expressing the wishes, starting to think about the future, trying to unhinge the clichés about movement and air pollution, working in a team, rethinking sustainability in pro-active terms.	> Reflecting upon the experience of the monitoring campaign; > Reading together the results, and collecting them to the neighborhood map; > Expressing and visualizing wishes and expectations about the future focusing on new forms of home-to-school mobility to fight pollution > Sharing ideas and analyzing everyone's needs and requests in a creative way; > Prioritizing alternatives.	☺ Presentation of the neighborhood monitoring campaign results; ☺ Implementing the neighborhood map with the new collected elements ☺ Presentation of the personal monitoring project to the children; ☺ Activitiy: what can we do? How be a researcher can counteract Black Carbon diffusion. ☺ Discussing and visualizing how to encourage low-carbon behaviours and identifying less polluted home-to-school paths
ACTION FOR CHANGE	From being a researcher to act as an agent of changing: we are not alone, how the world is trying to fight against Black Carbon? Understanding how to be part of the change, and how to spread our awareness.	> Summarising the work done and reflecting on the main achievements > Introducing the Global Goals and the main planned actions > Identifying the most effective way to counteract Black Carbon; > Working on material and a schedule to spread awareness	☺ Playing with hourly trend of BC graphs to reacquaint with the topic; ☺ Presentation of the Global Goals ☺ Selection of the most important ones ☺ Designing an awareness-raising campaign and working on communication materials ☺ Presenting the work to other actors

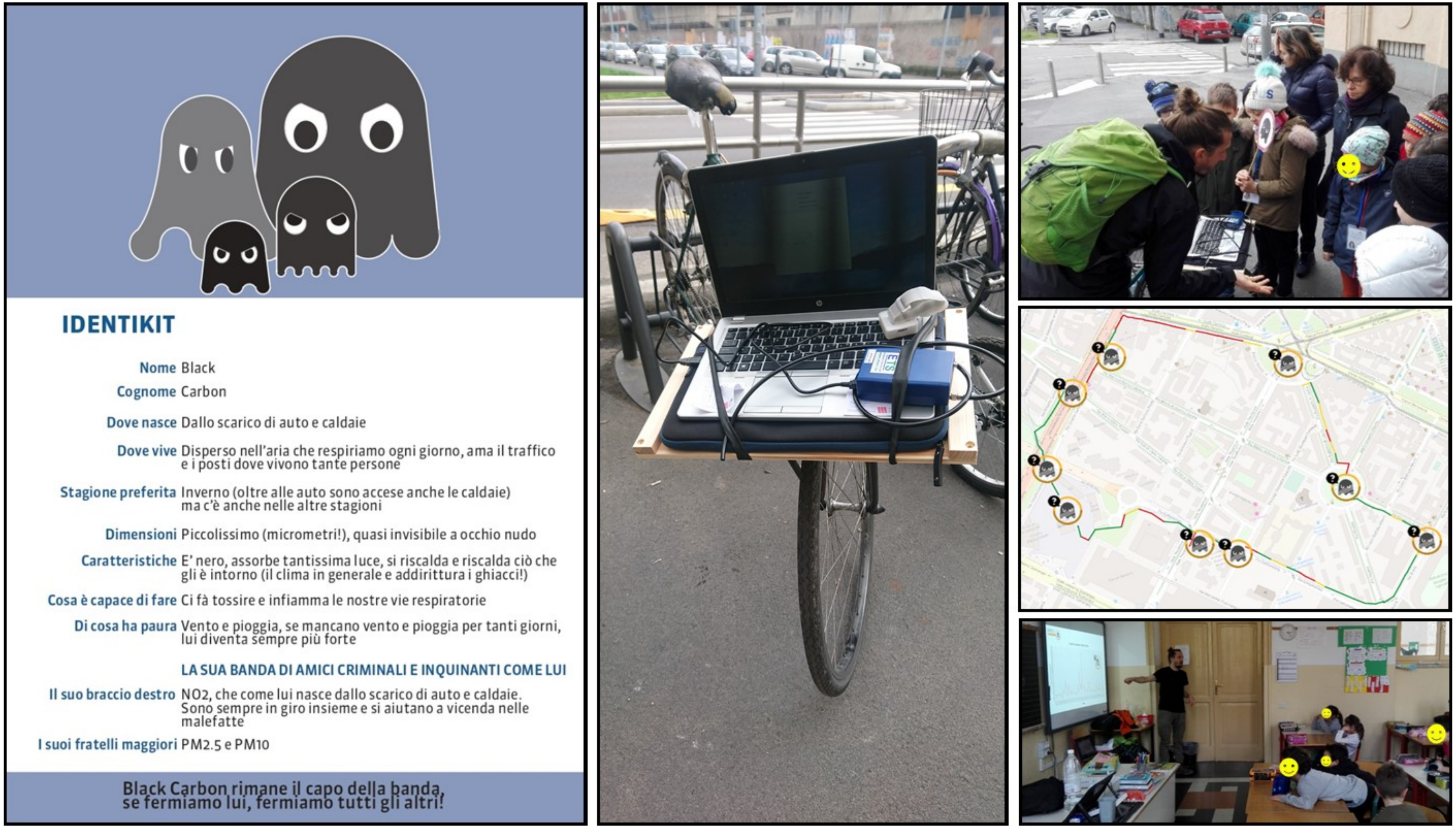


Figure 30. On the left, the identikit of BC and other pollutants presented as characters is reported. In the middle a bicycle equipped with a laptop and a microaethalometer AE51. The bicycle was used for the online measurements in the neighbourhood. On the top-right a moment during which children were asked to say if there was normal, high or very high level of BC according to the location and their perceives; on the mid-right one of the maps developed using the data collected during each neighbourhood measurements; at the bottom-right of the figure. a moment during which children were asked to figure out the place according to the level of BC is reported.

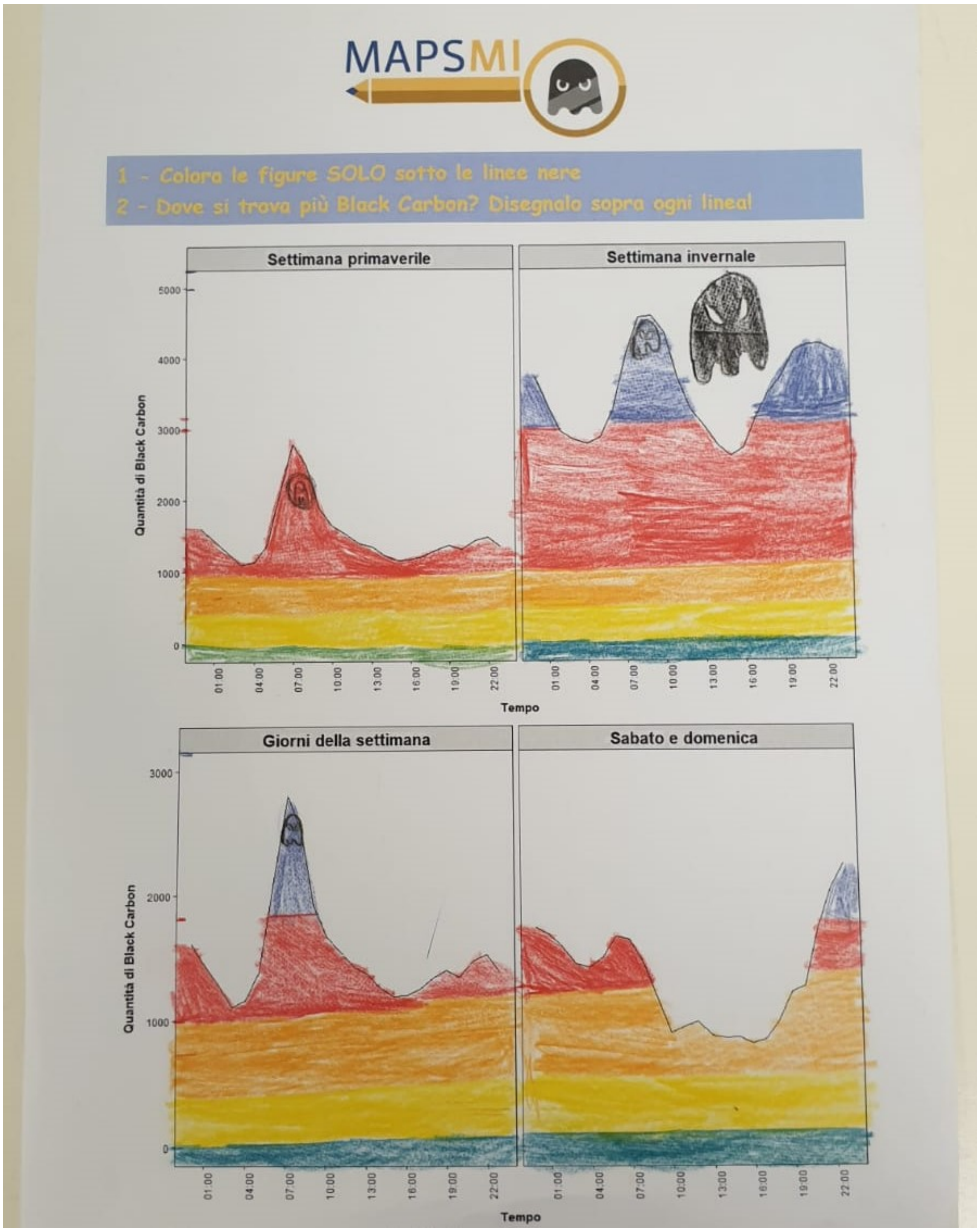


Figure 31. Example of one of the exercise in the frame of the environmental education intervention. This exercise was played at the beginning of the second module, during October 2018 to go over the topic previously learnt in the first module. Schoolchildren were asked to put a big black carbon inside the box with the highest concentration, while small black carbon close to all the peaks. Original data was used to build up the sheet. Translations: "Settimana primaverile" is "Spring week", "Settimana invernale" is "Winter week", "Giorni della settimana" is "days of the week", "Sabato e domenica" is "Saturday and sunday", finally "tempo" is "Time" and "Quantità di Black Carbon" is "Amount of Black Carbon".

Figure 32. SDGs-oriented posters produced by schoolchildren during the MAPS MI project. The main topics chosen by schoolchildren were: greenness, clean energy and active and sustainable mobility inside urban areas (SDGs 11). In the original IVAC framework, this was the "action" part.

4.2.3. Personal exposure during home-to-school paths and personal perceptions

Amidst the two environmental education modules and just after the last one, children and their parents were invited to take part in a two-season personal exposure assessment campaign (May-June 2018 and January-February 2019), that consisted in a 7-day GPS tracking, a 1-day air pollution personal exposure assessment, and a final biomonitoring.
In particular,
Finally, on the very last day of the cold-season, personal monitoring campaign and just after the home-to-school commuting, children were asked to draw their home-to-school paths and to colour it in green, yellow or red according to the perceived level of black carbon. In particular, the green colour was assimilated to a normal level of air pollution, yellow at a high level, red at an extremely high level. This classification had already been explained and experienced by the same schoolchildren during the whole process.
For each child, the coloured sections of the drawn home-to-school route were compared to the measured personal BC concentrations. In particular, the green sections were computed as values <50th percentile, the yellow sections as values in between of the 50th and the 75th percentiles, and the red sections as values >75th percentile. Moreover, it was assumed that children perceptions were only influenced by what happened during the home-to-school routes. Consequently, the percentiles of the measured BC concentrations to be compared were computed starting from each personal BC distribution of the home-to-school commuting.
Afterwards, we compared drawn segments with the data collected from the personal monitoring campaigns (Figure 33). This was possible by using GPS technology, which allowed us to link personal BC to each specific segment. The final sample was composed by 40 schoolchildren that went to school on foot, drawn and coloured properly their home-to-school route on the map, and finally had accurate and reliable GPS signals. All the spatial analysis were conducted in GIS environment.

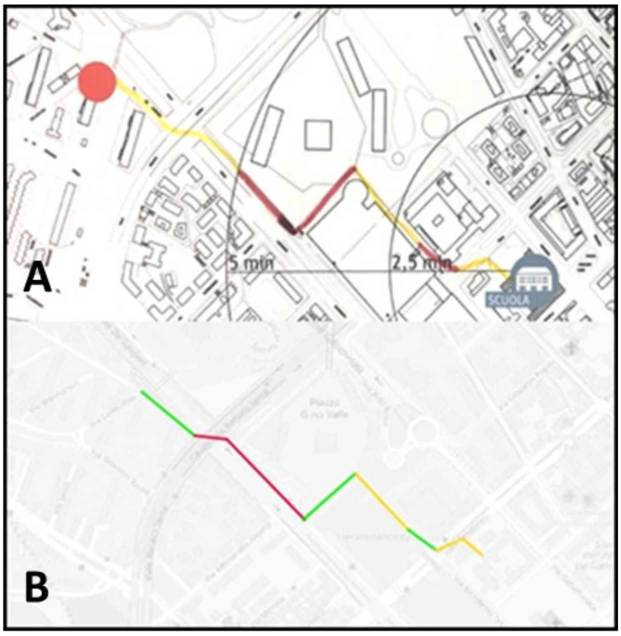


Figure 33. Picture A is an example of drawn home-to-school route coloured by schoolchildren according to their perception, while picture B is the same route re-drawn in GIS environment and coloured according to personal BC measures.

4.3. RESULTS AND DISCUSSION

The two environmental educational modules involved 128 children. Children pointing out the key places, both positive and negative, and the most critical areas according to their perception of pollution. They completed N.6 big posters featuring the neighbourhood and the catchment area of the school. Moreover, N.6 monitoring campaigns, one for each class, were successfully carried out in the neighbourhood in a participatory modality. BC data were collected and discussed with a gamification approach, focusing specifically on determinants. Children drew 120 alternative home-to-school routes with the aim to reduce their own perceived exposure. Among all SDGs, schoolchildren decided to focus on goals 3 “good health and well-being”, 7 “affordable and clean energy”, and 11 “sustainable cities and communities”, creating 8 posters on topics such as public transportation, bike sharing, green in the urban area and renewable energy. The posters were exhibited in a public event organized inside the school during which schoolchildren presented their works. Schoolchildren and parents involved in personal monitoring campaigns were 85 and 109, in May/June 2018 and January/February 2019 respectively. A response rate of 66% and an increment of +28% were observed for the warm- and the cold-season personal monitoring campaign recruitment respectively.. This result is probably connected to the level of engagement of both schoolchildren and teachers, that was likely to be achieved thanks to the planning of the ludical laboratories that were performed amidst the two personal monitoring campaigns.

Finally, Table 10 gives the results of the comparison between measured and perceived levels of BC during the on foot home-to-school commuting.

Table 10. Agreement between BC personal measures during home-to-school routes and BC concentration levels perceived by schoolchildren. In red overestimates, in light blue underestimates. The green lines were compared to the values <50th percentile, the yellow ones to the values included in 50-75th percentile range, the red ones to the values >75th percentile.

		Measured BC			TOT
		<50th	50th-75th	>75°	
Perceived BC	(green)	**39**	11	14	**64**
	(yellow)	50	**18**	21	**89**
	(red)	18	18	**15**	**51**
TOT		**107**	**47**	**50**	**204**

In particular, an agreement between perceptions and measurements was observed in the 25% of the cases. Children overestimated black carbon concentration in the 42% of the analysed segments. Finally, an underestimation of BC concentrations was observed in the remaining 23% of the cases.

Even if the Chi-squared test does not highlight differences (p=0.055), it is possible to see an overall tendency to overestimation. This is probably due to:

a) the higher concentration of air pollution that occurs during morning rush hour in Milan than in other time-windows of the day. This could in some way over-sensitize children;
b) the specific area that is one of the most congested in Milan, especially during the morning rush hour
c) a general over-sensitization due to the engagement in the MAPS MI project

4.3.1. Challenges of the participatory approach

Although the involvement in this kind of process it is likely to lead to interesting results and mutual learning, as a researcher it is important to be aware of the complexity of such an approach. Designing an education intervention, as well as conducting actively a part of the activities can be highly demanding. In particular, it is important that the involved researchers in the ludical laboratories are suited for this kind of intervention and show to be deeply committed. For instance, classrooms of more than 20 children are not simple to engage and manage. In a preparatory phase, it is important to be aware of this, otherwise the intervention could even lead to negative results in terms of engagement that could mean unsatisfactory rate of recruitment and low quality of data.

Moreover engage schoolchildren not always is equal to engage their parents. However, the engagement of the adults is fundamental if we consider that many of the activities planned for the personal monitoring campaign.

Moreover, due to schedule and funding issues, the “action” part of the intervention was limited to a single event organized inside the school during which the results of the two series of ludical laboratories were presented to all the school. A single event can’t be judged as sufficient to spread the content of the work and this was a source of discontent for all the partners. By treasuring this experience, in the future a more careful planning is needed.

4.4. CONCLUSION

A participatory approach that involves teachers, children and their families in a research project is a powerful way to raise awareness about scientific culture, air pollution and sustainable way of living. This approach can also help researchers to keep the lights on the project, increasing the level of engagement of the stakeholders. In this context, the partnership with the ABCittà cooperativa ONLUS proved to be an effective tool to widen the scope of the project. Moreover, the reached level of engagement allowed increasing the number of participants from the first to the second personal monitoring campaign. Finally, this approach helped to work together with active, engaged and well informed schoolchildren during the two personal exposure monitoring campaigns.

5. MEASURING PERSONAL EXPOSURE OF SCHOOLCHILDREN TO BLACK CARBON

RESEARCH QUESTIONS AND ANSWERS

Q7: Is transportation period an important factor to consider when analysing schoolchildren personal exposure in everyday life?

A7: Although it accounts for only 5-10% of the overall daily personal exposure, transportation-related personal exposure is actually the most intense, i.e. exposes schoolchildren to the highest peaks of concentration in a very short period. Moreover, the hourly trend of BC personal exposure highlights that morning rush hour, and especially the home-to-school commuting, is the most critical daily time-window for personal exposure for both warm- and cold-season.

ABSTRACT

Introduction: In the last decade, a multitude of new evidences show up on the relation between air pollution and both long- and short-term health outcomes on children, from airways disorders, to cognitive impairment and even cancer. According to the World Health Organisation, more than 98% of Italian children are exposed to average annual concentrations of PM2.5 above 10 $\mu g/m^3$. In the specific area of Milan, the biggest city in northern Italy, transportation is one of the main source of air pollution. This chapter aims to investigate the contribution of different microenvironments to the total amount of personal exposure to BC in a group of about 100 schoolchildren.

Methods: During January and February 2019, 82 and 98 children respectively were involved in two seasonal personal monitoring campaigns by measuring for approximately one day their personal exposure to BC, tracking their movements inside their living area with GPS technology, and collecting other information by means of time-activity diaries.

Results: The personal BC average (±sd) was 1399 (±431) and 4224 (±2220) during the warm- and the cold-season, respectively. According to both the seasons, children were exposed to the highest BC concentrations during the MRH, the home-to-school commuting time window. The overall weight of transportation on total exposure was relatively small, but relevant (5-10%). Furthermore, the exposure during transportation was found to be the most intense.

Discussion: Transportation is a relevant source of personal exposure to BC for schoolchildren. In particular, the home-to-school commuting period represents the highest critical daily time-window for personal exposure.

5.1. INTRODUCTION

According to the World Health Organisation, more than 98% of Italian children are exposed to average annual concentrations of PM2.5 above 10 μg/m^3 (WHO, 2018). This is the currently standard that has been identified to protect the health of the largest part of general population, including vulnerable groups, such as children (Makri and Stilianakis, 2008).

Children in the prenatal and early life, up to adolescence, are the most affected part of the general population due to:

1) their habits: children tends to be less inactive and to spend more time outdoor than adults;
2) their physiology: they have an higher respiratory rate, as well as an higher metabolic rate during inactivity and body weight/volume of air intake;
3) their natural barriers and body systems are still not completely developed (Bateson and Schwartz, 2008).

In the last decade many scientific works have investigated the effect of exposure to air pollution, and especially traffic related air pollution (TRAP), and children health (WHO, 2018). Among the other, acute lower respiratory infections, leukaemia, asthma, and cognitive impairment are the most alarming. Moreover, many new discovers has been found on how pollutants interact with human organism. For instance, Calderon-Garciduenas et al., (2015) showed that the blood-brain barrier and the nasal epitheliums can be compromised in children exposed to urban air pollution (Calderón-Garcidueñas et al., 2015). More recently, Bovè et al (2019) found an higher number of Black Carbon (BC) particles in the foetal side of placenta tissues of pregnant women with high residential BC exposure and living close to major streets than those living at least 500 meter far from major roads (Bove et al., 2019).

The urban environment is an important source of different health risk factors, among which air pollution is one of the most threatening (Nieuwenhuijsen et al., 2018). In the specific area of Milan, the biggest city in the northern Italy among the most polluted areas in Europe (EEA, 2018), transportation is one of the main source of air pollution (ARPA, 2018a). Given this, BC, a primary pollutant strictly linked with fossil fuels combustion (U.S.EPA, 2012), represents an ideal marker to study personal exposure to air pollution. Furthermore, it is a valuable indicator of adverse health effects related to airborne particles (Janssen et al., 2011), it has been recognized as a carrier of harmful chemical

components such as Polycyclic Aromatic Hydrocarbons (PAHs)(Dachs and Eisenreich, 2000) and it is an effective marker of diesel exhaust, both classified as carcinogen for humans (IARC, 2008; IARC, 2014).
In this chapter the first insights of a two-season personal monitoring campaign is reported. A special focus is given to the contribution of different microenvironments (MEs)/activities to the total amount of personal exposure to BC in the city of Milan.

5.2. MATERIALS AND METHODS

5.2.1. Study area and project design

For this contribution, a two-season personal monitoring campaign was carried out during spring 2018 (April, May and June) and winter 2019 (January and February) in Milan, the biggest city of the Northern Italy, with approximately 3.2 million residents in its greater area. Measurements were performed on children aged 8-11 years. All of the children attended the same school located in the northwest part of the city of Milan (Figure 23). The study area, which can be overlapped to the school catchment area, is affected by one of the major gateways into the city, with intense motorized traffic especially during the so-called morning rush hour. After being informed, to effectively take part in the project, children and parents were asked to sign three informed consent formats as required by the new General Data Protection Regulation of the European Union (EU, 2016). To identify possible confounders and other influencing variables and to investigate children health status, parents were asked to fill a specifically developed questionnaire.
The involved schoolchildren were asked to wear a GPS device for 7 days, to fill a 1-week time-activity diary (TAD) in order to collect valuable information on locations, habits and diet and finally, and finally to wear a shoulder bag equipped with a microaethalometer model AE51 to measure black carbon.
All the planned preliminary and logistic operations were carried out in the ex-medical room of the school with the permission of the school board. To complete all the steps, each child and his/her parents had to pass three times to the room (Table 11).

Table 11. List of the planned meeting between researchers and participant during each personal monitoring campaign

Meeting	Day of personal monitoring	Who	Motivation
First	1st	Children+parents	Training, informed consent, GPS, questionnaire and activity-diary handover
Second	6th	Children	Second training, other equipment handover
Third	7th	Children+parents	Equipment, questionnaire and activity diary restitution

In particular, starting from Monday afternoon and up to Friday morning, every school day a group of 4-5 children was expected to pass by the medical room at 4 pm to take and wear the shoulder bag, and then to handback the equipment on the very next morning, after the home-to-school commuting and as soon as entered the school. Moreover, in preparation of each personal monitoring period and before each meeting a standard message was sent to schoolchildren parents to remind the main requests related to the activities.

For the occasion, taking advantage from the two environmental education modules carried out in the classrooms just before the starting of each of the personal monitoring periods, parents and children were well informed on the objectives of the monitoring and the general procedures to follow. In particular, they were asked to behave as in a normal day, doing all the planned activities, wearing the shoulder bag as long as possible, and anyway to leave the equipment in their proximity. For instance, if the child planned to go to the swimming pool, it was asked to leave the shoulder bag in the dressing room, while in the presence of outdoor activities, it was asked to leave the equipment as close as possible in the outdoor environment. Moreover, children and parents were trained on how to put the equipment down, stressing the importance of leaving it in a relatively opened environment (i.e. not locked in a wardrobe) and with the inlet tube free from obstruction.

In addition to the personal monitoring campaign, a microaethalometer MA200 (Aethlabs, San Francisco, CA) was placed inside the ex-medical room and measured black carbon continuously during the two seasonal monitoring periods.

5.2.2. 24-hour exposure attribution

Schoolchildren were equipped with the AE51 monitor set up with a flowrate of 100 ml/min and a time resolution of 1 minute. Each monitoring period lasted for only about 16h and

30 min, from the 4 pm of the 6th day to the 8.30 am of the 7th day of personal monitoring. To profile the entire 24 hour of exposure, the MA200 device placed inside the ex-medical room of the school was used. Ultimately, for each schoolchildren the daily personal exposure profile is composed by:

a) From 12 am to 4 pm of the 6th day the concentration measured by the MA200 inside the school;
b) From 4 pm of the 6th day to the 8.40 am of the 7th day the concentration measured by the worn AE51;
c) From the 8.40 am to the 12 am of the 7th day the concentration measured by the MA200 inside the school.

The 8.40 am of the 7th day was the time threshold for AE51 data, and was chosen to include the home-to-school commuting of the latecomers.

Moreover, some failures of the MA200 sampling device occurred, especially during the warm season. To deal with this issue, we extrapolated hourly BC concentrations at the MA200 site based on the urban background station operated by the air quality network (AQN) of Milan (ID station 10283, via Ponzio 34/6 – Pascal Città Studi). The applied correction factors ranged from 0.75 to 1.25 and were similar to the regression slopes between the reference site and the AQN site computed separately for the two monitoring periods.

5.2.3. Data cleaning and quality control

A total of 6 microaethalometers, 5 AE51 and 1 MA200 were used during the two monitoring campaigns. BC raw data were post-processed by removing reported errors, by smoothing with the Optimized Noise-reduction Algorithm (ONA)(Hagler et al., 2011), by applying correction factors to account for differences between devices and finally by applying other correction factors to account for the loading effect of the particulate on the filter (Weingartner et al., 2003).

In particular, intercomparison exercises were conducted pre- and post-monitoring for each campaign; these were performed by running all devices simultaneously and next to each other for about 24 h. The MA200 was the most recent device calibrated by the manufacturer, so we decided to consider it as the gold standard. By comparing the MA200 with the AE51s, we calculated correction factors for each device that were applied to the raw data to obtain $BC_{correct}$. These values ranged from 0.78 to 1, and representing the regression slopes between MA200 and AE51s. The applied factors were calculated as the mean value between the pre- and post-monitoring inter-comparisons. The final correction algorithm to estimate $BC_{correct}$ is reported as follows:

$$BC_{correct} = BC_{raw} \times (1 + ATN \times 0.007) \times F_{IC}$$

Where F_{IC} is the intercomparison factor, while 0.007 is the chosen k Virkkula's factor, a parameter that account for the different type of sampled aerosols and the consequent loading effect. In this contribution it was decided to apply the k factor suggested in Good et al. (2017) that was found by analysing more than 100 previously sampled filters (Good et al., 2017).

5.2.4. Activity diaries and GPS

The information reported on the last day of personal monitoring campaign were firstly checked with the GPS data to avoid possible misclassification, and then used to characterise each 1-minute BC data. The information linked with the GPS and TAD were: the microenvironment (ME) (in transport, at school, at home, public park, other); the type of transportation mode (car, on foot/scooter/roller blade/skateboard, bike, subway, motorcycle or public bus); the presence/absence of active cooking stove; the type of MEs (indoor/outdoor).

Afterwards, the total measured BC associated to each microenvironments (BC_{ME}) was used to calculate the relative weight of each ME ($ME_{contrib}$) to the overall personal exposure (BC_{tot}) by applying the following equation:

$$ME_{contrib} = \frac{BC_{ME}}{BC_{tot}}$$

While to compute the related intensity of exposure ($ME_{intensity}$) we used:

$$ME/act_{int} = \frac{\frac{BC_{ME}}{BC_{tot}}}{\frac{t_{ME}}{t_{TOT}}}$$

Where t_{ME} is the total spent time in the selected ME and t_{TOT} is the total time of the personal monitoring campaign. The above-mentioned equations are the same used by Buonanno G et al (2013), Rivas et al (2016), and Jeong H et al (2017).

5.2.5. Statistical analysis

R studio and several R packaging were used to manipulate and clean data, as well as perform the statistical analysis. In particular, t-test for paired samples was used to test differences among different microenvironments

5.3. RESULTS AND DISCUSSION

5.3.1. Sample and general information

In Figure 34, the flow-chart of participants sums up the process that brought to the selection of the final sample. During the warm-season, personal monitoring campaign, from the starting 85 children that had answered the call, only 82 was confirmed and 73 were finally selected for the analysis. In this first case, the sample was composed by 57.5% of female and the average±sd age was 8.5 ± 0.7 years.

During the cold-season personal monitoring campaign, starting from the 109 children that had answered the new call, only 98 were confirmed and 89 were finally selected for the analysis. In this second time, the sample was composed by 51.7% female and the average±sd age was 9 ± 0.5 years. An increase in involvement was seen in the cold-season monitoring campaign that took place about 7 months later. This could be linked to the rising level of engagement of the third grade classes, teachers included, thanks to both:

a) the second series of ludical and experienced-based laboratories that took place amidst the two personal monitoring campaigns;
b) the word of mouth among schoolchildren and parents already involved in the first personal monitoring campaign.

A participatory approach that include environmental education intervention could lead to self-selection bias, by having the capacity to only involve those kids who have parents already sensitive about environmental issues (Hernan MA et al 2004). To control for this phenomenon, it was the teachers were involved from the very beginning in order to let them be part of the process. Consequently, the recruitment process was driven not only from the academic partner, but also from the teachers who may have offered greater guarantees of impartiality to the adults. However, since the original design of the project, this issue cannot be completely removed lowering the generalizability of the results.

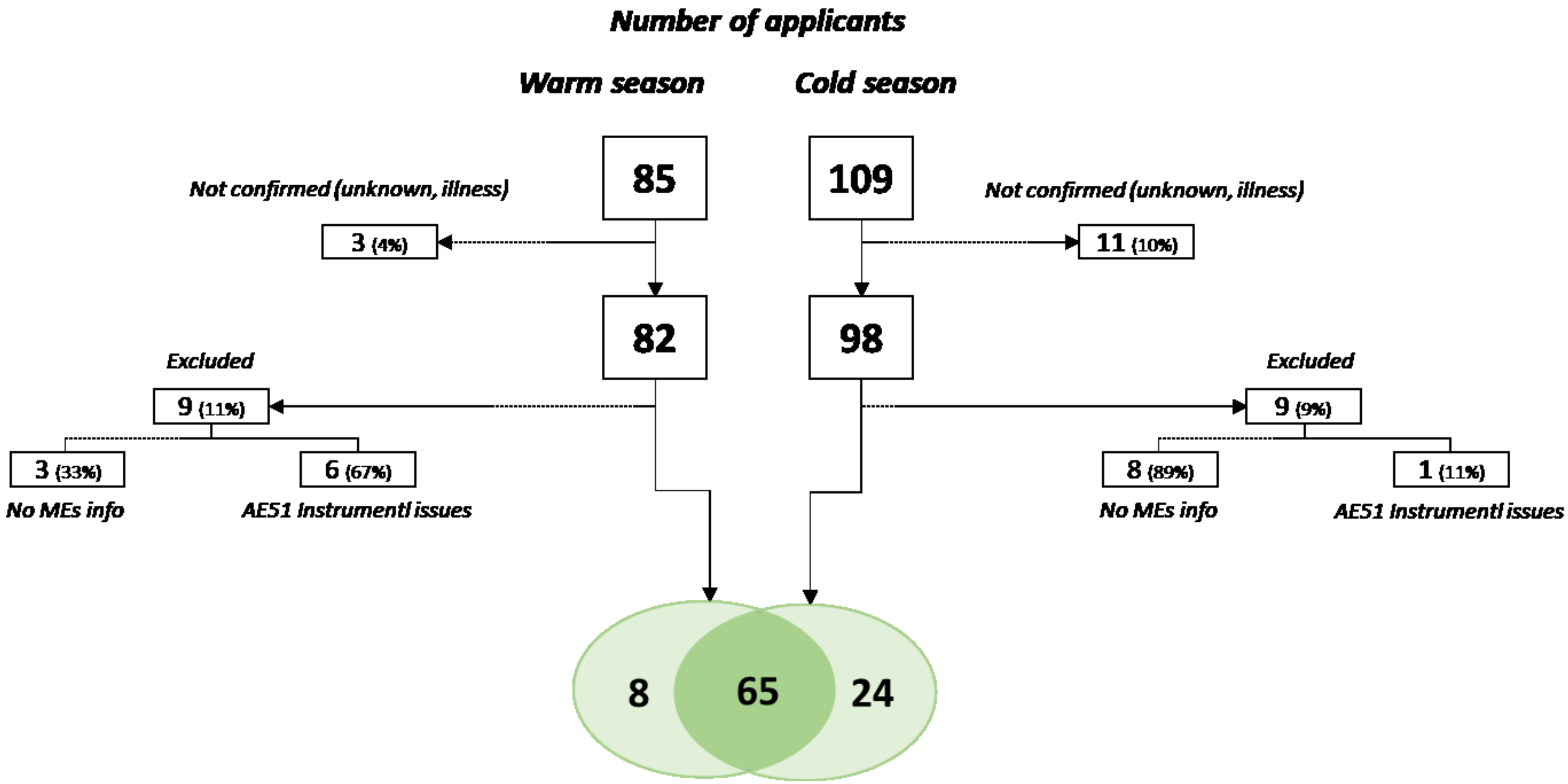


Figure 34. Flow chart of the personal monitoring campaign participants. Cases were excluded due to lack of information on microenvironments (MEs) and AE51 instrumental issues

The principal motivations for the exclusion from the analysis were:

a) lack of information due to low-quality data from time-activity diaries and/or from GPS devices;
b) AE51 instrumental issues.

In general, AE51 drawbacks are generally linked to a loss of battery linked with the impossibility to recharge the device from a day to another, and to the obstruction of sampling tube that may occur during the monitoring, especially when we talk about schoolchildren that usually moves and don't are expected to take too much care about devices. For the very same reason also GPS device can be easly forgotten in some microenvironment, or can be also put inside the schoolbag precluding its functioning.
Moreover, during the first personal monitoring campaign the latter motivation was the most frequent, while during the second personal monitoring campaign there was a higher level of lack of information due to low quality data. The lower percentage of instrument-related issues can be related to the increasing experience of the operators, while the low-quality data can be related to:

a) the newly and less experienced involved schoolchildren, who may even have been less supported by the parents;
b) the trouble for children to manage the TAD autonomously, and a contemporary lack of parents engagement.

Among all the participants included in the analysis, 65 were found to be involved in both warm- and cold-season monitoring campaigns. Among the 8 children that participated to the first monitoring campaign, but were not confirmed for the second one, only two decided voluntarily to not participate, while the others were either not confirmed due to illness or were excluded from the analysis for technical reasons.

5.3.2. Daily-seasonal time-activity pattern

In Figure 35 the pie charts show the relative contribution of MEs/activities in the two seasons. In particular, during the cold season children passed more time at home, while during the warm season spent more time in public parks and in other locations. However, these seasonal differences are not statistically significant. On the other hand, if we focus on the time spent indoor or outdoor, the t-test for paired samples shows a significant seasonal variation ($p<0.01$) with about the 96% of time spent indoor during the warm season, while the 94.5% during the cold season. Moreover, this difference could have been even stronger if we consider that we did not collect information on time spent in the playground during school time.

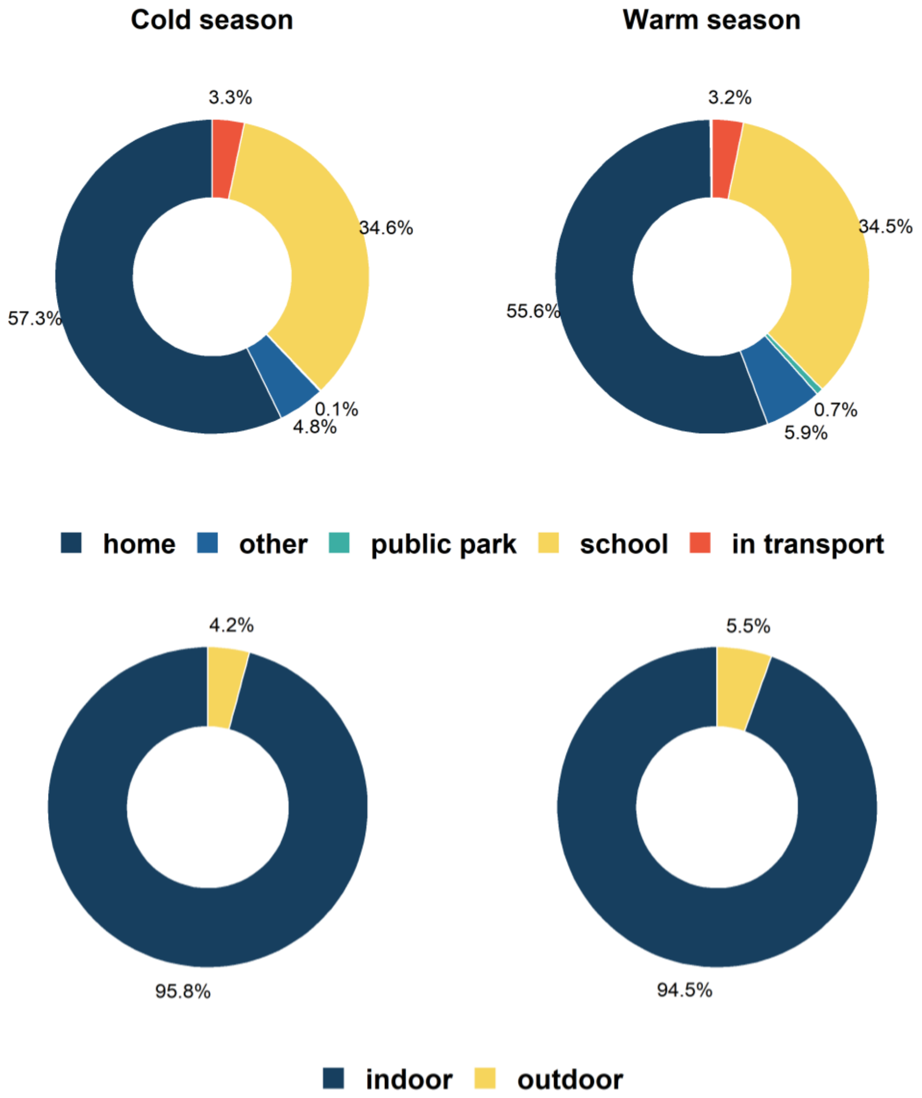


Figure 35. Seasonal time-activity pie charts

What we found seems to be comparable to other similar studies. For instance, Cunha-Lopes et al (2019), in a cohort of 9 schoolchildren (age 7-10 y) monitored for three consecutive working days in spring 2018, showed that children passed about 55% of their time at home, 30% at school and 5% in transport and 89% of the time in indoor environments (Cunha-Lopes et al., 2019). Moreover, Buonanno G et al (2013) in a cohort of 103 children (age 8-11 y) from an Italian middle town (resident population: 33,000 inhabitants) found that children spent 24% of their daily time-budget at school, the 64% at home and the 92% in indoor environment (Buonanno et al., 2013). In this case, the personal monitoring campaign was carried out between October 2011 and March 2012.

5.3.3. Overall seasonal personal exposure to BC

In Figure 35, the box plots of seasonal personal BC is reported. The strong difference between warm and cold season mirrors the same strong difference that we have already noted during the two seasonal fixed-sites monitoring campaigns (figure 26 among the other). In particular, on average personal exposure to BC was about 3.5 fold higher during the cold season than the warm season. This is probably due to the high BC concentration produced by both transportation, heating systems, and favoured by the frequent thermal inversions that usually occur in the so-called Po valley during winter.

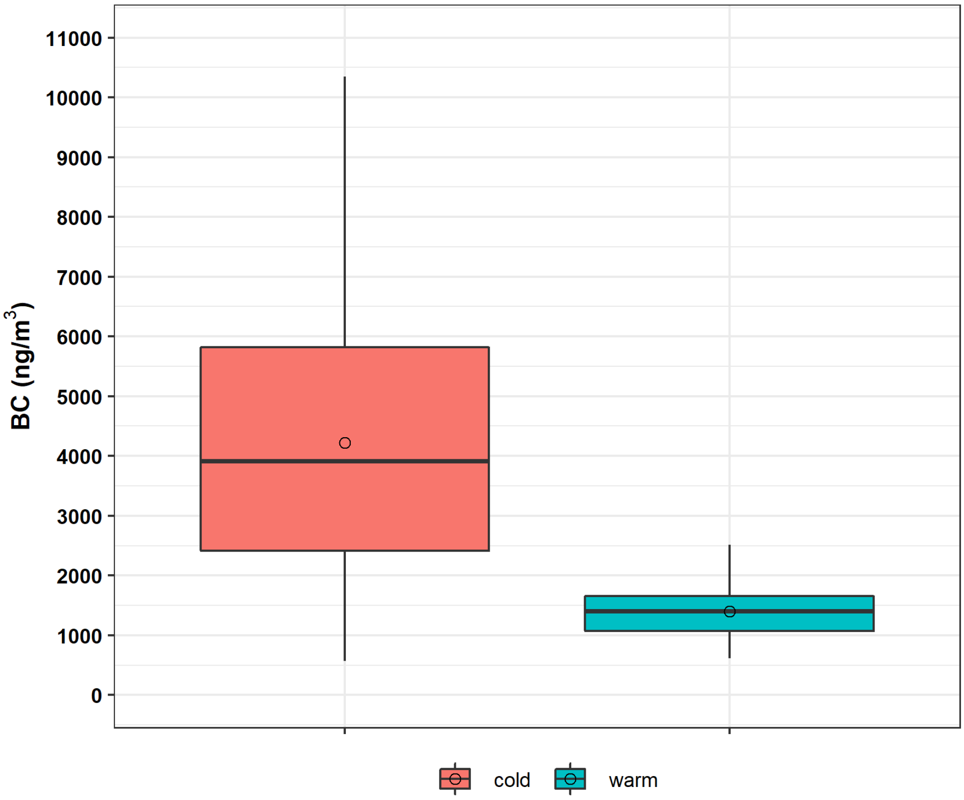


*Figure 36. Boxplots of seasonal personal BC. Inferior and superior whiskers represent: (Q1-1.5*IQR)<x < Q1, Q3<x<(Q3+1.5*IQR). Where x = data, Q = quartile and IQR is interquartile range.*

Moreover, during the cold season it is possible to observe a higher variability than during the warm season. This was expected and it is partly caused by the different time-activity patterns, but mostly it is caused by the different seasonal variability in background concentration (Figure 40). According to the boxplots, no outliers (x<Q1-1.5*IQR, x>Q3+1.5*IQR) were identified. The overall personal BC concentrations are given in Table 12.

Table 12. Statistics of measured personal BC concentrations (ng/m³), presented as average, standard deviation, minimum and maximum. The values are computed starting from the averages of all personal BC measured concentrations.

Season	n	mean	sd	min	max
Cold	89	4224	2220	574	10350
Warm	73	1399	431	618	2514

At a first analysis, concentrations are comparable to those measured in other scientific contributions. In particular, Buonanno G et al (2013) in the 2012 cold season measured an average of 5.1 μg/m³ in a cohort of 103 children (age 8-11 y) from an Italian congested (as reported in the paper) middle town (Buonanno et al., 2013). These measurements were made 7 years before ours, so it is possible that, for instance, the new emission standards for vehicles have influenced these concentrations. Moreover, only the 16% of the children went to school on foot. This can be read as an indicator of a lower inclination than ours participants (52% went to school on foot) to the active transportation that in general exposes people to lower air pollution concentration than those that use motorize vehicles (De Nazelle et al., 2017).

In a long-duration monitoring campaign in 2013/2014, Paunescu et al (2019) monitored 95 children (24h each, 47 during the warm season) aged 9 (sd ±0.2) years. The average personal BC measured concentrations were 1.27 μg/m³ and 1.73 μg/m³ in warm and cold season respectively. These results appear comparable limiting the analysis to the warm season, while cold season BC average is more than two fold lower than our result. This can be partially explained by the fact that in Paris air quality is better than in Milan (EEA, 2018), and it is also probably influenced by those measurements carried out during holidays according to which it is reasonable to expect lower values.

However, further investigation need to be done in order to identify all the determinants of this differences.

5.3.4. BC personal 15-min daily trend

In Figure 37, seasonal 15-min median and IQR BC trends during personal monitoring campaign days are presented; highest peaks were found corresponding to the time with the highest traffic, i.e. morning rush hour period. This is the daily time-window during which children commute to school (7-9 am).

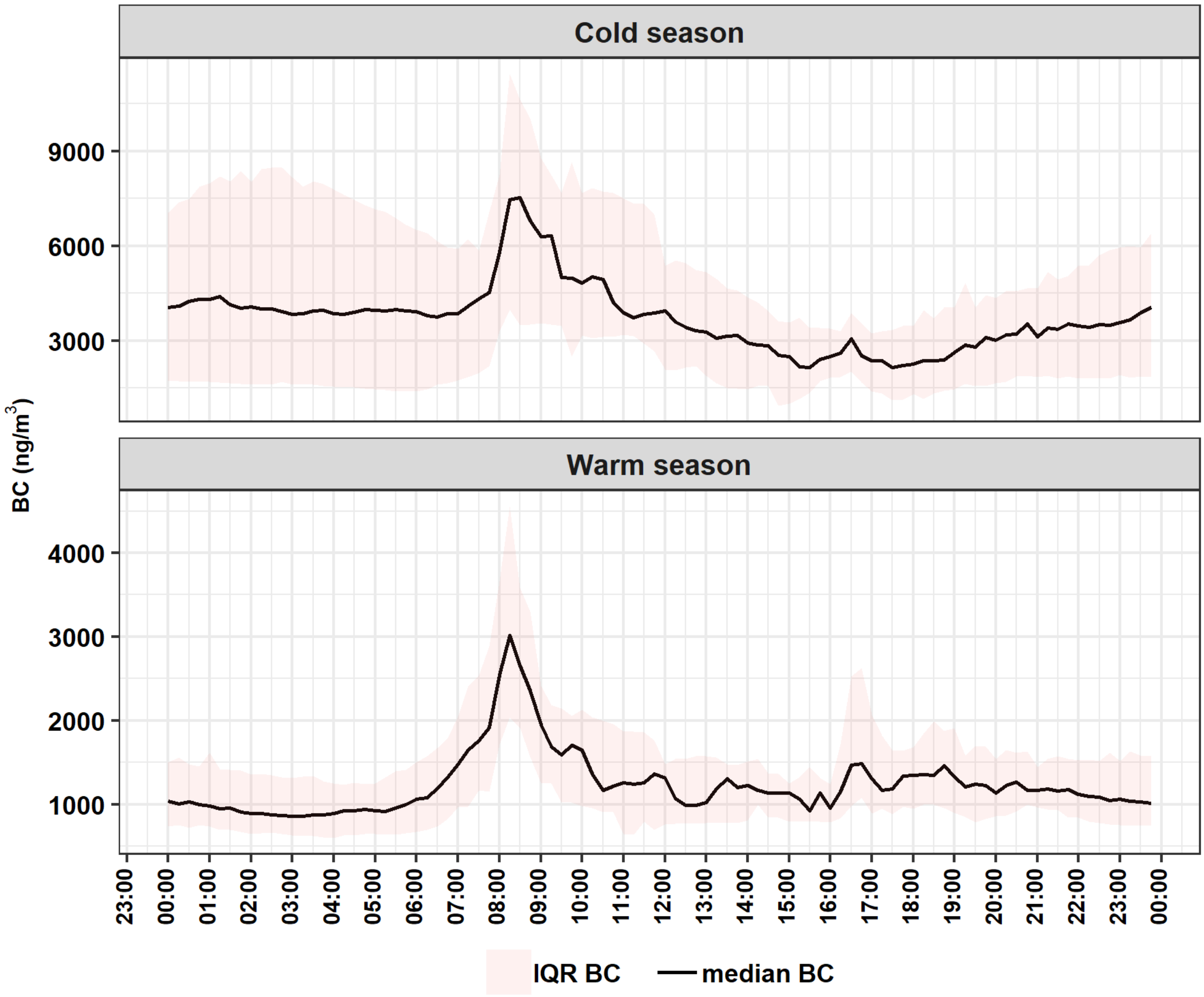


Figure 37. 15-min daily trend of personal BC concentrations during the warm- and the cold- season monitoring campaigns. Data are presented as median and IQR values for BC concentrations.

Moreover, it is possible to identify other peaks during both warm and cold seasons. In particular, between 4 pm and 5 pm it is clear the contribution of the end-time of the school and the consequent daily time-window during which children are involved in other activities such as transportation, sport, leisure time etc. (5-7 pm). Other less pronounced peaks are presented between 7 pm and 9 pm probably representing indoor sources such as second-hand smoke or cooking. Finally, the consistent increase in BC concentrations

that occurred during the cold-season night times is likely to be attributed to the frequent thermal inversions that characterize the Po valley.
The two just-mentioned seasonal trends appear slightly similar to the ones previously presented in figure 27 (left quadrants only) that was built up on fixed monitoring sites measurements. However, it is clear that the two can't be completely overlapped, especially for the different behaviour during the second part of the day. The lack of afternoon peaks of exposure during the cold season can be attributed to the fact that, once outside school, schoolchildren passed more time in indoor environments that constitute a filter to outdoor evening peak of concentration. In this case the peak of exposure is replaced by an increasing trend in concentration probably due to:

a) infiltration at home;
b) the meteorological condition that during the evening and the night favour the accumulation of contaminants at the ground.

This make emphasis to the fact that it is not possible to attribute a personal exposure value using only outdoor monitoring sites without introducing biases.

5.3.5. The role of time-activity patterns in personal exposure

As expected, home and school are the major contributors to the total BC exposure. Moreover, the same patterns seems to repeat in both seasons with an increase in weight of public garden, other extracurricular ME/activities and transport during the warm season. On the other hand, if we consider not only the relative contribution, but also the intensity of exposure, transportation represents the most critical microenvironments (Figure 38).

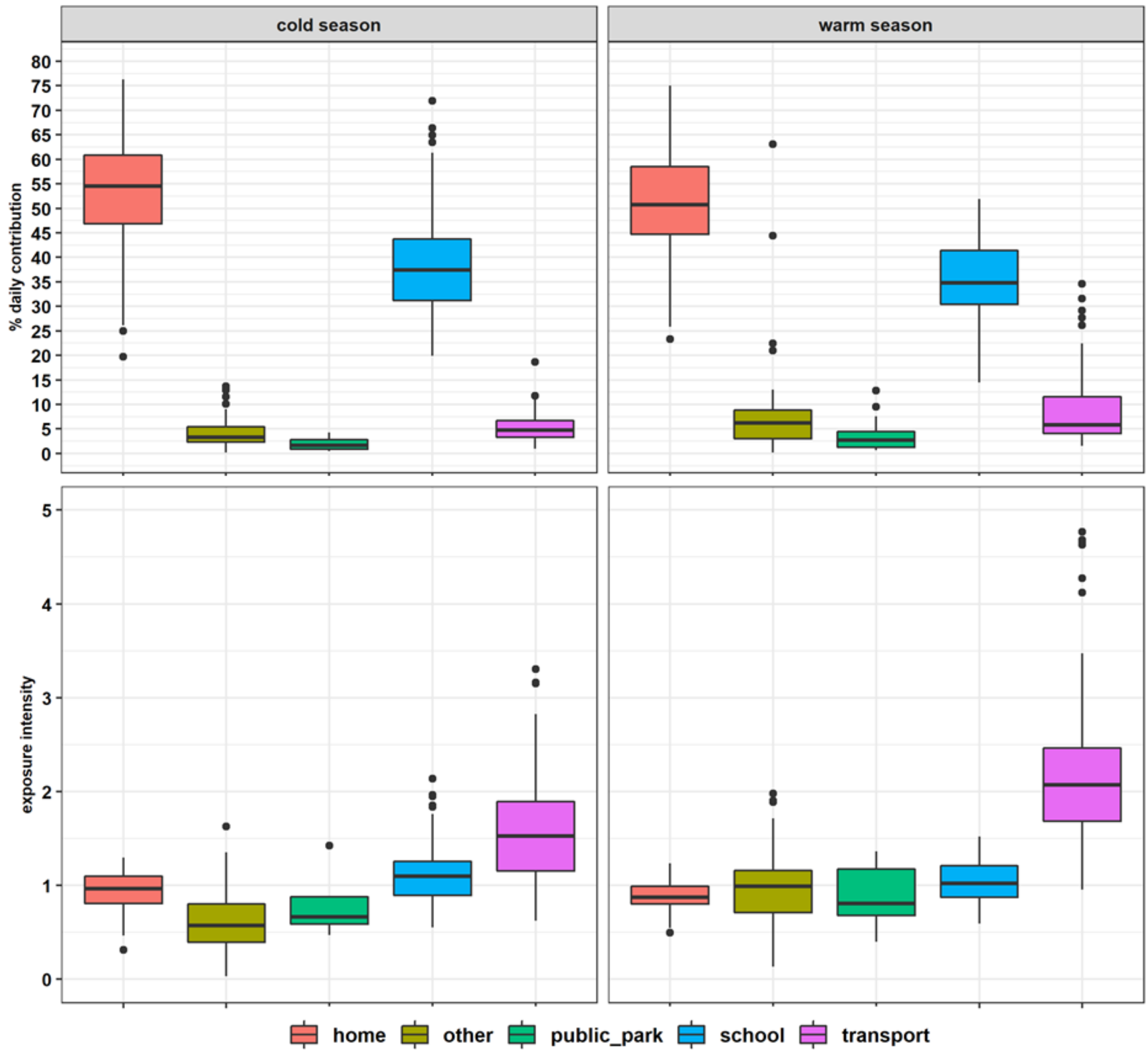


Figure 38. Seasonal relative contributions of MEs/activity on the total exposure (upper quadrants), and seasonal intensity of exposure per MEs/activity (lower quadrants)

These results are confirmed by other similar studies. In particular, Rivas et al (2016) found a very similar relation than the one we found (2.1 exposure:time). Moreover, using potential dose as numerator (i.e. exposure*inhalation rate:time), Buonanno et al. (2013) and Jeong H et al (2017) found a dose intensity linked to transportation equal to 2.8 and 2.2, respectively(Buonanno et al., 2013; Jeong and Park, 2017; Rivas et al., 2016).
These results confirm that to reduce air pollution exposure of schoolchildren it is fundamental to focus on home and school environment, however it is not possible to ignore the contribution of transportation related to which it is likely to find an high number of exposure peaks (*Dons et al., 2019)*.

5.4. CONCLUSION

The results suggest that home and school are the major contributors of the total personal exposure to BC among the recruited schoolchildren. However, exposure during transportation is relevant, and the most intense, i.e. its relative contribution to the total amount of BC exposure is very high if compared to its short duration. Moreover, hourly trends of BC personal exposure show that the highest peaks of exposure occur during the morning rush hour of both warm- and cold-season. Therefore, home-to-school commuting confirms to represent a highly critical moment for children personal exposure to air pollution in urban environment.

6. VALIDATION OF A LUR MODEL BY USING PERSONAL EXSPOSURE DATA AND IDENTIFICATION OF THE CLEANEST HOME-TO-SCHOOL ROUTES

This chapter is based on:

Boniardi, L; Dons, E; Campo, L; Van Poppel, M; Int Panis, L; Fustinoni, S; 2019. *Is a Land Use Regression Model Capable of Predicting the Cleanest Route to School?* Environments, 6, 90. DOI: 10.3390/environments6080090

RESEARCH QUESTIONS AND ANSWERS

Q8: Is it possible to apply a LUR model to mitigate the risk of exposure to air pollution, and in particular to identify the least expositive home-to-school paths?

A9: Despite the tendency to underestimate, the model estimates show moderate-to-good agreement with the personal measuring technique, explaining approximately the 55% of variability inside the personal BC distribution. In particular, our data suggest that a LUR model developed by using measured MRH-BC concentrations is a valuable tool to analyse home-to-school paths and select the cleanest one. This approach can help policy makers in the attempt to lower personal exposure of selected categories, i.e. schoolchildren going to school.

Q9: Can a LUR model developed on fixed monitoring sites help to reduce misclassification of exposure by integrating transportation period?

A9: Our exercise shows that by applying a LUR model to estimate personal exposure it is likely to obtain a systematic underestimation. Moreover, a trend to underestimate more was found when average personal BC was elevated. However, the moderate-to-good agreement between modelling approach and personal measuring technique suggests that this experience is a valuable starting point toward more refined tools for lowering exposure misclassification bias in the framework of environmental epidemiology studies.

ABSTRACT

Introduction: Land Use Regression (LUR) modeling is a widely used technique to model the spatial variability of air pollutants in epidemiology. In this study, we explore whether a LUR model can predict home-to-school commuting exposure to black carbon (BC).

Methods: During January and February 2019, 43 children walking to school were involved in a personal monitoring campaign measuring exposure to BC and tracking their home-to-school routes. At the same time, a previously developed LUR model for the study area was applied to estimate BC exposure on points along the route.

Results: Personal BC exposure varied widely with mean SD of 9003 4864 ng/m3. The comparison between the two methods showed good agreement (Pearson's r = 0.74, Lin's Concordance Correlation Coefficient = 0.6), suggesting that LUR estimates are capable of catching differences among routes and predicting the cleanest route. However, the model tends to underestimate absolute concentrations by 29% on average.

Discussion: A LUR model can be useful in predicting personal exposure and can help urban planners in Milan to build a healthier city for schoolchildren by promoting less polluted home-to-school routes.

6.1. INTRODUCTION

Land Use Regression (LUR) modelling is a widely used technique to model spatial variability of air pollutants. This approach was used in both urban and non-urban environments, usually with the aim of better predicting exposures in large epidemiological cohorts (Hoek et al., 2008; Ryan and LeMasters, 2007). Especially in cities, where an important part of pollution is from traffic, identifying spatial patterns of traffic-related air pollutants (TRAP) is fundamental to enhance the accuracy of exposure assessment (Dias and Tchepel, 2018). From personal monitoring studies, it is known that exposure while travelling is elevated mainly because of exposure peaks, and inhaled doses increase as well because of increased ventilation while traveling with active modes (Buonanno et al., 2013; Dons et al., 2019; Dons et al., 2012). Following this, TRAP in urban areas has been one of the main health issues in the past years (Nieuwenhuijsen et al., 2018) and among others, the traffic-related air pollutant Black Carbon (BC) has gained a primary role in this research field (Janssen et al., 2011).

Personal exposure to BC in urban environments is of high health concern to many people, and even more so for schoolchildren travelling to school during rush hours (Rivas et al., 2016). In particular, we recently found that morning rush hour (MRH) during weekdays is the most critical period for exposure to TRAP in Milan with an average increase of BC concentration of about 1 $\mu g/m^3$ in both spring and winter time (Boniardi et al., 2019).

Moreover, in the past few years, many studies found an association between BC, changes in respiratory and cardiovascular markers, and behavioral and cognitive skills and disorders in children (Chiu et al., 2013; Provost et al., 2017; Rice et al., 2016; Sunyer et al., 2015). Most of the time, exposure was inferred from monitoring sites of the official Air Quality Network (AQN) or estimated by a LUR at the residential address or school site. Recently, Alvarez Pedrerol M et al. (2017) linked a IQR increase of BC exposure during home-to-school commuting to a reduction in the growth of working memory in a Spanish cohort of 1,234 children (aged 7-10 y). In this study, both exposure and home-to-school routes were estimated for each child, and despite this the results suggested that focusing on commuting periods can play a major role in the effort to link exposure and health outcomes (Alvarez-Pedrerol et al., 2017).

Furthermore, LUR models can give valuable information for public health officials and urban planners to reduce population exposure to air pollution and design health-promoting cities with less polluted routes for pedestrian and cyclists. For instance, Hankey S et al.

2016 combined facility-demand and LUR models to highlight exposure patterns during active travel suggesting that it should be possible to reduce exposure by ~15% after intervening on the given scenario (Hankey et al., 2017). Recently, several studies confirmed that the health benefits linked to active travel outweigh the risks such as exposure to air pollution or accidents, suggesting that the attempt to build more walkable and bikeable urban environments is worth the effort (Mueller et al., 2017; Tainio et al., 2016).

Given this picture, applying LUR modelling together with GPS monitoring to the specific case of home-to-school commuting could be a valuable approach to both enhance the quality of exposure assessment in epidemiological studies and to develop new public health policies focused on the youngest generation. First, however, it is necessary to validate this approach with mobile air pollution measurements to check the effectiveness of the method.

The aim of the present study is to compare LUR model estimates and the personal BC measured concentrations of 43 schoolchildren during home-to-school commuting. Moreover, we discuss whether a LUR model can be applied to identify cleanest routes to school. The current analysis focuses on children walking to school only; commuting with other modes would imply several assumptions (such as indoor-outdoor ratios, position on the road, breathing rates) that might lead to differential misclassification (Alvarez-Pedrerol et al., 2017). This contribution is part of the “MAPS MI, Mapping Air Pollution in a School catchment area of Milan”, whose aim is to study exposure to air pollution of schoolchildren in Milan, using LUR models, personal air pollution monitoring, GPS tracking, and biological monitoring with a participatory approach.

6.2. MATERIALS AND METHODS

6.2.1. Study design

The study area is about 25 km^2 large and is located in the north-west of Milan, which is the biggest city in the Northern Italy basin, with an estimated population of about 3.2 million residents (ISTAT, 2018). This area represents the catchment area of an elementary school, which is attended by more than 700 children, aged 6 to 11. For the MAPS MI project, we recruited 92 schoolchildren from the school (aged 7 -11) to participate in a 7-day personal monitoring campaign, performed from January 14 to February 19, 2019. During the whole period children were asked to wear a GPS device, model i-gotU GT600 (Mobile Action, Taiwan) and to fill in an activity diary. Additionally, during the last day, children wore a shoulder bag equipped with a micro-aethalometer, model AE 51 (AethLabs, USA), for personal monitor of BC in the breathing zone (Figure 39). This included the commuting to school in the morning, between 7:30 and 8:30. Once to school the children, with the help of their accompanying person, were asked to draw their route from home-to-school on a paper map of the study area.

Figure 39. Picture of children wearing the shoulder bag equipped with a micro-aethalometer model AE51. GPSs were worn as wristwatch or necklace.

Micro-aethalometers are optical devices that estimate the BC concentration by measuring the rate of attenuation (ATN) of a beam of light (880 nm) that passes through a T60 Teflon-coated borosilicate glass fiber filter strip over which air samples are drawn. These devices are commonly used in BC personal monitoring assessment applications thanks to:

a) their high portability;

b) the long lasting internal battery that allows about 24 hours of continuous monitoring;
c) the possibility to set different flowrates and time resolutions according to the specific scenario.

During our monitoring campaign, the pump flowrate was set at 100 ml/s on a 60-second time resolution. The optical measurement technique on filters may present some artifacts, the most important of which are the so-called shadowing effect, and the 880 nm beam of light multiple scattering (Weingartner et al., 2003). In particular, the first relates to the increased filter loading, while the latter is linked to both filter material and aerosol composition. An overall underestimation of BC concentrations is reported in literature linked to high attenuation values and for this reason, post-processing methods are important to enhance the quality of data (Good et al., 2017).
The project was submitted to and approved by the ethical committee of the University of Milan and the elementary school board. Before the start of the monitoring period, information and explanations about the project were given to both parents and children and permission forms were signed.

6.2.2. Data analysis

For the present report, we focus on the route of children walking to school, resulting in a total of 43 cases (56% female). Only BC data associated with home-to-school commuting were used in this study. Raw BC data were post-processed by removing observations showing an error message, smoothing and accounting for the loading effect. In particular, we applied the Optimized Noise-reduction Algorithm (ONA) (Hagler et al., 2011), and the algorithm from Virkkula et al. (2007) (Virkkula et al., 2007) to account for the loading effect. Furthermore, correction factors were applied to each device to correct for differences among them. These factors resulted from two intercomparison monitoring exercises carried out both before and after the personal monitoring campaign by running all devices simultaneously and next to each other for 24 hours. The golden standard was micro-aethalometer model MA200-105 because of:

a) the device was equipped with the Dualspot© technology that automatically accounts for the loading effect;
b) the device was the most recent device calibrated by the manufacturer.

The final post-processing equation is the following:

$$BC_{correct} = BC_{raw} \times (1 + ATN \times K) \times F_{IC} \quad (1)$$

Where: $BC_{correct}$ is the post-processed BC personal exposure; BC_{raw} is the raw measurement performed by the micro-aethalometer; ATN is the measured rate of attenuation; K is the chosen Virkkula's factor; F_{IC} is the intercomparison factor. The K factor represents an empirically derived constant that has the aim to correct the BC concentration underestimates that occur in presence of filter overloading. In particular, we used the K factor equal to 0.0054 calculated from a long-term monitoring campaign at the urban site of Helsinki (Virkkula et al., 2007); F_{IC} ranged from 0.78 to 1.00, representing the regression slopes between MA200 and AE51s calculated by putting together both pre- and post- intercomparison datasets.

A Land Use Regression (LUR) model was previously developed (Boniardi et al., 2019), and was based on a 5-week multi-site BC monitoring campaign in the school catchment area in January and February 2018. 34 sites were sampled, one week each, using micro-aethalometers, model AE51. The cold-season MRH LUR model used in this paper was developed by using the ESCAPE methodology (Eeftens et al., 2012), and selecting only weekdays BC data measured from 7 am to 9 am. A supervised forward stepwise procedure was performed using as dependent variable the seasonal estimated BC concentrations and as explanatory variables a pool of traffic and land use variables calculated with QGIS software (QGIS *Team*, 2016). The best model was then selected according to the higher coefficient of determination (adjusted R^2) and lower Root Mean Square Error (RMSE). The final cold-season MRH LUR model was the following:

$$BC_{Cold\ MRH\ LUR} = 3706 + (12.24 \times TOT\_INVDist\_MRH) + (0.001007 \times TRAFLOAD\_100\_MRH) \quad (2)$$

Where *TOT_INVDist_MRH* is the ratio of the number of vehicles on the nearest road during MRH and the distance to that road; while *TRAFLOAD_100_MRH* is the sum of the number of vehicles on each road during MRH multiplied with the length of the roads in a circular buffer of 100 meter of radius. The model R^2 is 0.65, the RMSE is 434 ng/m^3. The Leave One Out cross Validation (LOOcV) resulted in a R^2 of 0.51 and a RMSE of 509 ng/m^3.

The routes from home-to-school were drawn in a GIS environment following the procedure below:

a) uploading GPS data and selecting only routes from home-to-school;

b) checking the paths by comparing them with the routes drawn by children and parents;
c) adjusting home-to-school routes, i.e. missing GPS data were replaced with the drawn path;
d) converting routes to 1 meter equidistant points along each line. Then, for each point we estimated the BC concentration by applying the MRH LUR model.

To remove possible outliers from the distribution of modelled BC values, a threshold equal to the highest seasonal BC value from the 2018 monitoring campaign +20% was set (Henderson et al., 2007).

Before comparing personal exposure data and MRH LUR estimates, $BC_{Cold\ MRH\ LUR}$ values were rescaled as measurements were done on different days with different background concentrations. For this, we retrieved data from an urban background site of the Air Quality Network (AQN) of Milan (ID station 10283, via Ponzio 34/6 – Pascal Città Studi), located ~6 km far from the study area. In particular, BC MRH data measured during the 2018 monitoring campaign period (BC_{AQN_2018}) were compared to those measured on the specific day of the 2019 personal monitoring campaign (BC_{AQN_day}). Finally, rescaled BC (BC_{LUR_day}) was obtained by applying the formula below:

$$BC_{LUR\_day} = BC_{Cold\ MRH\ LUR} \frac{BC_{AQN\_day}}{BC_{AQN\_2018}} \quad (3)$$

R (R Core Team, 2014) was used for the statistical analysis. In particular, we performed descriptive statistical analyses, Pearson correlation analysis to compare measured and modelled exposures along the routes, and we produced a Bland-Altman plot to assess agreement between the two methods. Lin's concordance correlation coefficient was used to compare BC_{LUR_day} model estimates and the gold standard represented by the average measured personal BC concentration. The coefficient ranges from 0 to ±1, showing:

a) high concordance near +1;
b) high discordance near -1;
c) no correlation around 0.

6.3. RESULTS

The average distance travelled by schoolchildren was 650 m (SD: 258 m), the longest route was 1403 m, while the shortest was 114 m (Table 13). The commuting trips were spread all around the school, covering approximately the entire school catchment area. Personal BC exposure while walking to school varied widely across the monitoring campaign. The mean ± SD measured BC was 9003 ± 4864 ng/m^3, while 1014 ng/m^3 and 25,097 ng/m^3 respectively, were the lowest and highest values. BC values measured at the AQN background station for the monitoring period showed on average lower concentration with mean ± SD equal to 6635 ± 3730 ng/m^3.

Table 13. Study characteristics. 43 children who walked to school were included in the analysis. 24 children were female, 19 were male.

	Mean ± SD	**Min-max**
Age (years)	9.1±0.7	7-11
Distance (m)	650 ± 258	114 – 1,403
Measured BC (ng/m^3)	9,003 ± 4,864	1,014 - 25,097
MRH LUR BC estimate (ng/m^3)	6,365 ± 3,676	1,365 - 12,886
MRH AQN background BC (ng/m^3)	6,635 ± 3,730	1,350 - 14,050

Figure 40 shows the temporal trend of BC concentrations during the 2019 monitoring campaign. The black line represents the MRH averaged values from the AQN monitoring site and shows a marked variability during the whole period. The circles represent the average BC exposure of the schoolchildren during their home-to-school commute.

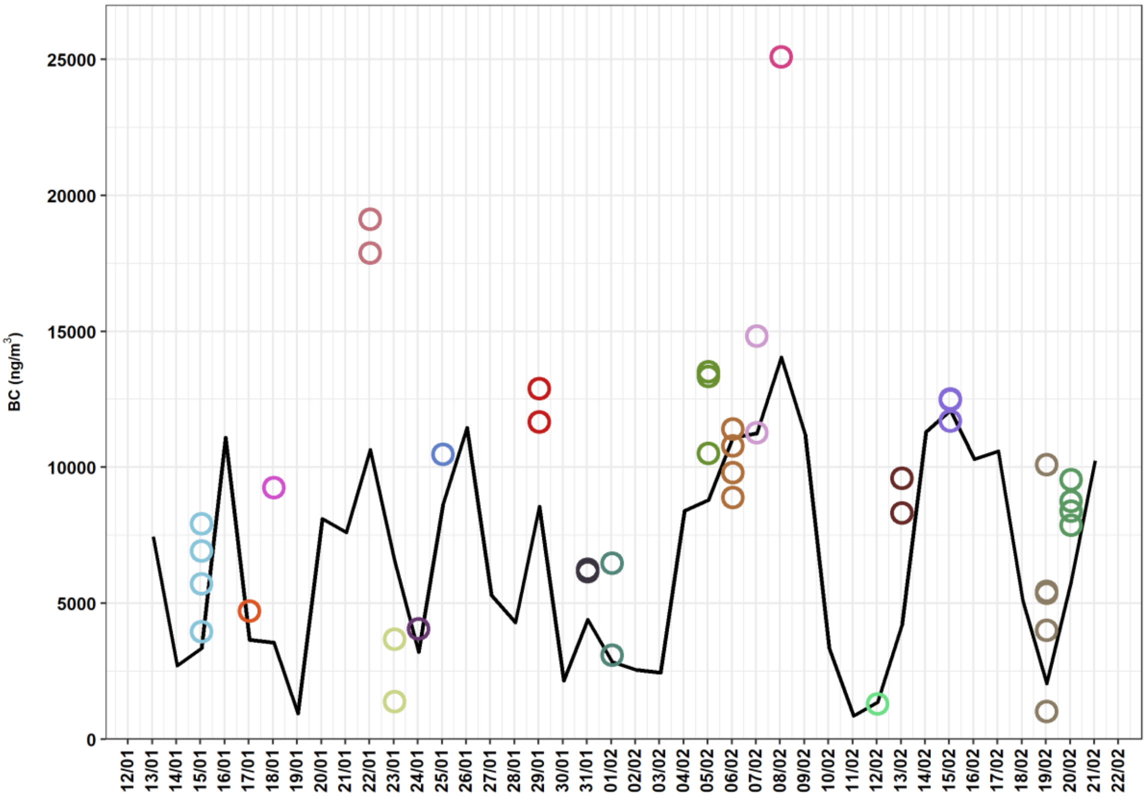


Figure 40. Average MRH BC concentrations measured at an urban background reference site (black line) and average home-to-school commuting personal exposure values (circles) during the 2019 personal exposure monitoring campaign. The colors of the circles correspond to the different days of monitoring.

Personal BC_{LUR_day} estimates averaged over all points along the route ranged from 1,365 ng/m^3 to 12,886 ng/m^3 with mean ± SD of 6365 ± 3676 ng/m^3. Figure 41A shows high correlation between average home-to-school estimates and personal BC measures (r=0.74, p<0.001). However, on average BC_{LUR_day} model showed to underestimate concentrations of about 29% (Table 14). The Bland-Altman plot visualizes this underestimate (blue line), and shows a slight trend in under- and over-estimating values at the extremes (Figure 41B). Lin's Concordance Correlation Coefficient is 0.6 (95% C.I.: 0.43 - 0.74) and shows moderate concordance between methods.

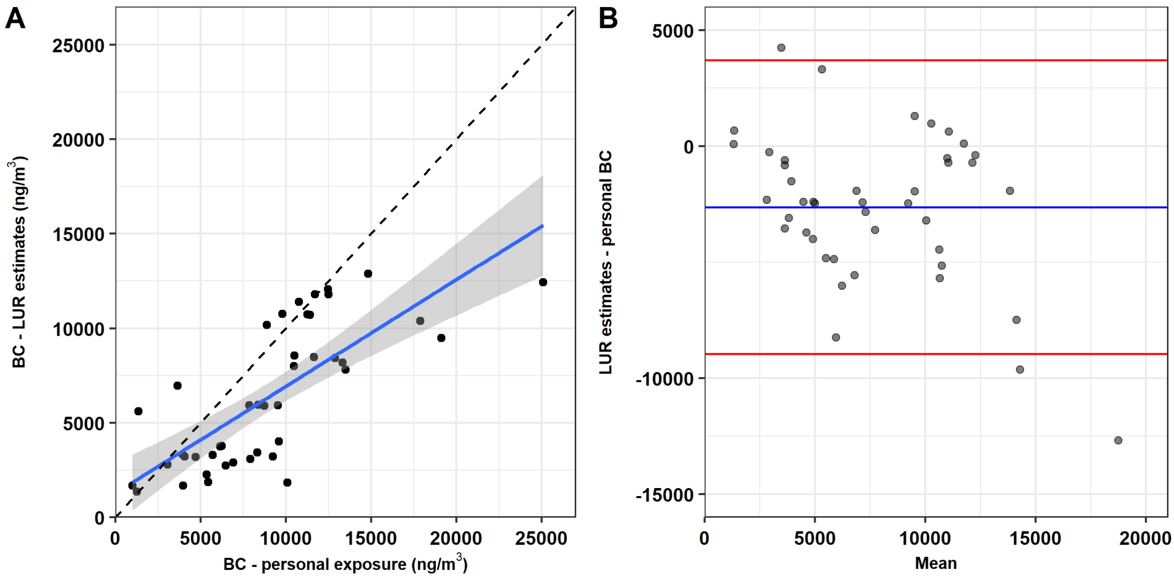


Figure 41. Correlation plot (A) with confidence interval set at 95% (shadowed area), and reference line (black dashed line). Bland-Altman plot (B) with average line (blue line), and ±1.96 SD lines (red lines). According to A, Pearson's correlation coefficient is 0.74. In the comparison between the two methods, Lin's Concordance Correlation Coefficient is 0.6 (95% CI: 0.43 - 0.74).

Table 14 and Figure 42 show five case studies comparing personal measured BC and BC_{LUR_day} estimates along home-to-school routes on two different days. On February 13, measured BC of Route 2 was higher by 15% than Route 1. This difference is similar to the one observed between BC_{LUR_day} BC estimates for the same routes, although in absolute terms these last were about 30% smaller than the measured BC. On February 06, measured BC of Route 5 was higher by 22% and 10% than Route 4 and Route 3, respectively; the BC_{LUR_day} estimates followed a similar trend, but differences were smaller. According to the BC_{LUR_day} estimates, for this day the model tends to overestimate measured BC of about 6-15%. A visual comparison between measured BC and BC_{LUR_day} estimates is given in Figure 42. According to both measured BC and BC_{LUR_day} estimates, near the school entrance there were high BC concentrations, probably because of vehicles dropping children in front of the school.

Table 14. Main information about the five case studies (see also Figure 4), such as home-to-school distance, measured and estimated BC statistics. For comparison, the mean concentration of BC at the AQN monitoring site is reported.

	Day	**Distance (m)**	**Measured BC (Mean ± SD, ng/m^3)**	**MRH LUR BC estimate (Mean ± SD, ng/m^3)**	**MRH AQN background BC (Mean, ng/m^3)**
Route 1	13/02/2019	482	8,320 ± 1,892	5,633 ± 761	4,200
Route 2	13/02/2019	486	9,591 ± 2,189	6,576 ± 871	4,200
Route 3	06/02/2019	939	9,798 ± 2,217	10,753 ± 2,510	11,100
Route 4	06/02/2019	492	8,884 ± 2,125	10,169 ± 1,954	11,100
Route 5	06/02/2019	1403	10,779 ± 4,594	11,390 ± 2,490	11,100

Meteorological parameters during both the 2018 and 2019 monitoring campaigns, as measured at the nearest Milan air quality network station (piazza Zavattari, ~ 1 km) are reported in Supplemental plot S11 and S12. Moreover, the statistics of BC concentrations for the same two periods are reported in Table S13, as measured at the background site of the Milan air quality network station (ID station 10283, via Ponzio 34/6 – Pascal Città Studi).

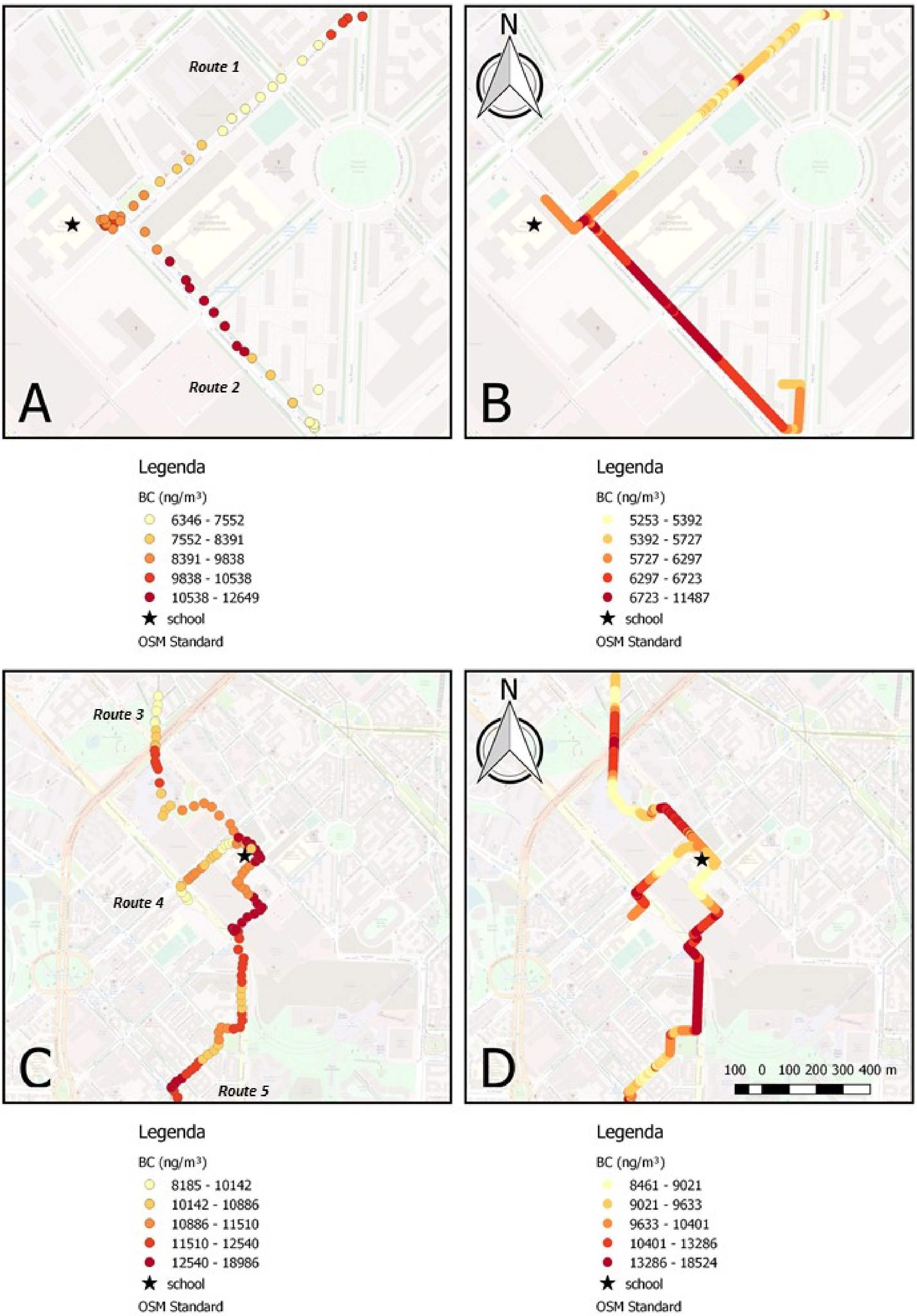


Figure 42. Visual comparison between measured BC and BC_{LUR_day} estimates of five different home-to school routes. In panel A and C there are the measured BC, while in panel B and D there are the corresponding BC_{LUR_day} estimates. The color is given by the quintile of the BC distribution for each day.

6.4. DISCUSSION

To the best of our knowledge, this is the first time that a LUR model was tested to assess its reliability in estimating BC exposure during home-to-school commuting. We measured personal exposure to BC along home-to-school walking routes for 43 schoolchildren showing considerable variability across the entire monitoring period. Furthermore, a rescaled MRH LUR model, previously developed for the study area, was applied to the same routes estimating personal exposure to BC. On average, the model underestimated the measured personal exposure; however, the correlation between the two methods was high. This suggests that LUR models could be successfully used to:

a) highlight relative differences among routes;
b) analyse spatial patterns inside the school catchment area during home-to-school commuting;
c) predict the cleanest route from a random home in the study area to the school (Figure 41, 42 and 43).

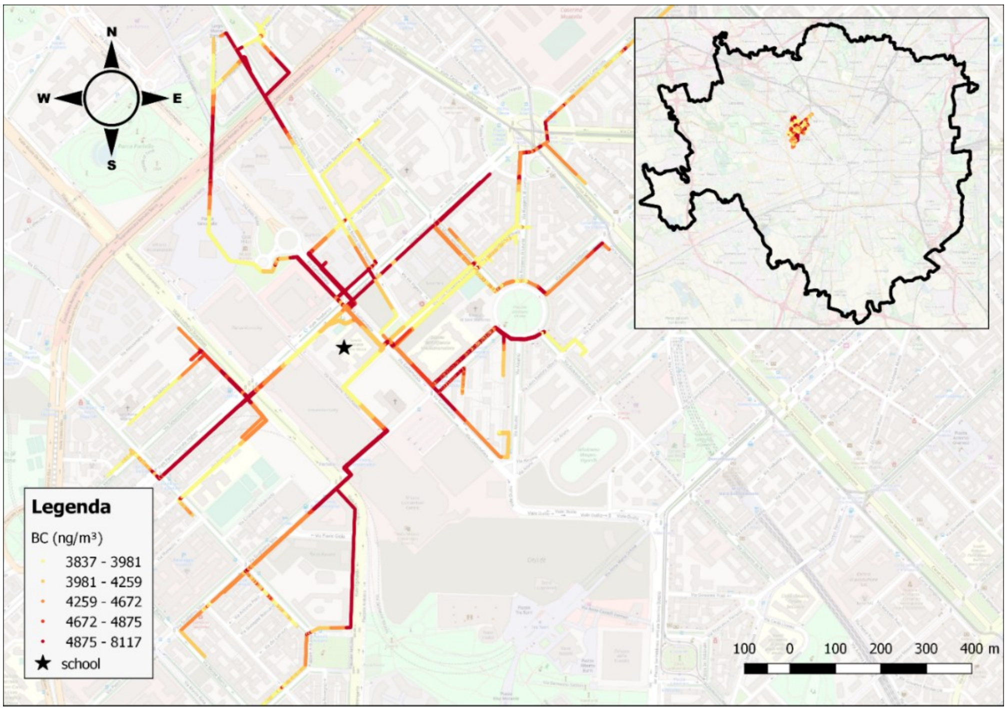


Figure 43. Study area and home-to-school routes. The lines were converted to equidistant points, located at 1-meter distance from each other. For each point, BC_{LUR_day} was applied to estimate BC concentrations. The colors are associated to the quantile of all estimates. The inset map represents the Municipality of Milan boundaries (black line) as well as the study area (yellow-to-red lines).

This paper presents some special features and in particular:

a) schoolchildren were all monitored in a relatively short period (i.e. across January and February 2019);
b) they belonged to the same school in Milan, so the resulting study area was relatively small;
c) the MRH LUR model was developed only using MRH data collected in the school catchment area;
d) a focus on home-to-school commuting on foot.

As expected, our average personal BC exposure (9003 ng/m^3) was higher than that reported in other studies, mainly because our data were measured during the most critical daily time-window for exposure in a congested urban environment, i.e. winter MRH in Milan. For instance, Buonanno et al. (2013) measured during winter an average daily BC personal exposure of 5100 ng/m^3 on 103 schoolchildren from Cassino, a middle town in the central part of Italy (Buonanno et al., 2013). Moreover, Nieuwenhuijsen MJ et. al (2015), Paunescu et al. (2017) and Cunha-Lopes I et al. (2019) found an average personal BC exposure during commuting time of 2800, 3230 and 2500 ng/m^3 respectively in Barcelona, Lisbon and Paris(Cunha-Lopes et al., 2019; Nieuwenhuijsen et al., 2015; Paunescu et al., 2019). These measures were conducted on three different cohorts of children; however, they were carried out in different seasons and considering all daily trips.

Previously, other studies compared LUR estimates with personal exposure during commuting. Nieuwenhuijsen MJ et al. (2015) found a lower correlation between LUR estimates at home and personal BC values during commuting (r = 0.32) than the one we found (r = 0.74)(Nieuwenhuijsen et al., 2015). Furthermore, Minet L et al. (2018) compared BC LUR derived surfaces (100x100 meters grid) to personal exposure measures finding that the latter (median = 1764 ng/m^3) were underestimated by the model (median = 1469 ng/m^3)(Minet et al., 2018). This result is comparable with our findings showing that short-term high exposure events are very hard to catch with a LUR approach. On the contrary, the correlation between personal and modelled exposures appeared very low probably due to the lack of temporal rescaling. Hankey et al. (2017) applied a LUR model based on mobile monitoring to predict concentrations at the midpoint of bike path segments for a complete urban area (Minneapolis, USA). Although an external validation was not provided, this analysis showed the potential of this approach for urban planning purposes (Hankey et al., 2017).

Figure 42 shows that the spatial pattern of the personal measures and the estimates along the home-to-school routes were not always in agreement. This is probably due to short-term exposure events that cannot be captured with a LUR model. Moreover, our BC_{LUR_day} model proved to behave differently by day according to the background concentration; in particular, it was able to detect relative differences between routes, but it seemed to over- or under-estimate personal BC depending on the background concentrations. This was partially expected because of the developing procedure of the model and the rescaled equation (2).

Our work has some limitations. In particular, to estimate 2019 BC concentrations we used a MRH LUR model developed using data measured by fixed monitoring sites in 2018. Then, BC estimates were rescaled only according to the concentrations at the AQN background site in 2019. This procedure has some weaknesses: it does not allow catching short-term spikes and the BC estimates are strongly connected to the behavior of the background site. Moreover, the traffic variables that we used to develop the model were only available as annual MRH estimates. Hence, we were not able to catch daily traffic conditions. Other limitations are linked to our LUR model: for instance, since we used only traffic variables, we were not able to catch the local influence of other important determinants such as the presence of restaurants or bus stops. These variables have already proved to be influential in previous works and could be useful to explain the differences between measured and modelled data (Tunno et al., 2018; van Nunen et al., 2017). Furthermore, we measured personal exposure to BC during home-to-school routes only on one day per child. This limited amount of data exposes our measurements to the bias linked with the temporal variation of different meteorological variables, such as wind direction and wind speed. In other words, LUR models are better suited to estimate longer-term concentrations rather than single events. Nevertheless, our results suggest that the model can be used in the study area to find relative differences between routes and to estimate the on-average cleanest walking route from an origin to a destination. Finally, in our case studies we compared only average values, without considering peak exposures or the total time of commuting. In the comparison between different routes with different distances, a cleanest route algorithm should preferably also take into account travel time. In fact, walking significantly longer to avoid polluted roads may result in a higher total uptake of pollutants; moreover, it is necessary to consider also the willingness of people to take longer routes (Anowar et al., 2017).

6.5. CONCLUSIONS

Our results suggest that a LUR model is capable of predicting the cleanest walking routes to school. A further analysis of the spatial patterns of the home-to-school commute and the BC distribution in the school catchment area of the city of Milan could provide valuable information to public health officials and urban planners. In the attempt of lowering exposure to air pollution and building a healthier city for schoolchildren, policy makers should promote less polluted home-to-school routes by, for instance, providing car-free school streets.

7. CONCLUSION

7.1. SUMMARY

This dissertation presents a novel approach to assess in a comprehensive way the exposure of schoolchildren to Black Carbon (BC) in an urban environment. The project started with a two-season monitoring campaigns of BC with the aim to analyse and to model the spatial distribution of the contaminant inside an elementary school catchment area. In this first stage, a participatory approach was adopted and consisted in the selection of monitoring sites by involving both schoolchildren parents and other citizens of the study area, and by asking them to host a monitoring device on their windowsills or balconies. Afterwards, an environmental education intervention consisted in ludical and experienced-based laboratories focused on air pollution was carried out in partnership with a non-profit organization, and involving 128 schoolchildren. This approach helped to engage teachers, schoolchildren, parents, and to recruit a total of 109 children in the last step of the research project: a two-season personal monitoring campaign. Finally, the collected personal exposure data were used to validate one of the model developed during the first stage of the research project. This last exercise, integrated with the time-activity and the GPS information helped to analyse at a high spatial definition one of the most critical period for the personal exposure of schoolchildren: the home-to-school commuting.

The present dissertation confirms that a participatory approach in exposure science is a suitable choice that can add value to the research project process without losing in quality.

7.2. MAIN CONTRIBUTION TO THE FIELD OF STUDY

7.2.1. Analysing and modelling the spatial distribution of black carbon in a school catchment area

Land Use Regression model is a well-known and intensively used technique in the fields of exposure science and environmental epidemiology. In chapter 3, our main contribution to the state of the art is represented by the participatory approach that we used to identify the monitoring sites inside the study area, as well as the special focus on both different seasons and morning rush hour, by highlighting peculiar spatial patterns. Being able to develop spatial models at both fine scale and high time resolution is the starting point toward an improvement of the exposure attribution accuracy in large-scale epidemiological studies.

7.2.2. A participatory approach to involve teachers, schoolchildren and their parents in the research process

In chapter 4, an environmental education intervention focused on air pollution in urban environment and based on both gamification of exposure science-related topics and IVAC methodology was presented. Moreover, such an approach was designed not only to raise awareness, but at the same time to favour the recruitment of volunteers in a two-season personal monitoring campaign, by scheduling the activities in order to increase the level of engagement of teachers, schoolchildren and their parents, and to favour their active and informed participation to the personal monitoring campaign.

7.2.3. Measuring personal exposure of schoolchildren to black carbon

In chapter 5, only the first insights of a two-season personal monitoring campaign are presented. The main objective of the contribution was to investigate personal exposure in different microenvironments with a focus on transportation. The main results confirm the findings already published in literature about both the role of home and school on the total exposure of schoolchildren, and the intensity of the exposure linked to transportation.

7.2.4. Validation and application of a Land Use Regression model

In chapter 6, for the first time to our knowledge, a Land Use Regression model developed specifically by using measured morning rush hour BC concentration in the study area was validated with personal exposure data collected during home-to-school commuting. This exercise shows that a Land Use Regression model is a suitable tool to identify less polluted routes, and therefore to be used as a tool for mitigating personal exposure.

7.3. MAIN WEAKNESSES

7.3.1. Analysing and modelling the spatial distribution of black carbon in a school catchment area

For this analysis, raw BC data were not post-processed to account for optical related artefacts (Good et al., 2017). This might have caused, especially during cold season, an underestimation of BC concentrations and it might have contributed to the lower performance of the cold season LUR models. Another limitation is that LUR models were developed using a pool of data collected in two seasonal 5-weeks monitoring campaigns, during which each site was monitored only for one week; this may have introduced some temporal variability bias. Moreover, for the cold season LUR models there is a lack of explanatory variables that properly account for the contribution of heating systems.

7.3.2. A participatory approach to involve teachers, schoolchildren and their parents in the research process

The main weakness that raised from the participatory approach developed inside the school is linked to the level of engagement of schoolchildren parents. In fact, engaging successfully schoolchildren is not always equal to engage their parents. To tackle the issue we engage teachers from the beginning part of the project, however more can be done. Then again, the engagement of the adults is fundamental if we consider that children can't carry out most of the planned activities for the personal monitoring campaign autonomously.

7.3.3. Measuring personal exposure of schoolchildren to black carbon

The two personal monitoring campaigns involved children for only one day. This brief period is likely to be not sufficient to profile entirely an individual exposure. However, the 7-day time-activity diary, as well as the GPS monitoring, will help us to fill this gap. Moreover, a participatory approach like the one proposed in the MAPS MI project is arguably linked to a selection bias, by favouring the engagement of those parents already sensitive about environmental issues.

Moreover, for this contribution, we limited our analysis on BC that is a primary air pollutant highly linked with traffic sources. For this reason, even if in the MAPS MI project we measured also other air pollutants, such as NO2 and BTEX, it is possible that we underestimated the influence of important sources, such as cooking activities. In particular, other studies have proved the influence of these kind of activities on UFP concentrations (Buonanno G 2013).

7.3.4. Validation of a LUR model by using personal exposure data and identification of the cleanest home-to-school routes

So far, the validation of the model performed through the comparison between estimates and personal measures was limited to the home-to-school commuting winter data.
Besides, this exercise was conducted by comparing seasonal averaged estimates and one-day personal measurement derived from different monitoring campaigns. In particular, estimates performed by a model developed on January/February 2018 data were compared to personal data measured during January/February 2019. Even if a rescale method was applied, it is likely that this approach introduced a bias in estimates. Moreover, one-day measurements are usually highly influenced by extemporary variables, such as direction and intensity of the wind, the presence of extemporaneous hotspots. Despite these limitations, our results suggest that this is a valuable analysis to perform and eventually refine in the future.

7.4. FURTHER STEPS AND CHALLENGES

One of the most important challenges that participatory scientific research should address in the future is the engagement of public authorities in terms of active partnership with precise functions. For instance, starting from the school catchment areas, urban planners could suite in this process by implementing policies oriented to design more walkable, bikeable and less polluted home-to-school routes, and consequently favouring active travel. This effort is likely to affect positively the health of citizens (De Nazelle et al., 2011) and could represent a valuable approach to tackle air pollution and mobility issues in one of the most polluted and congested city of Europe.
Indeed, our results suggest that the interest of community on air pollution can be prompted, and the answer to the call of participation can be very positive. In the frame of the new paradigm of exposure sciences, another important challenge would be to involve deeper the players, in particular the parents, by giving them the possibility to directly use low cost sensors, not only to monitor air pollution, but also to see possible subclinical effects (Ottaviano et al., 2019). Even if this approach could bring to less accurate data, it remains a valuable support to epidemiological studies (Jerrett et al.,

2017), and it is likely to be an even more powerful approach to raise awareness among citizens (English et al., 2018).
Moreover, from a technical point of view, although improvable, LUR models appear to be suitable tools for predicting the cleanest walking routes to school, therefore the next step should be finding resources and modifying the design of the project in order to broaden the analysis to more and more schools. Moreover, in the attempt to reduce the systematic underestimation of exposure performed by the model, this technique could be refined by using more sophisticated approaches such as machine learning.
In the attempt to develop highly-performant models collecting and measuring more and more explicative variables is a fundamental challenge. This is particularly true if we refer to the spatial distribution of black carbon during the cold season, related to which there seems to be a lack of variables capable to catch the spatial variability due to different sources than traffic.
Moreover, many technical and analytical challenges are related to the detection of BC. In particular, filter-based optical BC-detectors suffer from two important artefacts: the so-called shadowing effect and the multiple scattering of light related to the composition of the measured aerosol. In the future, it would be interesting to match light scattering measures with optical measures of BC on different classes of urban monitoring sites (UB, UT, S), as well as during personal monitoring campaigns.
One last research needed is about exposure to peaks of concentration. In fact, little is known about health-related effects and underlying mechanisms that could be trigged by highly intense exposure like those children experience when close to traffic sources.
Finally, the next planned steps of the MAPS MI project are:

a) going more in depth in the personal exposure assessment, by introducing the analysis of exposure-related dose and the detection of peaks of exposure;
b) estimating mid- and long-term children personal exposure to BC by integrating refined LUR estimates with the information collected with the time-activity diaries and the GPS;
c) linking together the different layers by analysing possible relationships between biomarkers of exposure, epigenetic markers, microbiota and personal air pollutants exposure measures and estimates.

SUPPLEMENTARY MATERIAL

CHAPTER 3: SPATIAL DISTRIBUTION OF BLACK CARBON IN A SCHOOL CATCHMENT AREA

S1. Explanatory variables used in the LUR models developing procedure

Predictor variable	Description	Buffer size (radius in meters)
ROADS_LENGTH_XX	Sum of the length of the roads in a certain buffer	50, 100, 300, 500, 1000
MAJORROADS_LENGTH_XX	Sum of the length of the major roads in a certain buffer[a]	50, 100, 300, 500, 1000
Distance_NR	The distance to the nearest road[b]	
INVDist_NR	1/distance to the nearest road[b]	
INVDist_NR2	1/(distance to the nearest road)^2[b]	
TOT_NR	Total daily or morning rush hour vehicles on the nearest road[b]	
TOT_INVDist_NR	TOT_NR/Distance_NR[b]	
TOT_INVDist_NR2	TOT_NR/(Distance_NR)^2[b]	
HEAVY_NR	Total daily or morning rush hour heavy commercial vehicles on the nearest road[b]	
HEAVY_INVDist_NR	HEAVY_NR/Distance_NR[b]	
HEAVY_INVDist_NR2	HEAVY_NR/(Distance_NR)^2[b]	
MR_Distance	The distance to the nearest major road[a]	
MR_INVDist	1/distance to the nearest major road[a]	
MR_INVDist2	1/(distance to the nearest major road)^2[a]	
MR_TOT	Total daily or morning rush hour vehicles on the nearest major road[a]	
MR_TOT_INVDist	MR_TOT/MR_Distance[a]	
MR_TOT_INVDist2	MR_TOT/(MR_Distance)^2[a]	
MR_HEAVY	Total daily or morning rush hour heavy commercial vehicles on the nearest major road[a]	
MR_HEAVY_INVDist	MR_HEAVY/MR_Distance[a]	
MR_HEAVY_INVDist2	MR_HEAVY/(MR_Distance)^2[a]	
TRAFLOAD_XX	Sum of (Total daily or morning rush hour vehicles * road length) in a certain buffer	50, 100, 300, 500, 1000

HEAVYLOAD_XX	Sum of (Total daily or morning rush hour heavy commercials vehicles * road length) in a certain buffer	50, 100, 300, 500, 1000
CONGESTION_NR	TOT_NR/Capacity of the road[b]	
CONGESTION_XX	average (TOT_NR/Capacity of the road) in a certain buffer	50, 100, 300, 500, 1000
MR_CONGESTION	MR_TOT/Capacity of the road[a]	
MR_CONGESTION_XX	Sum of (MR_TOT/Capacity of the road) in a certain buffer[a]	50, 100, 300, 500, 1000
HFRACTION_NR	Fraction of heavy commercial vehicles on the nearest road[b]	
HFRACTION_XX	Average fraction of heavy commercial vehicles in a certain buffer	50, 100, 300, 500, 1000
MR_TRAFLOAD_XX	Sum of (Total daily or morning rush hour vehicles * major road length) in a certain buffer[a]	50, 100, 300, 500, 1000
MR_HEAVYLOAD_XX	Sum of (Total daily or morning rush hour heavy commercials vehicles * major road length) in a certain buffer[a]	50, 100, 300, 500, 1000
ADDRESSES_XX	Number of addresses in a certain buffer	50, 100, 300, 500, 1000, 3000
POPRES_XX	Resident population in a certain buffer	50, 100, 300, 500, 1000, 3000
HDRES_XX	High residential areas in a certain areas	50, 100, 300, 500, 1000, 3000
LDRES_XX	Low residential areas in a certain buffer	50, 100, 300, 500, 1000, 3000
URBGREEN_XX	Urban green and other green areas in a certain buffer	50, 100, 300, 500, 1000, 3000
IND_XX	Industrial areas in a certain buffer	50, 100, 300, 500, 1000, 3000
SVF_XX	Sky View Factor	25, 50

[a]major roads: roads with an estimated traffic of more than 10000 vehicles per day

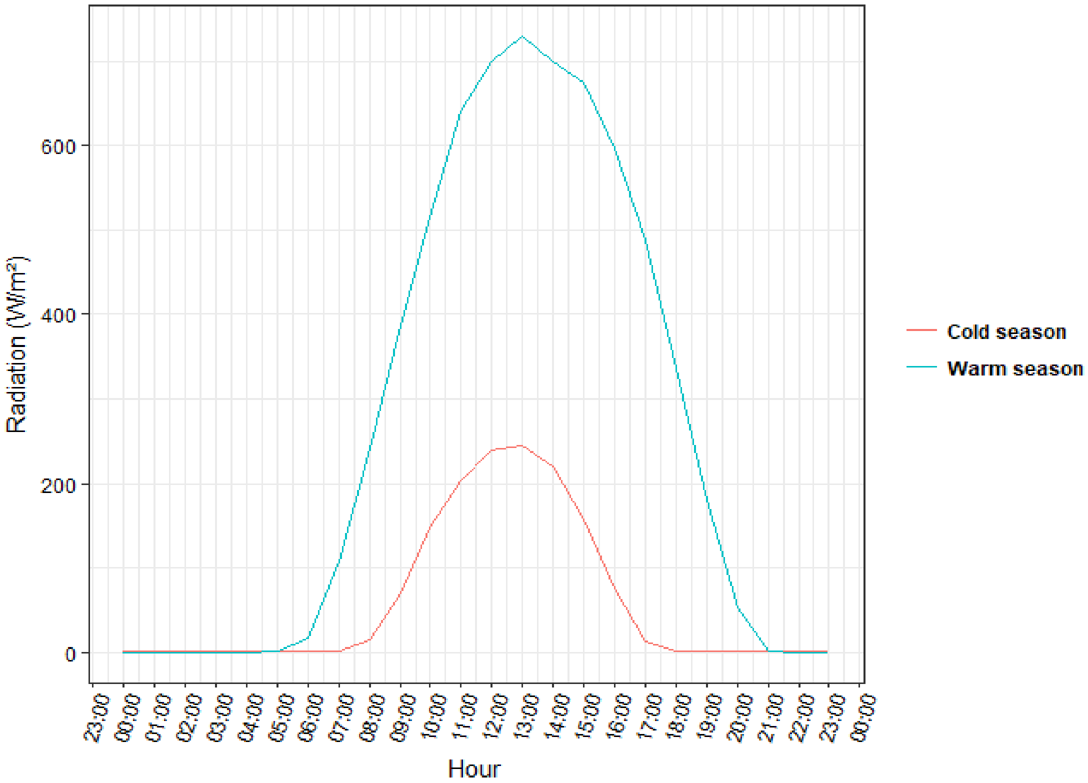
[b]only roads with estimated traffic where included in the network

S2. Statistics of the principal meteorological parameters during the two seasonal monitoring campaigns

	Warm season					Cold season				
	Mean	Median	SD	Min	Max	Mean	Median	SD	Min	Max
Temperature	21.7	21.6	3.3	16.6	27.1	5.8	5.6	1.8	2.9	9.5
Solar radiation	265.54	143.44	288.84	0.06	730.15	58.08	0.74	89.33	0.33	244.83
Relative Humidity (%)	54	53	12	36	76	83	86	8	63	94
Accumulated rain (mm)	0.045	0	0.138	0	0.7	0.065	0	0.010	0	0.5
Wind speed	1.35	1.4	0.28	0.8	1.8	1.12	1.1	0.23	0.7	1.8
Wind direction	207	203	23.8	166	250	219	216	40.8	112	319

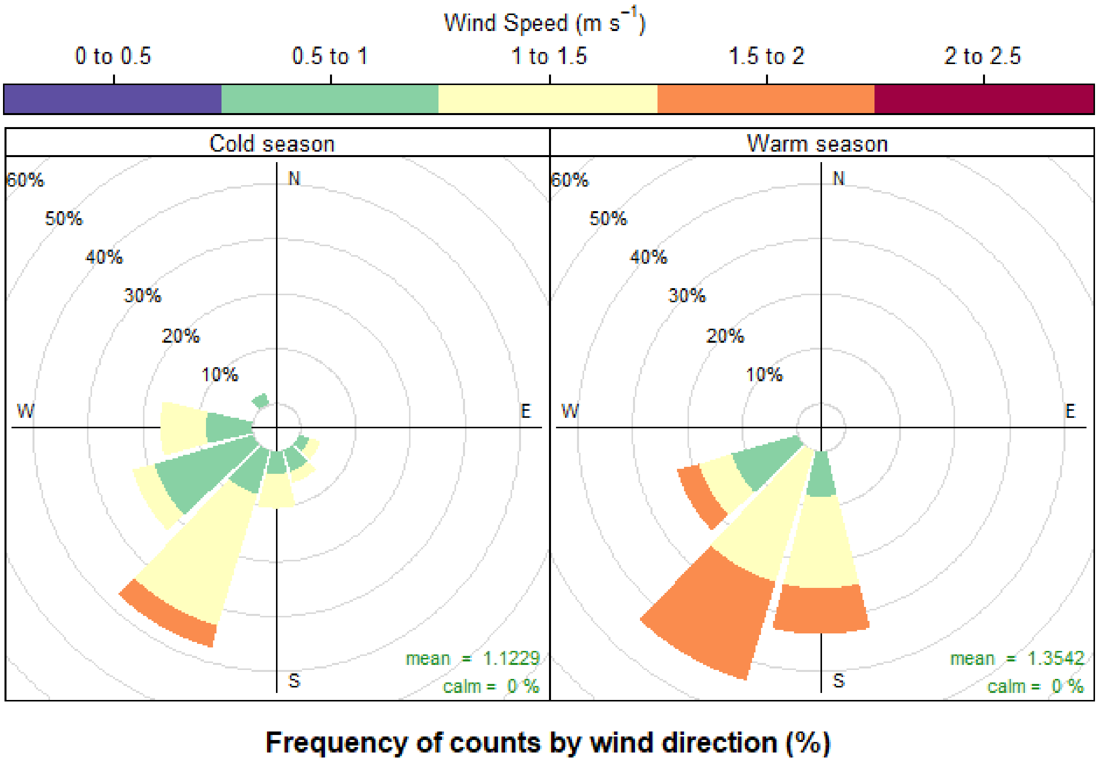
SD = standard deviation

***S3**. Averaged solar radiation daily trend during the two seasonal monitoring campaigns*

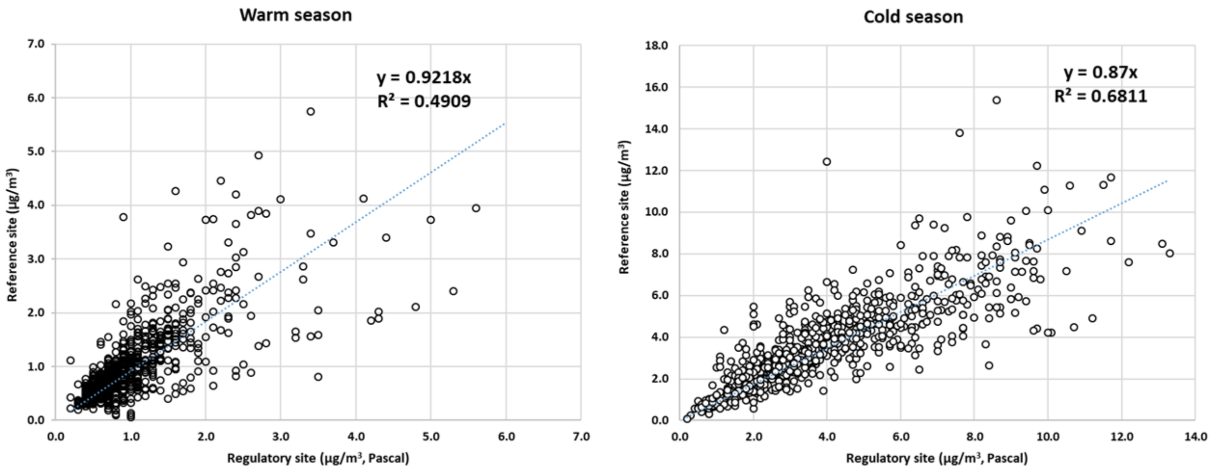


***S4**. Accumulated rain during the two seasonal monitoring campaigns*

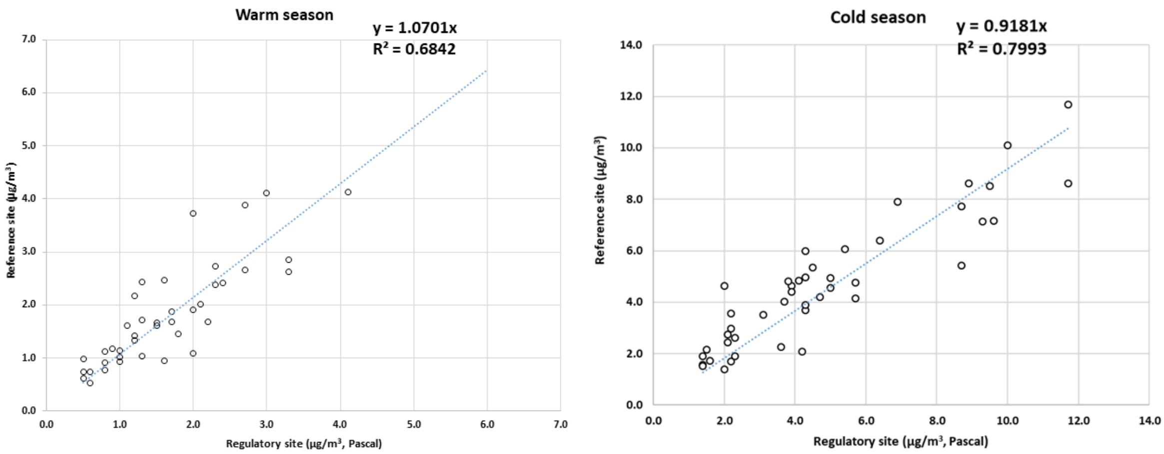
S5. Wind rose diagram of the two seasonal monitoring campaigns



S6. *Scatter plot of regulatory site (Pascal) and reference site during warm and cold season monitoring campaigns*



S7. *Scatter plot of regulatory site (Pascal) and reference site during the MRH (7 am – 9 am) warm and cold season monitoring campaigns*



***S8**. Kruskal-Wallis and Bonferroni post-hoc tests applied to test the differences among BC concentrations of the different monitoring sites classes, divided in seasonal, annual estimates, non-MRH and MRH data. The significance (*) was set at a = 0.05 and rejected H_o if $p <= a/2$.*

		S-UT	S-UB	UB-UT
Non-MRH BC	**Warm**	0.0042*	0.0000*	0.0403
	Cold	0.0782	0.0021*	0.0674
	Annual	0.0074*	0.0000*	0.0232*
MRH BC	**Warm**	0.0013*	0.0001*	0.1796
	Cold	0.0064*	0.0010*	0.2941
	Annual	0.0017*	0.0000*	0.0938

S9. *Translated recruitment letter*

UNIVERSITÀ DEGLI STUDI DI MILANO

DIPARTIMENTO DI SCIENZE CLINICHE E DI COMUNITA'

Department of Clinical Sciences and Community Health

Milan, 8 April 2017

To the attention of the Citizens

of the 8th local borough of the Municipality of Milan

Oggetto: **MAPS MI: Mapping Air Pollution in a elementary School catchment area of Milan and exposure assessment to Black Carbon during home-school commuting**

Dear citizen,

in the next three years, the University of Milan will conduct within the area of the 8th local borough of the Municipality of Milan, a project that we are going to summarize briefly in this letter and in the attached brochure.

We are currently organizing Stage I, which will consist in a 5-week environmental monitoring of the Black Carbon atmospheric pollutant. In order to successfully carrying out the monitoring campaign, we aim to identify about 30 sampling sites; in these locations, small air samplers (11cm x 6cm x 4cm approximately) will be placed to measure the Black Carbon airborne contaminant during the next May and June.

The identification of the monitoring sites is not always an easy process and for this reason we invite you, if interested in the project, to contact us to verify the possibility of a collaboration. At the bottom of this letter you will find our contact details: you can send an e-mail, or, if you prefer, give us a call.

The commitment required consists in making available a small space outside your house (balcony, windowsill, garden) where to place a Black Carbon sampler. This commitment will last for a maximum of 7 consecutive days, in a week to be established together, between Monday 8 May and Sunday 9 June.

The measurements obtained from the first phase of the project will be followed by the data processing stage, thanks to which we are going design the first seasonal air pollution map with high spatial resolution in the study area, focusing in particular on the entry of children to school, in order to easily identify the safest home-school commuting routes.

Hoping to have aroused your interest in our project, we thank you for your kind attention and best regards,

Dr. Luca Boniardi

Luca Boniardi

Prof. Silvia Fustinoni

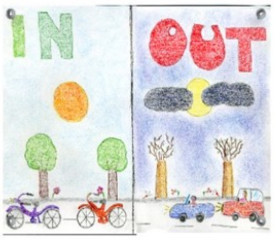
Silvia Fustinoni

Environmental sciences PhD student
Epiget research group
Mail: labtox.discco@unimi.it; luca.boniardi@unimi.it
Tel: 0250320110; 0255032633
Web site: http://users.unimi.it/toxlab/

S10. Brochure of the project (front/rear)

Urban designers, transport planners, environment and health professionals need to collaborate more closely in the design of "active community environments" that support childhood physical activity and mobility.

World Health Organization



UNIVERSITÀ DEGLI STUDI DI MILANO

Laboratorio di Tossicologia Ambientale ed Industriale

Dipartimento di Scienze Cliniche e di Comunità (DISCCO)

Via San Barnaba 18
Milano, MI 20144

0250320158

luca.boniardi@unimi.it

Fondazione CARIPLO

http://users.unimi.it/toxlab/

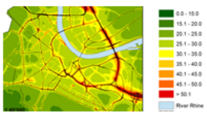
Valutazione dell'esposizione a Black Carbon nei tragitti casa-scuola:

mappatura delle concentrazioni nel bacino d'utenza e individuazione dei percorsi sicuri

Il progetto

1. monitoraggio ambientale
Sono previste due campagne stagionali (Maggio/giugno-Novembre/Dicembre) della durata di circa 4 settimane nell'area del bacino d'utenza della scuola

2. mappatura
Verranno disegnate le mappe stagionali sulla base delle misure effettuate sul campo



3. laboratori
I risultati verranno condivisi nelle classi aderenti al progetto, verranno svolti interventi di sensibilizzazione sul tema "mobilità, ambiente e salute"; verranno raccolti dati oggettivi sulle abitudini in relazione ai percorsi casa-scuola

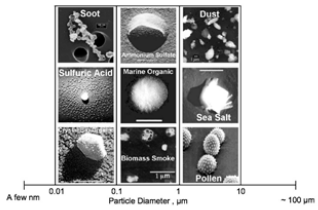
4. monitoraggio personale
Su base volontaria i bambini verranno monitorati stagionalmente con appositi strumenti non invasivi lungo i percorsi casa-scuola con un focus sulle diverse modalità di spostamento

5. conclusione
I risultati verranno condivisi con la scuola e con le autorità di riferimento, le mappe costituiranno la base per la scelta dei percorsi casa-scuola meno espositivi

Perchè le scuole?

- l'esposizione ad imquinanti atmosferici quali il Black Carbon rappresenta una minaccia soprattutto per i più piccoli;
- le malattie respiratorie, in particolare l'asma, sono in crescita tra i giovani (Galassi, 2006);
- esiste una forte relazione tra densità di traffico e problematiche respiratorie (Esposito, 2013; Migliore, 2009);
- buona parte di queste possono essere evitate intervenendo sul traffico urbano (Ministero della Salute, gruppo GARD, 2015);
- il 20% del traffico milanese tra le 8 e le 9 del mattino è dovuto ai percorsi casa-scuola (PUMS, 2013).

Costruire una città a misura di bambino più favorevole agli spostamenti attivi e sostenibili può portare benefici all'intera cittadinanza.



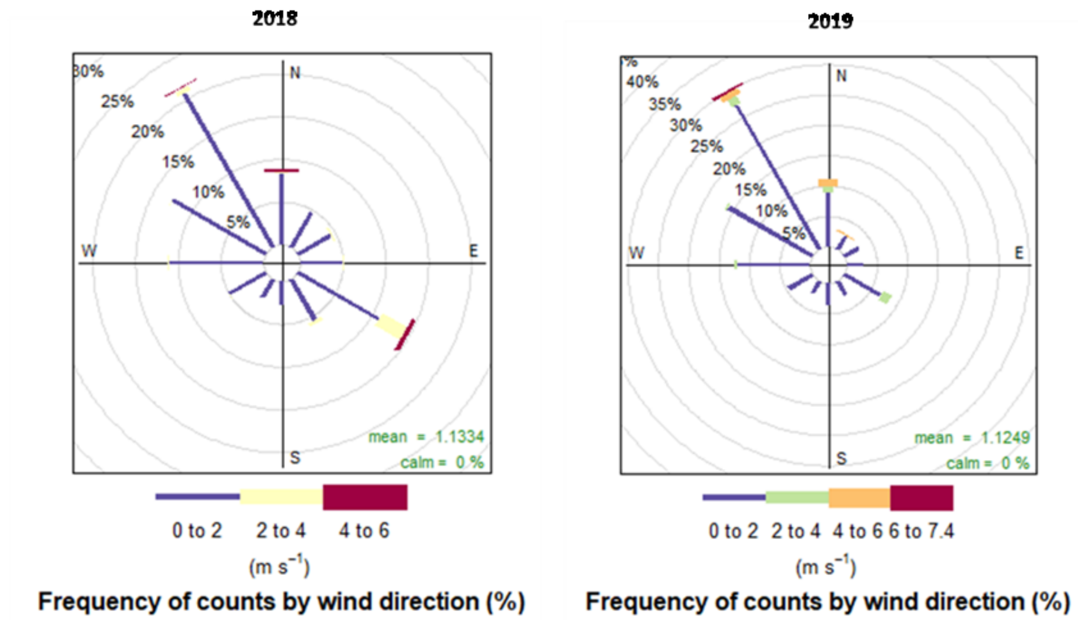
Perchè il Black Carbon?

- è un inquinante primario che si forma dalla combustione incompleta di biomasse, biocarburanti e carburanti fossili (EPA, 2010);
- per le sue dimensioni ridotte è una delle frazioni del Particolato atmosferico (PM) che minacciano maggiormente la salute dell'uomo (WHO, 2011);
- è l'inquinante ufficiale individuato dalla UE per valutare l'efficacia degli interventi di riduzione del traffico (UNECE, 2013);
- è uno degli inquinanti che contribuisce direttamente al riscaldamento globale (EPA, 2010).

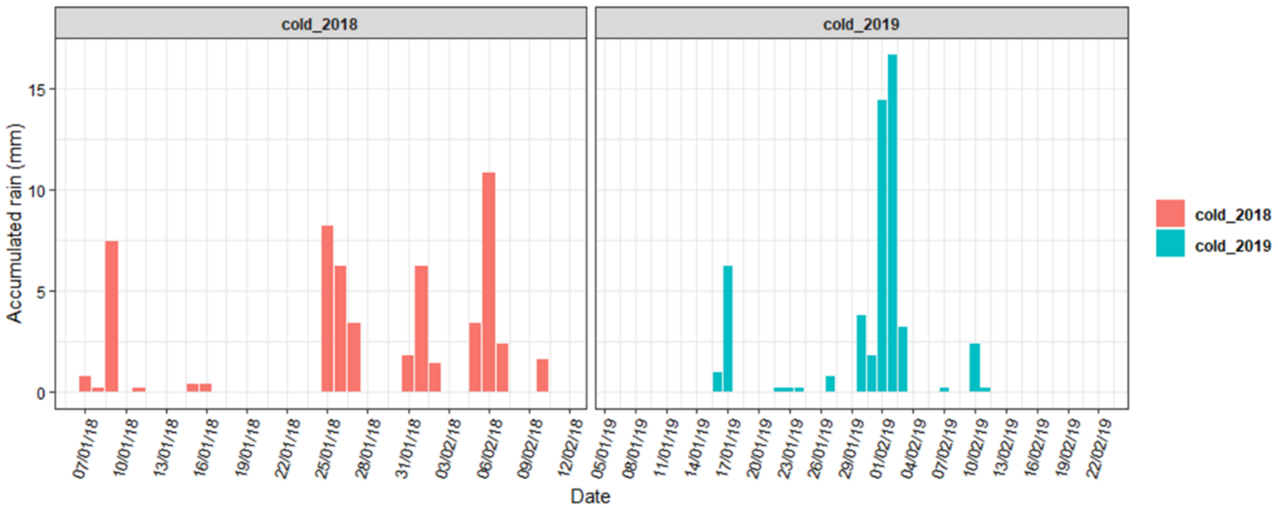
Le strategie di mitigazione del Black Carbon possono portare benefici sostanziali all'ambiente e alla salute pubblica.

CHAPTER 6: ESTIMATING BC PERSONAL EXPOSURE AND DESIGNING LESS POLLUTED HOME-TO-SCHOOL STREETS

S11. *Wind rose diagram of the two cold-season monitoring campaigns carried out in January and February 2018 and 2019. The selected Air Quality Network site that collected the data was located about 1 km away from the school*



S12. *Accumulated rain during the two cold-season monitoring campaigns carried out in January and February 2018 and 2019 (2018 mean = 54.8 mm, 2019 mean = 51.2 mm).*



S13. *Statistics of BC concentrations according to the urban background monitoring site of the Air Quality Network for the city of Milan (ID station 10283, via Ponzio 34/6 – Pascal Città Studi). The data were selected for January and February 2018 and 2019.*

id	n	median	min	max	p25	p75	mean	sd	IQR	T (˚C)
pascal_cold_2018	843	3.5	2	13.3	2	5.5	3.9	2.5	3.5	5.9
pascal_cold_2019	888	4.2	2	15.5	2.4	7.6	5.1	3.4	5.2	5

BIBLIOGRAPHY

Alvarez-Pedrerol, M., et al., 2017. Impact of commuting exposure to traffic-related air pollution on cognitive development in children walking to school. Environmental Pollution. 231, 837-844.

AMAT, Urban sustainable mobility plan of milan (PUMS) 2015.

Andreae, M. O., Gelencser, A., 2006. Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. Atmospheric Chemistry and Physics. 6, 3131-3148.

Anowar, S., et al., 2017. Quantifying the value of a clean ride: How far would you bicycle to avoid exposure to traffic-related air pollution? Transportation Research Part a-Policy and Practice. 105, 66-78.

ARPA, AIRUSE Project - Report 4 - PM speciation and source apportionment. Agenzia Regionale per la Protezione Ambientale, 2016.

ARPA, INEMAR - Inventario Emissioni in Atmosfera. Agenzia Regionale per la Protezione Ambientale, 2018a.

ARPA, Progetto Supersiti: la stazione di Milano Via Pascal. 2018b.

Bateson, T. F., Schwartz, J., 2008. Children's response to air pollutants. Journal of Toxicology and Environmental Health - Part A: Current Issues. 71, 238-243.

Bernstein, J. A., et al., 2004. Health effects of air pollution. Journal of Allergy and Clinical Immunology. 114, 1116-1123.

Bollati, V., Baccarelli, A., 2010. Environmental epigenetics. Heredity (Edinb). 105, 105-12.

Bond, T. C., Bergstrom, R. W., 2006. Light absorption by carbonaceous particles: An investigative review. Aerosol Science and Technology. 40, 27-67.

Bond, T. C., et al., 2013. Bounding the role of black carbon in the climate system: A scientific assessment. Journal of Geophysical Research-Atmospheres. 118, 5380-5552.

Boniardi, L., et al., 2019. Annual, seasonal, and morning rush hour Land Use Regression models for black carbon in a school catchment area of Milan, Italy. Environmental Research. 176, 11.

Bove, H., et al., 2019. Ambient black carbon particles reach the fetal side of human placenta. Nature Communications. 10, 7.

Bowatte, G., et al., 2015. The influence of childhood traffic-related air pollution exposure on asthma, allergy and sensitization: a systematic review and a meta-analysis of birth cohort studies. Allergy. 70, 245-56.

Bower, J., et al., 1999. Monitoring ambient air quality for health impact assessment. World Health Organization Regional Publications - European Series. III-196.

Brauer, M., et al., 2012. Exposure Assessment for Estimation of the Global Burden of Disease Attributable to Outdoor Air Pollution. Environmental Science & Technology. 46, 652-660.

Brauer, M., et al., 2003. Estimating long-term average particulate air pollution concentrations: application of traffic indicators and geographic information systems. Epidemiology. 14, 228-39.

Briggs, D., 2005. The role of GIS: coping with space (and time) in air pollution exposure assessment. J Toxicol Environ Health A. 68, 1243-61.

Briggs, D. J., et al., 1997. Mapping urban air pollution using GIS: a regression-based approach. International Journal of Geographical Information Science. 11, 699-718.

Brockmeyer, S., D'Angiulli, A., 2016. HOW AIR POLLUTION ALTERS BRAIN DEVELOPMENT: THE ROLE OF NEUROINFLAMMATION. Translational Neuroscience. 7, 24-30.

Brokamp, C., et al., 2019. Assessing exposure to outdoor air pollution for epidemiological studies: Model-based and personal sampling strategies. Journal of Allergy and Clinical Immunology. 143, 2002-2006.

Buonanno, G., et al., 2013. Children exposure assessment to ultrafine particles and black carbon: The role of transport and cooking activities. Atmospheric Environment. 79, 53-58.

Cabada, J. C., et al., 2004. Mass size distributions and size resolved chemical composition of fine particulate matter at the Pittsburgh supersite. Atmospheric Environment. 38, 3127-3141.

Calderon-Garciduenas, L., et al., 2015. Air Pollution and Children: Neural and Tight Junction Antibodies and Combustion Metals, the Role of Barrier Breakdown and Brain Immunity in Neurodegeneration. Journal of Alzheimers Disease. 43, 1039-1058.

Calderón-Garcidueñas, L., et al., 2015. Mexico City normal weight children exposed to high concentrations of ambient PM2.5 show high blood leptin and endothelin-1, vitamin D deficiency, and food reward hormone dysregulation versus low pollution controls. Relevance for obesity and Alzheimer disease. Environ Res. 140, 579-92.

Cape, J. N., et al., 2012. The atmospheric lifetime of black carbon. Atmospheric Environment. 59, 256-263.

Cargo M et al. 2008. The Value and Challenges of Participatory Research: Strengthening Its Practice. Annu. Rev. Public Health 2008.29:325-350.

Carugno, M., et al., 2018. PM10 exposure is associated with increased hospitalizations for respiratory syncytial virus bronchiolitis among infants in Lombardy, Italy. Environ Res. 166, 452-457.

Caserini, S., et al., 2017. Influence of climate change on the frequency of daytime temperature inversions and stagnation events in the Po Valley: historical trend and future projections. Atmospheric Research. 184, 15-23.

Castell, N., et al., 2017. Can commercial low-cost sensor platforms contribute to air quality monitoring and exposure estimates? Environ Int. 99, 293-302.

Chiu, Y., et al., 2016. Prenatal particulate air pollution and neurodevelopment in urban children: Examining sensitive windows and sex-specific associations. Environment International. 87, 56-65.

Chiu, Y. H., et al., 2013. Associations between traffic-related black carbon exposure and attention in a prospective birth cohort of urban children. Environ Health Perspect. 121, 859-64.

Ciarelli, G., et al., 2019. Long-term health impact assessment of total PM2.5 in Europe during the 1990–2015 period. Atmospheric Environment: X. 3.

Cofala, J., et al., 2010. INTEGRATED ASSESSMENT OF AIR POLLUTION AND GREENHOUSE GASES MITIGATION IN EUROPE. Archives of Environmental Protection. 36, 29-39.

Cohen, A. J., et al., 2017. Estimates and 25-year trends of the global burden of disease attributable to ambient air pollution: an analysis of data from the Global Burden of Diseases Study 2015. Lancet. 389, 1907-1918.

Commodore, A., et al., 2017. Community-based participatory research for the study of air pollution: a review of motivations, approaches, and outcomes. Environ Monit Assess. 189, 378.

Costabile, F., et al., 2015. Partitioning of Black Carbon between ultrafine and fine particle modes in an urban airport vs. urban background environment. Atmospheric Environment. 102, 136-144.

Croner, C. M., et al., 1996. Geographic information systems (GIS): new perspectives in understanding human health and environmental relationships. Stat Med. 15, 1961-77.

Cunha-Lopes, I., et al., 2019. Children's exposure to sized-fractioned particulate matter and black carbon in an urban environment. Building and Environment. 155, 187-194.

Dachs, J., Eisenreich, S. J., 2000. Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons. Environmental Science & Technology. 34, 3690-3697.

De Nazelle, A., et al., 2017. Comparison of air pollution exposures in active vs. passive travel modes in European cities: A quantitative review. Environment International. 99, 151-160.

De Nazelle, A., et al., 2011. Improving health through policies that promote active travel: a review of evidence to support integrated health impact assessment. Environ Int. 37, 766-77.

De Prins, S., et al., 2014. Airway oxidative stress and inflammation markers in exhaled breath from children are linked with exposure to black carbon. Environ Int. 73, 440-6.

Dias, D., Tchepel, O., 2018. Spatial and Temporal Dynamics in Air Pollution Exposure Assessment. International Journal of Environmental Research and Public Health. 15, 23.

Dockery, D. W., et al., 1993. An association between air pollution and mortality in six U.S. cities. N Engl J Med. 329, 1753-9.

Dong, X. Y., et al., 2019. Evaluating Recent Updated Black Carbon Emissions and Revisiting the Direct Radiative Forcing in Arctic. Geophysical Research Letters. 46, 3560-3570.

Dons, E., et al., 2011. Impact of time-activity patterns on personal exposure to black carbon. Atmospheric Environment. 45, 3594-3602.

Dons, E., et al., 2017. Wearable Sensors for Personal Monitoring and Estimation of Inhaled Traffic-Related Air Pollution: Evaluation of Methods. Environ Sci Technol. 51, 1859-1867.

Dons, E., et al., 2019. Transport most likely to cause air pollution peak exposures in everyday life: Evidence from over 2000 days of personal monitoring. Atmospheric Environment. 213, 424-432.

Dons, E., et al., 2012. Personal exposure to Black Carbon in transport microenvironments. Atmospheric Environment. 55, 392-398.

Dons, E., et al., 2014. Land use regression models as a tool for short, medium and long term exposure to traffic related air pollution. Sci Total Environ. 476-477, 378-86.

Dons, E., et al., 2013. Modeling temporal and spatial variability of traffic-related air pollution: Hourly land use regression models for black carbon. Atmospheric Environment. 74, 237-246.

Dratva, J., et al., 2016. Early Life Origins of Lung Ageing: Early Life Exposures and Lung Function Decline in Adulthood in Two European Cohorts Aged 28-73 Years. PLoS One. 11, e0145127.

Drinovec, L., et al., 2015. The "dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation. Atmospheric Measurement Techniques. 8, 1965-1979.

DTU, Global Wind Atlas 2.0. 2019, pp. <p class="MsoCaption" style="margin-bottom:0cm;margin-bottom:.0001pt;text-align: justify;line-height:200%">Map obtained from the] “Global Wind Atlas 2.0, a free, web-based application developed, owned and operated by the Technical University of Denmark (DTU) in partnership with the World Bank Group, utilizing data provided by Vortex, with funding provided by the Energy Sector Management Assistance Program (ESMAP). For additional information: https://globalwindatlas.info”.

EEA, Air quality in Europe. 2018.

EEA, Data and maps. Vol. 2019, 2019.

Eeftens, M., et al., 2013. Quantifying urban street configuration for improvements in air pollution models. Atmospheric Environment. 72, 1-9.

Eeftens, M., et al., 2012. Spatial variation of PM2.5, PM10, PM2.5 absorbance and PMcoarse concentrations between and within 20 European study areas and the relationship with NO2 - Results of the ESCAPE project. Atmospheric Environment. 62, 303-317.

English, P. B., et al., From Crowdsourcing to Extreme Citizen Science: Participatory Research for Environmental Health. In: J. E. Fielding, et al., Eds.), Annual Review of Public Health, Vol 39. Annual Reviews, Palo Alto, 2018, pp. 335-350.

EPA, Guidelines for Human Assessment Exposure. 1992.

EPA, Report to Congress on Black Carbon. Environmental Protection Agency, 2012.

ERS, Air quality and health. European Respiratory Agency, 2010.

EU, 2008/50/EU. 2008.

EU, GDPR, 2016/679/EU. 2016.

EUROSTAT, Transport statistics at regional level. 2019.

Faustini, A., et al., 2015. Short-term effects of particulate matter on mortality during forest fires in Southern Europe: results of the MED-PARTICLES Project. Occupational and Environmental Medicine. 72, 323-329.

Ferrari, L., et al., 2019. Particulate matter exposure shapes DNA methylation through the lifespan. Clin Epigenetics. 11, 129.

Filippini, T., et al., 2019. Association between Outdoor Air Pollution and Childhood Leukemia: A Systematic Review and Dose-Response Meta-Analysis. Environ Health Perspect. 127, 46002.

Fultescu, V., et al., Estimating emissions of Black Carbon and other SLCFs within CCAC activities. 2018.

Gehring, U., et al., 2013. Air pollution exposure and lung function in children: the ESCAPE project. Environ Health Perspect. 121, 1357-64.

Gerharz, L. E., et al., 2013. Spatio-temporal modelling of individual exposure to air pollution and its uncertainty. Atmospheric Environment. 64, 56-65.

Good, N., et al., 2017. An accurate filter loading correction is essential for assessing personal exposure to black carbon using an Aethalometer. Journal of Exposure Science and Environmental Epidemiology. 27, 409-416.

Greenwald, R., et al., 2019. Estimating minute ventilation and air pollution inhaled dose using heart rate, breath frequency, age, sex and forced vital capacity: A pooled-data analysis. PLoS One. 14, e0218673.

Gruzieva, O., et al., 2019. Prenatal Particulate Air Pollution and DNA Methylation in Newborns: An Epigenome-Wide Meta-Analysis. Environ Health Perspect. 127, 57012.

Gulliver, J., et al., 2011. Comparative assessment of GIS-based methods and metrics for estimating long-term exposures to air pollution. Atmospheric Environment. 45, 7072-7080.

Hagler, G. S. W., et al., 2011. Post-processing Method to Reduce Noise while Preserving High Time Resolution in Aethalometer Real-time Black Carbon Data. Aerosol and Air Quality Research. 11, 539-546.

Hankey, S., et al., 2017. Population-Level Exposure to Particulate Air Pollution during Active Travel: Planning for Low-Exposure, Health-Promoting Cities. Environmental Health Perspectives. 125, 527-534.

Hansen, A. D. A., et al., 1984. THE AETHALOMETER - AN INSTRUMENT FOR THE REAL-TIME MEASUREMENT OF OPTICAL-ABSORPTION BY AEROSOL-PARTICLES. Science of the Total Environment. 36, 191-196.

Harrison, R. M., et al., 2004. Major component composition of PM10 and PM2.5 from roadside and urban background sites. Atmospheric Environment. 38, 4531-4538.

Heck, J. E., et al., 2013. Childhood cancer and traffic-related air pollution exposure in pregnancy and early life. Environ Health Perspect. 121, 1385-91.

HEI, Traffic-Related Air Pollution: A Critical Review of the Literature on Emissions, Exposure, and Health Effects. Health Effects Institute, Boston, Massachus ets, 2010.

Henderson, S. B., et al., 2007. Application of land use regression to estimate long-term concentrations of traffic-related nitrogen oxides and fine particulate matter. Environmental Science & Technology. 41, 2422-2428.

Hernan MA, Hernandez-Diaz S, Robins JM. A structural approach to selection bias. Epidemiology 2004; 15:615–625.

Hitzenberger, R., et al., 2006. Intercomparison of thermal and optical measurement methods for elemental carbon and black carbon at an urban location. Environmental Science & Technology. 40, 6377-6383.

Hoek, G., 2017. Methods for Assessing Long-Term Exposures to Outdoor Air Pollutants. Curr Environ Health Rep. 4, 450-462.

Hoek, G., et al., 2008. A review of land-use regression models to assess spatial variation of outdoor air pollution. Atmospheric Environment. 42, 7561-7578.

Hoek, G., et al., 2013. Long-term air pollution exposure and cardio- respiratory mortality: a review. Environ Health. 12, 43.

Hägerstrand, T., 1970. What about people in Regional Science? Papers of the Regional Science Association. 24, 6-21.

IARC, 2008. Polycyclic aromatic hydrocarbons. IARC monographs. 92.

IARC, 2014. Diesel and gasoline engine exhausts and some nitroarenes. IARC Monographs on the evaluation of carcinogenic risks to humans. International Agency for Research on Cancer, Lyon, France.

IARC, IICC-3, International incidence of childhood cancer., Vol. 3, 2016a.

IARC, 2016b. Outdoor air pollution. International Agency for Research on Cancer (IARC), Lyon.

Int Panis, L., et al., 2010. Exposure to particulate matter in traffic: A comparison of cyclists and car passengers. Atmospheric Environment. 44, 2263-2270.

Invernizzi, G., et al., 2011. Measurement of black carbon concentration as an indicator of air quality benefits of traffic restriction policies within the ecopass zone in Milan, Italy. Atmospheric Environment. 45, 3522-3527.

ISTAT, Population census 2011. Italian National Statistics Institute, 2018.

Janssen, N. A. H., et al., 2011. Black Carbon as an Additional Indicator of the Adverse Health Effects of Airborne Particles Compared with PM10 and PM2.5. Environmental Health Perspectives. 119, 1691-1699.

Jedrychowski, W., et al., 2013. Intrauterine exposure to fine particulate matter as a risk factor for increased susceptibility to acute broncho-pulmonary infections in early childhood. International Journal of Hygiene and Environmental Health. 216, 395-401.

Jeong, H., Park, D., 2017. Contribution of time-activity pattern and microenvironment to black carbon (BC) inhalation exposure and potential internal dose among elementary school children. Atmospheric Environment. 164, 270-279.

Jensen BB, Schnack K. The action competence approach in environmental education. Environmental Education Research (1997) 3(2), pp. 163–178.

Jensen BB. A case of two paradigms within health education. Health Education Research (1997). 12(4), pp. 419-428

Jerrett, M., et al., 2005. A review and evaluation of intraurban air pollution exposure models. J Expo Anal Environ Epidemiol. 15, 185-204.

Jerrett, M., et al., 2017. Validating novel air pollution sensors to improve exposure estimates for epidemiological analyses and citizen science. Environmental Research. 158, 286-294.

Jerrett, M., et al., 2010. Spatial Modeling in Environmental and Public Health Research. International Journal of Environmental Research and Public Health. 7, 1302-1329.

Jung, K. H., et al., 2017. Effect of personal exposure to black carbon on changes in allergic asthma gene methylation measured 5 days later in urban children: importance of allergic sensitization. Clin Epigenetics. 9, 61.

K, H., DEMtools. 2014.

Kanaroglou, P. S., et al., 2005. Establishing an air pollution monitoring network for intra-urban population exposure assessment: A location-allocation approach. Atmospheric Environment. 39, 2399-2409.

Khreis, H., et al., 2017a. Exposure to traffic-related air pollution and risk of development of childhood asthma: A systematic review and meta-analysis. Environ Int. 100, 1-31.

Khreis, H., et al., 2017b. How to Create Healthy Environments in Cities. Epidemiology. 28, 60-62.

Kirchstetter, T. W., et al., 2004. Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon. Journal of Geophysical Research-Atmospheres. 109, 12.

Kistemann, T., et al., 2002. New perspectives on the use of Geographical Information Systems (GIS) in environmental health sciences. Int J Hyg Environ Health. 205, 169-81.

Klepeis, N. E., 1999. An introduction to the indirect exposure assessment approach: modeling human exposure using microenvironmental measurements and the recent National Human Activity Pattern Survey. Environ Health Perspect. 107 Suppl 2, 365-74.

Klepeis, N. E., et al., 2001. The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. J Expo Anal Environ Epidemiol. 11, 231-52.

Klimont, Z., et al., 2017. Global anthropogenic emissions of particulate matter including black carbon. Atmospheric Chemistry and Physics. 17, 8681-8723.

Knox, A., et al., 2009. Mass Absorption Cross-Section of Ambient Black Carbon Aerosol in Relation to Chemical Age. Aerosol Science and Technology. 43, 522-532.

Kot-Wasik, A., et al., 2007. Advances in passive sampling in environmental studies. Anal Chim Acta. 602, 141-63.

Kumar, P., et al., 2015. The rise of low-cost sensing for managing air pollution in cities. Environ Int. 75, 199-205.

Kwan, M. P., 2000. Interactive geovisualization of activity-travel patterns using three-dimensional geographical information systems: A methodological exploration with a large data set. Transportation Research Part C: Emerging Technologies. 8, 185-203.

LaRosa, L. B., et al., 2002. Real-time indoor and outdoor measurements of black carbon in an occupied house: An examination of sources. Journal of the Air & Waste Management Association. 52, 41-49.

Lepeule, J., et al., 2012. Chronic exposure to fine particles and mortality: an extended follow-up of the Harvard Six Cities study from 1974 to 2009. Environ Health Perspect. 120, 965-70.

Lioy, P. J., Smith, K. R., 2013. A discussion of exposure science in the 21st century: a vision and a strategy. Environ Health Perspect. 121, 405-9.

Madl, P., Exposure to Nano-Sized Particles and the Emergence of Contemporary Diseases with a Focus on Epigenetics. InTech, 2012, pp. 305-336.

Makri, A., Stilianakis, N. I., 2008. Vulnerability to air pollution health effects. International Journal of Hygiene and Environmental Health. 211, 326-336.

Mallone, S., et al., 2011. Saharan Dust and Associations between Particulate Matter and Daily Mortality in Rome, Italy. Environmental Health Perspectives. 119, 1409-1414.

Manara, V., et al., 2019. 1951–2017 changes in the frequency of days with visibility higher than 10 km and 20 km in Italy. Atmospheric Environment. 214.

Mariani, J., et al., 2018. Short-term particulate matter exposure influences nasal microbiota in a population of healthy subjects. Environ Res. 162, 119-126.

Martinsson, J., et al., 2017. Carbonaceous aerosol source apportionment using the Aethalometer model - evaluation by radiocarbon and levoglucosan analysis at a rural background site in southern Sweden. Atmospheric Chemistry and Physics. 17, 4265-4281.

Milan, S. o. o. t. M. o., Census Data: Analysis of the Commuting for Work and Study in Milan., 2011.

Mills, N. L., et al., 2007. Ischemic and thrombotic effects of dilute diesel-exhaust inhalation in men with coronary heart disease. N Engl J Med. 357, 1075-82.

Minet, L., et al., 2018. Development and Comparison of Air Pollution Exposure Surfaces Derived from On-Road Mobile Monitoring and Short-Term Stationary Sidewalk Measurements. Environmental Science & Technology. 52, 3512-3519.

Minkler, M., 2005. Community-based research partnerships: challenges and opportunities. J Urban Health. 82, ii3-12.

Minkler, M., 2010. Linking science and policy through community-based participatory research to study and address health disparities. Am J Public Health. 100 Suppl 1, S81-7.

Morawska, L., et al., 2018. Applications of low-cost sensing technologies for air quality monitoring and exposure assessment: How far have they gone? Environ Int. 116, 286-299.

Mueller, N., et al., 2017. Health impacts related to urban and transport planning: A burden of disease assessment. Environment International. 107, 243-257.

Muñoz, X., et al., 2019. Diesel exhausts particles: Their role in increasing the incidence of asthma. Reviewing the evidence of a causal link. Sci Total Environ. 652, 1129-1138.

Nawrot, T. S., et al., 2011. Public health importance of triggers of myocardial infarction: a comparative risk assessment. Lancet. 377, 732-40.

Nhung, N. T. T., et al., 2017. Short-term association between ambient air pollution and pneumonia in children: A systematic review and meta-analysis of time-series and case-crossover studies. Environ Pollut. 230, 1000-1008.

Nieuwenhuijsen, M. J., 2016. Urban and transport planning, environmental exposures and health-new concepts, methods and tools to improve health in cities. Environmental Health. 15, 11.

Nieuwenhuijsen, M. J., et al., 2015. Variability in and Agreement between Modeled and Personal Continuously Measured Black Carbon Levels Using Novel Smartphone and Sensor Technologies. Environmental Science & Technology. 49, 2977-2982.

Nieuwenhuijsen, M. J., et al., 2018. Air Pollution, Noise, Blue Space, and Green Space and Premature Mortality in Barcelona: A Mega Cohort. International Journal of Environmental Research and Public Health. 15, 12.

Nieuwenhuijsen, M. J., et al., 2017. Participatory quantitative health impact assessment of urban and transport planning in cities: A review and research needs. Environment International. 103, 61-72.

Niranjan, R., Thakur, A. K., 2017. The Toxicological Mechanisms of Environmental Soot (Black Carbon) and Carbon Black: Focus on Oxidative Stress and Inflammatory Pathways. Frontiers in Immunology. 8, 20.

O'Fallon, L. R., Dearry, A., 2002. Community-based participatory research as a tool to advance environmental health sciences. Environ Health Perspect. 110 Suppl 2, 155-9.

Oravisjärvi, K., et al., 2011. Effects of physical activity on the deposition of traffic-related particles into the human lungs in silico. Sci Total Environ. 409, 4511-8.

Ott, W. R., 1982. Concepts of human exposure to air pollution. Environment International. 7, 179-196.

Ottaviano, M., et al., 2019. Empowering Citizens through Perceptual Sensing of Urban Environmental and Health Data Following a Participative Citizen Science Approach. Sensors. 19, 19.

Panis, L. I., 2010. New Directions: Air pollution epidemiology can benefit from activity-based models. Atmospheric Environment. 44, 1003-1004.

Park, K., et al., 2006. Comparison of continuous and filter-based carbon measurements at the Fresno Supersite. Journal of the Air & Waste Management Association. 56, 474-491.

Paunescu, A. C., et al., 2019. Associations of black carbon with lung function and airway inflammation in schoolchildren. Environ Int. 131, 104984.

Perrone, M. G., et al., 2012. Sources of high PM2.5 concentrations in Milan, Northern Italy: Molecular marker data and CMB modelling. Science of the Total Environment. 414, 343-355.

Petzold, A., et al., 2002. Continuous measurement of atmospheric black carbon using a multi-angle absorption photometer. Environmental Science and Pollution Research. 78-82.

Poplawski, K., et al., 2009. Intercity transferability of land use regression models for estimating ambient concentrations of nitrogen dioxide. Journal of Exposure Science and Environmental Epidemiology. 19, 107-117.

Poschl, U., 2003. Aerosol particle analysis: challenges and progress. Analytical and Bioanalytical Chemistry. 375, 30-32.

Provost, E. B., et al., 2017. Recent versus chronic fine particulate air pollution exposure as determinant of the retinal microvasculature in school children. Environ Res. 159, 103-110.

Putaud, J. P., et al., 2004. European aerosol phenomenology-2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. Atmospheric Environment. 38, 2579-2595.

Ran, L., et al., 2016. Black carbon and wavelength-dependent aerosol absorption in the North China Plain based on two-year aethalometer measurements. Atmospheric Environment. 142, 132-144.

Ranzi, A., 2012. [Estimate of the spatial variability of exposure to airborne pollutants in urban areas]. Epidemiologia e prevenzione. 36, 287-295.

Reche, C., et al., 2011. New considerations for PM, Black Carbon and particle number concentration for air quality monitoring across different European cities. Atmospheric Chemistry and Physics. 11, 6207-6227.

Rice, M. B., et al., 2016. Lifetime Exposure to Ambient Pollution and Lung Function in Children. American Journal of Respiratory and Critical Care Medicine. 193, 881-888.

Rivas, I., et al., 2016. Spatiotemporally resolved black carbon concentration, schoolchildren's exposure and dose in Barcelona. Indoor Air. 26, 391-402.

Rundle, A., et al., 2012. Association of childhood obesity with maternal exposure to ambient air polycyclic aromatic hydrocarbons during pregnancy. Am J Epidemiol. 175, 1163-72.

Ryan, P. H., LeMasters, G. K., 2007. A review of land-use regression models for characterizing intraurban air pollution exposure. Inhal Toxicol. 19 Suppl 1, 127-33.

Ryan, P. H., et al., 2008. A land-use regression model for estimating microenvironmental diesel exposure given multiple addresses from birth through childhood. Science of the Total Environment. 404, 139-147.

Saenen, N. D., et al., 2016. Recent versus chronic exposure to particulate matter air pollution in association with neurobehavioral performance in a panel study of primary schoolchildren. Environ Int. 95, 112-9.

Sandradewi, J., et al., 2008. Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter. Environmental Science & Technology. 42, 3316-3323.

Sbihi, H., et al., 2019. Thinking bigger: How early-life environmental exposures shape the gut microbiome and influence the development of asthma and allergic disease. Allergy.

Seinfeld, J. H., Pandis, S. N., 2016. Atmospheric chemistry and physics: from air pollution to climate change.

Snyder, D. C., Schauer, J. J., 2007. An inter-comparison of two black carbon aerosol instruments and a semi-continuous elemental carbon instrument in the urban environment. Aerosol Science and Technology. 41, 463-474.

Snyder, E. G., et al., 2013. The changing paradigm of air pollution monitoring. Environ Sci Technol. 47, 11369-77.

Stone, V., et al., 2017. Nanomaterials Versus Ambient Ultrafine Particles: An Opportunity to Exchange Toxicology Knowledge. Environmental Health Perspectives. 125, 17.

Suades-González, E., et al., 2015. Air Pollution and Neuropsychological Development: A Review of the Latest Evidence. Endocrinology. 156, 3473-82.

Suglia, S. F., et al., 2008. Association of black carbon with cognition among children in a prospective birth cohort study. Am J Epidemiol. 167, 280-6.

Sunyer, J., et al., 2015. Association between traffic-related air pollution in schools and cognitive development in primary school children: a prospective cohort study. PLoS Med. 12, e1001792.

Tainio, M., et al., 2016. Can air pollution negate the health benefits of cycling and walking? Preventive Medicine. 87, 233-236.

Team, Q. D., QuantumGIS software. 2016.

Team, R. C., R: A Language and Environment for Statistical Computing., 2014.

Tobias, A., et al., 2014. Effects of black carbon on respiratory health in the city of Barcelona. European Respiratory Journal. 44.

Tunno, B. J., et al., 2018. Spatial Patterns in Rush-Hour vs. Work-Week Diesel-Related Pollution across a Downtown Core. International Journal of Environmental Research and Public Health. 15, 15.

Turnbaugh, P. J., et al., 2007. The human microbiome project. Nature. 449, 804-10.

U.S.EPA, Report to Congress on Black Carbon. Environmental Protection Agency, 2012.
UN, Sustainable Development Goals. 2015.
UN, Revision of world urbanization prospects. United Nations, 2018.
UN, Global Warming of 1.5°C. United Nation's Intergovernmental Panel on Climate Change (IPCC), 2018.
UNEP, WMO, Integreted assessment of Black Carbon and Tropospheric Ozone. United Nations Environment Programme,
World Meteorological Organization, 2011.
Van Nunen, E., et al., 2017. Land Use Regression Models for Ultrafine Particles in Six European Areas. Environmental Science & Technology. 51, 3336-3345.
Vanos, J. K., 2015. Children's health and vulnerability in outdoor microclimates: A comprehensive review. Environment International. 76, 1-15.
Vecchi, R., et al., 2004. The role of atmospheric dispersion in the seasonal variation of PM1 and PM2.5 concentration and composition in the urban area of Milan (Italy). Atmospheric Environment. 38, 4437-4446.
Viidanoja, J., et al., 2002. Organic and black carbon in PM2.5 and PM10: 1 year of data from an urban site in Helsinki, Finland. Atmospheric Environment. 36, 3183-3193.
Virkkula, A., et al., 2007. A simple procedure for correcting loading effects of aethalometer data. Journal of the Air & Waste Management Association. 57, 1214-1222.
Wang, J., Christopher, S. A., 2003. Intercomparison between satellite-derived aerosol optical thickness and PM2.5 mass: Implications for air quality studies. Geophysical Research Letters. 30.
Wang, M., et al., 2012. Systematic Evaluation of Land Use Regression Models for NO2. Environmental Science & Technology. 46, 4481-4489.
Weingartner, E., et al., 2003. Absorption of light by soot particles: determination of the absorption coefficient by means of aethalometers. Journal of Aerosol Science. 34, 1445-1463.
WHO, Air quality guidelines: global update 2005. 2005.
WHO, 2016. Ambient air pollution: a global assessment of exposure and burden of disease.
WHO, Air pollution and child health: prescribing clean air. 2018.
Wolffe, A. P., Guschin, D., 2000. Review: chromatin structural features and targets that regulate transcription. J Struct Biol. 129, 102-22.
Zartarian, V. G., et al., 1997. A quantitative definition of exposure and related concepts. J Expo Anal Environ Epidemiol. 7, 411-37.