# OPERATIONAL CONTEXT: AIR QUALITY MONITORING SYSTEMS

## SUB- ACTION A1.3

## Annex 3 of Abacus on operational context on Noise Low Emission Zone

Life MONZA

Methodologies fOr Noise low emission Zones introduction And management

# LIFE15 ENV/IT/000586

# LIFE MONZA
## Methodologies fOr Noise low emission Zones introduction And management

### Technical Report - A1.3 Operational context: Air Quality Monitoring Systems

| | |
|---|---|
| **Deliverable** | **Operational context: Noise Monitoring Systems**<br>**Annex 3 of Abacus on operational context on Noise Low Emission Zone** |
| **Action/Sub-action** | Action A1 - Operational context for Noise Low Emission Zones (LEZ) detection and management<br>Sub-action A1.3 - Operational context: Air Quality Monitoring Systems |
| **Authors** | Giorgio Cattani, Alessandro Di Menno di Bucchianico, Alessandra Gaeta, Gianluca Leone |
| **Status** | Final Version |

| | |
|---|---|
| **Beneficiary:** | ISPRA |
| **Contact person:** | Giorgio Cattani |
| **E-mail:** | giorgio.cattani@isprambiente.it |
| **Project web-site** | - |

# Table of contents

# 1 Introduction

## 1.1 Air pollution: sources, status and trend legislation

Air pollution is considered as a major environmental risk for human health; it increases the incidence of a wide range of diseases and has several environmental impacts, damaging vegetation and ecosystems.

The road transport sector provides a significant contribution to the total anthropogenic emissions, together with other mobile sources, non industrial combustion plants and combustion in energy and transformation industries. Other undesired substances (known as secondary pollutants e.g. ozone) may be formed in the atmosphere due to chemical reaction between pollutant directly emitted.

Control of exposure to air pollutants requires public authorities actions at global, regional and local level. WHO produced and subsequently revised air quality guidelines (WHO, 2000, 2005) that contain recommendations of targets for air quality and limits for the concentration of selected air pollutants derived from epidemiological and toxicological evidence.

The Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe defined and established objectives for ambient air quality designed to avoid, prevent or reduce harmful effects on human health and the environment as a whole. The ambient air quality in Member States must be assessed on the basis of common methods and criteria. Results of the ambient air quality assessment should be used in order to help combat air pollution and nuisance and to monitor long-term trends and improvements. Air quality plans should be developed for zones within which concentration of pollutants in ambient air exceed the relevant air quality target value. Moreover it is mandatory for the member states to ensure that such information on ambient air quality is made available to the public.

The pollutants targeted by the 2008/50/EC directive include particulate matter ($PM_{2.5}$, $PM_{10}$), ozone ($O_3$), nitrogen dioxide ($NO_2$), sulfur dioxide ($SO_2$), carbon monoxide (CO), and lead (Pb), while similar provisions were established for benzo(a)pirene, arsenic cadmium and nickel as high concern $PM_{10}$ toxic components by the 2004/107/EC directive.

Over the last twenty five years, the emissions of pollutants in Europe and in Italy have generally decreased considerably. The major drivers for the trend are reductions in the industrial and road transport sectors, due to the implementation of various European Directives which introduced new technologies, plant emission limits, the limitation of sulphur content in liquid fuels and the shift to cleaner fuels (natural gas in place of coal and fuel oil). Nevertheless there are some relevant countertrend, for instance in Italy $PM_{10}$ emissions from non industrial combustion plants, representing about 40% of the total, show a strong increase between 1990 and 2012, equal to 149% due to the increase of wood combustion for heating (ISPRA 2014).

Atmospheric pollution is an extremely complex phenomenon. The burden of pollutant resulting from human activities and natural source evolve in time and space trough the atmosphere. The transport, dilution, transformation and deposition mechanisms are driven by specific reactivity of the substances and the meteorological conditions, that are as well largely variable in time and space, and govern the dynamics of air pollutants after emission. This lead to a non-linear relationships between emission and outdoor air pollutants concentrations.

In the EU particulate matter, ozone and nitrogen oxides are the most critical pollutants, given the still high concentrations founded in the air, compared both with the European target and the WHO guidelines, despite the emissions reduction. A statistically significant moderate decreasing trend was found in the majority of the $PM_{10}$, and $NO_2$ Europe wide concentration time series, while any downward trend was found in the large majority of ozone time series.

Cities are major sources of pollution, due to city heating, energy production and transport. The majority of the people in the world live in urban areas.

## 1.2 Health effects of air pollution

Air pollution has been widely accepted and recognized by this time to have an impact in terms of cardio-vascular as well as respiratory diseases than can lead to premature mortality. Ambient (outdoor air pollution) in both cities and rural areas was estimated to cause 3.7 million premature deaths worldwide in 2012 (WHO, 2014).
Recently the International Agency for Research on Cancer (IARC) concluded that there is sufficient evidence that exposure to outdoor air pollution causes lung cancer. Particulate matter was evaluated separately and was also classified as carcinogenic to humans (IARC, 2013).
In recent years, 16 – 21 % of Europe's urban population may have been exposed to ambient $PM_{10}$ concentrations above the EU limit set to protect human health. Up to 17 % of the population living in urban areas may have been exposed to levels of ozone that exceed the EU target value.
Estimates of the health impacts attributable to exposure to air pollution indicate that PM2.5 concentrations in 2013 were responsible for about 467 000 premature deaths in Europe (41 countries), and around 436 000 in the EU-28, originating from long-term exposure. Fine particulate matter (PM2.5) in air has been estimated to reduce life expectancy in the EU by more than eight months. The estimated impacts on the population in the same 41 European countries of exposure to NO2 and O3 concentrations in 2013 were around 71 000 and 17 000 premature deaths per year, respectively, and in the EU-28 around 68 000 and 16 000 premature deaths per year, respectively (EEA, 2016).
Children and young adult represent the largest subpopulation of those susceptible to the adverse effects of air pollution. Compared to adults, they express a greater vulnerability, which can be explained by differences in the circumstances of exposure related to age, their activities, their child status, differences in lung anatomy and physiology, differences in the clinical expression of disease, and their organ maturity (WHO, 2013).

# 2 Air quality assessment

## 2.1 Conceptual framework on LEZs

Low emission zones (LEZs) have been established to reduce air pollutant emissions and to improve urban air quality in European countries. LEZs usually regulate the access to a zone depending on the vehicle emission standards or the vehicle type (heavy-duty vehicles, light-duty vehicles, moped etc.). LEZs may cover a variable area that can include few roads or a large part of an urban area. Those zones aims mainly at reducing exhaust emissions of traffic related pollutant, particularly PM and nitrogen oxides $NO_X$. Policy measures (as LEZs) to reduce traffic by banning the most polluting vehicles are generally able to reduce circulating vehicles but they gave conflicting results on air pollution level.

*Evaluating the effectiveness of a LEZ*

Evaluate the effect of a LEZ on pollution level ($PM_{10}$, $PM_{2.5}$, $NO_X$) is not an easy task because of several confounding factors: meteorological conditions, regional background levels of pollutants, other concomitant air quality policy measures (Holman C. et al., 2015). To assess the impact of the LEZs, taking into account the confounding factors, it needs to remove the influence of non local traffic pollution sources. Advanced statistical techniques are necessary to achieve this aim.

Meteorology has a great impact on yearly and daily variation of PM concentration and therefore it is necessary make adjustment over long periods to remove seasonal biases. Such circumstance makes even more difficult assessing the environmental impact of LEZs in terms of PM level reduction with regard to the short term air quality standards.
When the contribution of exhaust emissions from local traffic to PM concentration levels is very small compared to the contribution of other emission sources and to secondary PM (regional background), the reduction achievable with the LEZ implementation has, very often, a negligible impact on PM mass concentration levels. Such situation is typical in the region of our study (Po valley region). Focusing on specific components of PM, like black carbon, or parameter (e.g. particle number concentration) more related with exhaust vehicles emission seems to be more suitable for assessing the impact of LEZs on local scale air quality (C. Holman et al., 2015), particularly when the LEZs involve traffic restriction for heavy duty diesel vehicles (Jones at al., 2012).
The other concomitant air quality/transport/energy policy measures (e.g. implementation of Euro standards, vehicle fleet composition change, etc.) represent relevant confounding factors, and affect the evaluation process making hard to isolate the impact of LEZs on air quality.

*LEZs European cases of impact assessment on air quality*

In the period from the end of 2007 until 2008 it was implemented the introduction of "sulphur free" diesel fuel and the London Low Emission Zone for heavy goods vehicles in the London urban area. A great reduction in particle number concentration was occurred in London (59%) in a monitoring site used to assess the impact on air quality (Jones at al., 2012). This large reduction was mainly due to the "sulphur free" diesel measure and secondly correlated with the introduction of London's LEZ.
The impact assessment of LEZs on nitrogen oxides air concentration was analysed in 17 German cities in period from 2005 until the end of 2009 (Morfeld P. et al., 2014). The effect of LEZs on nitrogen oxides levels was estimated as a mean reduction of 2 $\mu g/m^3$ (4%).
Munich (Germany) has been establishing a LEZ and transit bans for heavy duty vehicles since 2008. The observed concentration of $PM_{10}$ were reduced by between 4.5% (urban background monitoring site) and 13% at traffic monitoring site (Fensterer V.et al., 2014).
A black carbon monitoring campaign was carried out in Milan (Italy) to estimate the potential impact of the congestion traffic charge zone (in the Ecopass zone, all vehicles prior Euro 4 standards have to buy a ticket) and the new pedestrian zone on air quality (Invernizzi G. et al., 2011). Black carbon and PM mass concentrations was analysed in three different days and in three different site. The first site was located outer the Ecopass zone, the second one within Ecopass zone and the last one in the pedestrian area. A reduction by 47% (Ecopass zone) to 62% (pedestrian zone) was found in the ratio of Black Carbon to $PM_{10.}$

## 2.2 Macrositing and micrositing criteria concerning fixed and passive sampling

A correct location of monitoring equipments is a crucial aspect in air quality assessment.
An adequate choose of macro and micrositing criteria to be adopted can be based on European AQ directives and scientific literature references and research experience.
The European Directive 2008/50/EC states some general criteria for siting fixed sampling points addressed to the protection of human health, they are as follows:

Macroscale siting criteria according to European Directive 2008/50/EC

*(a) Sampling points directed at the protection of human health shall be sited in such a way as to provide data on the following:*
*— the areas within zones and agglomerations where the highest concentrations occur to which the population is likely to be directly or indirectly exposed for a period which is significant in relation to the averaging period of the limit value(s),*
*— levels in other areas within the zones and agglomerations which are representative of the exposure of the general population,*
*(b) Sampling points shall in general be sited in such a way as to avoid measuring very small micro-environments in their immediate vicinity, which means that a sampling point must be sited in such a way that the air sampled is representative of air quality for a street segment no less than 100 m length at traffic-orientated sites and at least 250 m × 250 m at industrial sites, where feasible;*
*(c) Urban background locations shall be located so that their pollution level is influenced by the integrated contribution from all sources upwind of the station. The pollution level should not be dominated by a single source unless such a situation is typical for a larger urban area. Those sampling points shall, as a general rule, be representative for several square kilometres;*
*(d) Where the objective is to assess rural background levels, the sampling point shall not be influenced by agglomerations or industrial sites in its vicinity, i.e. sites closer than five kilometres;*
*(e) Where contributions from industrial sources are to be assessed, at least one sampling point shall be installed downwind of the source in the nearest residential area. Where the background concentration is not known, an additional sampling point shall be situated within the main wind direction;*
*(f) Sampling points shall, where possible, also be representative of similar locations not in their immediate vicinity;*
*(g) Account shall be taken of the need to locate sampling points on islands where that is necessary for the protection of human health.*

Microscale siting criteria according to European Directive 2008/50/EC

*— the flow around the inlet sampling probe shall be unrestricted (free in an arc of at least 270°) without any obstructions affecting the airflow in the vicinity of the sampler (normally some metres away from buildings, balconies,*
*trees and other obstacles and at least 0,5 m from the nearest building in the case of sampling points representing air quality at the building line),*
*— in general, the inlet sampling point shall be between 1,5 m (the breathing zone) and 4 m above the ground. Higher positions (up to 8 m) may be necessary in some circumstances. Higher siting may also be appropriate if the station is representative of a large area, — the inlet probe shall not be positioned in the immediate vicinity of sources in order to avoid the direct intake of emissions unmixed with ambient air,*
*— the sampler's exhaust outlet shall be positioned so that recirculation of exhaust air to the sampler inlet is avoided,*
*— for all pollutants, traffic-orientated sampling probes shall be at least 25 m from the edge of major junctions and no more than 10 m from the kerbside.,*
*The following factors may also be taken into account:*

- *interfering sources,*
- *security,*
- *access,*
- *availability of electrical power and telephone communications,*
- *visibility of the site in relation to its surroundings,*
- *safety of the public and operators,*
- *the desirability of co-locating sampling points for different pollutants,*

— *planning requirements.,*

Other criteria for siting passive samplers, to assess ambient air quality by indicative measurement, are suggested in the ESCAPE Study manual and related scientific literature (Brunekreef, 2008; Cyrys et al., 2012):

Sampling sites will be selected to represent the spatial variation of air pollution in the study domain. Monitoring sites will be selected with help according to Regional Environmental Agencies know-how together with available maps and satellite data. Sampling sites should be classified in regional, suburban and urban background and street traffic oriented and industrial sites.
An urban background site is defined as a site that is not specifically influenced by sources in the neighborhood. In a circle of 50 m around the site no more than 3.000 vehicles should pass daily. Within a circle of 100 meter around the site no other important sources of *anthropic* pollutants should be present (combustion sources, construction works, small industries, district heating plant, parking or garages). The distance to big sources should be considerably larger than 100 meter, depending on the specific emission characteristics (chimney height, temperature of flue gases). In order to obtain sufficient variability in the predictor variables, sites should be distributed well over the city, that is some sites in the city centre and several sites more in the suburbs of the city.
A traffic site is a site representing exposure to pollution generated by cars, buses or transport trucks. According to the ESCAPE Study manual, a traffic intensity above 10,000 vehicles per day is considered as a traffic site. In order to obtain sufficient variation among the predictor variables streets that cover the full range of traffic intensities and, possibly, composition in the city of interest should be selected. It’s also significant to include open and some street canyon type streets. Do not select only streets with the highest traffic intensity, but also more intermediate streets. It is important that sites cover locations with varying air pollution concentrations, traffic intensities and different land uses.
Guidelines for the selection of sites are in summary:

1. Visit the study area and get a general understanding of the range of air pollution environments that need to be monitored and modeled.
2. Sites should be broadly distributed in the study area. Make also sure that there is enough variation in air pollution concentrations and predictor variables at the selected sites. Each cohort should be characterized with respect to locations of homes. Make sure that some monitoring sites are included near the boundaries of the study areas, such that the developed models can be applied in the entire study area.
3. Assess which previously used predictor variables are likely important in your study area. Urbanization and traffic may be important key variables, and therefore sites could be divided in regional background, urban background and traffic sites.
4. Select sites that provide contrast in predictor variables (e.g. provide a range of traffic intensities rather than one extremely high and others with low intensities; provide also a range in urbanization).
Oversampling is needed in areas where pollution is higher and more variable (e.g. traffic areas) compared with other areas.
5. Select sites that are representative for homes of your study population, and, where applicable, also schools and day care centers. Try to avoid extreme situations, it is thus not a good idea to attach samplers to lampposts in the middle of major roads (too close to traffic) when these sites do not represent homes of the study population (a site should be at least 2 meters from the roadside, if there is more than 2 m distance between road and building). Public buildings may be appropriate if their location to roads is comparable to homes (for background locations more flexibility is present).

Microenvironmental criteria for site selection the ESCAPE Study manual are described below:

Unrestricted air flow around the sampler: sampler inlet should be placed at least 20 cm from any vertical surface (such as a wall), and if possible the sampler inlet should be located at least twice the distance from an obstacle as the height of that obstacle.

- Inlet should be at least 2 m from a High volume sampler inlet and 1 meter from a medium volume sampler, and at least 50 cm from a $NO_X$ measurement. Sampling inlet should be at least 3 m from the outlet of a pump.
- Sampler inlet should not be near exhaust flues or vents from homes or other buildings (at least 5 m away).
- Preferably the sampler inlet should also be at least 5 m away from air conditioning.
- Sampling height (inlet) at least 1.5 m (preferably 2 m) above the surface on which the sampler is placed and preferably between 1.5 and 3 m above the ground.
- The sampler should not be placed near the drip line of trees.
- Electricity available (active sampling only).
- Safe from vandalism or accidental damage.
- Accessible for field workers.

Other practical criteria:

- Do not locate the monitoring site within 25 m of a traffic light or traffic junction / intersection.
- A site should be at least 2 meters from the roadside (when there is more than 2m distance between road and building).
- Do not locate the monitoring site within 100 m of locations where construction works are ongoing or where construction works are planned during the measurement periods (contact the local authorities for information about planned construction works) or at locations that are likely to be subject to maintenance (e.g. affected by street-cleaning operations).
- Do not locate the monitoring site in a street where large changes in traffic intensities are to be expected in the future (for example due to traffic regulations).
- When using a residential address a nonsmoking family is preferred. Do not use a balcony where cigarettes are smoked as a location for a monitoring site.
- Do not locate the monitoring site within 25 m of locations where smokers are allowed to smoke and/or gather (for example close to the entrance of restaurants, hospitals, schools or other public buildings, because smokers usually congregate close to the entrance of these buildings).
- Do not use a location within 100 m of road tunnels, small industries and carparks as these locations may be affected by local emission sources.
- Do not use a location where there are a lot of birds.

## 2.3 Passive sampler review

To assess the exposure gradients within a city as well as to assess the effectiveness of measures addressed to reduce the air pollution, reliable estimate of both temporal and spatial variability in the study domain are needed. Two general approach can be identified as for assess small scale spatial variability: deterministic modelling (i.e. dispersion model) and empirical modelling (e.g. land use regression). Whatever the modelling approach, fixed point measurement are used to develop and or

to validate the models. Thus, ad hoc monitoring are needed, since routine networks in most urban areas are not dense enough. In fact, existing monitoring networks have insufficient density to capture small-scale spatial variation of air pollution. Moreover several areas, particularly small-medium cities in Italy, have only 1-2 fixed sites belonging to the regional air pollution monitoring network, if any. Furthermore, purpose-designed monitoring allows the investigators the control over the type of sites (e.g. traffic, background) they wish to include in model development.
Disadvantages of purpose-designed monitoring include the additional cost and the limited temporal coverage of the measurements. To date, most purpose-designed monitoring campaigns consisted of between one and four 7–14 days sampling campaigns, spread over a full year, in order to catch the seasonal variability, whereas routine monitoring is typically continuous, especially for the gaseous components.
Diffusive sampling technique are of particular interest, because of their relatively low cost, no need of any pump or electrical power and simple operation, allowing for deploying a large number of samplers over the study area.
A diffusive sampler is a device which is capable of taking samples of gases or vapours from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or a porous material and/or permeation through a membrane, but which does not involve the active movement of pumped air through the device.
The diffusive samplers are suitable for long-term monitoring of several gases in ambient air (e.g. nitrogen oxides, ozone, several volatile organic compounds).
The samplers, provided with weather protective shelters, can be easily deployed at a suitable height above the ground (2 -3 m), placed on lamp post, utility poles or street signals (see section 2.2).

Duplicate or triplicate samples should be collected during each measurement periods, as well as three to five field blanks in order to calculate the limits of detection and precision following a stated protocol (e.g. Cyris et al., 2012).
The averaged concentration over the exposure time is calculated using the following general equation, derived from Fick’s first law:

$$[X]_t = \frac{(m_s - m_b)}{d \cdot v \cdot t \cdot 10^{-6}} \qquad (1)$$

where
$[X]_t$ = concentration of pollutant X in µg/m³ at actual average temperature and pressure during the exposure;
$m_s$ = mass of X measured in the exposed sampler in µg;
$m_b$ = mass of X in the blank in µg;
v = uptake rate in cm³/min;
$t$ = sampling time in min.
d = desorption efficency

From Fick's Law, we know that the sampling rate (v) is a function of the diffusion coefficient of a given analyte (D) and the geometric constant of the sampler (K). The diffusion coefficient (D) always remains constant for a given analyte; therefore, to improve sampling rate (v), the geometric constant (K) must be improved: K = S/l where S is diffusive surface and l is the distance between the diffusive and adsorbing surface.
The theoretical uptake rate ($cm^3$ of gas in a given period of time) is calculated using the diffusion coefficient of the target gas in air and the dimensions of the sampler. The actual uptake rate however, depends, for a given gas, by the influential environmental parameters (air temperature pressure, wind speed, relative humidity) during exposure. Thus, an empirical equation for the uptake rate is proposed, applied and verified in laboratory experiments and in the field for each sampler and pollutant.

Exposure periods of 1 to 8 weeks are feasible, with important differences among specific gases and devices. Generally the allowed exposure time is chosen within the range found during field validation tests obtained from many sites across Europe.

Potential interferences must also be considered carefully. For instance, interferences from nitrous acid (HONO) and peroxyacetyl nitrate (PAN) which give rise to nitrite ion must be recognised for $NO_2/NO_X$ passive sampler, or the chemical reaction between $O_3$ and NO within diffusion tubes that may lead to an overestimation of the measured $NO_2$ concentration. However, in ambient air monitoring over long sampling times, both contaminants are generally present at low concentrations relative to $NO_2$. Moreover, these species can also interfere with the measurement of $NO_2$ when applying the EU reference method for $NO_2$ monitoring based on chemiluminescence.
Several different types of diffusive samplers in general use were identified. Based on their shape, they can be classified as tube-type, badge-type, and radial type.

Recently studies aimed to assess the equivalence to the reference methods of diffusive samplers for ozone, benzene and nitrogen dioxide were carried out. The procedure of demonstration of equivalence for diffusive samplers is given in the guide Demonstration of Equivalence of Ambient Air Monitoring Methods (EC-JRC, 2008).
As a result, standard methods to assess outdoor air Nitrogen dioxide and benzene concentrations using diffusive sampling have been developed.
Based on the state-of-art knowledge, the samplers used in the European Union for $NO_2$ ambient air quality monitoring purposes should be of the tube-type design with triethanolamine as sorbent.
The $NO_2$ Palmes diffusion tube is a small cylinder that is about 7 cm long and 1 cm wide, one end of which contains a small amount of triethanolamine (TEA) as an absorbent for gaseous $NO_2$. The other end is sealed with a membrane shortly before use.
Its capacity to remove $NO_2$ from the sampled air is high (90-100%), as demonstrated using sequential sampling. Humidity is probably the most important environmental variable that affects the performance of diffusive samplers using TEA as absorbent since TEA does not perform

quantitatively at low humidity: a minimum of around 3 g $H_2O$ $m^{-3}$ is required for TEA to be effective as a sorbent in diffusive samplers.
Sufficient information was available to underpin its potential for meeting European Union data quality objectives. The relative expanded uncertainty of $NO_2$ measurements performed using these tube-type diffusive samplers can potentially be lower than 25 % for individual measurements. When aggregating results to form annual average values, the relative expanded uncertainty can be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.
The recently published European Standard (EN 16339-2013) specifies a method for the sampling and analysis of $NO_2$ in ambient air using diffusive sampling. The collected $NO_2$ is extracted as nitrite using water. The resulting extract may be analyzed by:
— Colorimetry after derivatization of the nitrite, using the Griess-Saltzman method (Atkins et al., 1986);
— Ion chromatography with conductivity detection (Miller et al., 1984).
It can be used for the $NO_2$ measurement in a concentration range of approximately 3 µg/m³ to 130 µg/m³.
The European Standard UNI EN 14662-5 gives general guidance for the sampling and analysis of benzene in air, by diffusive sampling.
A number of devices are recommended for the sampling of benzene, each device having a different range of applicability, particularly with regard to the optimum period of exposure.
More specifically a radial type sampler (a sintered microporous polyethylene cylinder as a diffusive surface containing an inner coaxial stainless steel cylindrical adsorbing cartridge containing activated charcoal) and a tube type (an open-ended glass tube containing granular coconut shell charcoal) exposed for 14 days gave satisfying results showing the ability of the sampler to meet the DQO of the reference method.
After sampling, aromatic VOCs trapped by the cartridge will be extracted with carbon disulfide then detected and quantified using internal standard capillary gas chromatography, and a flame ionization detector (FID).
Benzene in a concentration range of approximately 0,5 µg/m³ to 50 µg/m³ can be detected, in an air sample typically collected over a period of several days or several weeks, allowing for the determination of benzene in ambient air for the purpose of comparison of measurement results with limit values with a one-year reference period.

## 2.4 Assessment of spatial variability: Land Use Regression models

Current methods for assessing intra-urban air pollution spatial variability have recently been reviewed (Jerrett et al., 2005). Conventional dispersion models and empirical techniques, in particular geo-statistical interpolation methods and Land Use Regression models (LURs), were the most common approaches described in most of the studies. Application of LUR model was introduced for the first time in the SAVIAH (Small Area Variations in Air quality and Health) study (Briggs et al., 1997). After the successful pioneering work in SAVIAH, LURs have been getting increasingly: further developments have been focalized on additional variables (Rosenlund et al., 2008, Arain et al., 2007,), transferability to other locations, combination with dispersion model outputs (Zwack et al., 2011) and, more recently, on spatio-temporal aspects (Patton et al, 2014).
To evaluate the efficacy of Low Emission Zones (LEZ) in urban areas, the models that were commonly used to give a reliable estimations of air pollution, were dispersion models (photochemical or lagrangian model in according to the scale of impact and the complexity of scenario’s simulation). However, in recent years, LURs have been achieved best performances and results in order to capture small scale variations in air pollution concentrations, particularly from traffic sources, with sensible low costs. In fact, higher spatial resolution of pollutant concentration

estimation with a cost-effective approach was the main improvement of LURs in comparison to other techniques.
LURs have been performed particularly in North America and Europe within a number of studies in the last two decades (Hoek et al., 2008).
LURs combine experimental measures of air pollutants at various locations representative of the study area, and the development of a regression model using predictor variables, obtained through geographic information system (GIS). Development in GIS have contributed to the popularity of LUR methods.
Pollutant measurements were the dependent variable. A spatially network of pollutant monitoring sites must be planned: the performance of the model depends on the number and distribution of the samplers. In urban areas, routine networks (fixed monitoring stations) were not able to capture small scale variability: consequently, it was necessary to design monitoring *ad hoc* campaigns. $NO_2$, $NO_X$, NO and Volatile Organic Compounds (VOCs) were generally measured with passive sampling method that was easy, inexpensive and reliable, whereas PM ($PM_{10}$, $PM_{2.5}$, ultrafine particles) was typically measured with active samplers. There is no rigorous methodology to determine the required number of monitoring locations given a certain study objective and setting; the right choose should be take into account the size of population and city to determine the right number.
Predictors were the independent variables. Significant predictors should include traffic-related variables (distance to the nearest road, road length, traffic density), population density in the census area, land use information offered by Corine Land Cover (e.g. high and low density residential area, urban green) physical geography (latitude and longitude), meteorological parameters (temperature, wind velocity, pressure, precipitation, mixing height) and emission data (available on National Emission Inventories, produced by ISPRA).
In recent works (Tang et al., 2013), other variables were investigated. By combining data on building heights and high resolution topographical data, typical of LEZ characterisation, enhanced variables can be offered to account for the effects of building volume, road and width length (street canyon).
Predictor variables were usually computed in circular buffers around each monitoring size: the selection of buffer size (Jerrett et al., 2009, Stephaning von Klot, 2011) is crucial to determining the model performance and the spatial resolution of the estimates. Ideally, buffer sizes should be selected to take account of known dispersion pollutant patterns and the urban configuration around the study domain (heights buildings and street width).
A stochastic model is then applied to predict the concentrations in the whole selected area, including sites where the measures were not carried out.
A standardized approach in a LUR model development was performed in the European Study of Cohorts for Air Pollution Effects (ESCAPE) (Eeftens et al, 2012). Following the ESCAPE protocol, a stepwise forward regression method should be applied to develop the model from a large set of predictor variables that maximizes the percentage of explained variability ($R^2$, $R^2$ adjusted) and minimizes the Root Mean Square Error (RMSE). The forward selection process started with the variable that maximizes the adjusted $R^2$; in every iteration, all the potential predictor variables were entered independently. The predictor variable, producing an increase in the adjusted $R^2$ higher than 1%, was added to the model if the direction of the association with pollutant was as expected. The procedure was repeated until no additional variables could increase the adjusted $R^2$. Covariates with p-value higher than 0.1 were sequentially removed from the model.
Standard diagnostic tests for ordinary least regression (t-test, influential observation by Cook's Distance, homoschedasticity, normality of the residuals and spatial autocorrelation) should be applied to the final model to assess the linearity and independence of errors assumptions.
Finally, model validation through Leave-One-Out Cross Validation (LOOCV) method should be taken to asses the predictive ability of the model to a new dataset.

# 3 Study protocol

The objectives of action B5 will be to assess whether the implementation of the noise low emission zone contributes, as an ancillary effects, to reduce air pollution levels in the study area.

To assess the impact of Monza LEZs will be used the follow approach which arises from the previous analyses:

- Assessment will be carried out on the basis of monitoring campaign which will include at least particle number concentration parameter in addition to standard pollutant measurements (PM, $NO_X$, benzene, etc.);
- Advanced statistical techniques will be used to try to remove the influence of confounding factors at local level.

In order to compare the spatial variability of air pollution before and after the noise LEZ implementation, $NO_2$ and benzene land use regression models in a 16 $km^2$ of the urban area of Monza, (Italy) including the noise LEZ, will be developed.
Moreover the temporal pattern of several traffic related pollutant will be continuously monitored.
The variation in the temporal profile of each pollutant that could be due to the LEZ implementation will be studied by comparing the co-located measurement carried out inside and outside the LEZ.
The study area will be chosen with the aim to be representative of the potential impact of the measure to be undertaken, due to the overall emissions potentially reduced, particularly those coming from truck traffic, that most likely significantly affect the surrounding air quality.

*Temporal pattern*

Measurement campaigns will be performed before and after the noise LEZ implementation using a mobile laboratory located in Via della Libertà (inside the LEZ) and contemporary taken at a fixed site in the urban area of Monza (outside the LEZ) belonging to the regional air quality network. Measurements will lasts 8 weeks in 2017, (2 weeks by each Seasons) and will be repeated during 2019 with the same schedule.
Hourly ($SO_2$, CO, $NO_2$, $NO_X$) and daily ($PM_{10}$, $PM_{2.5}$) averages will be measured using the respective European reference methods.
Moreover the particle number concentration (PNC) and size distribution in the 0.3 ÷ 10 µm range, will be measured with an aerosol particle sizer, while continuous measurement of black carbon and aerosol light absorption properties will be carried out using a Multi Angle Absorption Photometer.
Contemporary the same pollutants will be monitored with the same schedule at a fixed site in the urban area of Monza (outside the LEZ) belonging to the regional air quality network.

*Spatial pattern*

The low cost and easy operation of the diffusive sampling technique will be used for a large scale air pollution surveys with a high spatial resolution.
NO2 and benzene, as traffic sources indicators, will be measured at 30 locations, within and outside the noise LEZ, in winter and summer (14 days each) before the noise LEZ implementation (2017) and after the implementation (2019).
Each selected site will be chosen following the provision on macro and micro siting criteria described in the section 2.2.
The sites will be visited and geo-coded using a high sensitivity GPS receiver (eTrex Vista HCx, Garmin), before and after each measurement campaign. Coordinates will be checked on GIS map, and if necessary, corrected manually.

Palmes-type diffusion tubes will be used for $NO_2$ sampling, with triethanolamine as sorbent. Radiello RAD 130 will be used for aromatic VOCs (Sigma-Aldrich) and only benzene will be quantitatively detected.
Duplicate $NO_2$ and VOCs samplers, provided with weather protective shelters, will be deployed at 2.5 m above the ground, placed on lamp post, utility poles or street signals.
All $NO_2$ and aromatics VOCs samplers will be removed 14 days after their installation.
Three field blanks will be also collected during each monitoring campaign for the different passive samplers. The limits of detection and precision will be calculated following the protocol used in the European Study of Cohorts for Air Pollution Effects (ESCAPE) (Cyris et al., 2012; Eeftens et al., 2012).
Co-location of passive samplers at a few sites with continuous monitors has generally shown good agreement, but it remains important to include co-location in each new study.
In order to compare $NO_2$ and benzene measurements with the corresponding European reference method (EN 14211, 2005; EN 14622-3, 2005) two diffusive samplers will be co-located at two monitoring stations managed by the Environmental Protection Agency of Lombardia (ARPA LOMBARDIA) in the urban area of Monza.
The $NO_2$ analysis will be spectrophotometrically based upon the Saltzman method.
Aromatic VOCs will be extracted with carbon disulfide then detected and quantified using internal standard capillary gas chromatography performed on a HP-6890 Gas Chromatograph (HewlettePackard Inc., USA) (column VOCOL 25m x 0.25 mm x 0.25 µm, Supelco, Bellefonte, PA, USA) with FID detection.
The airborne 14 day $NO_2$ and benzene, mean concentrations will be then calculated using standard procedure (EN 13528-2, 2003). Quality control and quality assurance procedures for all laboratory analyses based on the manufacturer's specifications and the ISO standard methods guidelines will be strictly followed (EN 13528-3, 2004).
For each site, results from the four campaigns will be averaged to estimate the annual mean. Concentrations will be adjusted for temporal variation using a centrally located reference site.
The land use regression models for average $NO_2$ and benzene spatial pattern in the study area before and after the LEZ implementation will be developed and evaluated following the standardized approach described in the section 2.4.

# 4 References


Arain et al., "the use of wind fields in a land use regression model to predict air pollution concentrations for health exposure studies", Atmos. Environ. 41, 3453-3464, 2007.

D. Atkins, J. Sandalls, D. Law, A. Hough, K. Stevenson. The measurement of nitrogen dioxide in the outdoor environment using passive diffusion tube samplers. United Kingdom Atomic Energy Authority, Harwell Laboratory, Report AERE R12133, 1986.

Briggs et al., "Mapping urban air pollution using GIS: a regression-based approach", International Journal of Geographical Information Science, volume 11, 1997 -Issue 7

Buzica et al., The equivalence of diffusive samplers to reference methods for monitoring O3, benzene and NO2 in ambient air J. Environ. Monit., 2008, 10, 1052–1059

Cyrys, J. Et al. Variation of NO2 and NOx concentrations between and within 36 European study areas: Results from the ESCAPE study. Atmos. Environ. 62, 374- 390, 2012.

Brunekreef, B. Study manual ESCAPE - European Study of Cohorts for Air Pollution Effects. Institute for Risk Assessment Sciences Utrecht University, 2008

Eeftens et al., Development of land use regression models for PM2.5, PM2.5 absorbance, PM10 and PMcoarse in 20 European study areas; results of the ESCAPE project. Environ. Sci. Technol. 46, 11195-11205, 2012.

EN 13528-2, 2003. Ambient air quality - diffusive samplers for the determination of concentrations of gases and vapours - Requirements and test methods. Part 2: Specific requirements and test methods.

EN 13528-3, 2004. Ambient air quality - diffusive samplers for the determination of concentrations of gases and vapours - Requirements and test methods. Part 3: Guide to selection, use and maintenance.

EN 14211, 2005. Ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence.

EN 14662-3, 2005. Ambient Air Quality - Standard method for the measurement of benzene concentrations - Part 3: Automated pumped sampling with in situ gas chromatography.

EN 14662-5:2005 Ambient air quality - Standard method for measurement of benzene concentrations - Part 5: Diffusive sampling followed by solvent desorption and gas chromatography

EN 16339:2013 Ambient air - Method for the determination of the concentration of nitrogen dioxide by diffusive sampling

Fensterer V.et al., Evaluation of the Impact of Low Emission Zone and Heavy Traffic Ban in Munich (Germany) on the Reduction of PM10 in Ambient Air, Int. J. Environ. Res. Public Health, 11, 5094-5112, 2014.

Guidance on air quality assessment under the Air Quality Directive 2008/50/EC – European Commission, Dg Environment, May 2010.

Guide to the demonstration of equivalence of ambient air monitoring methods, in P. Pérez Ballesta, " Proceedings of Equivalence of Ambient Air Analytical Methods", EUR 23216 EN, ISBN 978-92-79-08205-4, ISSN 1018-5593, DOI 10.2788/63342, 2008.

Hafkenscheid T., et al. Review of the application of diffusive samplers in the European Union for the monitoring of nitrogen dioxide in ambient air. European Commission, Joint Research Centre Institute for Environment and Sustainability. Luxembourg: Office for Official Publications of the European Communities European Communities, 2009.

Hoek et al., "A review of land-use regression models to asses spatial variation of outdoor air pollution", Atmos. Environ., 42, 7561-7578, 2008.

Holman C. et al., "Review of the efficacy of low emission zones to improve urban air quality in European cities", Atmospheric Environment, 111, 161-169. 2015.

International Agency for Research on Cancer (IARC). Outdoor Air Pollution. IARC monographs on the evaluation of carcinogenic risk to humans. Volume 109. Lyon, France: IARC; 2015. http://monographs.iarc.fr/ENG/Monographs/vol109/index.php

Invernizzi G. et al., "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, 2011.

ISO 11222:2002. Air quality – Determination of the uncertainty of the time average of air quality measurements

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

Jerrett et al., “A distance-decay variable selection strategy for land use regression modelling of ambient air pollution exposures”, Science of the Total Environment, 407, 3890–3898, 2009.

Jones A.M. et al., “A large reduction in airborne particle number concentrations at the time of the introduction of “sulphur free” diesel and the London Low Emission Zone”, Atmospheric Environment, 50, 129-138, 2012.

Miller D. Ion chromatographic analysis of Palmes tubes for nitrite. Atmos. Environ. 18 (1984) 891–892.

Morfeld P,et al. (2014) “Effectiveness of Low Emission Zones: Large Scale Analysis of Changes in Environmental NO2, NO and NOx Concentrations in 17 German Cities”,PLoS ONE 9(8): e102999. doi:10.1371/journal.pone.0102999, 2014.

Patton et al., “An hourly regression model for ultrafine particles in a near-highway urban area”, Environ. Sci. Technol, 48, 3272-3280, 2014.

Rosenlund et al., “Comparison of regression models with land use and emissions data to predict the spatial distribution of traffic-related air pollution in Rome”, J. Expo. Sci. Environ. Epidemiol, 18, 192-199, 2008.

Tang et al., “using Building Heights and Street configuration to Enhance interurban PM10, NOx and NO2 Land Use Regression Models”, Environ. Sci. Technol, 47, 11643-11650, 2013.

UNI EN 13528-1:2003. Campionatori diffusivi per la determinazione della concentrazione di gas e vapori. Requisiti e metodi di prova - Requisiti generali

UNI EN 13528-2:2003. Campionatori diffusivi per la determinazione della concentrazione di gas e vapori. Requisiti e metodi di prova - Requisiti specifici e metodi di prova

UNI EN 13528-3:2004. Campionatori diffusivi per la determinazione della concentrazione di gas e vapori - Requisiti e metodi di prova Parte 3: Guida per la scelta, l’utilizzo e la manutenzione.

UNI EN 14662-4:2005. Metodo normalizzato per la misurazione delle concentrazioni di benzene Parte 4: Campionamento diffusivo seguito da desorbimento termico e gascromatografia

Stephanie von Klot, “ Equivalence of using nested buffers and concentric adjacent rings as predictors in land use regression models, Atmos. Environ., 45, 4108-4110, 2011

Van Roosbroeck, S. et al. 2006. Long-term personal exposure to traffic-related air pollution among school children, a validation study. Sci. Tot. Environ. 368, 565-573.

WHO, 2000, Air quality guidelines for Europe, World Health Organization, Regional Office for Europe, Copenhagen (http://www.euro.who.int/__data/assets/pdf_file/0005/74732/E71922.pdf) accessed 4 September 2015.

WHO, 2006, Air Quality Guidelines: Global update 2005. Particulate matter, ozone, nitrogen dioxide and sulphur dioxide, World Health Organization, Regional Office for Europe, Copenhagen.

World Health Organization. Review of evidence on health aspects of air pollution – REVIHAAP Project. Copenhagen, Denmark: WHO; 2013. http://www.euro.who.int/en/health-topics/environment-and-health/air-quality/publications/2013/review-of-evidence-on-health-aspects-of-air-pollution-revihaap-project-final-technical-report Accessed 11 May 2016.

Zwack et al., “using dispersion models and mobile monitoring to characterize spatial patterns of ultrafine particles in urban area”, Atmos. Environ., 45, 4822-4829, 2011.