



# Air Quality Study for a new Thermal Treatment Facility (TTF)

PA/06096/23


# Report



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# 1 INTRODUCTION

This report outlines the results from an air dispersion model carried out for the proposed new Maghtab Thermal Treatment Facility (MTTF). The assessment has been requested by the ERA to evaluate various operational scenarios and thus obtain a good understanding of the impacts from the proposed facility. The assessment has been based on the Terms of Reference (ToRs) issued by ERA for a new Thermal Treatment Facility (PA/6096/23).

The modelling suite used throughout this exercise has been capable of incorporating all the substances included in the terms of reference. Specifically, the same suite of dispersion modelling was used, in order to assess for the likelihood of significant effect on ambient air quality (including exceedances of the ambient limit values in SL.549.59) as well as on the deposition levels of particular components, due to the operation of the new plant MTTF.

Under normal operations, the project designers have stated that the MTTF will operate a thermal load ranging between 60% and 100% (and at 110% for 1 hour every 24hours). The waste type and quantities being incinerated shall influence the thermal load. The facility is not designed to operate outside the aforementioned range and would thus automatically shut down.

Therefore, the analysis was developed with three different scenarios in mind:

- Typical operations (Scenario A): 60% thermal load for 24hours, with a flue gas flow per line of 4116 Nm<sup>3</sup>/h for 24 hours;
- Maximum operating conditions (Scenario B): 100% thermal load for 23hours (flue gas flow per line of 6860 Nm<sup>3</sup>/h) and 110% load for 1 hour (a flue gas flow per line of 7814 Nm<sup>3</sup>/h);
- Abnormal operating conditions (Scenario C): based on the limits defined in Schedule 2 of S.L.549.81, a dust concentration of 150 mg/Nm<sup>3</sup> shall be set at the stack at maximum operating conditions

All simulations were conducted by considering the optimal height of the stack at 25 meters defined on the basis of the results of a previous study which compared three chimney stack heights for the MTTF, at 25m, 30m and 35m respectively. The study had revealed that there were no significant variations in the impacts on air quality for the three different stack height scenarios, and thus the designers opted for a shorter chimney stack to minimise visual impacts and associated costs.

The model also considered the cumulative air quality impacts from the operation of the adjacent Waste-to-Energy facility.



## 2 METHODOLOGY

The impact of air quality emissions is determined by applying a mathematical model of dispersion and atmospheric fallout, which calculates the concentration of substances emitted by the incinerator in ambient air at ground level, integrating and processing the emission data, the data meteorological and geomorphological (see figure 1). The following regulatory references have been considered for the preparation of this document:

- a) UNI EN 13725: 2004 "Air quality. Determination of odor concentration by dynamic olfactometry".
- b) UNI 10796: 2000 "Evaluation of the dispersion of aeriform effluents into the atmosphere. Guide to the selection criteria of mathematical models".
- c) UNI 10964: 2001 "Environmental impact studies. Guide to selecting mathematical models for predicting impact on air quality".

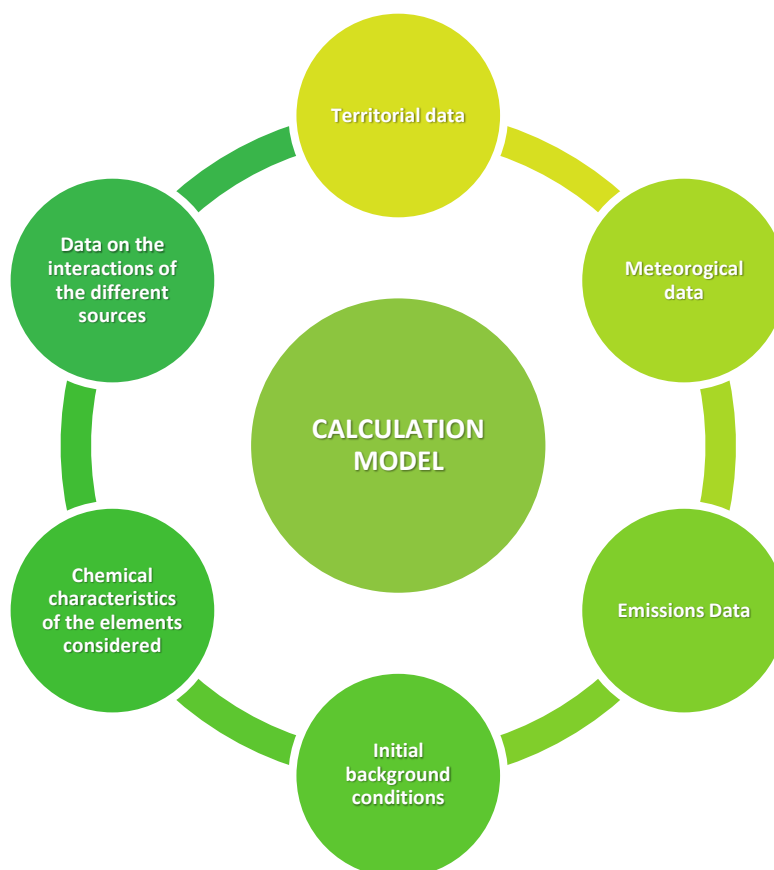


FIGURE 1: SCHEMATIC REPRESENTATION OF THE TYPE OF INFORMATION AND INPUT DATA REQUIRED BY THE MODEL

The emission factors used are the provisional limit values in normal operating conditions based on "Tentative limit values under normal operating conditions based on BAT and IED" shown in Table 3 of the EIA TORs dated 05/08/2024. The model used in this study is capable of predicating the dispersion and deposition of pollutants under variable meteorological conditions ranging from the most favorable to the least favorable. The modelling suite permitted the annual calculation of the

required parameters. The spatial resolution obtained by the model is equal to 5 x 5 m, to enable the identification of impacts at sensitive receptors.

Generally, an air quality model (or "atmospheric dispersion model") is a mathematical algorithm that has as its objective the calculation of the concentrations in the atmosphere of one or more pollutants emitted by a defined set of sources. The two main categories of models are *stochastic* and *deterministic* models.

The *stochastic* do not refer to physical cause-and-effect relationships but only to statistical correlations, for which they are characterized by a series of intrinsic limits and are mainly used to formulate semi-quantitative forecasts on air pollution, which must however be validated by an experienced operator.

The *deterministic* models, on the contrary, are made up of mathematical algorithms which reproduce (more or less according to the typology of the model itself) the diffusion, transport and chemical transformation processes to which the pollutants are subjected once emitted into the atmosphere.

The information presented here refers mainly to this second category of models: it is in fact to the deterministic models that the legislation refers (in particular the DM 261/2002 - *Regulation containing the technical directives for the preliminary assessment of the quality of the ambient air, the criteria for the preparation of the plan and the programs referred to in articles 8 and 9 of the legislative decree 4 August 1999, n.351*), as they potentially allow to face any type of simulation scenario.

Deterministic models, by their own nature, need a series of input data, which can be divided into three general types:

- a) *geographical data*, which describe the geographical characteristics of the territory in which the emissive phenomenon occurs, in particular the topography and roughness. The territorial context in which the model is applied is called the calculation domain;
- b) *emission data*, which describe the characteristics of the sources of atmospheric pollution that are taken into consideration, in particular the quantity and type of pollutants emitted;
- c) *meteorological data*, which describe the ways in which pollutants are dispersed in the atmosphere, in particular anemology and phenomena related to turbulence and atmospheric stability. A typical set of weather data needed for an analysis is made up of an annual data set.

They provide the spatial distribution of one or more pollutants in a given area, the so-called concentration fields which, in the case of the most advanced models, have a three-dimensional character.

The most advanced air quality models require real input data pre-processing modules, in particular as regards meteorological data; in this case we speak more properly of modeling chain since the pre-processing modules of meteorological data

are in turn real models that provide output fields of quantities such as: wind characteristics, temperature, atmospheric turbulence etc.

There are two basic categories of deterministic models, depending on the spatial coordinate system which they refer. The *Eulerian models* refer to a fixed coordinate system, while the *Lagrangian models* use a mobile coordinate system that follows the movements of the air masses. The Eulerian models are divided into *analytical models*, and into *grid models*. In the analytical ones, through the introduction of a series of simplifications, it is possible to analytically solve the general differential equation that describes transport and diffusion.

The so-called "*plume*" *Gaussian models*, which constitute the simplest tool in the field, and the "*puff*" *models*, belong to the analytical Eulerian models. The fundamental difference consists in the fact that the Gaussian models assume that the process is stationary (ie that in every point of the domain the variation in concentration over time is zero), while the "puff" models allow a treatment, albeit simplified, also of non-stationary processes. Both solutions assume that the emission originates at a point in space (point source) and also the meteorological geometries considered are very simplified.

In grid models, however, the calculation domain is always three-dimensional, it is divided into a series of cells through a suitable grid and the general transport and diffusion equation is taken in a more complete (non-stationary) form that requires resolution by numerical methods. To this category belong the photochemical models capable of describing, in addition to diffusion and transport, also the phenomena of chemical transformation to which pollutants are subjected once they are released into the atmosphere.

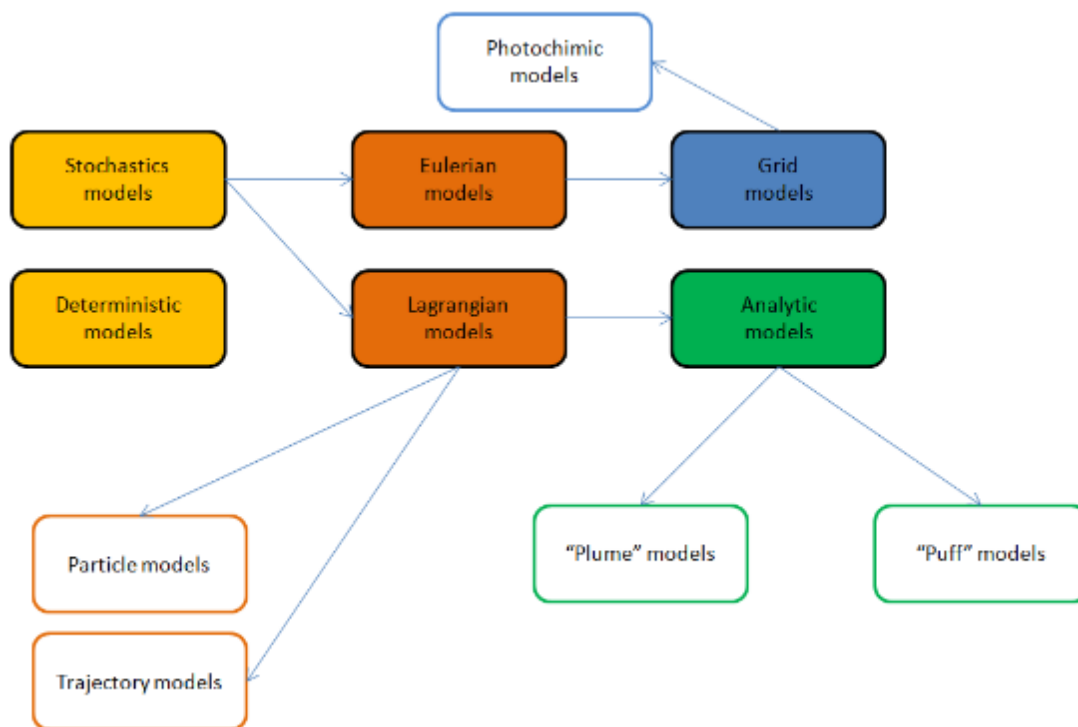


FIGURE 2: MAIN TYPES OF MODELS

Lagrangian models, which are also capable of describing non-stationary processes, are divided into *particle* and *trajectory models*. The emission of each pollutant is represented, in the first case through a series of small units of known mass (called particles), in the second by one-dimensional vertical columns. In both cases, these are models that use a three-dimensional computation domain, but while particle models are also suitable for simulations of high spatial detail, trajectory models are used in the study of phenomena at a very large spatial scale, of the order thousands of kilometers, as in the case of cross-border pollution.

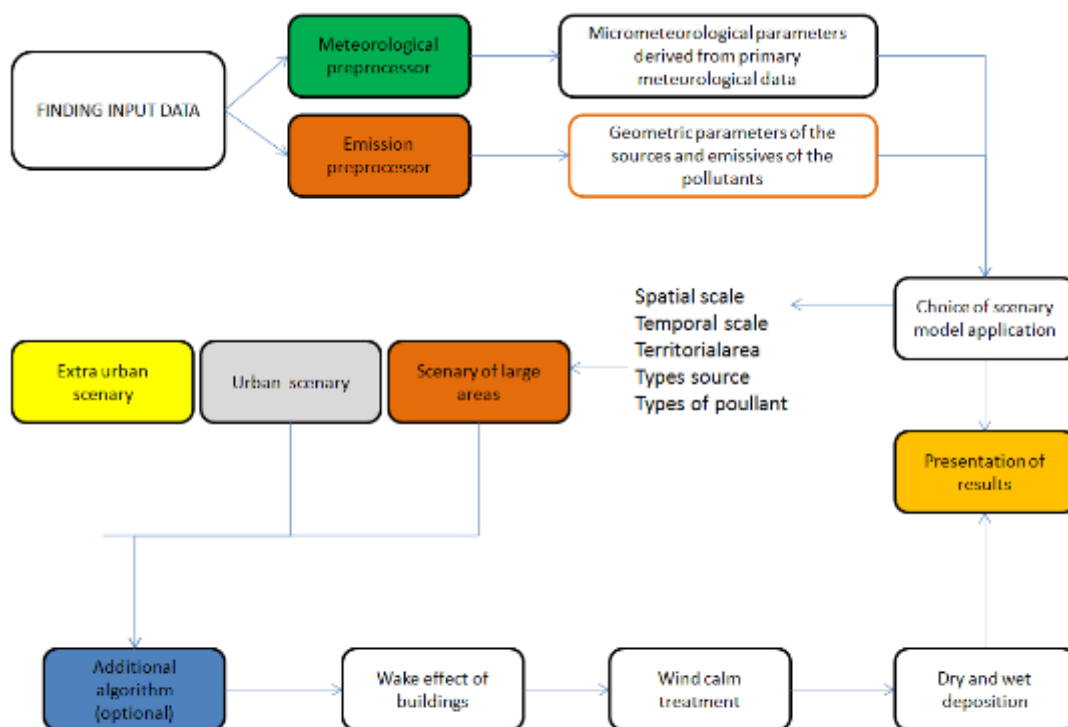


FIGURE 3: REALIZATION PHASES OF A DIFFUSION MODEL IN THE ATMOSPHERE.

## 2.1 MODEL APPLICATION

When making the choice of an air quality model (or a modeling chain), it is necessary to bear in mind the nature of the problem to be addressed. For this purpose, the notion of scenario is very useful, that is, the set of elements that characterize a specific application. Based on the Guidelines for the selection and application of atmospheric dispersion models for assessing air quality, a scenario is defined by five elements:

- the *spatial scale*, for which micro-scale applications (up to 1 km), local scale (up to 10 ÷ 20 km), mesoscale (up to 100 ÷ 200 km) are distinguished;
- the *time scale*, for which short-term (roughly a few minutes to a few days) and long-term (seasonal and annual periods) applications are distinguished.
- the *territorial context*, for which applications on a simple site (flat terrain, homogeneous territorial and meteorological characteristics) and on a complex site (complex orography, territorial and / or uneven meteorological characteristics) are distinguished.
- the *types of source* present, for which point, linear and areal sources are distinguished.
- the *types of air pollutant* taken into consideration, whereby a distinction is made between non-reactive (or reactive to the first order, that is, decay expressed by means of time constant) and reactive pollutant.

From the choice of the different types of elements, one of the three different types of possible scenarios emerges:

1. Urban areas
  - 500x500 m<sup>2</sup> spatial staircase (typical size of a block that houses buildings and roads), up to 10x10 km<sup>2</sup> (surface within which the entire urban area can be included).
  - This scenario is dominated by pollutants emitted above all at ground level by vehicular traffic, and is characterized by a marked spatio-temporal variability of concentrations. It can be described with analytical models that allow the treatment of linear sources in the form of a road graph and of areal sources as a composition of emissions from domestic heating or in cases where it is desired to describe the contribution of a network of roads without distinguishing the individual contributions.
2. Extra urban areas
  - This scenario is dominated by the typical emissions of a given production area (e.g. sulfur dioxide and nitrogen oxides due to the combustion processes of fossil fuels), generally conveyed into chimneys (emissions from point sources) and / or from emissions of extra-urban road arteries (emissions from linear sources).
  - This is the case most frequently treated with models: since the 1960s simulations of the dispersion of radionuclides emitted in the event of accidental release from nuclear plants were carried out and then the study was carried out of the behavior of plumes of pollutants emitted into the atmosphere by large industrial plants through chimneys (point sources) or from the buildings of the plants (area sources)
3. Extended areas
  - This scenario is the most general one and considers the set of polluting sources located on spatial scales ranging from extended urban realities, such as large metropolitan areas to aerological basins affecting multiple regions (as in the case of the Po valley). The treated domains can therefore be of the order from 50x50km<sup>2</sup> up to 500x500km<sup>2</sup> and consider both primary and secondary pollutants.

## 2.2 TYPE OF SOURCES AND ASSIGNMENT CRITERIA

There are three types of sources: *point, linear and areal*.

Generally, the assignment of a source to one of these classes takes place on the basis of several criteria: the form (typically, for example, the emissions distributed on a line such as road, air transport infrastructures etc.) fall within the line, whether or not to relocate the source in the form of point or linear. In this regard, for example, the position of large industrial plants is usually sufficiently characterized, therefore emissions are generally attributed to a specific source, vice versa, emissions from heating systems for civil use, since they cannot be georeferenced individually due to

their number, are usually attributed to the emissions of the polygon corresponding to the census / municipality / province / region to which they belong according to the detail and therefore treated as areal.

A similar example concerns road traffic emissions, in fact usually the main road arches are treated individually while the secondary ones are sometimes considered as a whole, corresponding to the neighborhood or cell to which they belong. A further classification criterion involves the identification of appropriate threshold values, i.e. emission values on the basis of which to differentiate between sources that must be considered stand-alone if the emissions exceed the established threshold or can be grouped with others, similar for type of pollutant and process. On the basis of these considerations, the sources are then divided between punctual, to be considered individually, and areal.

In the impossibility of treating all the sources individually, it is evident that the choice of the threshold values sometimes depends on the resources available and the purposes of the inventory or modeling application.

### 2.3 EMISSIONS PREPROCESSOR

An emissions preprocessor is a SW tool that processes the information relating to the emissions necessary for the execution of an air quality model using appropriate estimation methods or from existing data (emission inventories, measurements). Usually for modelling purposes, emissions are treated as:

- punctual
- linear
- areal and volumetric

The emissions present in the simulation domain, once assigned with appropriate criteria to one of these types, must be adequately characterized according to the information required by the models. The main sources for obtaining this information are the emission inventories which are prepared both on a national scale by the APAT (Agency for the Protection of the Environment and for Technical Services), and on a local (regional, provincial etc.) scale by the related entities. The input relating to emissions generally represents one of the most complex input data to be obtained both for the small number of local inventories available on the national territory and for the complexity of the processing to be performed on the data coming from the inventories, as it is generally aimed at other purposes and not equipped with sufficient spatial and temporal detail to be directly usable by a model.

It is therefore necessary to use more or less complex emission processors depending on the availability of the initial data and the type of QA model to be applied, on which the complexity of the input to be prepared depends. The case of a three-dimensional model for reactive pollutants undoubtedly represents the most complex one since it requires the emissions specified for each cell of the grid, for each hour of simulation, for each chemical species treated individually or combined.

A processor for the predisposition of the emissions must therefore allow to carry out:

- a) the spatial allocation to allow the passage from the territorial detail (common for example) to the cell;
- b) the temporal breakdown to allow the estimates to be reduced from annual to hourly basis;
- c) speciation to transform the overall information of VOCs and PTSs into group species required by the model;
- d) the particle size distribution to derive PTS estimates in particle size classes according to the requests of the model.

This obviously applies in a completely general way, this does not exclude that, in some cases, the available emissions may already exhaustively cover one or all four of the desired details (spatial and / or temporal and / or chemical-physical of the polluting species) and therefore the use of the processor is limited to the supply of the missing detail or to the reading / writing of the emissions in the requested IT format.

## 2.4 TYPE OF DATA REQUIRED BY A QA MODEL

Usually, a model requires the following groups of information about the source:

- a) coordinates (coordinates of the extremes of the arc usually described by means of broken lines in the case of linear ones, coordinates of an angle in the case of areas usually treated as a composition of square-shaped area sources, of the center of gravity of the chimney in the case of points);
- b) physical-geometric parameters (height and diameter of the chimney, temperature and speed of the fumes or equivalent parameters such as the flow rate, in the case of the linear ones, for example, the slope may be required, if above / below high etc.);
- c) quantity of polluted emissions per unit of time or emission accruals for each pollutant. The emission accruals are usually deducted either from direct measurements or from estimates according to the reference methodologies.
- d) a time modulation profile referring to the year / month / day.

This applies in the simplest case, for example referred to the Gaussian models. The numerical dispersion models for the study of reactive pollutants, taking instead the more complex but more significant case in order to better highlight all the critical issues, require hourly emission values for the entire simulation period, specified for each cell of the grid, and for about twenty species containing either single chemical species or group species, that is, they treat groups of compounds similar in structure and reactivity as a single chemical species. The discussion is further complicated if you also want to model the particulate matter, in which case it is necessary to know the distribution by particle size classes (knowledge of the finest particles of particular interest) and the chemical composition.

During the development and analysis of the emission pre-processors, the definition of some strictly spatial and geographical parameters, such as the coordinate system,

the dimensions and plans of the receptor grid, the orographic data and the any effects of the orography if considered complex.

## 2.5 METEOROLOGICAL PREPROCESSOR

The most frequently used models for the simulation of point and linear sources from extra-urban traffic (Gaussian or "puff" analytics) generally require primary meteorological data (wind speed and direction, temperature). Stability classes (eg Pasquill-Gilford) and mixing height, micrometeorological parameters derived from primary meteorological data, are generally used to characterize stability.

To derive these quantities, it is possible to use a one-dimensional meteorological preprocessor applied to the data collected as close as possible to the release point. It is very useful to have vertical wind and temperature profiles. Since there are no on-site stations, it is possible to use meteorological information suitably processed using a three-dimensional meteorological preprocessor applied using all the meteorological information available on a given area (ground stations and radio soundings).

### EXAMPLE 1 - Point source simulation

In these cases the source term is generally known or easily estimated (from the fuel used or the number of vehicles present), as well as the characteristics of the emission (emitting surface, height of release, temperature of fumes, etc.); the size of the domain of interest for assessing the impact of these sources varies from a few hundred meters for releases of cold fumes near the ground or for the estimation of concentrations near road viaducts, to a few tens of kilometers for releases from chimneys high (> 200m) of hot fumes or for the emissions of a motorway section.

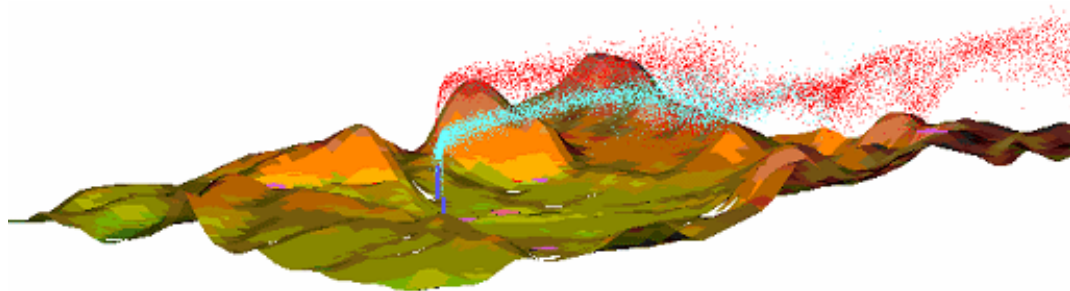


FIGURE 4: POINT SOURCE SIMULATION

The models historically developed and used for these cases are the "Gaussians"; however, it is necessary to take into account the limitations to their use: in fact the application of these models in incorrect conditions has often led to very disappointing results in the comparison between simulated and measured concentrations. Its use can be recommended for sites that are not orographically complex, with very low percentages of calm and weak winds and for emissions close to the ground; in these cases, even with few meteorological data (the historical series of the data of an anemometer placed at altitude release is sufficient) it is possible to obtain useful indications on the concentrations on the ground; it is necessary to pay attention to the choice of the dispersion parameters and to be guided in the choice

between the different families of curves (Pasquill, Briggs, etc.) by comparing them with measured data.

To simulate emissions in all other conditions (releases above 100m of hot fumes, complex sites) it is necessary to collect an adequate data-set of meteorological measurements at ground level and at altitude which describe in detail the weather-diffusive phenomena acting on the site, so to be able to activate the simulation models for the dispersion of pollutants as closely as possible to the actual conditions of the atmosphere. In these cases, puff and particle models can be used, supported by appropriate meteorological models for the reconstruction of wind fields on sites with complex orography.

Depending on the resources available, two different simulation models can be used.

- Short Term Calculation (punctual)
- Long Term calculation (climatological)

In the first, a sort of snapshot of the diffusion of a certain pollutant is represented on the basis of precise data such as direction and wind speed, and this makes it possible to calculate and evaluate any legal limits on the pollutants emitted in each receptor of the grid.

The second, on the other hand, allows to simulate a significant number of days representative of the different types of weather and therefore, based on their frequency of occurrence, to reconstruct the climatological indicators. Generally, a temporally broad set of starting data is needed in order to characterize the "diffusion trends" in the area of pollutants according to the climatology typical of the study area.

Based on the scenario in question and the characteristics of the area, it may be necessary to calculate some downwash effects (deflection) of the flow, such as the wake effect of the chimney itself and / or the wake effect of the buildings when they are upwind at the point emission (building downwash). The effects of these phenomena therefore entail a lowering of the effective height of the plume and this can increase the spread of pollutants at lower altitudes. In defining the emissions dispersion model and in the study report, the geographical coordinates of each of the buildings and the height of the building relative to the ground must be reported for each of the buildings that generate wake effect.

## 2.6 WIND CALM TREATMENT

Often the more precise dispersion models have a special method for treating calm winds. Many of the available software have a significantly different algorithm from the regular one for calm winds for all those hours of the simulation time domain in which the wind speed is lower than a certain defined threshold value.

It is also necessary that the percentage of hours for which the model uses the special method is minimal, and possibly less than 2% since:

- a) the olfactory impact parameter to be expressed as the final result of the simulations is in the form of the 98th percentile;
- b) in calm wind conditions the maximum olfactory impact is often obtained, since the pollutants are less effectively mixed in the atmosphere.

Some dispersion models that operate with very rich or very poor weather data on rainy days often need to activate the calculation algorithms relating to the deposition processes that take place within the air mass. These processes are:

- a) Dry Deposition: Mechanism always present in the PBL (Planet boundary layer) which eliminates a part of the pollutant present in the plume and transfers it to the ground without intervention of the water present in the atmosphere.
- b) Wet deposition: Elimination mechanism caused by the action of rainwater on the plume.

In many cases studied however, these algorithms are not often necessary and are cautiously deactivated in the modeling phase.

## 2.7 DESCRIPTION OF THE SITE AND ITS SURROUNDINGS

The proposed site for the TTF forms part of the ECOHIVE complex, located in Maghtab, a village within the locality of Naxxar. This area forms part of the North-east coastal zone of Malta, as shown in Figure 5, and in greater detail in Figure 6. It is mainly characterised by rural and agricultural land. The satellite map of the scheme size and location, and its 100 m boundary are shown in Figure 7.



FIGURE 5: THE GEOGRAPHICAL LOCATION WITHIN THE MALTESE ISLANDS (SOURCE: GOOGLE EARTH)



FIGURE 6: SCHEME LOCATION IN MALTA (Source: Google Earth)



FIGURE 7: PROPOSED SCHEME SITE FOOTPRINT AND IMMEDIATE SURROUNDINGS

## 2.8 DESCRIPTION OF THE PRODUCTION PLANT (MTTF)

The ECOHIVE complex in which the TTF is proposed consists of several other waste management facilities, which to date include the ground work for the Waste to Energy facility, a proposed Material Recovery Facility, an Organic Processing Plant, Biowaste Treatment Plant. The TTF site is an irregular shape, with the longest part measuring 220m. The total site footprint is 18,185m<sup>2</sup> of land which will undergo a change in use from non-intensive agriculture to accommodate the Thermal Treatment Facility as shown in Figure 8.

This scheme is being proposed to establish a new hazardous waste incineration plant and centralise all the major waste operations carried out by Wasteserv Malta. The project entails the preparation of a new hazardous waste incineration plant with two independent lines, and space for a potential third independent line in the future. The proposed development will form part of the ECOHIVE Complex and will operate in conjunction with the other waste management facilities at Maghtab.



FIGURE 8: RENDER OF THE PROPOSED THERMAL TREATMENT FACILITY

The plant shall comprise of two independent lines, with space for an additional third line. Each line will have an incineration/boiler and Flue Gas Treatment (FGT) that can operate independently of each other. Each line consists of a rotary kiln, a waste heat boiler with combustion air fans, economiser, FGT reactor and bag house filter.

## 2.9 FALLOUT MODEL ELABORATION

### 2.9.1 Model - Windimula

WinDimula is a plume Gaussian model that allows performing diffusion calculations in the atmosphere of non-reactive pollutants emitted from multiple point and area sources, scattered over an area that represents the domain of calculation of the model, in the presence of complex orography. The model allows to perform both "Short Term" and "Climatological" simulations. WinDimula also allows to evaluate the effective heights of pollutants emitted by chimneys for each class of atmospheric stability. The model allows the calculation of the concentrations of pollutants in all the receptors defined within the calculation domain (both Cartesian and discrete) and of both dry and wet deposition.

A "Short Term" or punctual calculation represents a sort of "snapshot" of the diffusion of a certain pollutant based on "punctual" meteorological data (ex: hourly wind direction and speed).

The WD calculation code allows the user to perform multiple point simulations in sequence; in this way it is possible to evaluate any legal limits on the pollutants emitted. In particular, if an annual sequence of hourly meteorological data is available, it is possible to perform WD on the entire sequence of data, evaluating for example in each receptor of the calculation grid the maximum hourly concentration value detected during the whole considered sequence.

With the WDPRO postprocessor it is possible to evaluate other legal limits both in terms of values and percentiles for the pollutants considered. A climatological simulation, on the other hand, does not allow to make assessments on the limits of the law but allows to evaluate the "diffusion trends" in the area of interest (calculation domain), that is those areas of the calculation domain mainly affected by the atmospheric diffusion of pollutants.

A climatological calculation is basically a set of point calculations (by sectors) weighted however with respect to their statistical occurrence frequency. Having therefore available suitable series of meteorological data it is possible to climatologically characterize a certain area through the definition of a suitable JFF (Joint Frequency Function).

The calculation model also allows to evaluate the diffusion of the pollutant into the atmosphere even in situations of "calm wind". In these cases WD integrates a suitable model (Cirillo Poli model) for calm winds. The model has no limitations. The execution times of a simulation depend on the type of calculation required, the size of the grid (number of grid nodes), the number of sources considered, the type of meteorological data used. The presence of calm wind situations always leads to an increase in the temporal performance of the execution, as this is not a directional calculation but carried out on a 360 ° angle around each source.

APAT (Italian agency for environmental protection and technical services) has included WinDimula in the models to be applied for the evaluation of air quality.

### 2.9.2 Size and unit of measure

- Height (m)
- Internal diameter of the chimney (m)
- Flue gas temperature (° K)
- Total emission rates relating to the pollutants considered (m(mass)/s)
- Flow rate (m(mass)/s)
- Sedimentation speed (m/s)
- Wind direction (degrees) in the case of the short-term model
- Wind direction (degrees / sector) in the case of the climatological model
- Wind speed (m / s)
- Temperature (° K)
- Height of inversion (m)
- for all that information that needed georeferencing, the UTM Coordinates fused 33N Datum WGS 84 were used

For the mixing heights, rural Briggs, urban Briggs and possible roughness-dependent Briggs were taken into account.

### 2.9.3 Calculation domain

The calculation grid represents the geographical space within which the diffusion simulation is processed, has been defined geographically according to the following parameters:

- Abscissa and ordinate of the origin of the calculation grid: 446844 AND 3974993 N
- Number of links in x direction and y direction: 120 x, 120 y
- Reticle pitch right and right: 50 m x 50 m
- Height of ground receptors: 2 meters, indicative value obtained from the average height at which the concentration is perceived;
- Absence of discrete receptors;
- Standard control parameters, with the use of the non-conservative approach for the term of reflections in the presence of gravitational sedimentation;
- The resolution of the calculation of the concentrations/deposition is equal to 5x5m.

The figure below shows the extension of the calculation domain used for this study. The subsequent spatial elaborations were produced on a "mask" of territory adapted to the extension of the results obtained in order to emphasize the areas most affected.



FIGURE 9: CALCULATION DOMAIN BASED ON 3 KM RADIUS

#### 2.9.4 Meteorological Dataset

The meteorological dataset required for the development of the dispersion model have been collected from the weather station of Luqa Hourly-Malta Airport.

#### 2.9.5 Pluvio-thermometric regime

The raw meteorological dataset acquired from weather station of Luqa Hourly, related to temperature and precipitation values for the entire year 2021, has been checked for excluding the presence of no-data values (errors and/or 0-data values), and the hourly values has been merged together using a spreadsheet management SW, to obtain the daily mean values for Temperature and Precipitation.

The time lapses taken into account are 24-hours intervals, (for example from 01/01-00:00 to 01/01-24:00), that were plotted on monthly graphs, shown below.

Final dataset was therefore plotted and represented on various histogram-type and rose diagram-type charts.

These histograms show the total annual precipitation and annual temperature, with daily frequency for both. Have been produced 13 final combined graphs (Histogram + Lines) which shows the trend monthly, as well a final summary all year long.

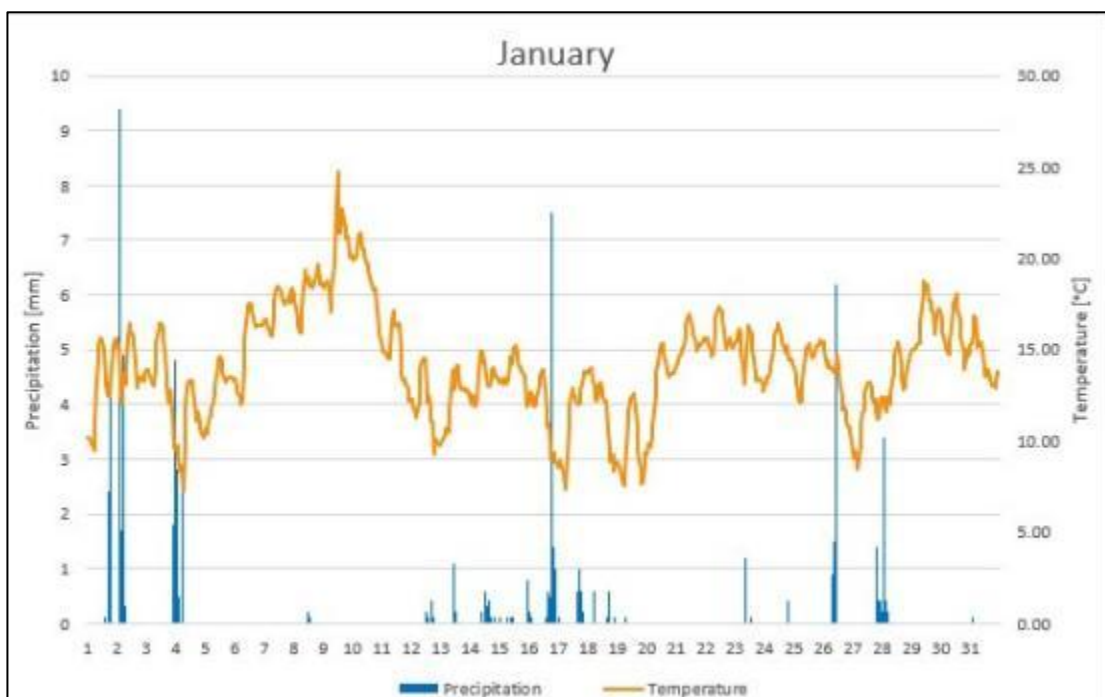
In these graphs, the two vertical axis allows to read at the same time the daily precipitation values expressed in millimeters (left axis) and the mean daily temperature expressed in Celsius degrees (right axis). The horizontal axis on the bottom shows instead the days of the corresponding month.

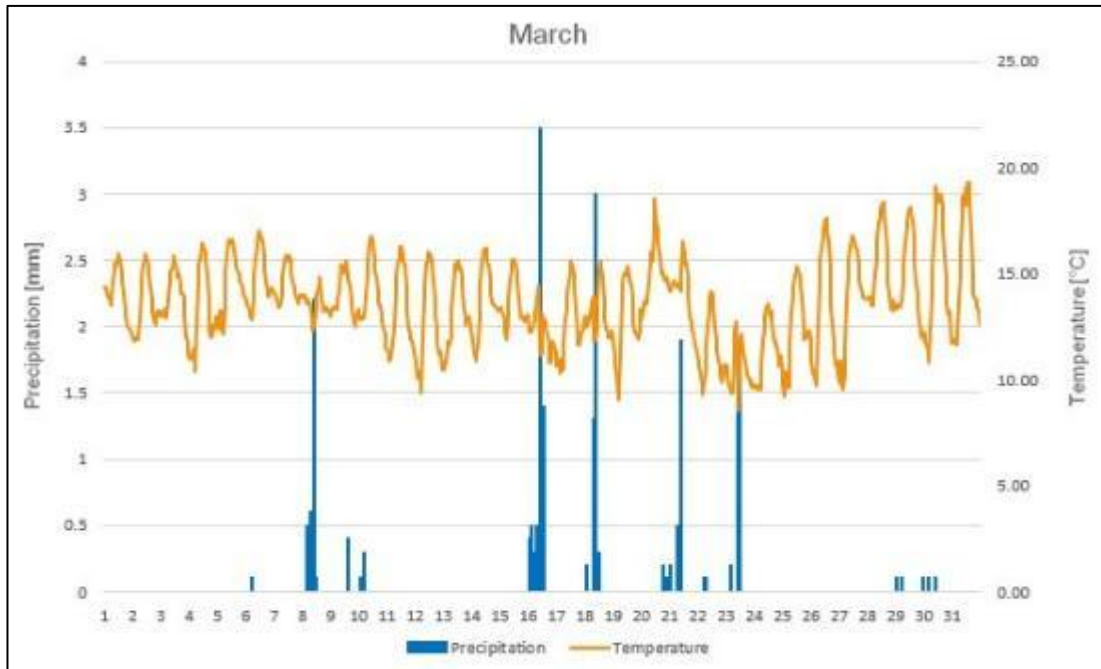
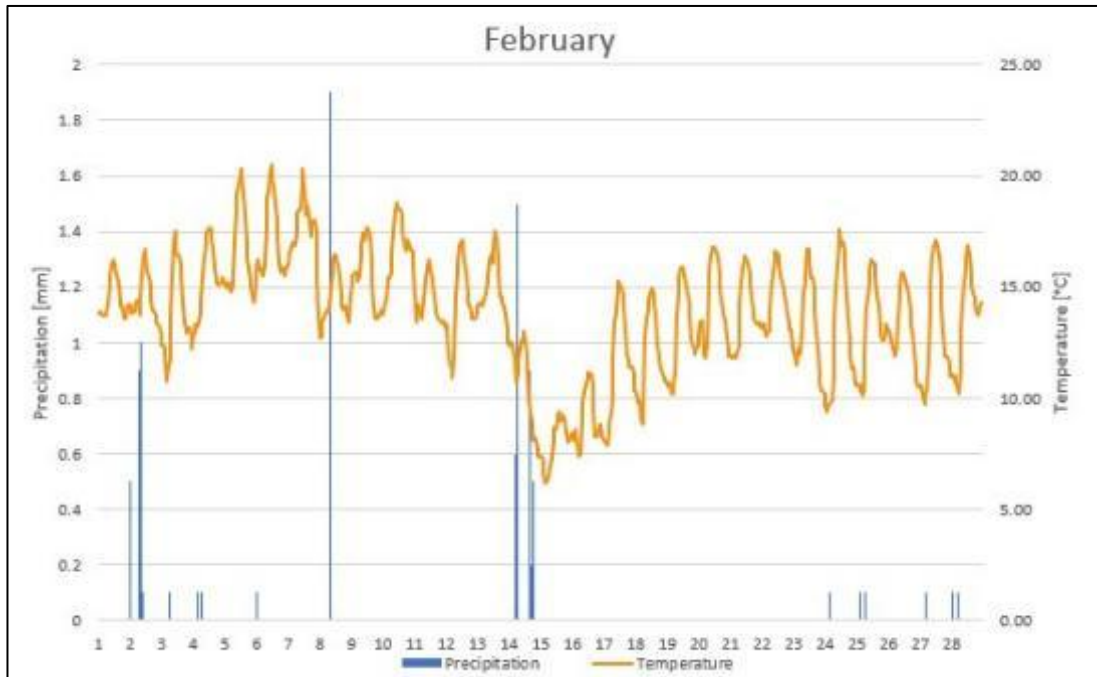
Analysis of temperature trends for example shows:

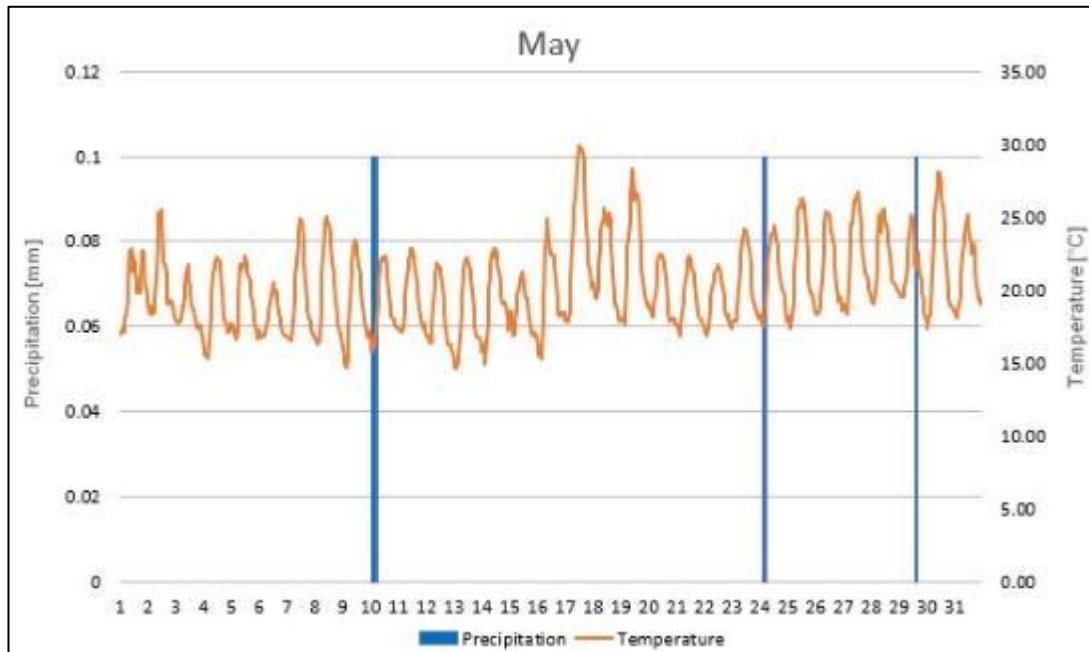
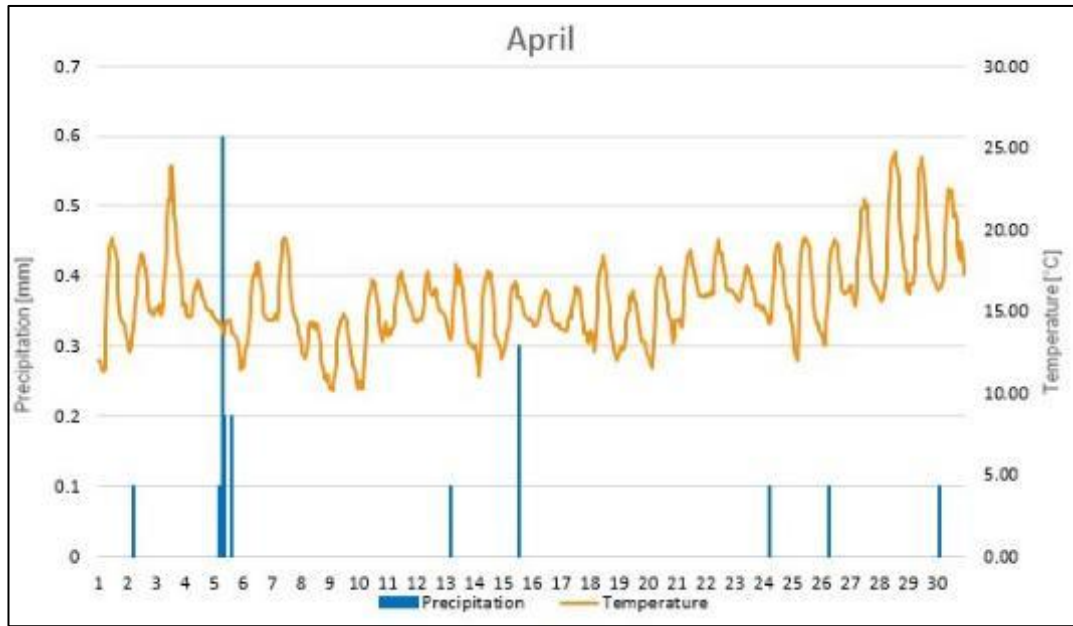
- A very regular and typical trend of mean daily temperature, which during the year follows a normal or “Gaussian” distribution. The temperature range varies from 39.60C° to + 6.20C° and indicates a strong thermal mitigating effect due to the sea proximity.

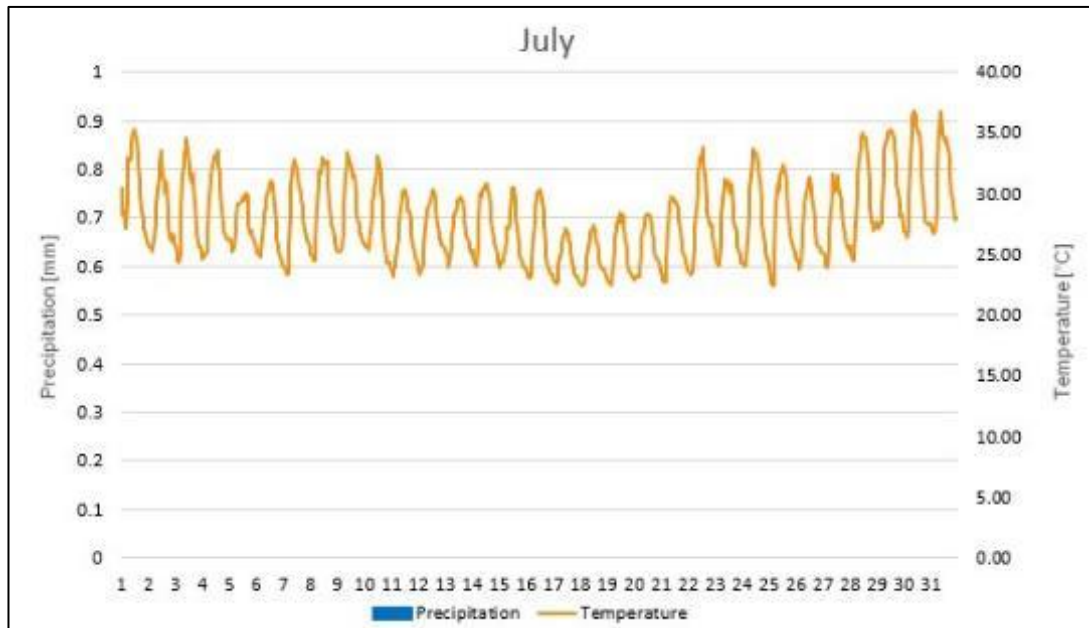
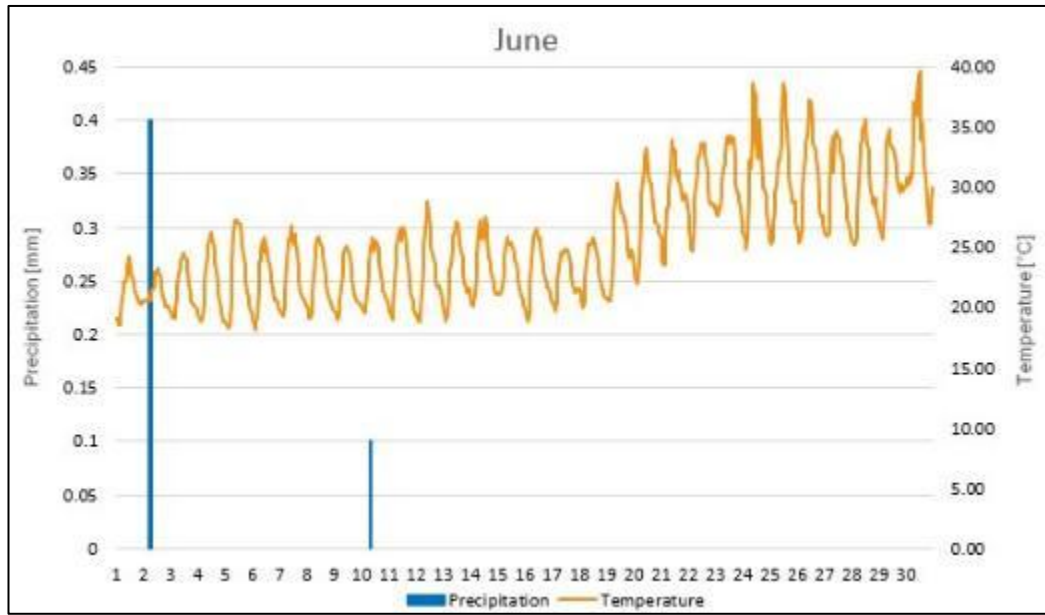
This underlined trend is typical of Mediterranean near-sea and insular areas, with poor rainfall in summer seasons and high peaks of precipitations in winter and spring seasons. The total annual rainfall in this type of climatic area are however low and above average.

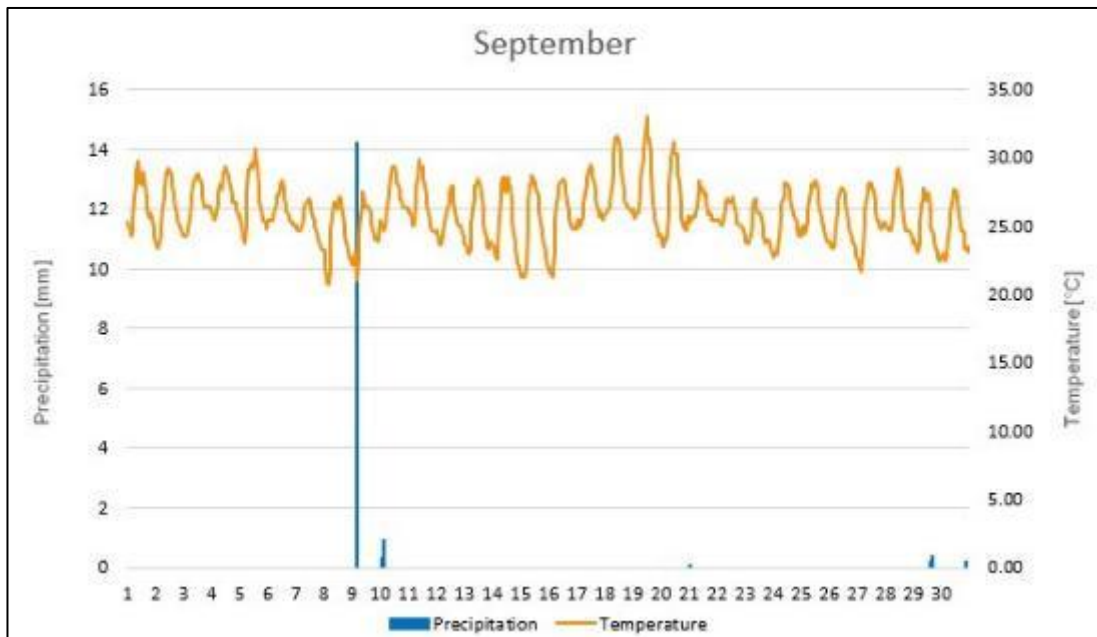
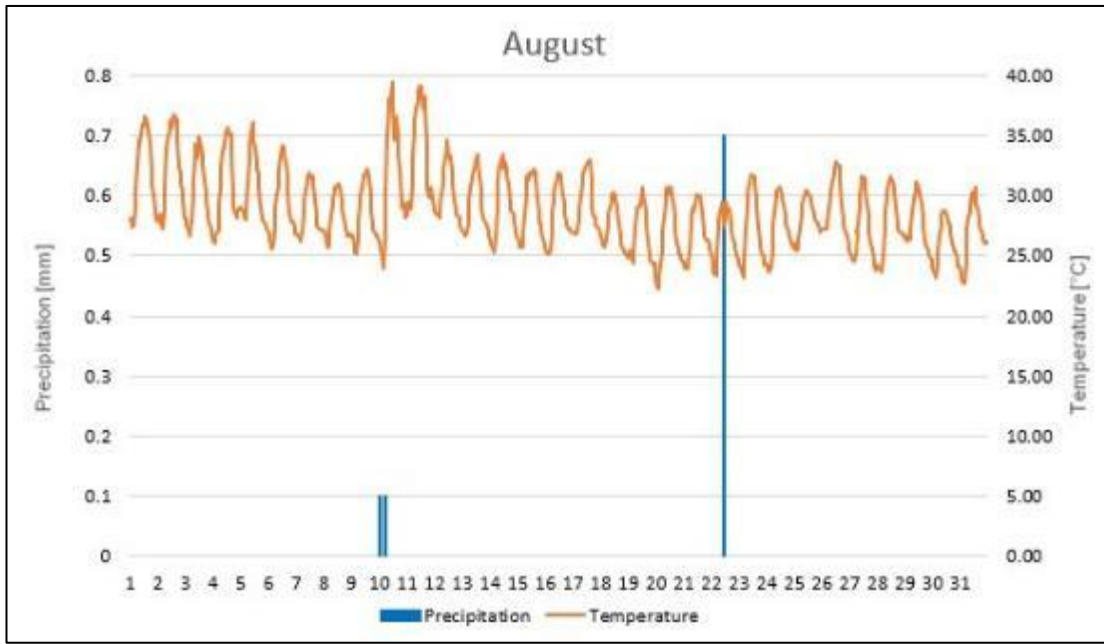
The analysis of annual precipitation or rainfall trend, shows instead the existence of one main peak of rainfall occurring in the October- November period (34-38 mm).

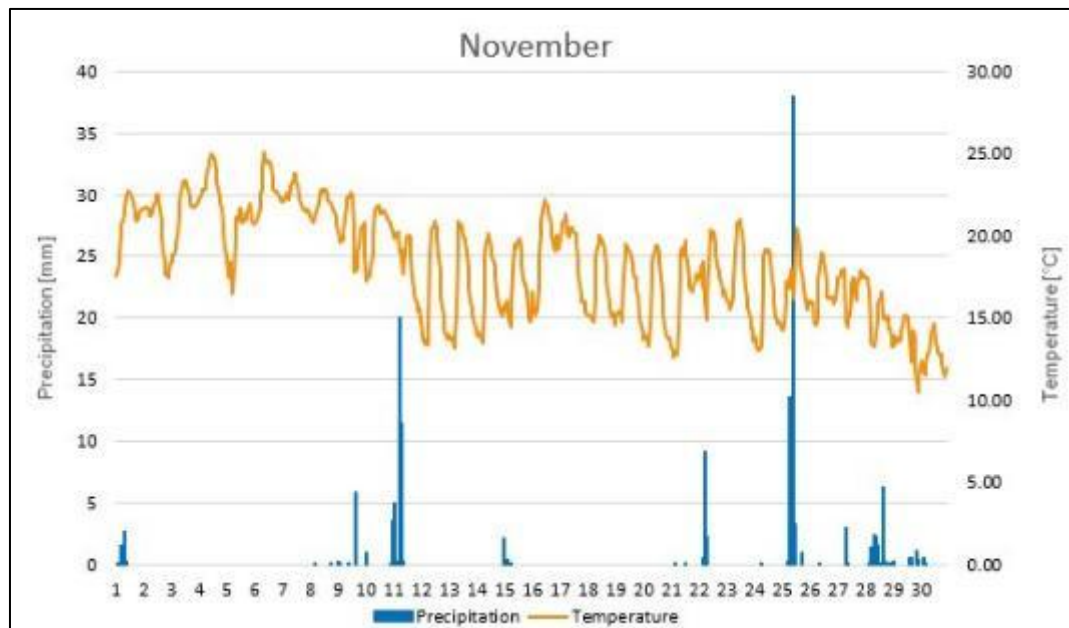
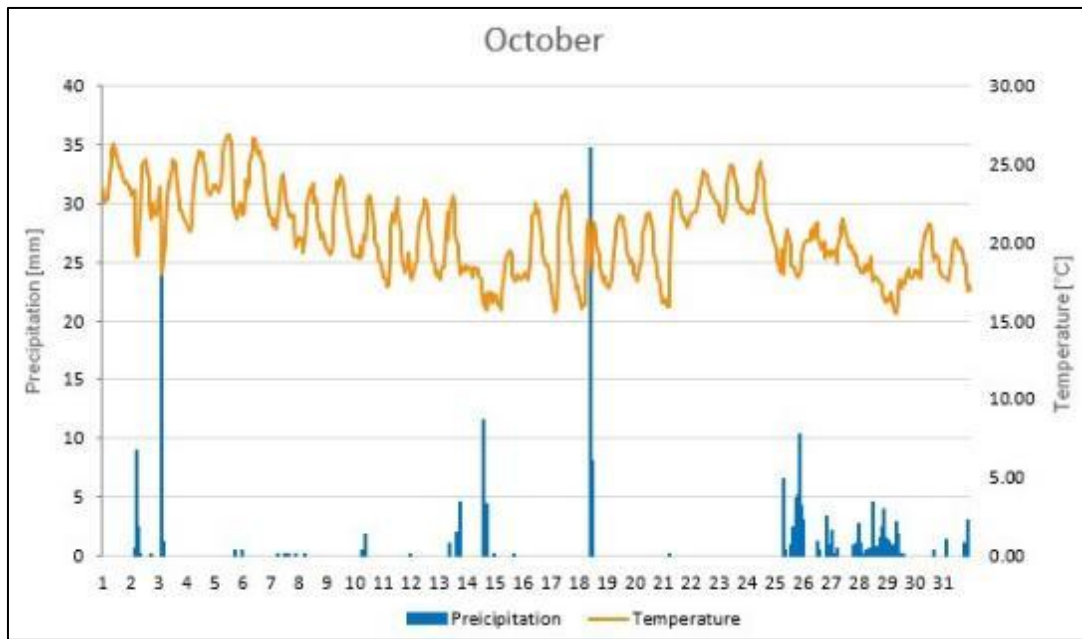


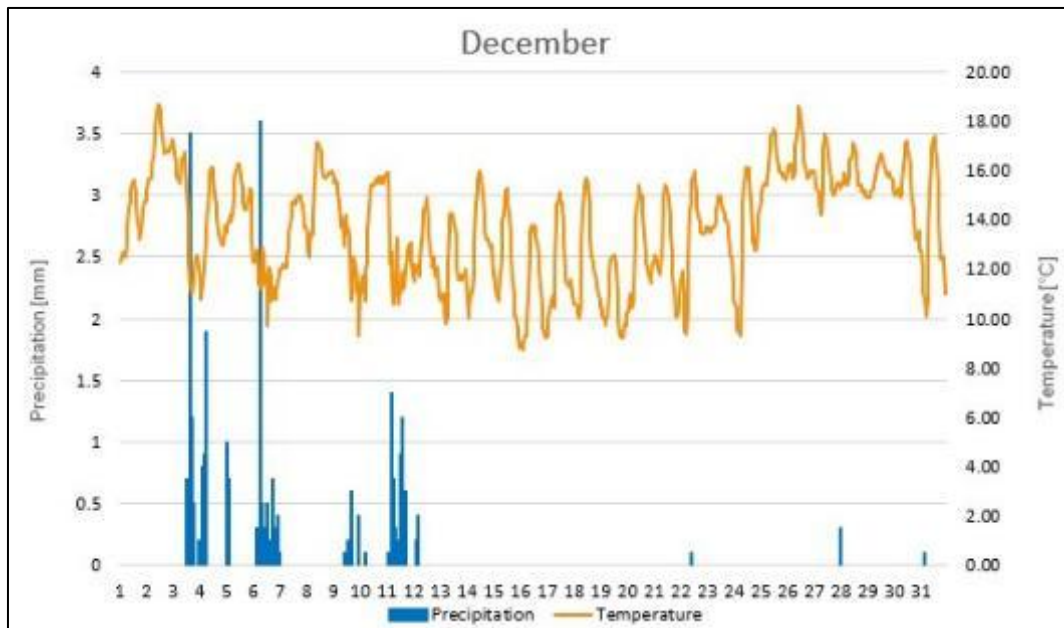












### 2.9.6 Anemometric regimes

As usual in meteorology studies, in the presented wind rose diagrams, has been indicated the angle or the direction of the wind (the direction in which the wind is coming), clockwise relative to the North.

For example, when indicated that the wind has angle of 90° (East), it is meant that it blows from East to West. Instead, into simulation scenarios and taking into account pollutant dispersion it's more effective to represent the wind vector (the direction in which the wind heads) rather than the direction of coming.

The general wind rose diagram, derived from the data of the whole year 2021, shows two predominant directions of the wind:

- The first, from Northwest to Southeast.
- The second one, almost in perpendicular direction than the first, from West-Southwest to East-Northeast.

The winds are oriented mainly into preferential directions that reflects the geographical and orographic settings of the area, as well the positioning of the major airport structures like the two main landing strips. The distance from the sea (6km in almost all directions) does not allow the development of any significant phenomena of sea breeze or land breeze.

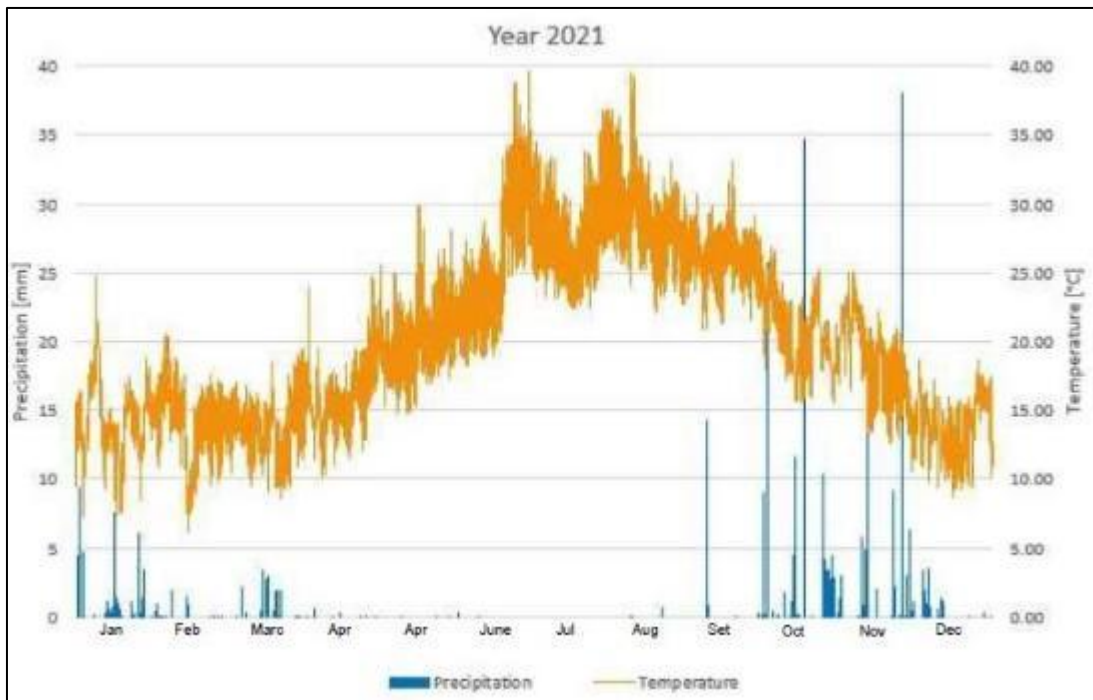


FIGURE 10: WIND YEAR 2021 (8760 OBSERVATIONS)

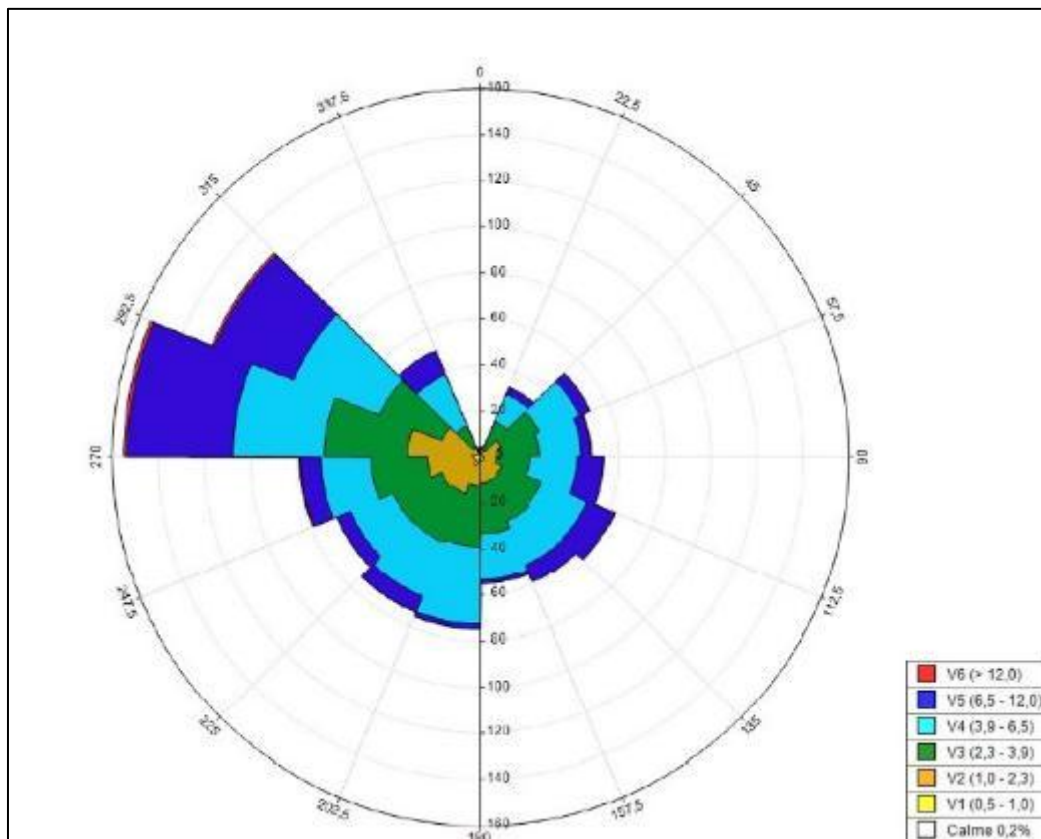


FIGURE 11: WIND-ROSE FOR YEAR 2021

- The almost total absence of winds blowing from Northwest to Southeast and from Southwest to Northeast, can be caused by the presence of low hills that

surround the west side of the area, leading to a poor air circulation in those directions.

The seasonal wind rose-diagrams instead, highlights the following:

- Autumn and Winter wind directions resemble each other and are similar to the main trend for the entire year. The predominant direction is from Northwest to Southeast.
- Spring and Summer wind directions resemble each other too but are more often contributing the winds blowing from the other main direction (West-Southwest to East-Northeast).

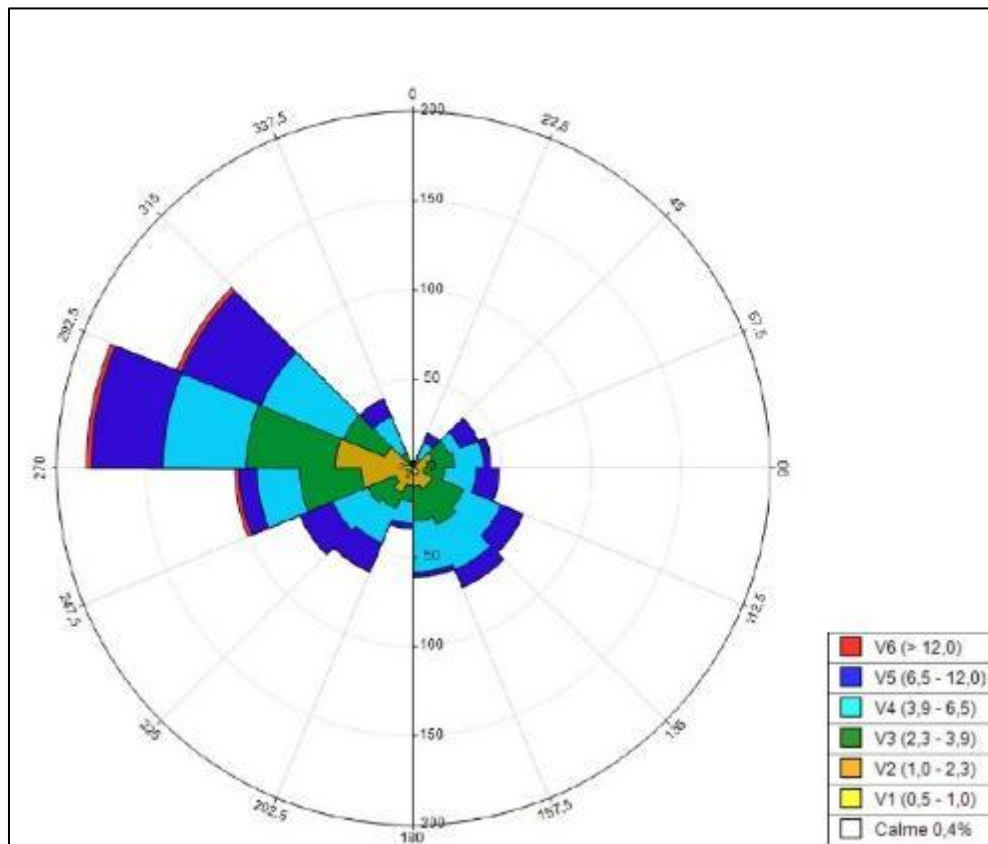


FIGURE 12: SEASONAL WIND ROSE-DIAGRAMS –AUTUMN

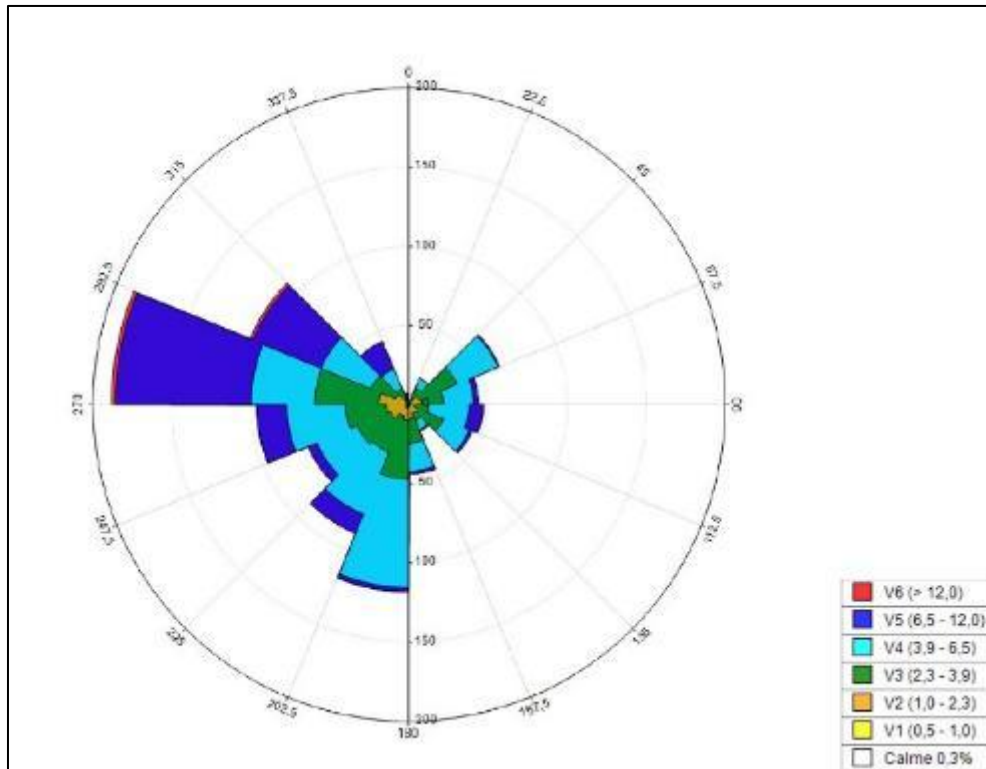


FIGURE 13: SEASONAL WIND ROSE-DIAGRAMS WINTER

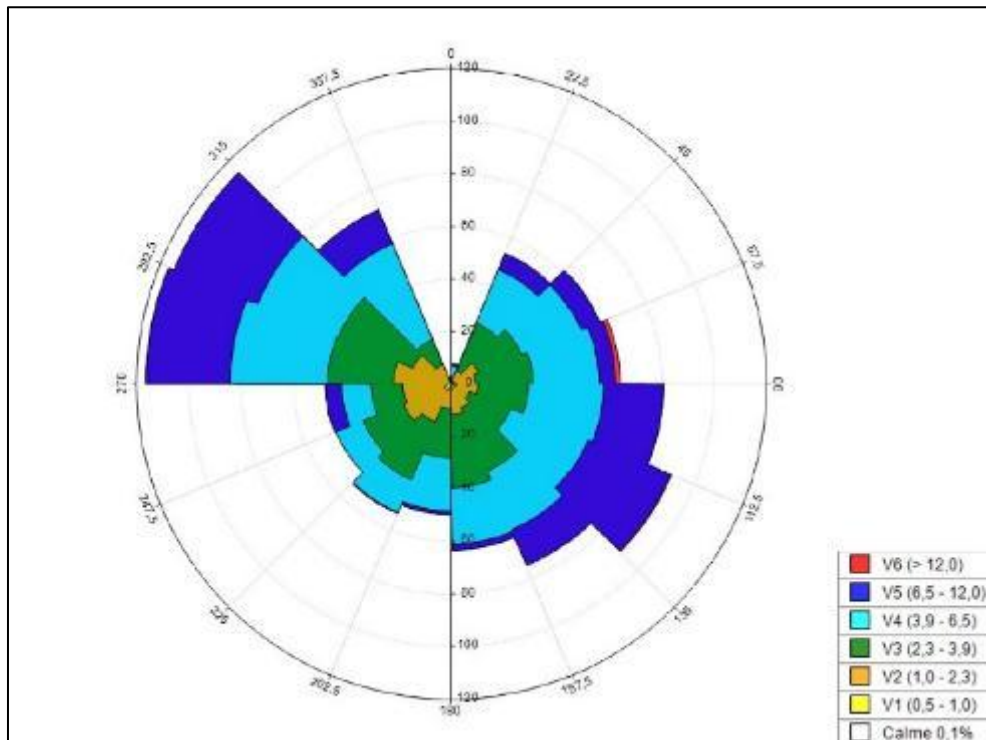


FIGURE 14: SEASONAL WIND ROSE-DIAGRAMS SPRING

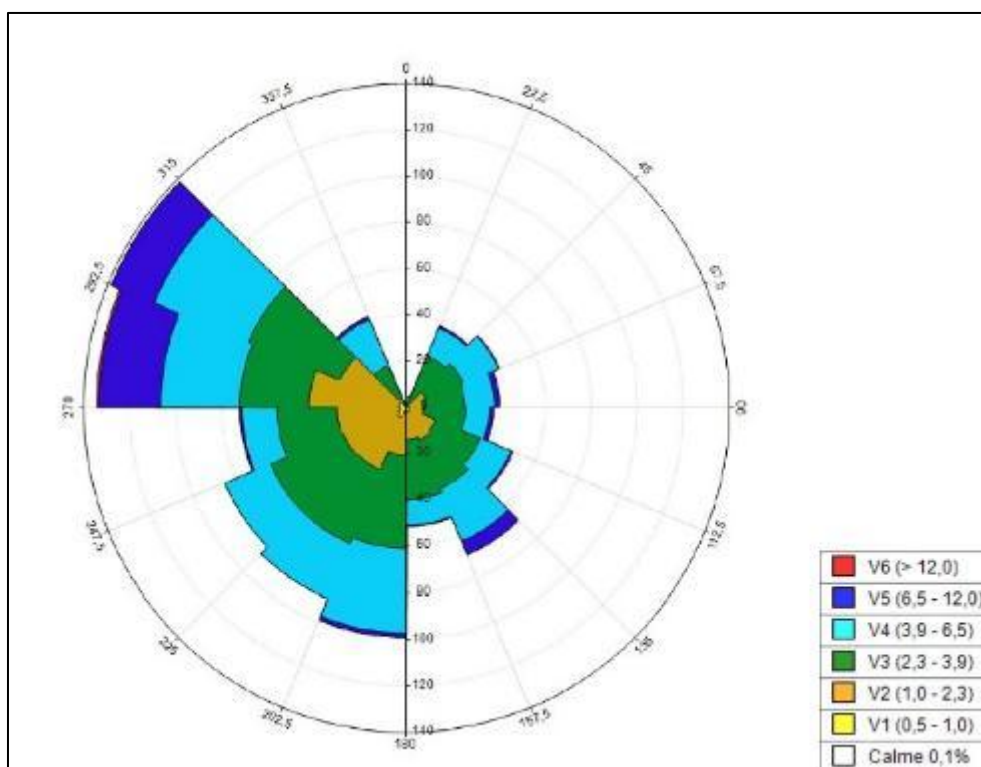


FIGURE 15: SEASONAL WIND ROSE-DIAGRAMS SUMMER

The anemometric data files were created according to the format used by Aeronautica Militare (Joint Frequency Function) and compatible with the calculus module DIMULA.

The climatological model use as raw data the so-called *Joint Frequency Function*. These “functions” are statistical aggregation of meteorological observation derived from historical data series.

Data are aggregated into seven tables that represents six classes of atmospheric stability A, B, C, D, E, F + G (Fog Class). Each table contain 18 rows and 6 columns of 1000-normalized data.

Columns represent the aggregation based on the wind intensity and velocity; rows represent the aggregation based on the direction in which the wind is coming.

Especially:

- the first 16 rows represent the 16 sectors of direction of the wind, starting from North and going clockwise (each sector has width of 22,5°);
- row 17 contains variable data, for which was possible to establish the intensity but not the direction of the wind;
- row 18 contains wind calm data, not measurable from the instruments.
- the first column contains just data from wind calm, every other wind episode has value set to 0.
- the velocity value written on every column represent the reference value of the velocity class used for the aggregation.

- In addition to the data on the wind condition, the “Joint Frequency Function” contains the following data too:
- A table of occurrence frequencies of single classes normalized to 1000
- Mean temperature of air and altitude of the meteorological station above the ground
- The altitudes of thermal inversion typical for each stability class
- A table normalized to 1000 with the occurrence frequency of the 14 classes of thermal inversion utilized only for Fog Class.
- The wind velocity and the standard deviation, for use in calculations within the wind model.

Direzione	1.5	1.56	3.12	5.2	9.36	32
Settore 1	0	0.67	0	0	0	0
Settore 2	0	1.34	5.36	0	0	0
Settore 3	0	55.97	45.91	0	0	0
Settore 4	0	81.43	77.41	0	0	0
Settore 5	0	30.16	19.1	0	0	0
Settore 6	0	38.07	18.43	0	0	0
Settore 7	0	43.57	33.18	0	0	0
Settore 8	0	18.77	12.4	0	0	0
Settore 9	0	0.67	9.72	0	0	0
Settore 10	0	1.34	1.01	0	0	0
Settore 11	0	0	0	0	0	0
Settore 12	0	0	0	0	0	0
Settore 13	0	0	0	0	0	0
Settore 14	0	0	0	0	0	0
Settore 15	0	0.34	0	0	0	0
Settore 16	0	1.68	1.34	0	0	0
Variabili	0	0	2.68	0	0	0
Calma	498.66	0	0	0	0	0

FIGURE 16: EXAMPLE OF A JFF FILE TABLE

### 2.9.7 Definition of the emission sources

The main problem to estimate the emissions into the atmosphere is linked to the definition of emission source and to the chemical-physical characterization of the fumes. In the following, both geometrical characteristics of the chimney and chemical-physical characteristics of the fumes for the new Thermal Treatment Facility (MTTF) for the three scenarios have been defined.

### 2.9.8 Geometric characteristics of the emission chimney

- Geographical coordinates of the chimney: 449834 mE; 3977782 mN
- Altitude of the base: 33.20m from MSL
- Diameter: 2.50 m
- Height: 25m (58.20m from MSL)

The emission factors used are the provisional limit values in normal operating conditions are based on “Tentative limit values under normal operating conditions based on BAT and IED” as shown in Table 3 of the EIA TORs dated 05/08/2024.

For the following parameters:

- Total dust, total volatile organic carbon (TVOC), hydrochloric acid, hydrofluoric acid, sulfur dioxide, carbon monoxide, nitrogen oxide and ammonia, the Daily Average Value was used;
- Cadmium and Thallium and Total Metals and their compounds (As, Cr, Co, Cu, Mn, Pb, Sb, V and Ni) and Mercury, the Average value over 30 min to 8 hours was used;
- Polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/F) + dioxin-like polychlorinated biphenyls (PCBs), the Average value over 6 to 8 hours was adopted.

TABLE 1: CHARACTERISTICS OF THE EMISSIONS FOR EACH POLLUTANT EXPRESSED AS DAILY AVERAGES (MTTF)

POLLUTANT	EMISSION LEVEL ASSOCIATED BAT-AEL (NEW PLANT)	UNIT
Dust	5	mg/Nm <sup>3</sup>
NO <sub>x</sub>	120	mg/Nm <sup>3</sup>
NH <sub>3</sub>	10	mg/Nm <sup>3</sup>
CO	50	mg/Nm <sup>3</sup>
SO <sub>2</sub>	30	mg/Nm <sup>3</sup>
HCl	6	mg/Nm <sup>3</sup>
HF	1	mg/Nm <sup>3</sup>
TVOC	10	mg/Nm <sup>3</sup>
Hg	0.02	mg/Nm <sup>3</sup>
PCDD/F+PCB dioxine	0.08	ng WHO-TEQ/Nm <sup>3</sup>
Cd+Tl	0.02	mg/Nm <sup>3</sup>

Group III Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V	0.03	mg/Nm <sup>3</sup>
Table Notes:		
a) Concentrations referenced to temperature 273 K, pressure 101.3 kPa, 11% oxygen, dry gas.		
b) Metal groups are as follows:		
Group 1: Cadmium (Cd) and thallium (Tl)		
Group 2: Mercury (Hg)		
Group 3: Antimony (Sb), arsenic (As), lead (Pb), chromium (Cr), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), and vanadium (V).		
c) The emission limit value refers to the total concentration of dioxins and furans calculated using the concept of toxic equivalence (TEQ).		

The gas conditions at the chimney top are estimated at:

	Unit	Line 1	Line 2
Normalised flue gas flow, wet at full load	Nm <sup>3</sup> /h @ 11%O <sub>2</sub> dry gas	6860	6860
Anticipated temperature	°C	120-180	120-180
Anticipated O <sub>2</sub> content	% dry gas	5 - 9	5-9
Actual flue gas flow, wet (@ 7% O <sub>2</sub> dg and 150°C). Note 1	m <sup>3</sup> /h	7594	7594
Velocity at stack top, full load. Note 2	m/s	20	20
Velocity at stack top, minimum load (60%) Note 2	m/s	12	12

Notes:

1. The actual flue gas is re-calculated from the normalised using the actual temperature and oxygen content. Accordingly, the actual flue gas will vary depending on the actual data of the gasses. Note that on overload the flue gas flow will be 7,814Nm<sup>3</sup>/h.
2. The full load velocity at stack top is set in order to avoid stack noise. The EPC will adjust the flue dimensions to achieve correct velocity at the actual gas data of their specific design during the engineering phase. The full load velocity may be increased up to approximately 23 m/s if the part load velocity is too low to achieve sufficient dispersion.

Below are the model simulation scenarios:

- Typical operations (**Scenario A**): 60% thermal load for 24 hours, also meaning a flue gas flow per line of 4116 Nm<sup>3</sup>/h for 24 hours;
- Maximum operating conditions (**Scenario B**): 100% thermal load for 23 hours (flue gas flow per line of 6860 Nm<sup>3</sup>/h) and 110% load for 1 hour (a flue gas flow per line of 7814 Nm<sup>3</sup>/h);

- Abnormal operating conditions (**Scenario C**): based on the limits defined in Schedule 2 of S.L.549.81, a dust concentration of 150 mg/Nm<sup>3</sup> shall be set at the stack at maximum operating conditions.

The following abatement technologies were also considered:

POLLUTANT	ABATEMENT TECHNOLOGIES
Particulate matter (dust)	Cyclones, Electrostatic Precipitators (ESP) or Bag filters
Oxides of nitrogen (NO <sub>x</sub> )	SNCR, a sodium bicarbonate abatement system, activated carbon injection and bag filters.
Acid Gases (Sulphur dioxide & Halides (HCl & HF)	Dry sorbents (hydrated lime or possibly sodium bicarbonate) + Bag filter
Heavy Metals	Activated Carbon Injection & Bag filters
Dioxins & furans	Activated Carbon Injection & Bag filters + Combustion control and possibly flue gas recirculation

### 2.9.9 Orographic data and surface roughness

The WinDimula calculation module provides for the insertion of the orographic data within the model for the study of the interference of the conformation of the territory with atmospheric diffusion.

The implementation of the orographic data in the model was made by producing an auxiliary calculation file (\*.oro) which was produced on a rectangular mesh of the 50 \* 50m pitch for a number of points equal to 36,000,000.

The file with the orographic data is a square matrix that contains the extrapolated altitude value on the intersection of all coordinates. To know the altitude values to be included in the file, a DTM (Digital Terrain Model) was produced starting from georeferenced topographic cartography.

The digital terrain model was produced by triangulating the inserted points, it is based on square areas with regular mesh integrated with a series of points quoted for the areas with more complex orography.

The DTM has the important characteristic of describing an irregular surface by means of a finite set of points with coordinates (X, Y, Z) in space. The original dimensioned

points are generally spaced irregularly and according to the technique used for the measurements.

To obtain the model of soil for the present study, an exact interpolator IDW (Inverse Distance Weighting) was used as an interpolation algorithm, i.e. an interpolator capable of returning the exact value at each measuring instrumental point.

The three-dimensional model was developed not only for a useful representation of the territory but also for all derivation and analysis operations that can be carried out with it.

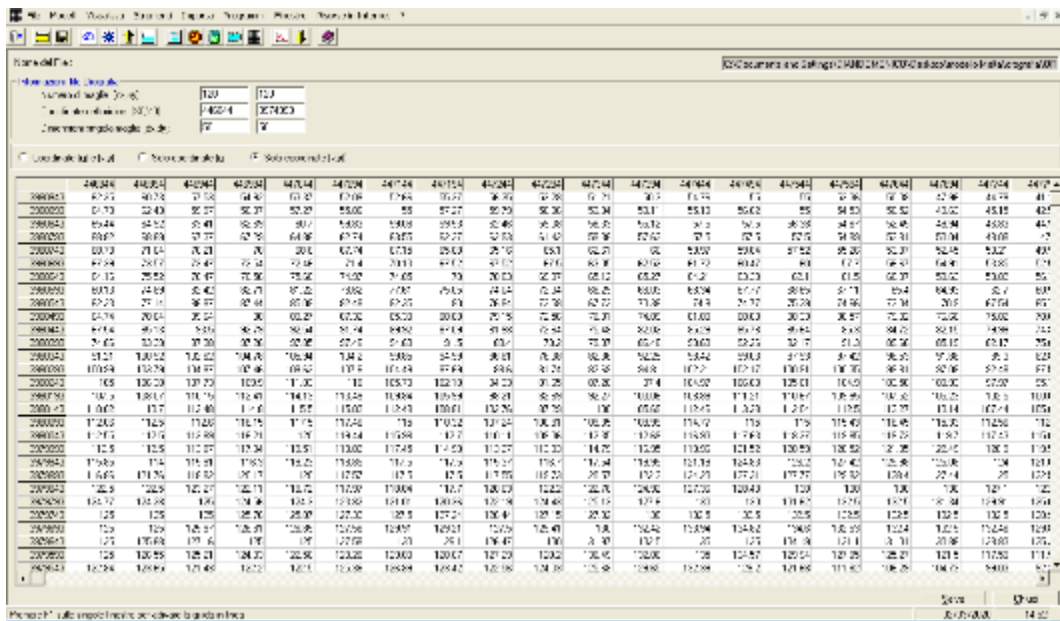


FIGURE 17: EXAMPLES OF AN OROGRAPHIC MATRIX USED BY THE SOFTWARE

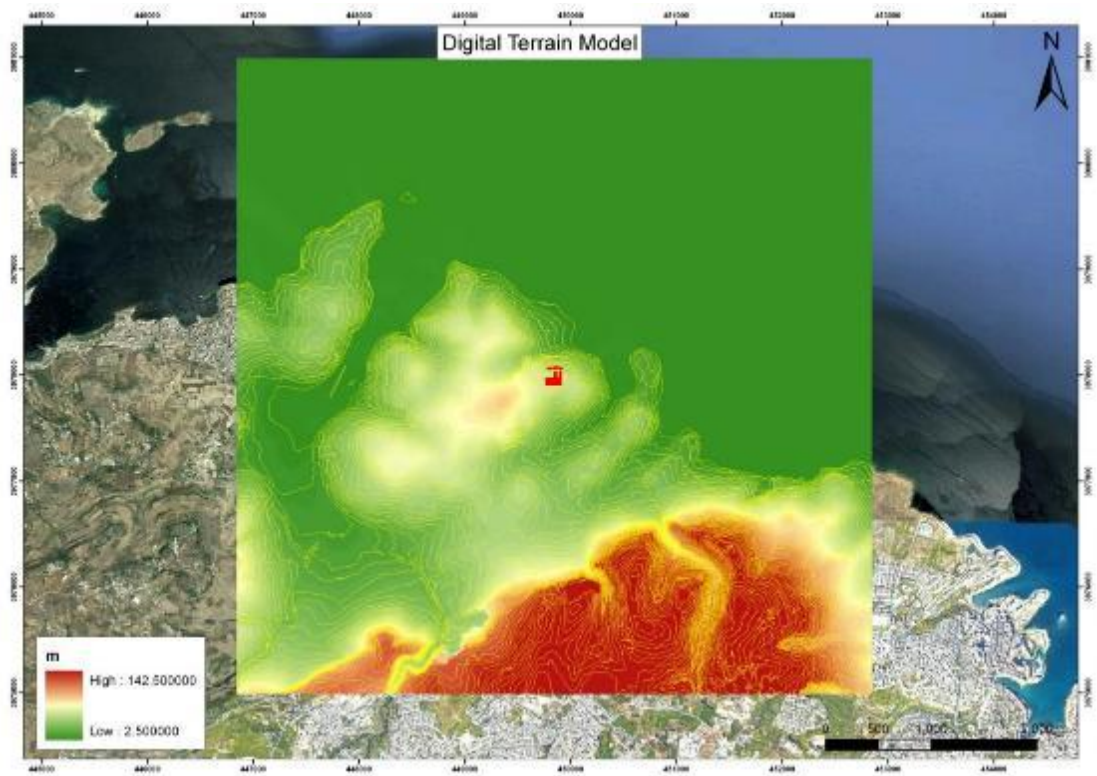


FIGURE 18: EXTRACT OF DTM WITH GIS SOFTWARE

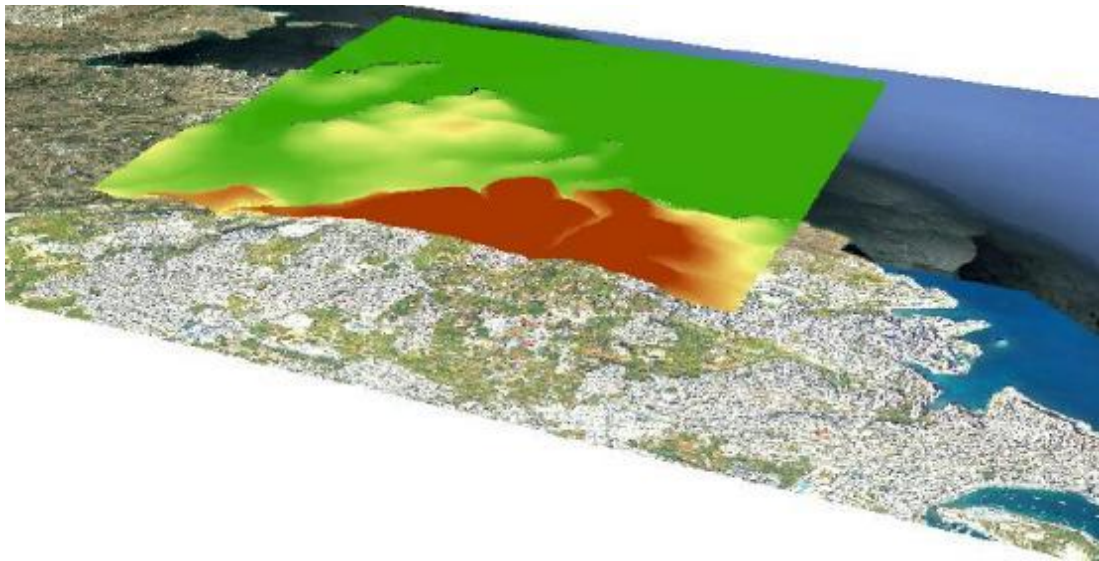
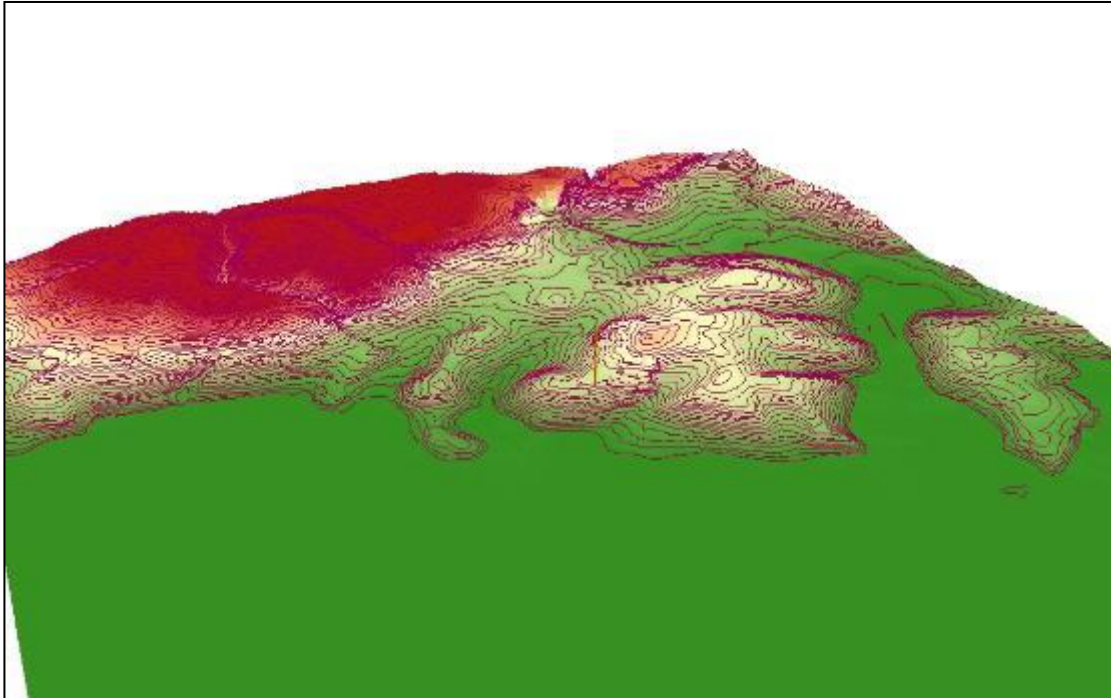


FIGURE 19: EXTRACT OF DTM WITH GIS SOFTWARE

### 2.9.10 Equations

The Gaussian equation that expresses the concentration for high point sources with continuous emissions takes the following form:

$$C(x, y, z) = \frac{Q}{2\pi\sigma(x)_y\sigma(x)_z} \exp\left[-\frac{y^2}{2\sigma(x)_y^2}\right] \cdot V \cdot D$$

*Q: pollutant emission expressed as mass per unit of time*

*V: vertical term*

*D: decay term*

$\sigma(x)_y, \sigma(x)_z$ : lateral and vertical dispersion coefficients (m)

$\mu$ : wind speed at the altitude of the release (m / s)

*x: leeward distance between the source and the receptor with respect to the wind direction*

*y: distance perpendicular to the wind direction between the plume axis and the receptor*

*z: altitude of the receptor relative to the ground*

This equation is obtained on the basis of the following hypotheses:

- Stationary process
- Constant weather conditions
- Turbulent transport along the x axis negligible compared to advection transport
- Constant dispersion coefficients in y and z
- Constant emission
- Reflective ground

The climatological calculation uses the Gaussian formulation evaluated on the sectors of origin of the wind. In addition to the basic assumptions already described for the Short-Term model, the following assumptions are made:

- the wind rose is divided into 16 sectors with a width of 22.5 °, the sectors are divided starting from the north in a clockwise direction;
- within each sector the concentration depends only on the radial distance between the source and the receptor (therefore there is no dependence on the distance perpendicular to the wind direction y);

In these hypotheses the equation used for climatological calculation is the following:

$$C(R, \Delta\vartheta, z) = \frac{Q}{\sqrt{2\pi} \cdot u \cdot R \cdot \sigma(R)_z \cdot \Delta\vartheta} \cdot V \cdot D \cdot S$$

*Q: pollutant emission expressed as mass per unit of time*

*V: vertical term*

*D: decay term*

*R: source receptor radial distance in the calculation sector*

*$\Delta\theta$ : size of the single sector*

*u: wind speed at altitude of release (m / s)*

*z: altitude of the receptor relative to the ground*

*S: smoothing function*

$\sigma(R)_z$ : source area

This equation represents the contribution to the concentration at a point R of a single point source. The total concentration value produced by a single source will be given by:

$$C_{tot} = \sum_{istab, idir, ivel} C(R, z) \cdot \frac{f(istab) \cdot f(istab, idir, ivel)}{10^6}$$

*istab*: sum on the stability classes (A, B, C, D, E, F + G, Mists)

*idir*: sum on the sectors of origin of the wind

*ivel*: sum on the speed classes

*f(istab)*: frequency normalized to 1000 of occurrence of the *istab*-th stability class

*f(istab, idir, ivel)*: normalized frequency at 1000 of the occurrence of the *idir*-th direction and the *ivel*-th speed class of the *istab*-th stability class

### 2.9.11 Post Processor

The WinDimula calculation model incorporates the WDPstProc program, this is the post-processing module of the results calculated by the model.

The program analyzes the output files (\*.mbf -MaindBinaryFile-) produced by WinDimula and evaluates the concentrations relative to:

- average hourly concentrations
- average daily concentration over eight hours
- daily average concentration
- annual concentrations
- winter concentrations
- exceeding of threshold values for consecutive hours.

It is possible to use one of the predefined pollutants using the values provided by the Ministerial Decree or to enter a new type of pollutant specifying the limits and exceedances allowed. In addition to the results of the verification calculation, it is possible to display the time series of each receptor and the results calculated by WinDimula in each meteorological situation analyzed.

## 2.10 CALIBRATION - SAMPLING CAMPAIGN

### 2.10.1 PM<sub>10</sub>

In line with S.L. 549.59, baseline levels of PM<sub>10</sub> were measured on site using the reference method (MSA EN 12341:2014), which describes both sampling and measurement methods for PM<sub>10</sub>. Other specific details regarding the measurement of PM<sub>10</sub> can be found in the Terms of Reference provided by ERA.

In line with Annex B and Section IV of Annex IX of the said standard, the monitoring of PM<sub>10</sub> was carried out using a Sequential Automatic Sampler (Skypost PMHV,

GEMINI or GIANO DADO LAB SEQUENTIAL AUTOMATIC SAMPLER). Since this sampler functions with a constant flow rate of 2.3 m<sup>3</sup>/h ± 2% (EN 12341), the Sequential Automatic Sampler has a dry gas meter within 2% precision installed. The sampler can also electronically control the flow. The Sequential Automatic Sampler is also equipped with a sensor to measure the atmospheric pressure and temperature and the pressure drop on the filter. This sensor is installed on the suction tube and is protected against adverse meteorological conditions.

The clean filter reservoir can contain up to 18 filter cassettes and can therefore allow a maximum of 18 days of monitoring without the need for a site visit to replace new filters. Unloaded filters were conditioned in the weighing room for a minimum of 48 h before weighing. Filters were weighed twice, with an interval of at least 12 hours, to confirm that the filter weight has stabilized. Loaded filters were placed in the weighing room for a minimum of 48 hours before weighing, and then weighed again after a further 24 to 72 hours, whilst being retained in the appropriate conditions.

The monitoring phase lasted a total of 45 days (6 weeks), but a scale up factor of 0.85 (based on Zejtun 2023 data) provided by ERA was used to scale the values of PM<sub>10</sub> to yearly values. Any PM<sub>10</sub> readings which were influenced by Saharan dust intrusions were discarded. The specific details on the methodology and instrumentation that were applied for the sampling and analysis of PM<sub>10</sub> are listed in the table hereunder. The instrumentation can be seen in Figure 20. The PM10 sampler was positioned at 35°56'24.85"N, 14°26'29.99"E.

TABLE 2 – DETAILS ON THE METHODOLOGY AND INSTRUMENTATION OF THE PM<sub>10</sub> ANALYSIS

PM10

<b>Description of activity:</b>	<p>Sampling was carried out with a sampling constant flow set equal to 38.3 L/min using the appropriate sampling heads: LVS for PM<sub>10</sub>. The filter sampled was delivered to the laboratory for analysis and then weighed with an analytical balance.</p> <p>The scale was positioned inside a room with controlled temperature and humidity. The flow is programmable under the conditions of temperature and pressure of the sampling point (Qa), or standard (Qs) at 101.3 kPa, 0°C.</p>
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## PM10

<b>Instrument used:</b>	<p>Skypost PM with the following features:</p> <ul style="list-style-type: none"><li>» Flow Range: 0.5 to 50 L/min</li><li>» Autonomy: 16 filters</li><li>» Electronic measurement of flow</li><li>» Sensors measure of parameters:<ul style="list-style-type: none"><li>Atmospheric Pressure</li><li>Pressure drop filter</li><li>Ambient temperature</li><li>Temperature volumetric</li></ul></li><li>» Volumetric measurement meter with accuracy of <math>\pm 2\%</math></li></ul> <p>As per specifications of the ISO standard, the room temperature and the relative humidity of the weighing room are continuously monitored and controlled to <math>20^{\circ}\text{C} \pm 1 \text{ K}</math> and <math>(50 \pm 5) \% \text{ RH}</math> respectively. Unloaded filters were conditioned in the weighing room for a minimum of 48 hours before weighing. Filters were weighed twice, with an interval of at least 12 hours, to confirm weight stabilisation. Loaded filters were placed in the weighing room for at least 48 hours before weighing, and then weighed again after a further 24-72 hours, whilst being retained in the appropriate conditions. The balance resolution is of <math>10 \mu\text{g}</math>.</p>
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FIGURE 20: SEQUENTIAL AUTOMATIC SAMPLER INSTALLED ON SITE

#### 2.10.2 NO<sub>2</sub>

In line with S.L. 549.59, baseline levels of NO<sub>2</sub> were determined using the reference method, which describes both sampling and measurement methods for NO<sub>2</sub>. Other specific details regarding the measurement of NO<sub>2</sub> can be found in the Terms of Reference provided by ERA.

The monitoring of NO<sub>2</sub> was carried out using a type of passive sampler known as Passam Diffusion Tubes. These are cylindrical containers whose mechanism is based on the principle of diffusion through a surface. Pollutants which passively pass through the surface are adsorbed to the filter which should be manually replaced with a clean one every 7 days. The monitoring phase lasted a total 6 weeks, but a scale up factor of 0.96, provided by the ERA, was used to scale the values of NO<sub>2</sub> to yearly values. The sampler was positioned at 35°56'16.83"N 14°26'58.17"E.

The tubes used for the monitoring of NO<sub>2</sub> were then sent to Passam ag, where they were treated to extract the pollutants and analysed. As a result, the analytical technique is divided into two distinct phases: sampling and analysis.

As required by the ToRs, the Consultant should provide at least one article in a peer-reviewed journal which showcases that the equivalence of these tubes has been demonstrated in at least 1 EU Member State. An article by Hafkenscheid et al. (2009) on the application of diffusive samplers in the European Union for the monitoring of nitrogen dioxide in ambient air was chosen, and is enclosed in Appendix 3. This article indicates that in France, Passam samplers were compared to the standard reference method in line with the Guidance to Demonstration of Equivalence (2010). The study found the Passam tubes to be equivalent to the reference method, with an

uncertainty of 6.4% at a 95% confidence level, thus fulfilling the 15% uncertainty level for fixed NO<sub>2</sub> measurements.

The specific details on the methodology and instrumentation that were applied for the sampling and analysis of NO<sub>2</sub> can be seen in Table 3. This methodology was outlined in the Method Statement, which was subsequently approved by the ERA. The instrumentation can be seen in Figure 21.

TABLE 3: DETAILS ON THE METHODOLOGY AND INSTRUMENTATION OF THE NO<sub>2</sub> ANALYSIS

NITROGEN DIOXIDE

<b>Description of activity:</b>	The passive sampler that was used (type Passam) is equipped with an adsorbant (in this case triethanolamine) on which NO <sub>2</sub> adsorbs.	
	The radially symmetrical diffusive body is fixed to a metal plate and is exposed to air between 1.5 and 4 meter above the ground level.	
	The passive sampler is analyzed in the laboratory to determine the amount of NO <sub>2</sub> . The uptake rate will be calculated at 298.15K and will then be used to determine the average concentration of the pollutant during the exposure period.	
	Further details on the analyser used are given below:	
<b>Instruments used:</b>	Principle of method	Passive sampler
	Instrumentation	Passam tube
	Lower detectable limit	0.3 µg/Nm <sup>3</sup>

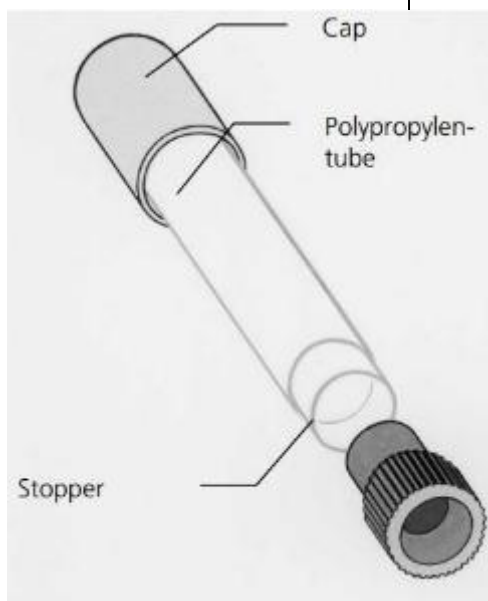


FIGURE 21: PASSAM TUBE

### 2.11 SIGNIFICANCE CRITERIA

A significance criteria tool provided by the ERA was used to determine the significance of the impact at all sensitive receptors and at any point within the investigated area.

To determine the impact, the tool considers the following inputs:

- The annual limit value ( $\mu\text{g}/\text{m}^3$ );
- The baseline concentration ( $\mu\text{g}/\text{m}^3$ ) - The baseline concentration value considered was the average daily value;
- The change ( $\mu\text{g}/\text{m}^3$ ) - the worst-case emissions reported from the air dispersion model was considered for the determination of the exchange rate.

TABLE 4 – IMPACT CRITERIA TOOL FOR  $\text{PM}_{10}$

		CHANGE IN THE ANNUAL $\text{PM}_{10}$ DAA LEVELS DUE TO SCHEME				
		CAA	DAA $\leq 0,4$ $\mu\text{G}/\text{M}^3$	$0,8 \mu\text{G}/\text{M}^3 \leq$ DAA $\leq 2,0$ $\mu\text{G}/\text{M}^3$	$2,4 \mu\text{G}/\text{M}^3 \leq$ DAA $\leq 4,0$ $\mu\text{G}/\text{M}^3$	DAA $> 4$ $\mu\text{G}/\text{M}^3$
CAA FOR $\text{PM}_{10}$	$\text{CAA} \geq 44 \mu\text{G}/\text{M}^3$		Moderate	Major	Major	Major
	$43,6 \mu\text{G}/\text{M}^3 \leq$ $\text{CAA} \leq 41,2$ $\mu\text{G}/\text{M}^3$		Moderate	Moderate	Major	Major
	$40,8 \mu\text{G}/\text{M}^3 \leq$ $\text{CAA} \leq 38 \mu\text{G}/\text{M}^3$		Minor	Moderate	Moderate	Major
	$37,6 \mu\text{G}/\text{M}^3 \leq$ $\text{CAA} \leq 30,4$ $\mu\text{G}/\text{M}^3$		Not significant	Minor	Moderate	Moderate
	$\text{CAA} \leq 30 \mu\text{G}/\text{M}^3$		Not significant	Not significant	Minor	Moderate

For the calculation of the CAA of  $\text{PM}_{10}$ , that is the corrected annual average, the following formula has been proposed

$$\text{CAA} = \frac{P_{y+1}^{x \text{ weeks}}}{P_y^{x \text{ weeks}}} \times P_y^{52 \text{ weeks}}$$

Where:

- CAA is the corrected annual average;

- $P_{y+1}^{x weeks}$  is the concentration of NO<sub>2</sub> or PM<sub>10</sub> measured by the consultants throughout the 6 (9) week (baseline) monitoring period;
- $P_y^{x weeks}$  is the concentration of NO<sub>2</sub> or PM<sub>10</sub> measured throughout the same 6 (9) week monitoring period of the preceding year at a comparable ERA fixed station;
- $P_y^{52 weeks}$  is the annual average of NO<sub>2</sub> or PM<sub>10</sub> measured at the comparable ERA fixed station.

The annualization factor for PM<sub>10</sub> considered is 0,85 (based on the Zejtun 2023 data).

TABLE 5 – IMPACT CRITERIA TOOL NO<sub>2</sub>

		CHANGE IN THE ANNUAL NO <sub>2</sub> DAA LEVELS DUE TO SCHEME				
CAA		DAA ≤ 0,4 µG/M <sup>3</sup>	0,8 µG/M <sup>3</sup> ≤ DAA ≤ 2,0 µG/M <sup>3</sup>	2,4 µG/M <sup>3</sup> ≤ DAA ≤ 4,0 µG/M <sup>3</sup>	DAA > 4 µG/M <sup>3</sup>	
CAA FOR NO <sub>2</sub>	CAA ≥ 44 µG/M <sup>3</sup>	Moderate	Major	Major	Major	
	43,6 µG/M <sup>3</sup> ≤ CAA ≤ 41,2 µG/M <sup>3</sup>	Moderate	Moderate	Major	Major	
	40,8 µG/M <sup>3</sup> ≤ CAA ≤ 38 µG/M <sup>3</sup>	Minor	Moderate	Moderate	Major	
	37,6 µG/M <sup>3</sup> ≤ CAA ≤ 30,4 µG/M <sup>3</sup>	Not significant	Minor	Moderate	Moderate	
	CAA ≤ 30 µG/M <sup>3</sup>	Not significant	Not significant	Minor	Moderate	

The annualization factor for NO<sub>2</sub> considered is 0.96 (based on GHR 2024 data).

### 3 RESULTS OBTAINED FROM THE MODEL

The data obtained from the model consist of the outputs at average hourly concentrations on an annual basis at each point of the investigated area within a radius of influence equal to 6 km from the chimney.

From the hourly concentrations it was possible to evaluate the concentrations of each pollutant investigated in relation to each month, therefore, the behavior of the fallout for the entire year.

The data obtained were processed with the MMS RunAnalyzed which allows to perform various elaborations such as the calculation of statistical indices (such as averages and percentiles) on the specified time intervals, useful for comparison with the regulatory reference levels for each pollutant or for discriminating analysis in the various receptor points.

The data obtained with the modeling simulation were standardized and organized (XYZ-ASCII format) in order to be imported into software for interpolation and spatial processing, in this case the SURFER 8.0 program was used (Golden Software Inc. 2001). The interpolation results were exported in format (.GRD) inserted in a GIS software and reported on cartography using the QGIS program.

This representation is documented by the forecast emission maps shown in the Annexes 1.

By observing the diffusion maps, it was possible to draw further considerations relating to the dispersion of substances from the chimney (for three scenarios) and to deposition on the ground.

#### 3.1 DETERMINATION OF THE AREA OF INFLUENCE

A specific spatial processing of the data obtained from the model was carried out, in order to assess the probability of significant effects on the quality of the ambient air (including exceeding the environmental limit values) as well as on the deposition levels of particular components. The analysis focused on an area of influence estimated within a radius of 6 km from the chimney.

The “Area of Influence – AOI” has been defined as the largest area around the plants obtained considering the areas where the contribution of the plant to the annual environmental levels of NO<sub>2</sub>, PM<sub>10</sub> or PM<sub>2,5</sub> is as follows, whichever results in the largest AoI. If the AoI is <11.3km<sup>2</sup> then the AoI shall be assumed to be a circle of 6km radius centred on the chimney:

- PM<sub>10</sub> → 0.3 µg / m<sup>3</sup>
- NO<sub>2</sub> → 0.3 µg / m<sup>3</sup>
- PM<sub>2,5</sub> → 0.19 µg / m<sup>3</sup>

### 3.2 IDENTIFICATION AND SELECTION OF SENSITIVE RECEPTORS

The consultants have identified a number of sensitive receptors that could potentially be affected by the proposed development. The list of sensitive receptors has been derived by adopting a risk-based approach based on the pollution contours presented by the ERA's NO<sub>2</sub> passive diffusion tube network in 2023 as depicted below.

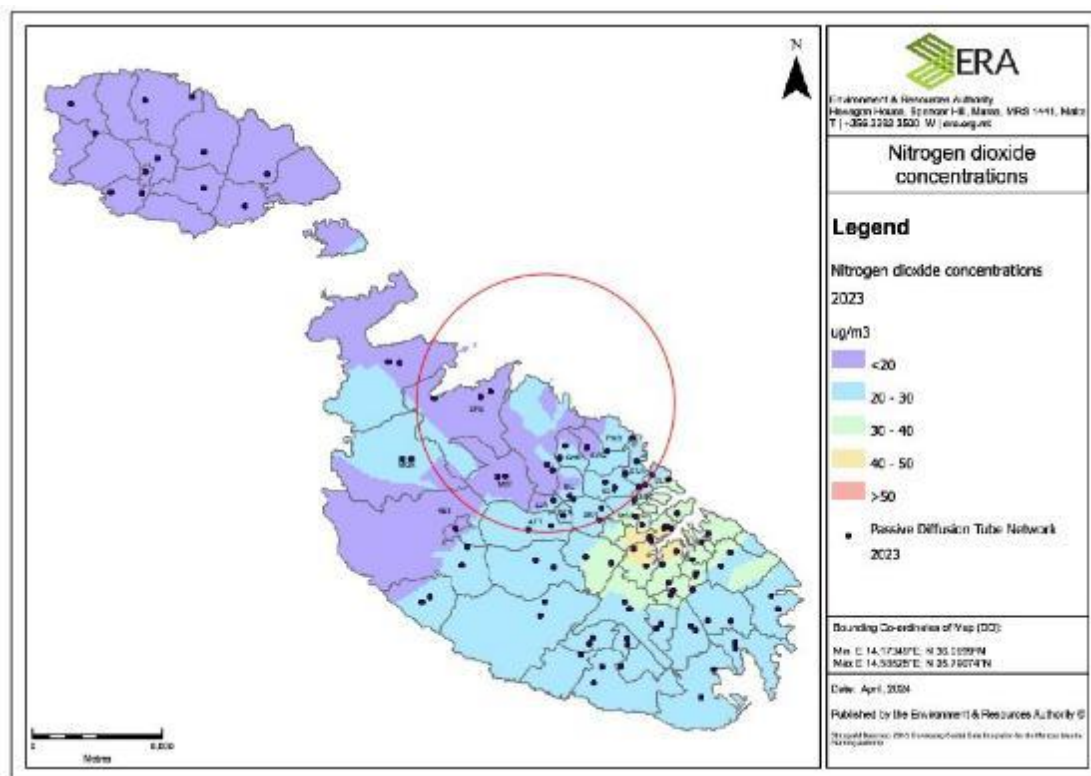


FIGURE 1. NO<sub>2</sub> CONTOUR MAP BASED ON 2023 DATA OBTAINED FROM ERA AND SUPERIMPOSITION OF THE 6KM AOI

The local council boundaries which fall within the 6km radius AoI are: SPB – St’ Paul’s Bay; NXR – Naxxar; MST – Mosta; GHR – Gharghur; LJA – Lija; ATT – Attard; BZN – Balzan; IKL – Iklin; BKR – Birkirkara; SGN – San Gwann; MSD – Msida; SWQ – Swieqi; PMB – Pembroke; STJ – St Julians; SLM – Sliema; GZR – Gzira; RBT – Rabat; MGR – Mgarr.

A risk-based approach has been adopted to select the sensitive receptors considered the distance away from the source and the current pollution levels (as shown in the contour map). Consequently, a hierarchy of risk level has been adopted to establish the location of the sensitive receptors.

TABLE 6 – DEFINITION OF CRITERIA USED FOR THE RISK-BASED APPROACH TO IDENTIFY SENSITIVE RECEPTORS

Criterion	Level	Definition
Closest Distance	Short (3)	Located at <2km away from the scheme site
	Medium (2)	Located at 2-4km away from the scheme site
	Far (1)	Located at >4km away from the scheme site
Current pollution	High (3)	Ambient 2019 pollution levels are >40 µg/m <sup>3</sup> NO <sub>2</sub>
	Medium (2)	Ambient 2019 pollution levels are 30-40 µg/m <sup>3</sup> NO <sub>2</sub>
	Low (1)	Ambient 2019 pollution levels <30 µg/m <sup>3</sup> NO <sub>2</sub>
Risk Level	Major (5-6)	Risk level is considered major when sum of current pollution and closest distance is equal to Level 5-6
	Moderate (3-4)	Risk level is considered moderate when sum of current pollution and closest distance is equal to Level 3-4
	Low (2)	Risk level is considered low when sum of current pollution and closest distance is equal to Level 2

From the risk-assessment carried out above, one can conclude that the following localities pose the highest level of risk (Moderate - Level 4): Naxxar, Gharghur, Pembroke, Swieqi and San Gwann. Therefore, the consultant has identified a number of specific sensitive receptors within the aforementioned localities, that include: residential areas, schools, clinics, old people's home and hospitals. For the lower risk localities, a minimum of one sensitive receptor has also been included.

TABLE 7: RISK ASSESSMENT FOR EACH LOCALITY IN THE AOI

LOCALITY	DISTANCE [KM]	CURRENT POLLUTION	RISK LEVEL
SPB	1.6 - Short (3)	< 20 µg/m <sup>3</sup> - Low (1)	Moderate (4)
NXR	0.0 - Short (3)	20 - 30 µg/m <sup>3</sup> - Low (1)	Moderate (4)
MST	2.6 - Medium (2)	< 20 µg/m <sup>3</sup> - Low (1)	Moderate (3)
LJA	4.2 - Far (1)	< 20 µg/m <sup>3</sup> - Low (1)	Low (2)
BZN	4.6 - Far (1)	20 - 30 µg/m <sup>3</sup> - Low (1)	Low (2)
ATT	5.0 - Far (1)	20 - 30 µg/m <sup>3</sup> - Low (1)	Low (2)
IKL	3.0 - Medium (2)	20 - 30 µg/m <sup>3</sup> - Low (1)	Moderate (3)
BKR	4.6 - Far (1)	20 - 30 µg/m <sup>3</sup> - Low (1)	Low (2)
GHR	1.5 - Short (3)	20 - 30 µg/m <sup>3</sup> - Low (1)	Moderate (4)
PMB	1.9 - Short (3)	< 20 µg/m <sup>3</sup> - Low (1)	Moderate (4)
SWQ	1.5 - Short (3)	< 20 µg/m <sup>3</sup> - Low (1)	Moderate (4)
SGN	3.6 - Medium (2)	20 - 30 µg/m <sup>3</sup> - Low (1)	Moderate (3)
MSD	5.2 - Far (1)	20 - 30 µg/m <sup>3</sup> - Low (1)	Low (2)
STJ	4.7 - Far (1)	20 - 30 µg/m <sup>3</sup> - Low (1)	Low (2)
SLM	5.6 - Far (1)	20 - 30 µg/m <sup>3</sup> - Low (1)	Low (2)

LOCALITY	DISTANCE [KM]	CURRENT POLLUTION	RISK LEVEL
GZR	5.6 - Far (1)	20 - 30 µg/m <sup>3</sup> - Low (1)	Low (2)
RBT	5.3 - Far (1)	< 20 µg/m <sup>3</sup> - Low (1)	Low (2)
MGR	5.3 - Far (1)	20 - 30 µg/m <sup>3</sup> - Low (1)	Low (2)

TABLE 8 – SENSITIVE RECEPTORS

RECEPTOR NO.	NAME	COORDINATES	DISTANCE
R1	Verdala International School, Pembroke	35°55'33.67"N 14°28'49.07"E	3.80 km
R2	Chiswick House School, San Gwann	35°54'26.02"N 14°29'0.87"E	5.36 km
R3	St Catherine's High School, Pembroke	35°55'30.98"N 14°28'24.17"E	3.31 km
R4	St Michael's School, Pembroke	35°55'31.24"N 14°28'34.19"E	3.52 km
R5	St Michael's Foundation, San Gwann	35°54'43.73"N 14°27'53.62"E	3.92 km
R6	St Francis School, San Gwann	35°54'27.88"N 14°28'48.44"E	5.10 km
R7	St Clare Primary College, Pembroke	35°55'40.57"N 14°28'40.21"E	3.50 km
R8	Karmnu Sant Primary School, Gharghur	35°55'25.82"N 14°27'5.60"E	2.22 km
R9	Bice Mizzi Vassallo Primary School, Pembroke	35°55'29.92"N 14°28'27.30"E	3.40 km
R10	St Clare Secondary, Pembroke	35°55'47.69"N 14°28'19.09"E	2.93 km
R11	Sprachcaffe Language School, Pembroke	35°55'30.60"N 14°28'41.83"E	3.69 km
R12	San Miguel Resource Centre, Pembroke	35°55'41.26"N 14°28'30.65"E	3.28 km

RECEPTOR No.	NAME	COORDINATES	DISTANCE
R13	M.U.S.E.U.M Pembroke	35°55'35.46"N 14°28'42.10"E	3.62 km
R14	Risen Christ Church, Pembroke	35°55'34.72"N 14°28'39.08"	3.56 km
R15	National Sports School, Pembroke	35°55'27.69"N 14°28'26.35"E	3.42 km
R16	Simblija Care Home, Naxxar	35°54'42.13"N 14°26'50.75"E	3.49 km
R17	Golden Care Retirement Home, Naxxar	35°55'3.49"N 14°26'54.07"E	2.85 km
R18	Primary School, Naxxar	35°54'50.02"N 14°26'47.09"E	3.24 km
R19	MRC Middle School, Naxxar	35°54'37.01"N 14°26'52.35"E	3.65 km
R20	Giovanni Curmi Higher Secondary, Naxxar	35°54'35.28"N 14°26'48.54"E	3.69 km
R21	Naxxar Parish Church, Naxxar	35°54'52.52"N 14°26'39.98"E	3.16 km
R22	St Clare's Primary College, San Gwann	35°54'32.44"N 14°28'31.27"E	4.72 km
R23	San Gwann Parish Church, San Gwann	35°54'27.65"N 14°28'36.81"E	4.93 km
R24	Immaculate Mother of the Church, Swieqi	35°55'15.51"N 14°28'27.78"E	3.69 km
R25	St Bartholomew Parish Church, Gharghur	35°55'25.49"N 14°27'12.52"E	2.31 km
R26	Clubclass English School, Swieqi	35°55'10.80"N 14°28'50.10"E	4.20 km
R27	Agricultural land, Magħtab	35°56'22.21"N 14°26'45.34"E	0.43 km

RECEPTOR No.	NAME	COORDINATES	DISTANCE
R28	Żona fil-Baħar madwar Għawdex - MT0000112	35°56'52.41"N 14°27'0.53"E	0.79 km
R29	Żona fil-Baħar bejn Il-Ponta ta' San Dimitri (Għawdex) u Il-Qaliet (MT0000105)	35°56'54.63"N 14°27'17.86"E	1.18 km
R30	L-Għadira s-Safra (MT0000008)	35°57'2.52"N 14°26'43.28"E	0.86 km
R31	Is-Salini (MT0000007)	35°56'38.19"N 14°25'20.58"E	1.94 km
R32	Triq ir-Ramla, Magħtab Residential & Industrial Area	35°56'9.33"N 14°26'32.99"E	0.78 km
R33	Triq Jules Verne, Naxxar Residential Area	35°55'26.90"N 14°26'21.72"E	2.13 km
R34	Triq Fidel Zarb, Għargħur Residential Area	35°55'39.42"N 14°27'9.29"E	1.88 km
R35	Dawret il-Qawra, Qawra Residential Area	35°57'0.72"N 14°25'24.15"E	2.01 km
R36	Triq Napuljun Tagliaferro, Pembroke Residential Area	35°55'39.77"N 14°28'39.18"E	3.48 km
R37	Triq M. Pulis, Birkirkara Residential Area	35°53'57.91"N 14°27'55.10"E	5.21 km
R38	Constitution Road, Mosta Residential Area	35°54'34.35"N 14°25'34.08"E	4.04 km
R39	Triq San Guzepp, San Gwann Residential Area	35°54'26.90"N 14°28'37.06"E	4.95 km
R40	Parish Street, St Paul's Bay Residential Area	35°56'55.42"N 14°24'8.97"E	3.78 km
R41	Triq il-Maghsar, Burmarrad Residential Area	35°55'59.70"N 14°24'49.00"E	2.93 km
R42	Triq Preziosi, Lija Residential Area	35°54'13.20"N 14°26'42.79"E	4.37 km

RECEPTOR No.	NAME	COORDINATES	DISTANCE
R43	Triq Balaguer, Balzan Residential Area	35°53'59.04"N 14°27'4.81"E	4.85 km
R44	Triq Annabelle Preca, Attard Residential Area	35°53'49.31"N 14°26'15.74"E	5.13 km
R45	Triq il-Harruba, Iklin Residential Area	35°54'42.16"N 14°27'8.16"E	3.56 km
R46	Triq L.Apap, St Julian's Residential Area	35°55'16.57"N 14°29'22.03"E	4.78 km
R47	Mater Dei Hospital, Msida	35°54'4.63"N 14°28'35.51"E	5.49 km
R48	Tower Road, Sliema Residential Area	35°55'1.99"N 14°29'59.81"E	5.81 km
R49	Farm at Triq il-Katakombi, Salina	35°56'44.52"N 14°25'45.23"E	1.35 km
R50	Farm at Sqaq Habel Zwejra, Maghtab	35°56'15.73"N 14°26'8.07"E	0.95 km
R51	Farm and fields at Triq Burmarrad, Burmarrad	35°55'33.18"N 14°25'12.83"E	2.86 km
R52	Farms at Bahar ic-Caghaq	35°56'2.57"N 14°26'53.43"E	1.06 km
R53	Agricultural land at Triq il-Wardija, Wardija	35°56'18.06"N 14°24'38.77"E	3.02 km
R54	Agricultural land at Triq is-Sagra Familja, Bidnija	35°55'33.91"N 14°23'31.26"E	5.03 km
R55	Agricultural land, Triq Sir Temi Zammit, Mosta	35°54'33.82"N 14°24'6.01"E	5.32 km



FIGURE 2. MAP OF THE IDENTIFIED SENSITIVE RECEPTORS

### 3.3 SPATIAL ELABORATIONS

The area of influence - AOI, area around the plant in which the contribution of the plant to the annual ambient levels of NO<sub>2</sub>, PM<sub>10</sub> or PM<sub>2.5</sub> is 0.3 µg/m<sup>3</sup> for NO<sub>2</sub> or 0.3 µg/m<sup>3</sup> for PM<sub>10</sub> or 0.19 µg/m<sup>3</sup> for PM<sub>2.5</sub>, whichever results in the largest AOI. If the area of the AOI is < 11.3 km<sup>2</sup> then the AOI shall be assumed to be a circle of radius 6 km center on the chimney.

Below are the results obtained by the model for the three scenarios considered:

#### Scenario A

- a. NO<sub>2</sub>, the simulated concentrations are lower than 0.3 µg/m<sup>3</sup> on entire calculation domain and receptors. The maximum concentrations have been estimated in a radius centered on chimney equal to about 0.78 km;
- b. PM<sub>10</sub>, the simulated concentrations are lower than 0.3 µg/m<sup>3</sup> on entire calculation domain and receptors. The maximum concentrations have been estimated in a radius centered on chimney equal to about 0.78 km;
- c. PM<sub>2.5</sub>, the simulated concentrations are lower than 0.19 µg/m<sup>3</sup> on entire calculation domain and receptors. The maximum concentrations have been estimated in a radius centered on chimney equal to about 0.78 km.

#### Scenario B

- a. NO<sub>2</sub>, the simulated concentrations are lower than 0.3 µg/m<sup>3</sup> on entire calculation domain and receptors. The maximum concentrations have been estimated in a radius centered on chimney equal to about 0.78 km;
- b. PM<sub>10</sub>, the simulated concentrations are lower than 0.3 µg/m<sup>3</sup> on entire calculation domain and receptors. The maximum concentrations have been estimated in a radius centered on chimney equal to about 0.78 km;
- c. PM<sub>2.5</sub>, the simulated concentrations are lower than 0.19 µg/m<sup>3</sup> on entire calculation domain and receptors. The maximum concentrations have been estimated in a radius centered on chimney equal to about 0.78 km.

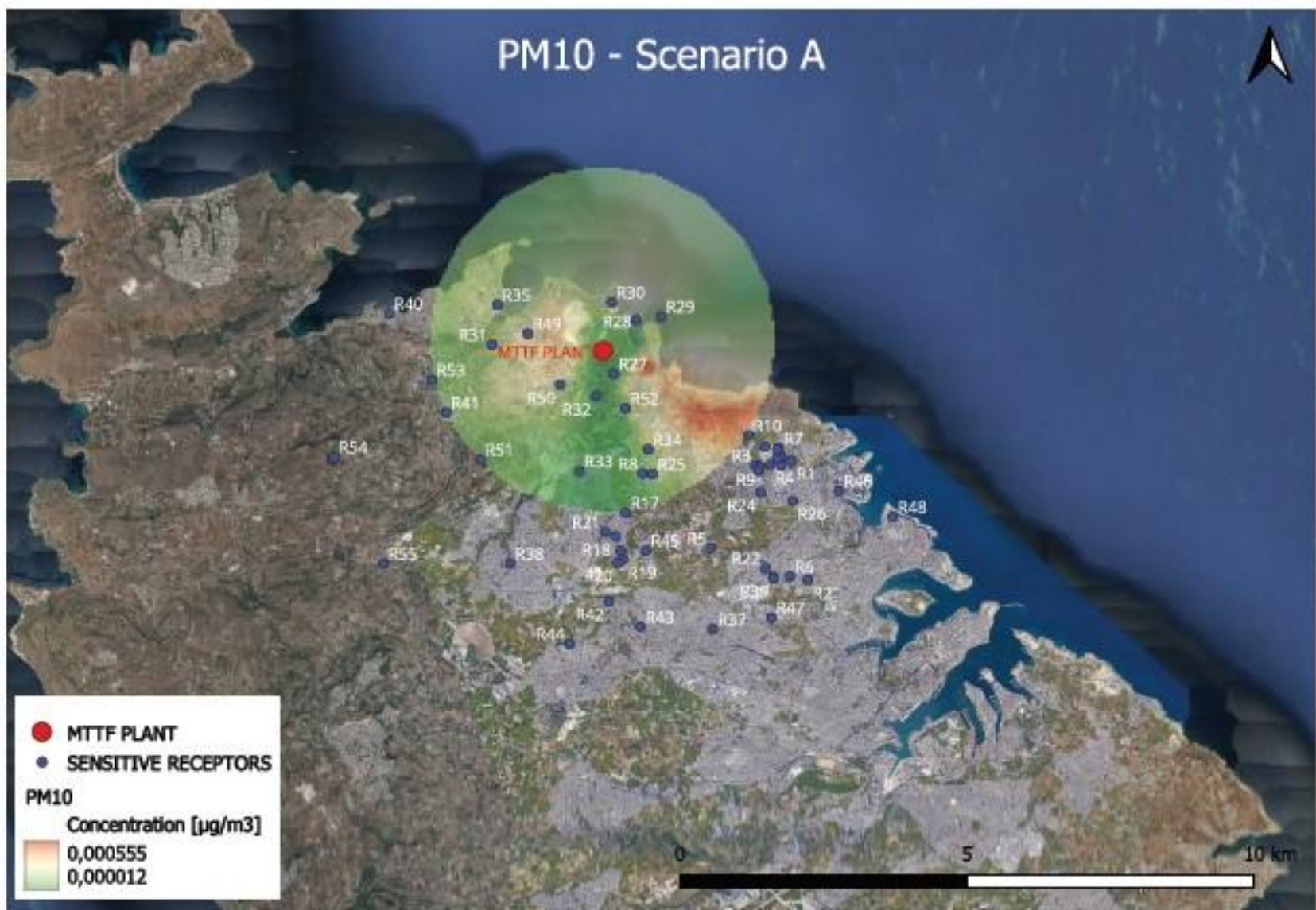
#### Scenario C

- a. PM<sub>10</sub>, the simulated concentrations are lower than 0.3 µg/m<sup>3</sup> on entire calculation domain and receptors. The maximum concentrations have been estimated in a radius centered on chimney equal to about 0.78 km;
- b. PM<sub>2.5</sub>, the simulated concentrations are lower than 0.19 µg/m<sup>3</sup> on entire calculation domain and receptors. The maximum concentrations have been estimated in a radius centered on chimney equal to about 0.78 km.

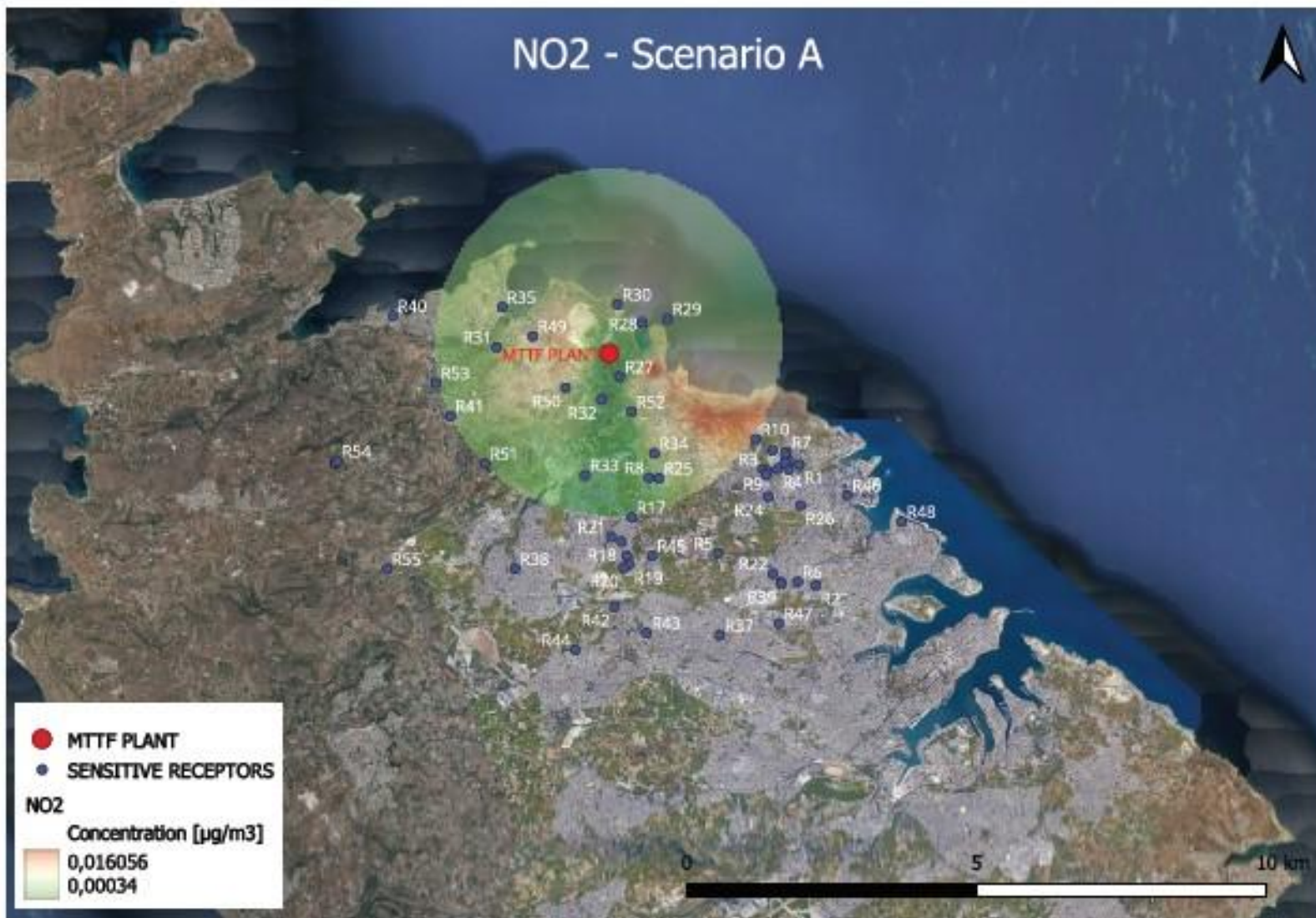
The isoconcentration maps have been created in order to define in detail the areas in which the calculated concentrations expressed as µg/m<sup>3</sup>. A color gradient between orange and red was used to highlight areas with higher concentrations. All maps are listed in Annex 1.

The simulations have revealed that the concentration of NO<sub>2</sub>, PM<sub>10</sub> and PM<sub>2.5</sub> are lower than the established thresholds. Consequently, an AoI with a radius of 6km has been established. The models and the spatial analysis was developed with the aim of obtaining a spatial data resolution of 5 × 5 m<sup>2</sup>.

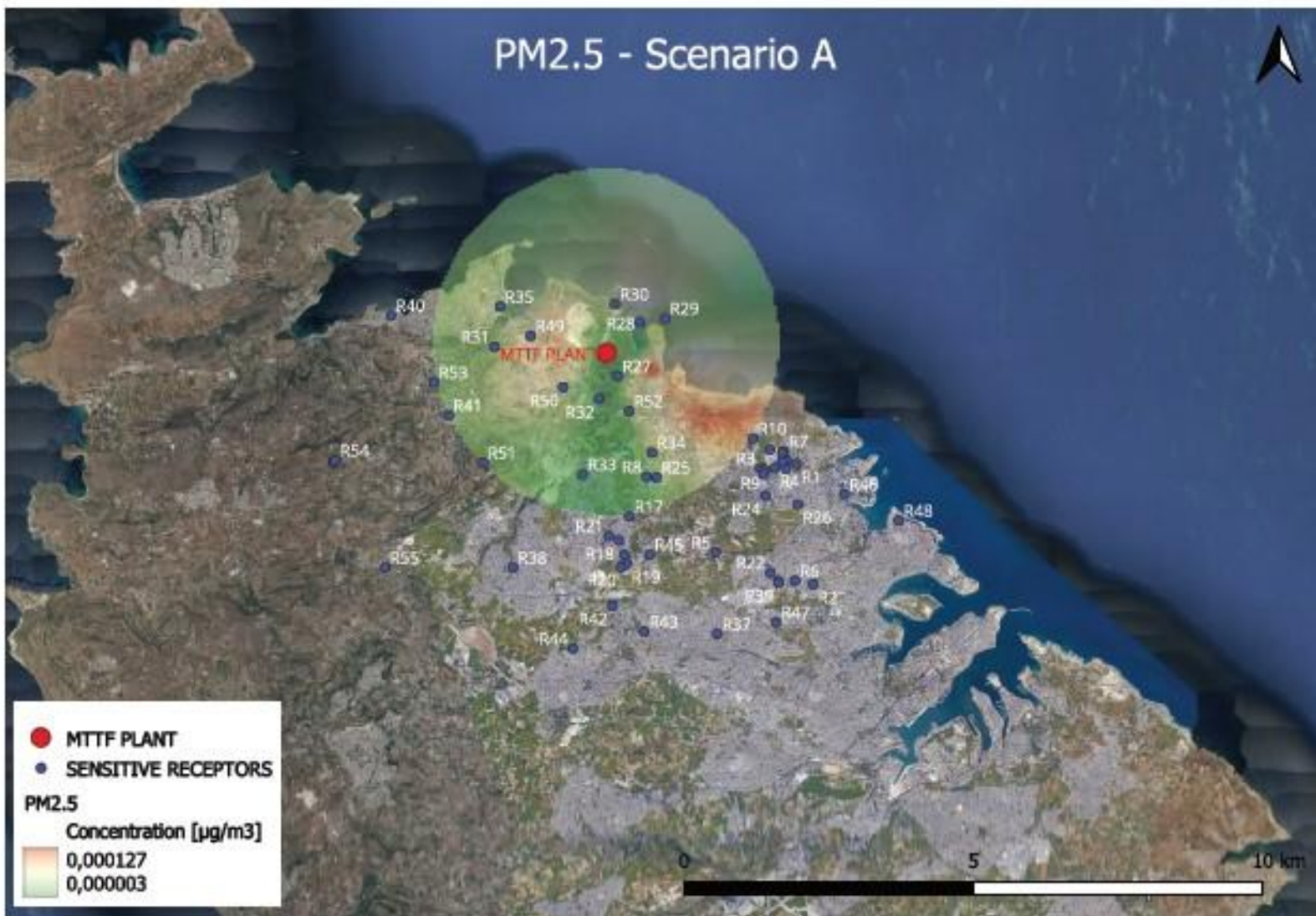
3.3.1 Isoconcentration map of PM<sub>10</sub> - Scenario A



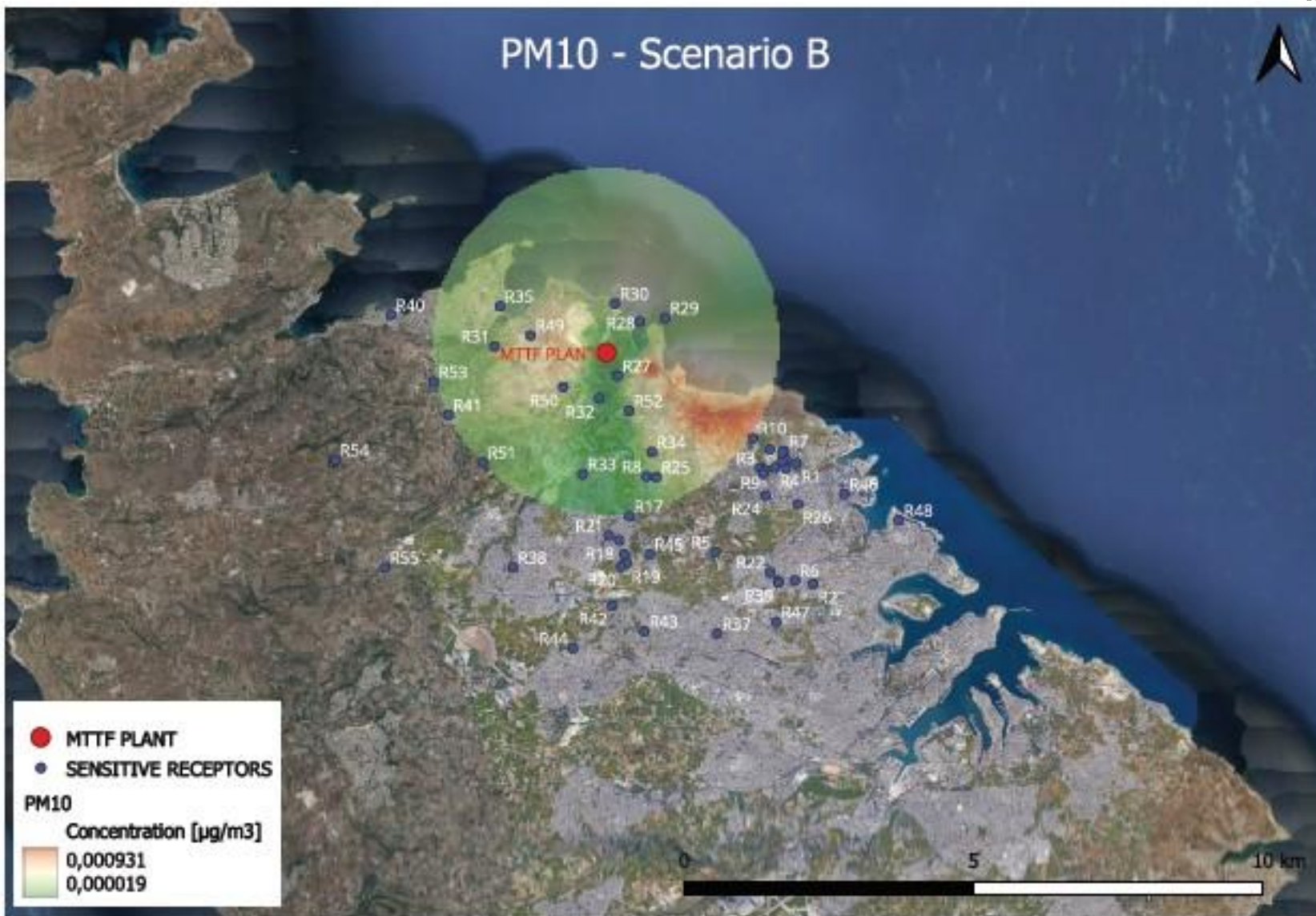
3.3.2 Isoconcentration maps of NO<sub>2</sub> - Scenario A



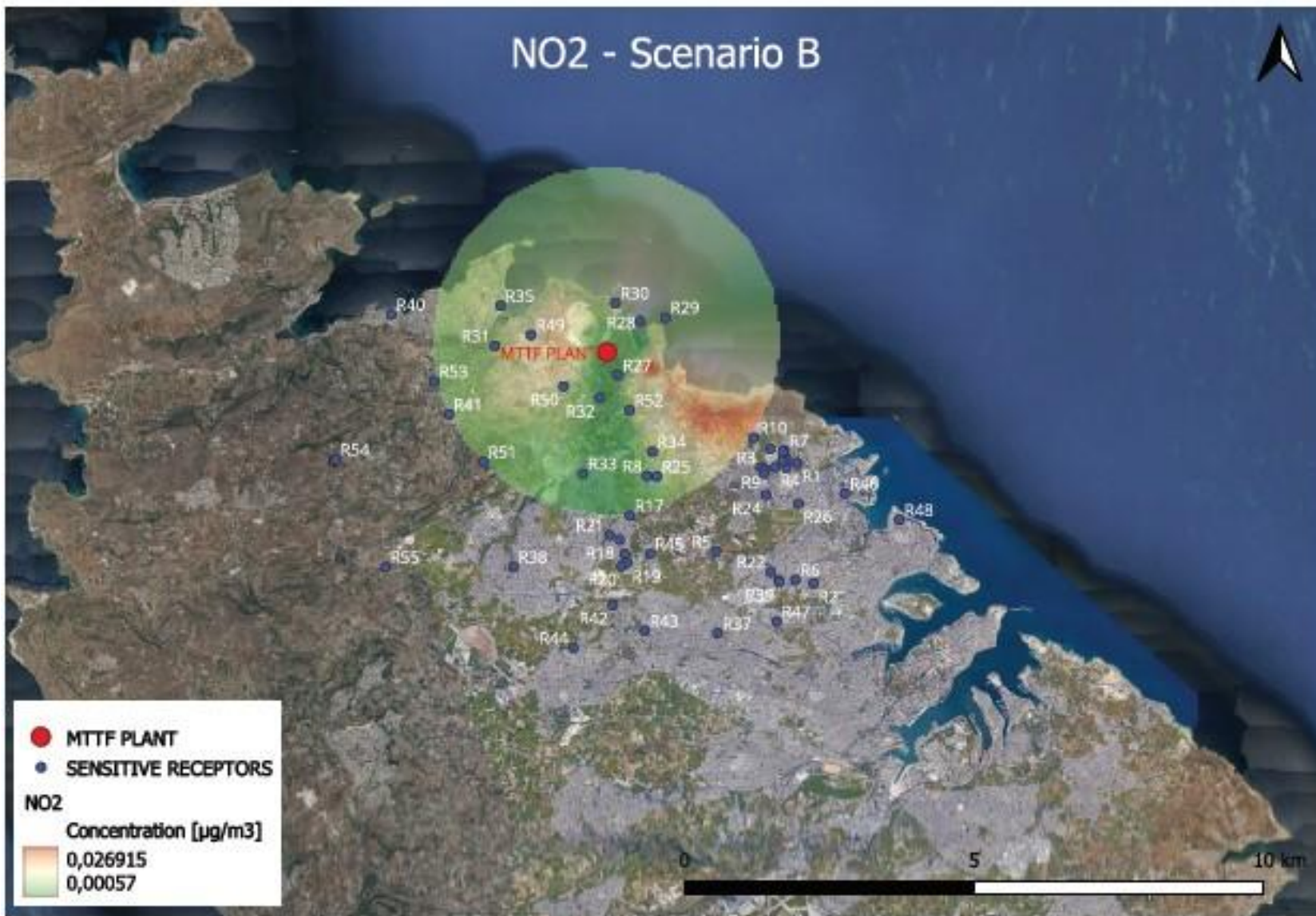
3.3.3 Isoconcentration maps of PM<sub>2.5</sub>- Scenario A



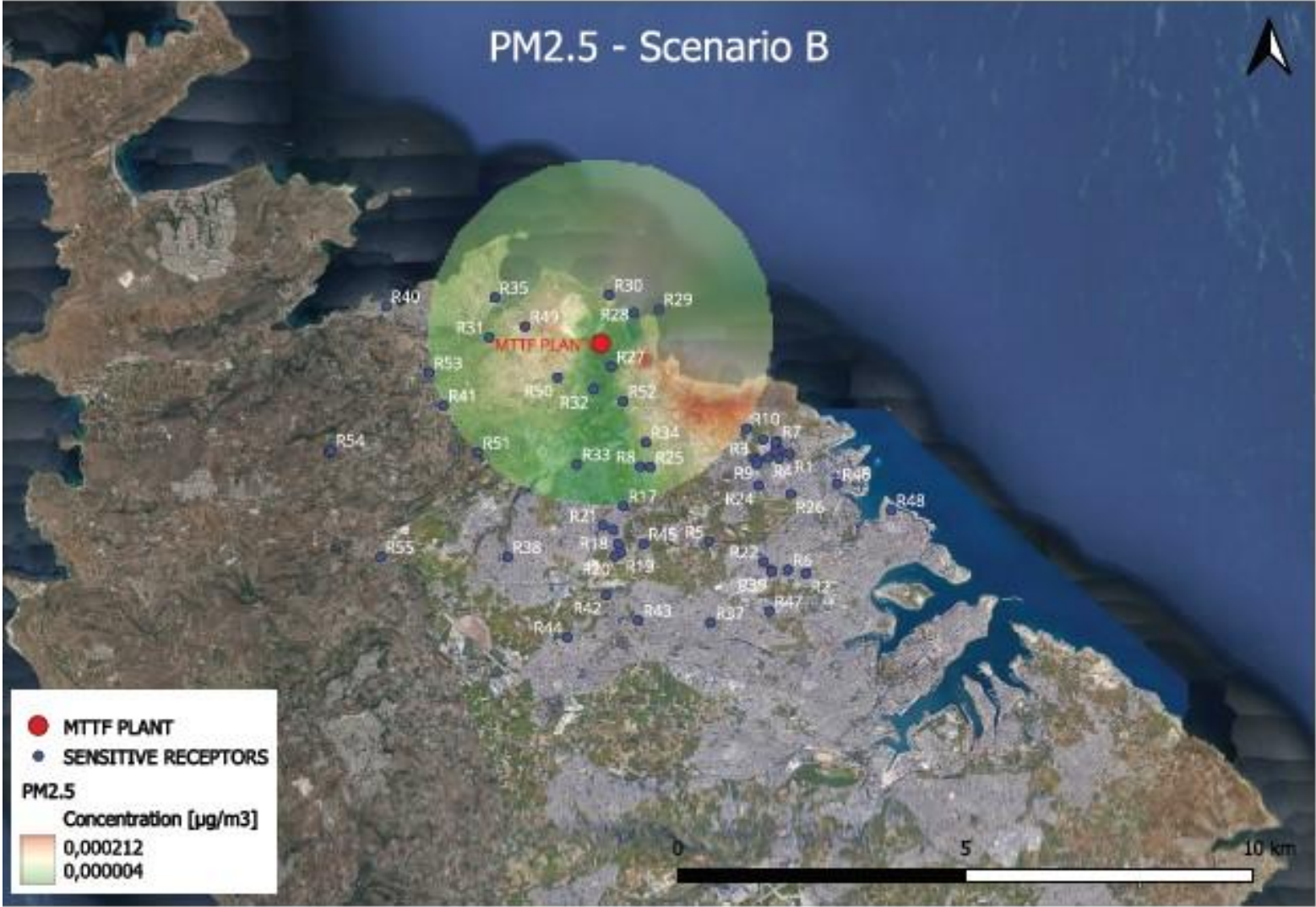
3.3.4 Isoconcentration map of PM10 - Scenario B



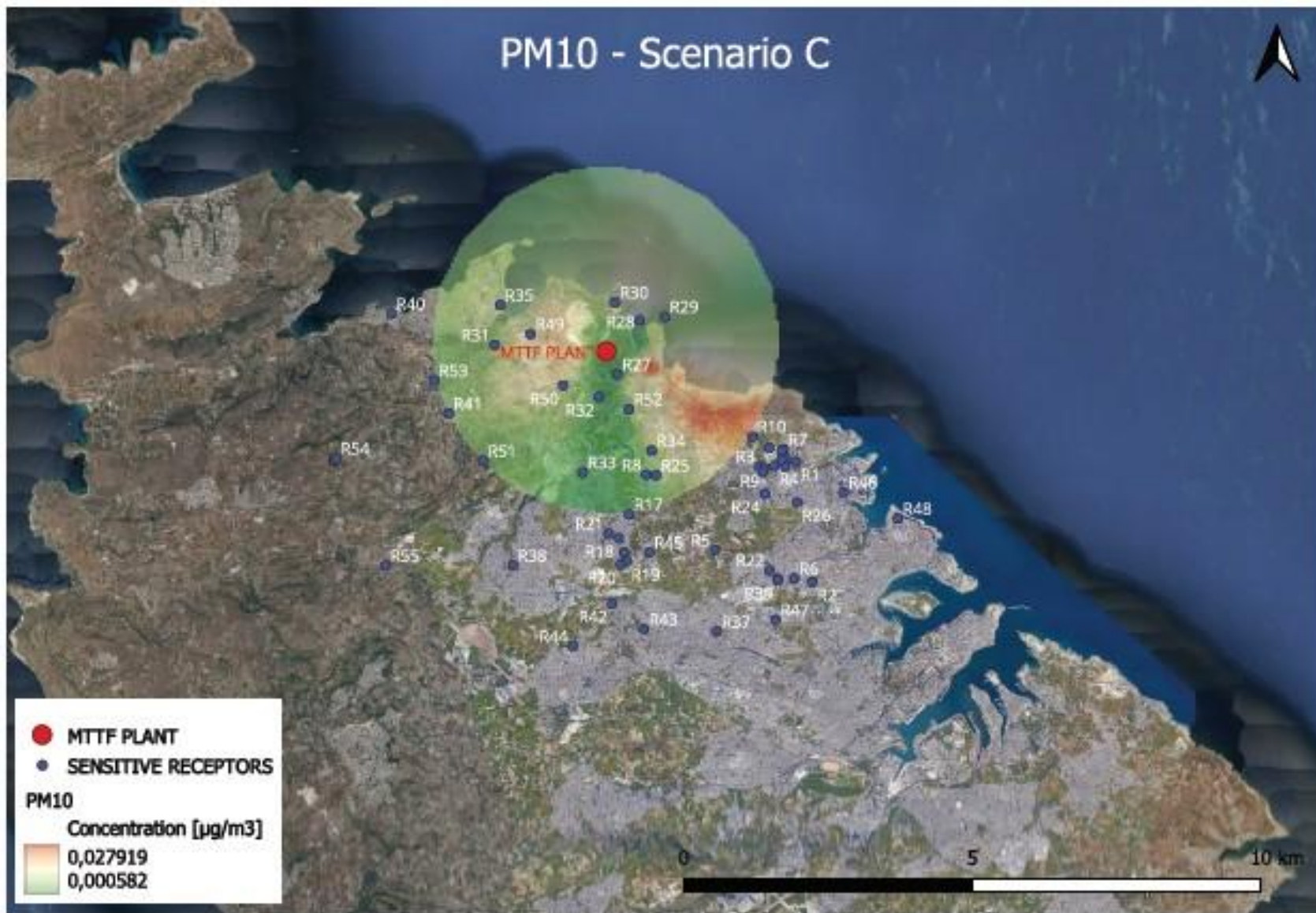
### 3.3.5 Isoconcentration maps of NO<sub>2</sub> - Scenario B



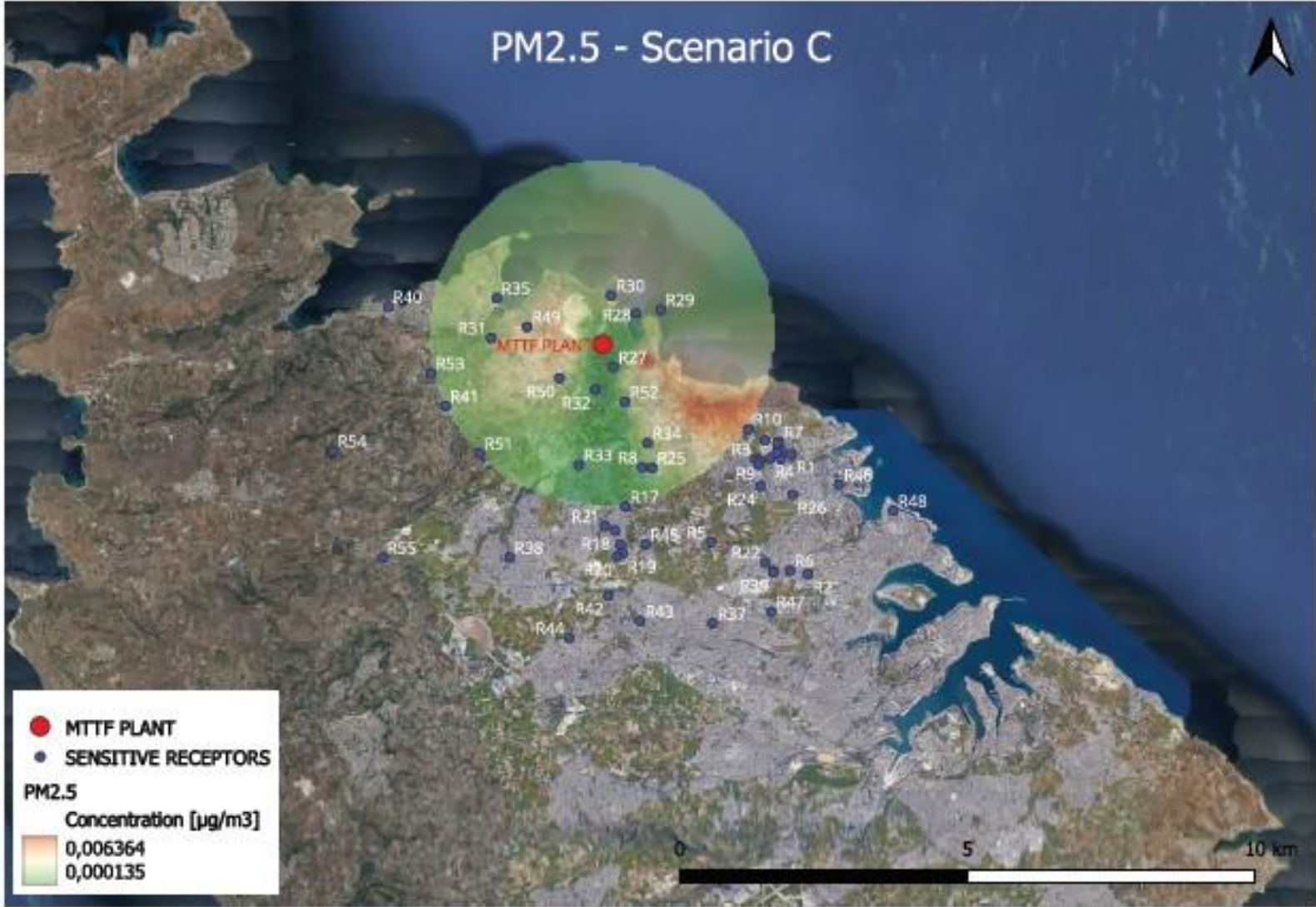
3.3.6 Isoconcentration maps of PM<sub>2.5</sub>- Scenario B



3.3.7 Isoconcentration maps of PM<sub>10</sub> - Scenario C



3.3.8 Isoconcentration maps of PM<sub>2.5</sub> - Scenario C



### 3.4 PERCENTILE EVALUATION

In accordance with the ERA TOR's, the 90.4th percentile of concentrations for PM<sub>10</sub> and the 99.8th percentile of concentrations for NO<sub>2</sub> were estimated.

With the aim of obtaining a comparable dataset, these statistical parameters have been calculated at the receptors for each parameter relation to a year (as shown in table 1 and table 2).

Part II of Schedule 7 to Regulation 29 of S.L. 549.59 sets the following (legally binding limit values):

- an annual limit value of 40 µg/m<sup>3</sup> for PM<sub>10</sub>, a daily limit value for PM<sub>10</sub> of 50 µg/m<sup>3</sup> which cannot be exceeded on more than 35 calendar days (90.4% of the daily readings in a calendar year should be < 50 µg/m<sup>3</sup>);
- an annual limit value of 40 µg/m<sup>3</sup> for NO<sub>2</sub> and an hourly limit value of 200 µg/m<sup>3</sup>, which cannot be exceeded more than 18 times per calendar year (99.8 % of the hourly readings in a calendar year should be < 200 µg/m<sup>3</sup>).

From the model results it emerges that:

- in the ***Scenario A*** the 90.4<sup>th</sup> percentile of concentrations for are below the regulatory limits of 50 µg/m<sup>3</sup> which cannot be exceeded on more than 35 calendar days and are below an annual limit value of 40 µg/m<sup>3</sup>; also, the 99.8th percentile of concentrations for NO<sub>2</sub> in the Scenario A are below an hourly limit value of 200 µg/m<sup>3</sup> which cannot be exceeded on more than 35 calendar days and are below an annual limit value of 40 µg/m<sup>3</sup>;
- in the ***Scenario B*** the 90.4<sup>th</sup> percentile of concentrations for are below the regulatory limits of 50 µg/m<sup>3</sup> which cannot be exceeded on more than 35 calendar days and are below an annual limit value of 40 µg/m<sup>3</sup>; also, the 99.8th percentile of concentrations for NO<sub>2</sub> in the Scenario A are below an hourly limit value of 200 µg/m<sup>3</sup> which cannot be exceeded on more than 35 calendar days and are below an annual limit value of 40 µg/m<sup>3</sup>;
- in the ***Scenario C*** the 90.4<sup>th</sup> percentile of concentrations for are below the regulatory limits of 50 µg/m<sup>3</sup> which cannot be exceeded on more than 35 calendar days and are below an annual limit value of 40 µg/m<sup>3</sup>; Also the 99.8th percentile of concentrations for NO<sub>2</sub> in the Scenario A are below an hourly limit value of 200 µg/m<sup>3</sup> which cannot be exceeded on more than 35 calendar days and are below an annual limit value of 40 µg/m<sup>3</sup> (evaluated in the Scenario B).

TABLE 9: MAXIMUM VALUES OF FALLOUT TO THE RECEPTORS (PM<sub>10</sub>) FOR THREE SCENARIOS

RECEPTORS	Distance from the chimney [km]	SCENARIO A		SCENARIO B		SCENARIO C		
		PM10		PM10		PM10		
		Avarege hourly value Annual limit value [40 µg/m <sup>3</sup> ]	Percentile 90.4 (PM10) Daily Limit Value [50 µg/m <sup>3</sup> ]	Avarege hourly value Annual limit value [40 µg/m <sup>3</sup> ]	Percentile 90.4 (PM10) Daily Limit Value [50 µg/m <sup>3</sup> ]	Avarege hourly value Annual limit value [40 µg/m <sup>3</sup> ]	Percentile 90.4 (PM10) Daily Limit Value [50 µg/m <sup>3</sup> ]	
R1	Verdala International School Pembrok	3,80 km	0.00023	0.00072	0.00039	0.00121	0.01170	0.03620
R2	Chiswick House School San Gwann	5,36 km	0.00009	0.00028	0.00016	0.00047	0.00464	0.01410
R3	St Catherine's High School Pembroke	3,31 km	0.00032	0.00096	0.00054	0.00161	0.01610	0.04830
R4	St Michael's School Pembroke	3,52 km	0.00032	0.00096	0.00053	0.00161	0.01590	0.04820
R5	St Michael's Foundation San Gwann	3,92 km	0.00007	0.00024	0.00012	0.00040	0.00348	0.01190
R6	St Francis School San Gwann	5,10 km	0.00009	0.00028	0.00015	0.00047	0.00444	0.01420
R7	St Clare Primary College Pembroke	3,50 km	0.00025	0.00078	0.00041	0.00130	0.01240	0.03900
R8	Karmnu Sant Primary School Gharghur	2,22 km	0.00008	0.00024	0.00013	0.00039	0.00379	0.01180
R9	Bice Mizzi Vassallo Primary School P	3,40 km	0.00031	0.00093	0.00051	0.00156	0.01540	0.04690
R10	St Clare Secondary Pembroke	2,93 km	0.00043	0.00138	0.00073	0.00231	0.02180	0.06920
R11	Sprachcaffe Language School Pembroke	3,69 km	0.00022	0.00065	0.00037	0.00109	0.01100	0.03280
R12	San Miguel Resource Centre Pembroke	3,28 km	0.00038	0.00117	0.00063	0.00196	0.01880	0.05890
R13	M.U.S.E.U.M Pembroke	3,62 km	0.00023	0.00069	0.00039	0.00115	0.01160	0.03460
R14	Risen Christ Church Pembroke	3,56 km	0.00023	0.00069	0.00038	0.00116	0.01140	0.03480
R15	National Sports School Pembroke	3,42 km	0.00029	0.00090	0.00049	0.00151	0.01470	0.04540
R16	Simblija Care Home Naxxar	3,49 km	0.00001	0.00004	0.00002	0.00006	0.00060	0.00176
R17	Golden Care Retirement Home Naxxar	2,85 km	0.00002	0.00006	0.00003	0.00011	0.00082	0.00323
R18	Primary School Naxxar	3,24 km	0.00001	0.00004	0.00002	0.00006	0.00060	0.00185
R19	MRC Middle School Naxxar	3,65 km	0.00001	0.00003	0.00002	0.00006	0.00058	0.00171
R20	Giovanni Curmi Higher Secondary Naxx	3,69 km	0.00001	0.00003	0.00002	0.00006	0.00056	0.00169
R21	Naxxar Parish Church Naxxar	3,16 km	0.00001	0.00003	0.00002	0.00006	0.00054	0.00171
R22	St Clare's Primary College San Gwann	4,72 km	0.00009	0.00026	0.00014	0.00043	0.00428	0.01300
R23	San Gwann Parish Church San Gwann	4,93 km	0.00009	0.00027	0.00014	0.00046	0.00431	0.01370
R24	Immaculate Mother of the Church Swie	3,69 km	0.00024	0.00074	0.00040	0.00124	0.01190	0.03710
R25	St Bartholomew Parish Church Gharghu	2,31 km	0.00011	0.00042	0.00019	0.00070	0.00564	0.02100
R26	Clubclass English School Swieqi	4,20 km	0.00016	0.00042	0.00026	0.00071	0.00777	0.02120
R27	Agricultural land Magtab	0,43 km	0.00003	0.00012	0.00005	0.00020	0.00156	0.00595
R28	?ona fil-Ba?ar madwar G?awdex - MT000	0,79 km	0.00017	0.00062	0.00029	0.00103	0.00875	0.03100
R29	?ona fil-Ba?ar bejn Il-Ponta ta? San	1,18 km	0.00017	0.00057	0.00028	0.00095	0.00833	0.02860
R30	L-G?adira s-Safra (MT0000008)	0,86 km	0.00022	0.00082	0.00037	0.00137	0.01120	0.04110
R31	Is-Salini (MT0000007)	1,94 km	0.00015	0.00057	0.00025	0.00095	0.00744	0.02850
R32	Triq ir-Ramla Magtab Residential &	0,78 km	0.00002	0.00007	0.00003	0.00011	0.00100	0.00335
R33	Triq Jules Verne Naxxar Residential	2,13 km	0.00003	0.00009	0.00005	0.00015	0.00148	0.00434
R34	Triq Fidel Zarb G?arg?ur Residential	1,88 km	0.00018	0.00065	0.00030	0.00109	0.00885	0.03280
R35	Dawret il-Qawra Qawra Residential Ar	2,01 km	0.00020	0.00065	0.00033	0.00109	0.00980	0.03270
R36	Triq Napuljun Tagliaferro Pembroke R	3,48 km	0.00024	0.00075	0.00040	0.00125	0.01190	0.03750
R37	Triq M. Pulis Birkirkara Residential	5,21 km	0.00003	0.00012	0.00005	0.00020	0.00161	0.00589
R38	Constitution Road Mosta Residential	4,04 km	0.00004	0.00011	0.00006	0.00018	0.00195	0.00541
R39	Triq San Guzepp San Gwann Residentia	4,95 km	0.00009	0.00027	0.00014	0.00046	0.00429	0.01370
R40	Parish Street St Paul's Bay Resident	3,78 km	0.00010	0.00033	0.00017	0.00056	0.00500	0.01670
R41	Triq il-Maghsar Burmarrad Residentia	2,93 km	0.00013	0.00040	0.00022	0.00067	0.00671	0.02010
R42	Triq Preziosi Lija Residential Area	4,37 km	0.00001	0.00003	0.00001	0.00005	0.00045	0.00137
R43	Triq Balaguer Balzan Residential Are	4,85 km	0.00001	0.00005	0.00002	0.00008	0.00058	0.00231
R44	Triq Annabelle Preca Attard Resident	5,13 km	0.00001	0.00004	0.00001	0.00006	0.00045	0.00191
R45	Triq il-Harruba Iklun Residential Ar	3,56 km	0.00002	0.00007	0.00003	0.00012	0.00095	0.00350
R46	Triq L.Apap St Julian's Residential	4,78 km	0.00020	0.00059	0.00034	0.00099	0.01010	0.02960
R47	Mater Dei Hospital Msida	5,49 km	0.00007	0.00023	0.00011	0.00038	0.00337	0.01140
R48	Tower Road Sliema Residential Area	5,81 km	0.00018	0.00054	0.00031	0.00090	0.00926	0.02710
R49	Farm at Triq il-Katakombi Salina	1,35 km	0.00031	0.00117	0.00052	0.00196	0.01570	0.05890
R50	Farm at Sqaq Habel Zwejra Magtab	0,95 km	0.00021	0.00077	0.00036	0.00130	0.01070	0.03890
R51	Farm and fields at Triq Burmarrad Bu	2,86 km	0.00010	0.00034	0.00016	0.00057	0.00480	0.01700
R52	Farms at Bahar ic-Caghaq	1,06 km	0.00008	0.00028	0.00014	0.00047	0.00422	0.01400
R53	Agricultural land at Triq il-Wardija	3,02 km	0.00011	0.00034	0.00018	0.00057	0.00537	0.01700
R54	Agricultural land at Triq is-Sagra Fa	5,03 km	0.00008	0.00023	0.00013	0.00038	0.00380	0.01130
R55	Agricultural land Triq Sir Temi Zamm	5,32 km	0.00006	0.00019	0.00009	0.00031	0.00280	0.00934

TABLE 1. MAXIMUM VALUES OF FALLOUT TO THE RECEPTORS (NO<sub>2</sub>) FOR TWO SCENARIOS

RECEPTORS	Distance from the chimney(km)	SCENARIO A		SCENARIO B	
		NO <sub>2</sub>		NO <sub>2</sub>	
		Avarege hourly value Annual limit value [40 µg/m <sup>3</sup> ]	Percentile 99.8 (NO <sub>2</sub> ) Hourly Limit Value [200 µg/m <sup>3</sup> ]	Avarege hourly value Annual limit value [40 µg/m <sup>3</sup> ]	Percentile 99.8 (NO <sub>2</sub> ) Hourly Limit Value [200 µg/m <sup>3</sup> ]
R1	Verdala International School Pembroke	3,80 km	0.00652	0.07920	0.13300
R2	Chiswick House School San Gwann	5,36 km	0.00257	0.04750	0.07960
R3	St Catherine's High School Pembroke	3,31 km	0.00898	0.11100	0.18600
R4	St Michael's School Pembroke	3,52 km	0.00886	0.10300	0.17200
R5	St Michael's Foundation San Gwann	3,92 km	0.00197	0.06370	0.10700
R6	St Francis School San Gwann	5,10 km	0.00246	0.04850	0.08120
R7	St Clare Primary College Pembroke	3,50 km	0.00691	0.08740	0.14700
R8	Karmnu Sant Primary School Gharghur	2,22 km	0.00218	0.18700	0.31300
R9	Bice Mizzi Vassallo Primary School P	3,40 km	0.00860	0.10800	0.18100
R10	St Clare Secondary Pembroke	2,93 km	0.01220	0.12700	0.21300
R11	Sprachcaffe Language School Pembroke	3,69 km	0.00611	0.08170	0.13700
R12	San Miguel Resource Centre Pembroke	3,28 km	0.01060	0.10900	0.18400
R13	M.U.S.E.U.M Pembroke	3,62 km	0.00647	0.08360	0.14000
R14	Risen Christ Church Pembroke	3,56 km	0.00637	0.08490	0.14200
R15	National Sports School Pembroke	3,42 km	0.00822	0.10800	0.18100
R16	Simblija Care Home Naxxar	3,49 km	0.00035	0.02770	0.04640
R17	Golden Care Retirement Home Naxxar	2,85 km	0.00048	0.03880	0.06500
R18	Primary School Naxxar	3,24 km	0.00035	0.02900	0.04860
R19	MRC Middle School Naxxar	3,65 km	0.00034	0.02680	0.04500
R20	Giovanni Curmi Higher Secondary Naxx	3,69 km	0.00033	0.02660	0.04460
R21	Naxxar Parish Church Naxxar	3,16 km	0.00032	0.02780	0.04650
R22	St Clare's Primary College San Gwann	4,72 km	0.00239	0.05060	0.08480
R23	San Gwann Parish Church San Gwann	4,93 km	0.00240	0.04940	0.08280
R24	Immaculate Mother of the Church Swie	3,69 km	0.00662	0.10300	0.17200
R25	St Bartholomew Parish Church Gharghu	2,31 km	0.00324	0.18500	0.31000
R26	Clubclass English School Swieqi	4,20 km	0.00431	0.06420	0.10800
R27	Agricultural land Mag'tab	0,43 km	0.00090	0.06640	0.11100
R28	?ona fil-Ba?ar madwar G?awdex - MT000	0,79 km	0.00503	0.29900	0.50000
R29	?ona fil-Ba?ar bejn Il-Ponta ta? San	1,18 km	0.00480	0.28100	0.47000
R30	L-G?adira s-Safra (MT0000008)	0,86 km	0.00645	0.35800	0.60000
R31	Is-Salini (MT0000007)	1,94 km	0.00428	0.18200	0.30500
R32	Triq ir-Ramla Mag'tab Residential &	0,78 km	0.00059	0.03900	0.06540
R33	Triq Jules Verne Naxxar Residential	2,13 km	0.00084	0.12300	0.20600
R34	Triq Fidel Zarb G?arg?ur Residential	1,88 km	0.00509	0.22800	0.38200
R35	Dawret il-Qawra Qawra Residential Ar	2,01 km	0.00562	0.18500	0.31000
R36	Triq Napuljun Tagliaferro Pembroke R	3,48 km	0.00664	0.08740	0.14600
R37	Triq M. Pulis Birkirkara Residential	5,21 km	0.00091	0.04480	0.07510
R38	Constitution Road Mosta Residential	4,04 km	0.00109	0.05700	0.09560
R39	Triq San Guzepp San Gwann Residentia	4,95 km	0.00239	0.04930	0.08260
R40	Parish Street St Paul's Bay Resident	3,78 km	0.00283	0.07260	0.12200
R41	Triq il-Maghsar Burmarrad Residentia	2,93 km	0.00380	0.11000	0.18500
R42	Triq Preziosi Lija Residential Area	4,37 km	0.00026	0.02340	0.03920
R43	Triq Balaguer Balzan Residential Are	4,85 km	0.00034	0.03250	0.05450
R44	Triq Annabelle Preca Attard Resident	5,13 km	0.00026	0.02160	0.03630
R45	Triq il-Harruba Iklin Residential Ar	3,56 km	0.00055	0.05420	0.09080
R46	Triq L.Apap St Julian's Residential	4,78 km	0.00555	0.05760	0.09660
R47	Mater Dei Hospital Msida	5,49 km	0.00188	0.04570	0.07660
R48	Tower Road Sliema Residential Area	5,81 km	0.00506	0.04940	0.08280
R49	Farm at Triq il-Katakombi Salina	1,35 km	0.00904	0.31300	0.52400
R50	Farm at Sqaq Habel Zwejra Maghtab	0,95 km	0.00617	0.40900	0.68600
R51	Farm and fields at Triq Burmarrad Bu	2,86 km	0.00271	0.10800	0.18100
R52	Farms at Bahar ic-Caghaq	1,06 km	0.00243	0.23200	0.39000
R53	Agricultural land at Triq il-Wardija	3,02 km	0.00306	0.10000	0.16800
R54	Agricultural land at Triq is-Sagra Fa	5,03 km	0.00210	0.04870	0.08160
R55	Agricultural land Triq Sir Temi Zamm	5,32 km	0.00154	0.04580	0.07680

### 3.5 DEPOSITION RATE EVALUATION

The dispersion model was used to define and calculate the areas in which the mass deposition rates on an annual daily basis are higher.

The results obtained were then compared with the limits indicated in the TOR's and shown below in the table.

TABLE 10: LIMIT OF POLLUTANT

POLLUTANT	LIMIT
Dioxin/Furans	4 pg WHO-TE/m <sup>2</sup> ·day (bulk deposition)
Cd	2 µg/m <sup>2</sup> ·day (bulk deposition)
As	4 µg/m <sup>2</sup> ·day (bulk deposition)
Hg	1 µg/m <sup>2</sup> ·day (bulk deposition)
Pb	100 µg/m <sup>2</sup> ·day (bulk deposition)
TI	2 µg/m <sup>2</sup> ·day (bulk deposition)

Corine land cover was used for the definition of the type of soil cover, this allowed to define the site-specific parameters for the calculation of the depositions.

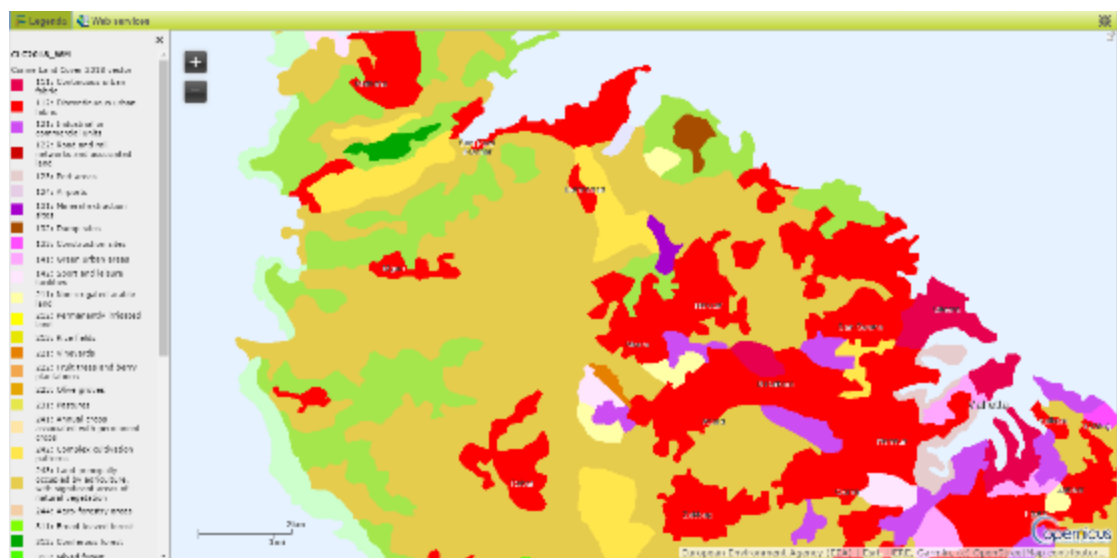


FIGURE 22: EXTRACT OF CORINE LAND COVER UTILIZED IN TO MODELLIZATION

The results obtained are listed below with the individual conservative assessments:

### 3.5.1 Scenario A

- Metals Group 1

From the model results it emerges that the maximum daily concentrations (calculated as the sum of hourly deposits for a single day) are equal to 0.0098 µg/m<sup>2</sup>-day, a much lower value than:

- the deposition limit imposed for Cadmium equal to 2 µg/m<sup>2</sup>-day;
- the deposition limit imposed for Thallium equal to 2 µg/m<sup>2</sup>-day;

This result is conservative because it comprises the total of Cd and Tl concentrations - metal of group 1-).

- Metals Group 2

From the model results it emerges that the maximum daily concentrations (calculated as the sum of hourly deposits for a single day) are equal to 0.0069 µg/m<sup>2</sup>-day, a much lower value than:

- the deposition limit imposed for mercury equal to 1 µg/m<sup>2</sup>-day.

- Metals Group 3

From the model results it emerges that the maximum daily concentrations (calculated as the sum of hourly deposits for a single day) are equal to 0.00486 µg/m<sup>2</sup>-day, a much lower value than:

- the deposition limit imposed for Arsenic equal to 4 µg/m<sup>2</sup>-day;
- the deposition limit imposed for Nickel equal to 15 µg/m<sup>2</sup>-day;
- the deposition limit imposed for Nickel equal to 100 µg/m<sup>2</sup>-day.

This result is a conservative result because it comprises the total of Sb-As-Pb-Cr-Co-Cu-Mn-Ni-V concentrations -metal of group 3-).

- Polychlorinated dibenzo-p-dioxins/ polychlorinated dibenzofurans (PCDD/F) + dioxin - like polychlorinated biphenyls (PCBs)

From the model results it emerges that the maximum daily concentrations (calculated as the sum of hourly deposits for a single day) are equal to 0.0339 pg WHO-TE/m<sup>2</sup>-day, a much lower value than:

- the deposition limit imposed for Polychlorinated dibenzo-p-dioxins/ polychlorinated dibenzofurans (PCDD/F) equal to 4 pg WHO-TE/m<sup>2</sup>-day.

TABLE 11: COMPARISON OF THE TABLE LIMITS IN EIA TORs WITH THE MAXIMUM CONCENTRATIONS – SCENARIO A

POLLUTANT	LIMIT TABLE NO.4 OF TORs 08/05/2024	MASS DEPOSITION RATES ON ANNUAL DAILY BASIS MAX CONC DOMAIN	DISTANCE FROM THE CHIMNEY (KM) MAX CONC DOMAIN	HOURLY AVERAGE VALUE - MAX CONC ON RECEPTORS	DISTANCE FROM THE CHIMNEY (KM) MAX CONC ON RECEPTORS
Cd [µg/m <sup>2</sup> .day]	2	0.0098	2.45	0.0085	2.93
Tl [µg/m <sup>2</sup> .day]	2	0.0098	2.45	0.0085	2.93
Hg [µg/m <sup>2</sup> .day]	1	0.0069	0.21	0.0009	1.18
Ni [µg/m <sup>2</sup> .day]	15	0.0486	2.45	0.0414	2.93
As [µg/m <sup>2</sup> .day]	4	0.0486	2.45	0.0414	2.93
Pb [µg/m <sup>2</sup> .day]	100	0.0486	2.45	0.0414	2.93
PCDD/F + PCB [pgWHO-TE/m <sup>2</sup> .day]	4	0.0339	2.45	0.0286	2.93

### 3.5.2 Scenario B

- Metals Group 1

From the model results it emerges that the maximum daily concentrations (calculated as the sum of hourly deposits for a single day) are equal to 0.0164 µg/m<sup>2</sup>-day, a much lower value than:

- the deposition limit imposed for Cadmium equal to 2 µg/m<sup>2</sup>-day;
- the deposition limit imposed for Thallium equal to 2 µg/m<sup>2</sup>-day;

This result is conservative because it comprises the total of Cd and Tl concentrations –metal of group 1-).

- Metals Group 2

From the model results it emerges that the maximum daily concentrations (calculated as the sum of hourly deposits for a single day) are equal to 0.0115 µg/m<sup>2</sup>-day, a much lower value than:

- the deposition limit imposed for mercury equal to 1 µg/m<sup>2</sup>-day.

- Metals Group 3

From the model results it emerges that the maximum daily concentrations (calculated as the sum of hourly deposits for a single day) are equal to 0.0814  $\mu\text{g}/\text{m}^2\text{-day}$ , a much lower value than:

- the deposition limit imposed for Arsenic equal to 4  $\mu\text{g}/\text{m}^2\text{-day}$ ;
- the deposition limit imposed for Nickel equal to 15  $\mu\text{g}/\text{m}^2\text{-day}$ ;
- the deposition limit imposed for Nickel equal to 100  $\mu\text{g}/\text{m}^2\text{-day}$ .

This result is conservative because it comprises the total of Sb-As-Pb-Cr-Co-Cu-Mn-Ni-V concentrations –metal of group 3-).

- Polychlorinated dibenzo-p-dioxins/ polychlorinated dibenzofurans (PCDD/F) + dioxin - like polychlorinated biphenyls (PCBs)

From the model results it emerges that the maximum daily concentrations (calculated as the sum of hourly deposits for a single day) are equal to 0.0568  $\text{pg WHO-TE}/\text{m}^2\text{-day}$  (scenario 1), a much lower value than:

- the deposition limit imposed for Polychlorinated dibenzo-p-dioxins/ polychlorinated dibenzofurans (PCDD/F) equal to 4  $\text{pg WHO-TE}/\text{m}^2\text{-day}$ .

TABLE 12: COMPARISON OF THE TABLE LIMITS IN EIA TORs WITH THE MAXIMUM CONCENTRATIONS – SCENARIO B

POLLUTANT	LIMIT TABLE NO.4 OF TORs 08/05/2024	MASS DEPOSITION RATES ON ANNUAL DAILY BASIS MAX CONC DOMAIN	DISTANCE FROM THE CHIMNEY (KM) MAX CONC DOMAIN	HOURLY AVERAGE VALUE - MAX CONC ON RECEPTORS	DISTANCE FROM THE CHIMNEY (KM) MAX CONC ON RECEPTORS
Cd [ $\mu\text{g}/\text{m}^2\text{.day}$ ]	2	0.0164	2.45	0.0142	2.93
Tl [ $\mu\text{g}/\text{m}^2\text{.day}$ ]	2	0.0164	2.45	0.0142	2.93
Hg [ $\mu\text{g}/\text{m}^2\text{.day}$ ]	1	0.0115	0.21	0.0015	1.18
Ni [ $\mu\text{g}/\text{m}^2\text{.day}$ ]	15	0.0814	2.45	0.0694	2.93
As [ $\mu\text{g}/\text{m}^2\text{.day}$ ]	4	0.0814	2.45	0.0694	2.93
Pb [ $\mu\text{g}/\text{m}^2\text{.day}$ ]	100	0.0814	2.45	0.0694	2.93
PCDD/F + PCB [ $\text{pgWHO-TE}/\text{m}^2\text{.day}$ ]	4	0.0568	2.45	0.0479	2.93

### 3.5.3 Scenario C

For Scenario C, the mass deposition rates on an annual daily basis are the same as those shown in Scenario B because in the simulation only modified the dust concentration, as defined by the limits in Schedule 2 of S.L.549.81.

## 3.6 COMPARISON WITH AIR QUALITY LIMITS

The following table shows the maximum concentration values of the pollutants calculated on the calculation domain and on the receptors when compared with the air quality limits established in DIRECTIVE 2008/50/EC ON QUALITY ENVIRONMENTAL AIR AND CLEANER AIR FOR LIVING IN EUROPE (Table n°2 and Table n°3 of EIA TORs). The results obtained from the air dispersion model show lower values than the limits set in the EIA TORs for each Scenario.

### 3.6.1 Scenario A

TABLE 13: COMPARISON WITH LIMITS – SCENARIO A

POLLUTANT	TYPE	RESULT - MAX CONC ON DOMAIN	RESULT - MAX CONC ON RECEPTORS	LIMIT AS PER EIA TORs
Average Hourly value of Group 1 elements [ng/m <sup>3</sup> ]	Value	0.002990	0.002291	Cd - 0.15 ng/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of Group 2 elements [ng/m <sup>3</sup> ]	Value	0.002978	0.002271	Hg - 1.5 ng/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of Group 3 elements [ng/m <sup>3</sup> ]	Value	0.004563	0.003560	Pb - 15 ng/m <sup>3</sup> As - 0.18 ng/m <sup>3</sup> Ni - 0.60 ng/m <sup>3</sup> Cr - 0.50 ng/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of PCDD/F+ PCB [ng/m <sup>3</sup> ]	Value	0.011893	0.009057	70 fg WHO-TE/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
	Value	0.000555	0.000433	1.2 µg/m <sup>3</sup>

POLLUTANT	TYPE	RESULT - MAX CONC ON DOMAIN	RESULT - MAX CONC ON RECEPTORS	LIMIT AS PER EIA TORS
Average hourly value of PM <sub>10</sub> [µg/m <sup>3</sup> ]	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of PM <sub>2.5</sub> [µg/m <sup>3</sup> ]	Value	0.000127	0.000097	0.6 µg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of NO <sub>2</sub> [µg/m <sup>3</sup> ]	Value	0.016056	0.012200	1.2 µg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93KM	
Average Hourly value of TVOC [mg/m <sup>3</sup> ]	Value	0.0000074333	0.0000011322	10 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of HCl [mg/m <sup>3</sup> ]	Value	0.0000008920	0.0000006793	6 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of HF [mg/m <sup>3</sup> ]	Value	0.0000001487	0.0000001132	1 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of SO <sub>2</sub> [mg/m <sup>3</sup> ]	Value	0.0000044600	0.0000033965	30 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
	Value	0.0000178398	0.0000135858	120 mg/m <sup>3</sup>

POLLUTANT	TYPE	RESULT - MAX CONC ON DOMAIN	RESULT - MAX CONC ON RECEPTORS	LIMIT AS PER EIA TORs
Average hourly value of NOx [mg/m <sup>3</sup> ]	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of NH <sub>3</sub> [µg/m <sup>3</sup> ]	Value	0.0000014867	0.0000011322	10 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of CO [µg/m <sup>3</sup> ]	Value	0.0000074333	0.0000056608	50 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93KM	

### 3.6.2 Scenario B

TABLE 14: COMPARISON WITH LIMITS – SCENARIO B

POLLUTANT	TYPE	RESULT - MAX CONC ON DOMAIN	RESULT - MAX CONC ON RECEPTORS	LIMIT AS PER EIA TORs
Average Hourly value of Group 1 elements [ng/m <sup>3</sup> ]	Value	0.00501	0.003840	Cd - 0.15 ng/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of Group 2 elements [ng/m <sup>3</sup> ]	Value	0.00499	0.003807	Hg - 1.5 ng/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of Group 3 elements [ng/m <sup>3</sup> ]	Value	0.0076	0.005963	Pb - 15 ng/m <sup>3</sup> As - 0.18 ng/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	Ni - 0.60 ng/m <sup>3</sup> Cr - 0.50 ng/m <sup>3</sup>
	Value	0.01994	0.015183	

POLLUTANT	TYPE	RESULT - MAX CONC ON DOMAIN	RESULT - MAX CONC ON RECEPTORS	LIMIT AS PER EIA TORs
Average Hourly value of PCDD/F+ PCB [ng/m <sup>3</sup> ]	Receptor/ distance from chimney	0.78km	R10 - 2.93km	70 fg WHO-TE/m <sup>3</sup>
Average hourly value of PM <sub>10</sub> [µg/m <sup>3</sup> ]	Value	0.00093	0.000726	1.2 µg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of PM <sub>2.5</sub> [µg/m <sup>3</sup> ]	Value	0.00021	0.000162	0.6 µg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of NO <sub>2</sub> [µg/m <sup>3</sup> ]	Value	0.02691	0.020500	1.2 µg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93KM	
Average Hourly value of TVOC [mg/m <sup>3</sup> ]	Value	0.0000024921	0.0000018979	10 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of HCl [mg/m <sup>3</sup> ]	Value	0.0000014953	0.0000011400	6 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of HF [mg/m <sup>3</sup> ]	Value	0.0000002492	0.0000001898	1 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
	Value	0.0000074763	0.0000056936	30 mg/m <sup>3</sup>

POLLUTANT	TYPE	RESULT - MAX CONC ON DOMAIN	RESULT - MAX CONC ON RECEPTORS	LIMIT AS PER EIA TORs
Average Hourly value of SO <sub>2</sub> [mg/m <sup>3</sup> ]	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average hourly value of NO <sub>x</sub> [mg/m <sup>3</sup> ]	Value	0.0000299053	0.0000227743	120 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of NH <sub>3</sub> [µg/m <sup>3</sup> ]	Value	0.0000024921	0.0000014867	10 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of CO [µg/m <sup>3</sup> ]	Value	0.0000124606	0.0000094893	50 mg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93KM	

### 3.6.3 Scenario C

TABLE 15: COMPARISON WITH LIMITS – SCENARIO C

POLLUTANT	TYPE	RESULT - MAX CONC ON DOMAIN	RESULT - MAX CONC ON RECEPTORS	LIMIT AS PER EIA TORs
Average hourly value of PM <sub>10</sub> [µg/m <sup>3</sup> ]	Value	0.00093	0.021800	1.2 µg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	
Average Hourly value of PM <sub>2.5</sub> [µg/m <sup>3</sup> ]	Value	0.00021	0.004854	0.6 µg/m <sup>3</sup>
	Receptor/ distance from chimney	0.78km	R10 - 2.93km	

### 3.7 CALIBRATION

The second phase of the study a 6-week monitoring was conducted to establish the baseline values of PM<sub>10</sub> (*Skypost*) and 6-week monitoring was conducted to establish the baseline values of NO<sub>2</sub> (*Passam*), the results obtained from the monitoring are reported in this chapter.

#### 3.7.1 Baseline results of PM<sub>10</sub>

The PM<sub>10</sub> concentrations detected by monitoring from 23 September 2024 to 9 November 2024 were influenced, on some days, by "Sahara Dust" and are therefore excluded from the scope of this work. Such events were observed on October 3<sup>rd</sup>, 9<sup>th</sup> and 10<sup>th</sup> 2024.

The analytical results obtained in the six weeks of PM<sub>10</sub> monitoring were compared with the data recorded from the Maltese "Air Quality" stations and in particular the four different types of stations, Gharb (Rural environment) and Msida (Traffic), Zetjun and Attard downloaded from the ERA website,

Below lies the data collected by the stations from October 2<sup>nd</sup> to November 4<sup>th</sup> from the ERA website and the printouts of the interactive maps downloaded from the ERA website on 3<sup>rd</sup>, 9<sup>th</sup> and 10<sup>th</sup> October.



FIGURE 3: DAILY MEAN SURFACE CONCENTRATION IN THE STATION OF GHARB, MSIDA, ZETJUN AND ATTARD

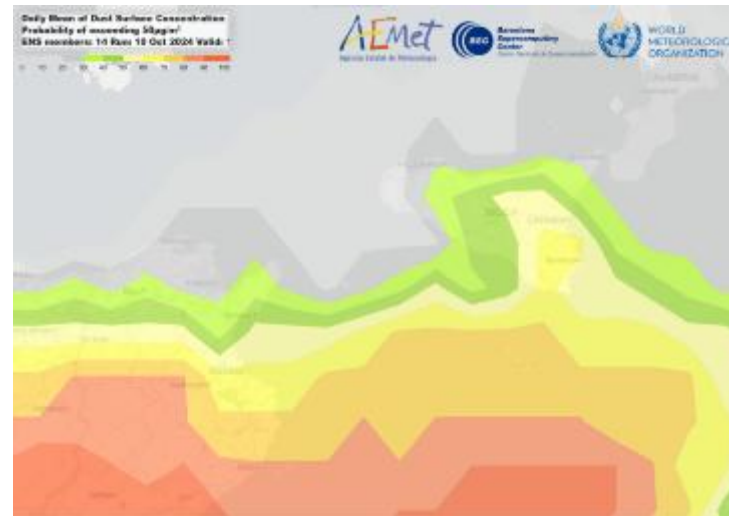
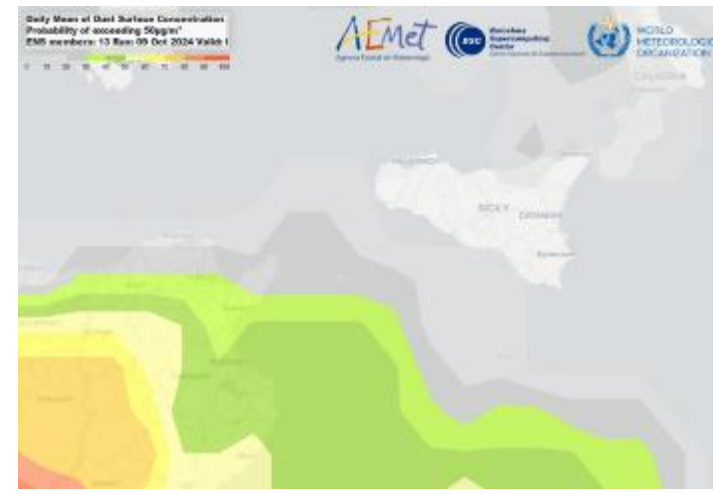
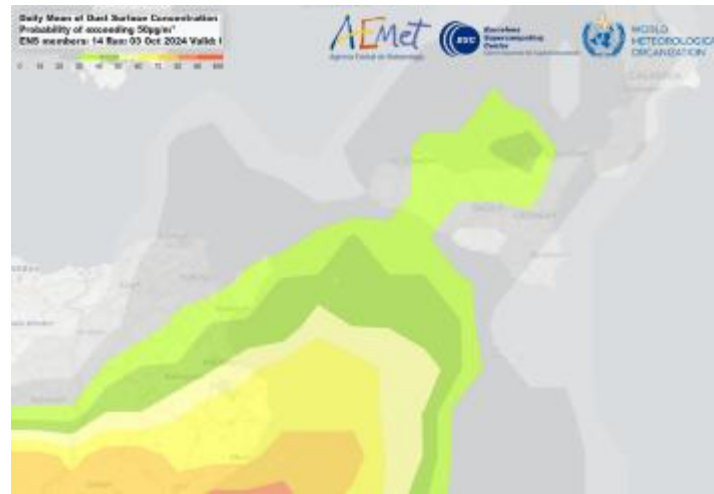


FIGURE 23: INTERACTIVE MAPS DOWNLOADED FROM THE WMO WEBSITE ON 3RD, 9TH AND 10TH OCTOBER

The analytical results obtained in the six weeks of PM<sub>10</sub> monitoring by the Skypost sequential sampler installed on site are shown below. Readings affected by Sahara dust events are marked with an asterisk (\*) as they were discarded from this analysis. Such events were observed on the 3<sup>rd</sup>, 9<sup>th</sup>, and October 10<sup>th</sup> 2024. For this reason, three additional days of monitoring were conducted, for a total of 45 days.

TABLE 16: PM<sub>10</sub> AIR QUALITY RESULTS OBTAINED FROM THE 6 WEEK SAMPLING CAMPAIGN

DATE	CONCENTRATION $\mu\text{G}/\text{M}^3$
23/09/2024	33
25/09/2024	34
26/09/2024	41
28/09/2024	29
29/09/2024	34
30/09/2024	29
01/10/2024	28
02/10/2024	52
03/10/2024	110*
04/10/2024	65
05/10/2024	31
06/10/2024	37
07/10/2024	35
08/10/2024	50
09/10/2024	63*
10/10/2024	134*
11/10/2024	75
12/10/2024	39
13/10/2024	35
14/10/2024	49
15/10/2024	41
16/10/2024	48
17/10/2024	71
18/10/2024	41
19/10/2024	30
20/10/2024	22
21/10/2024	35
22/10/2024	32
24/10/2024	83
25/10/2024	33
26/10/2024	65
27/10/2024	33
28/10/2024	26
29/10/2024	18
30/10/2024	32
31/10/2024	54

DATE	CONCENTRATION $\mu\text{g}/\text{M}^3$
01/11/2024	47
02/11/2024	43
03/11/2024	45
04/11/2024	69
05/11/2024	53
06/11/2024	30
07/11/2024	88
08/11/2024	22
09/11/2024	48

The statistical parameters obtained from the aforementioned baseline readings are summarised below:

TABLE 17: STATISTICAL PARAMETERS

AVERAGE	90,4° PERCENTILE	MIN	MAX	DEV.ST	MEDIAN
42.98	69.13	18.00	88.00	16.67	38.00

Considering a baseline value equal to  $42.98 \mu\text{g}/\text{m}^3$ , the annualization factor 0.85 the result of the CAA calculation is equal to  $36.53 \mu\text{g}/\text{m}^3$ .

### 3.7.2 Baseline Results of $\text{NO}_2$

The analytical results obtained in the six weeks of  $\text{NO}_2$  monitoring are shown below.

**Test Report Air Pollution Measurement**

**passam ag**  
air quality monitoring

**NO<sub>2</sub> Nitrogen dioxide measurement by means of passive sampler**

<b>customer information</b> customer: AIS Environment Ltd. customer ID: MNI contact person: Sacha Dunlop project: Air Quality Study for LITCM - reference: for Thermal Treatment Facility	<b>passive samplers</b> date received: 05.11.2024 type: tube (Palmer) pollutant: NO <sub>2</sub> limit of detection: 0.5 $\mu\text{g}/\text{h}$ (14 days) sampling rate: 0.734 (l/min) protective filter: yes	<b>analysis</b> method: SP91 photometer, Seitzmann analyte: NO <sub>2</sub> date: 12.11.2024 place: passam ag	<b>test report</b> created on: 13.11.2024 created by: K. Bockl checked on: 13.11.2024 checked by: I. Hangartner file name: MA012401 pages: 1
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note: applies to the sample as received, results below the detection limit are indicated with "<math>\leq</math>" and the associated value, this method is accredited to ISO/IEC 17025 measurement uncertainty <math>\leq 2.5\%</math>, sampling rate related to 20 °C, further information at www.passam.ch

measuring site	passive sampler		measuring period				temp. [°C]	blank [µg/24h]	measurement		result		Comment on the analysis
	label	lot no.	start date	start time	end date	end time			detection	value [µg/24h]	m. analyte [µg]	C-NO <sub>2</sub> [µg/m <sup>3</sup> ]	
35 908610, 14 440480	MAI-1	45402	23/09/2024	13:45	14/10/2024	14:08	504.6	0.002	1	0.113	0.25	11.1	
35 908610, 14 440480	MAI-3	45402	23/09/2024	13:45	14/10/2024	14:08	504.6	0.002	1	0.113	0.25	11.1	
35 908610, 14 440480	MAI-3	45402	14/10/2024	14:08	04/11/2024	13:45	503.6	0.002	1	0.132	0.29	13.0	
35 908610, 14 440480	MAI-4	45402	14/10/2024	14:08	04/11/2024	13:45	503.6	0.002	1	0.131	0.29	12.9	

The statistical parameters obtained from the aforementioned baseline readings are summarised below:

TABLE 18: STATISTICAL PARAMETERS  $\text{NO}_2$

AVERAGE	99,8° PERCENTILE	MIN	MAX	DEV.ST	MEDIAN
12.04	13.02	11.1	13.03	1.08	12.02

Considering a baseline value equal to  $12.04 \mu\text{g}/\text{m}^3$ , the annualization factor 0.96 the result of the CAA calculation is equal to  $11.56 \mu\text{g}/\text{m}^3$ .

### 3.8 IMPACT ASSESSMENT AT RECEPTORS

The thematic maps shown in the following figures describe the spatial distribution of the sensitive receptors with respect to the survey area and the relationships between each receptor and the calculated concentrations of PM<sub>10</sub>, and NO<sub>2</sub>. A color scale was used to emphasize the most disturbed sensitive receptors, the color scale varies from green (lower concentrations) to red (higher concentrations).

A summary table was also drawn up where the concentration value calculated by the model and integrated with the values obtained from monitoring was reported.

Following the instructions of the ERA, the impact assessment has taken into account only the sensitive aspects receptors that undergo a variation (dAA) greater than 0.3 µg/m<sup>3</sup> due to PM<sub>10</sub> and NO<sub>2</sub> emissions from the proposed project.

TABLE 19: IMPACT ASSESSMENT – SCENARIO A

RECEPTOR NO.	BASELINE PM <sub>10</sub> (CAA)	PREDICTED PM <sub>10</sub>	CHANGE PM <sub>10</sub> (DAA)	IMPACT <sup>1</sup>	BASELINE NO <sub>2</sub> (CAA)	PREDICTED NO <sub>2</sub>	CHANGE NO <sub>2</sub> (DAA)	IMPACT <sup>1</sup>
	µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>		µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>	
R1 to R55	36.53	36.530	0.00001 - 0.00043	N/S	11.56	11.558 - 11570	0.000259 - 0.0122	N/S

<sup>1</sup> Not Significant (N/S), Minor (MI), Moderate (MO), Major (MA)

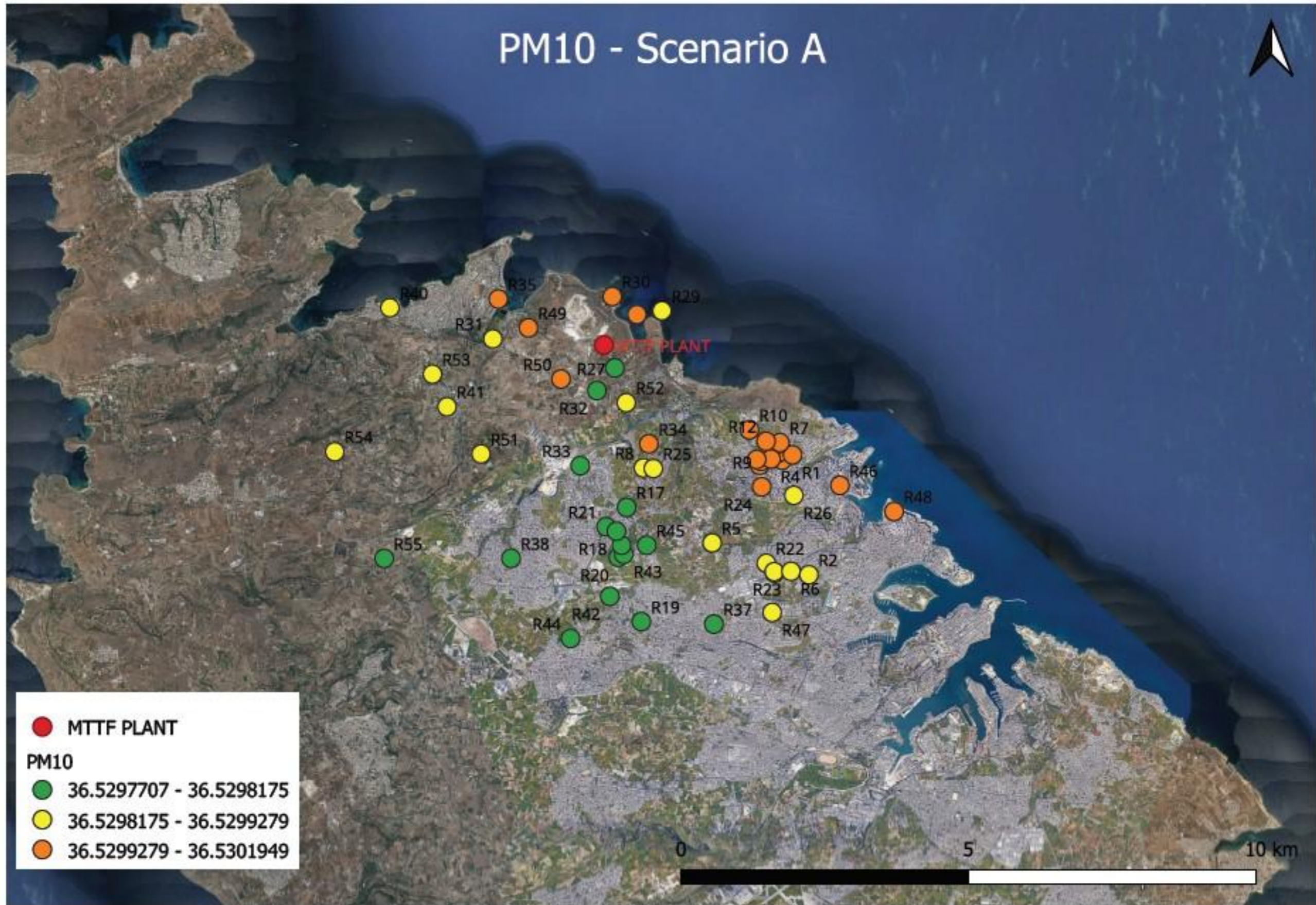


FIGURE 24: PM<sub>10</sub> RESULTS – SCENARIO A

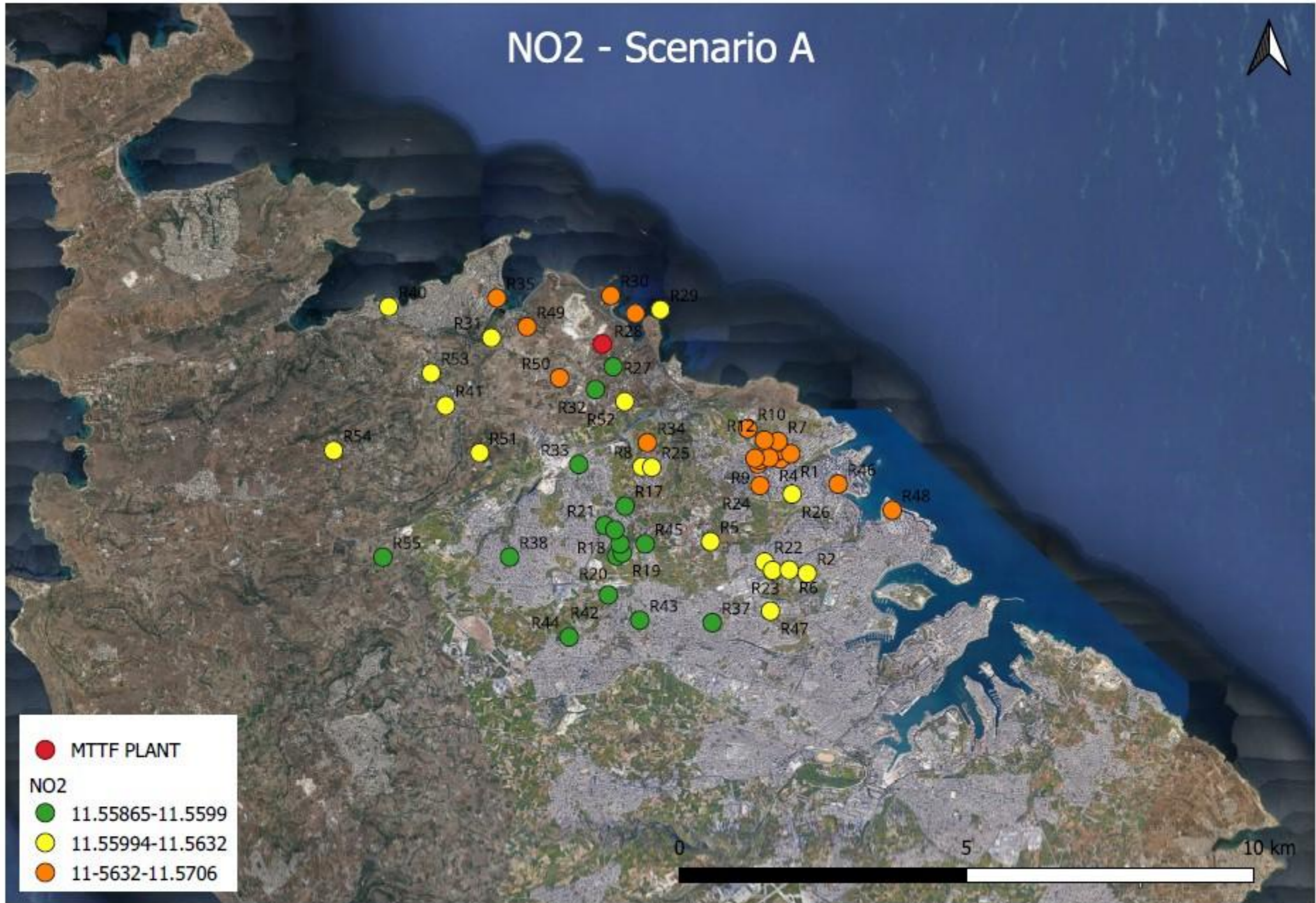


FIGURE 25: NO2 RESULTS – SCENARIO A

TABLE 20: IMPACT ASSESSMENT – SCENARIO B

RECEPTOR NO.	BASELINE PM <sub>10</sub> (CAA)	PREDICTED PM <sub>10</sub>	CHANGE PM <sub>10</sub> (DAA)	IMPACT <sup>1</sup>	BASELINE NO <sub>2</sub> (CAA)	PREDICTED NO <sub>2</sub>	CHANGE NO <sub>2</sub> (DAA)	IMPACT <sup>1</sup>
	µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>		µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>	
R1 to R55	36.53	36.530 - 36531	0.00001 - 0.00073	N/S	11.56	11.558 - 11578	0.00043 - 0.0205	N/S

<sup>1</sup>Not Significant (N/S), Minor (MI), Moderate (MO), Major (MA)

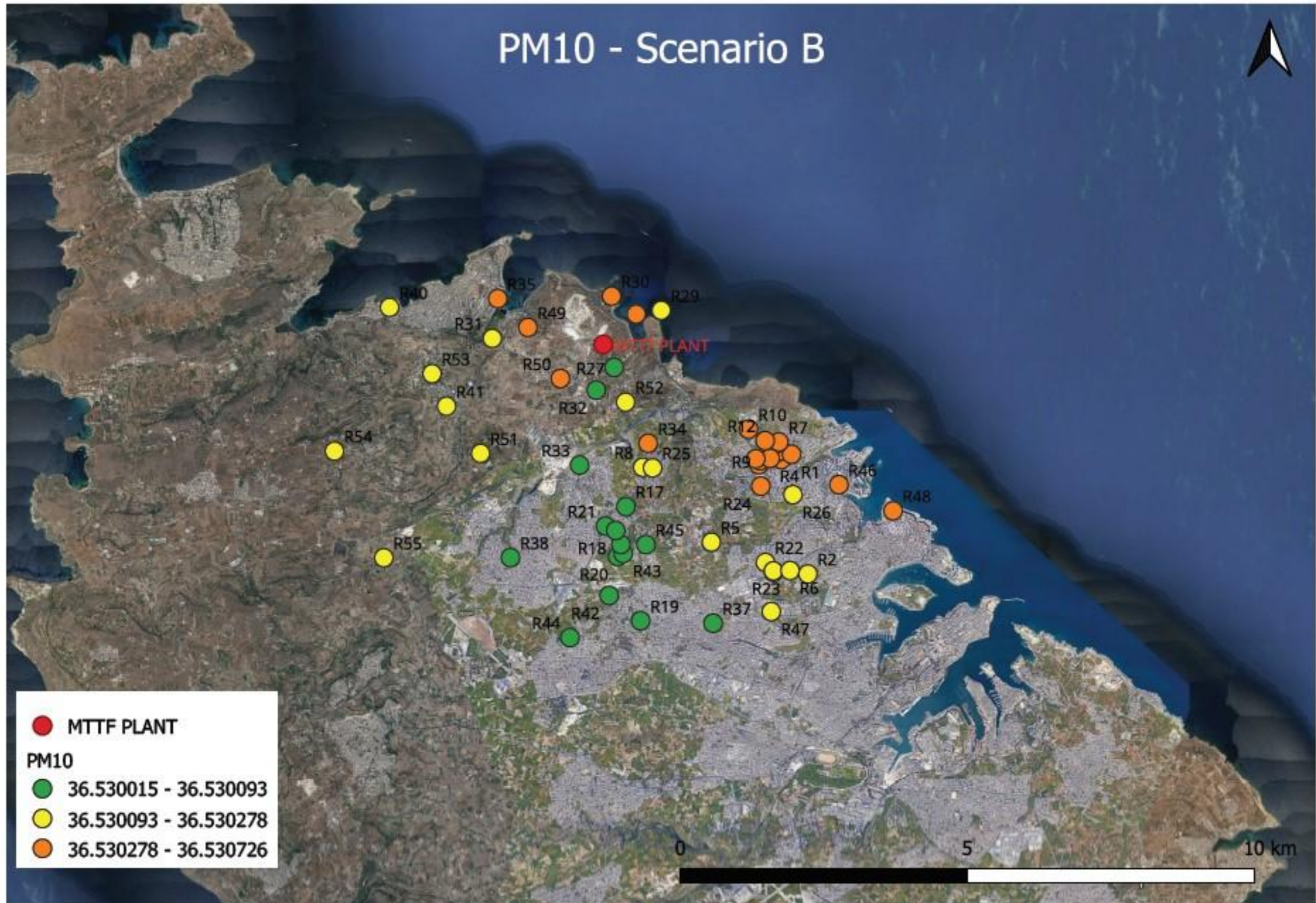


FIGURE 26: PM<sub>10</sub> RESULTS – SCENARIO B

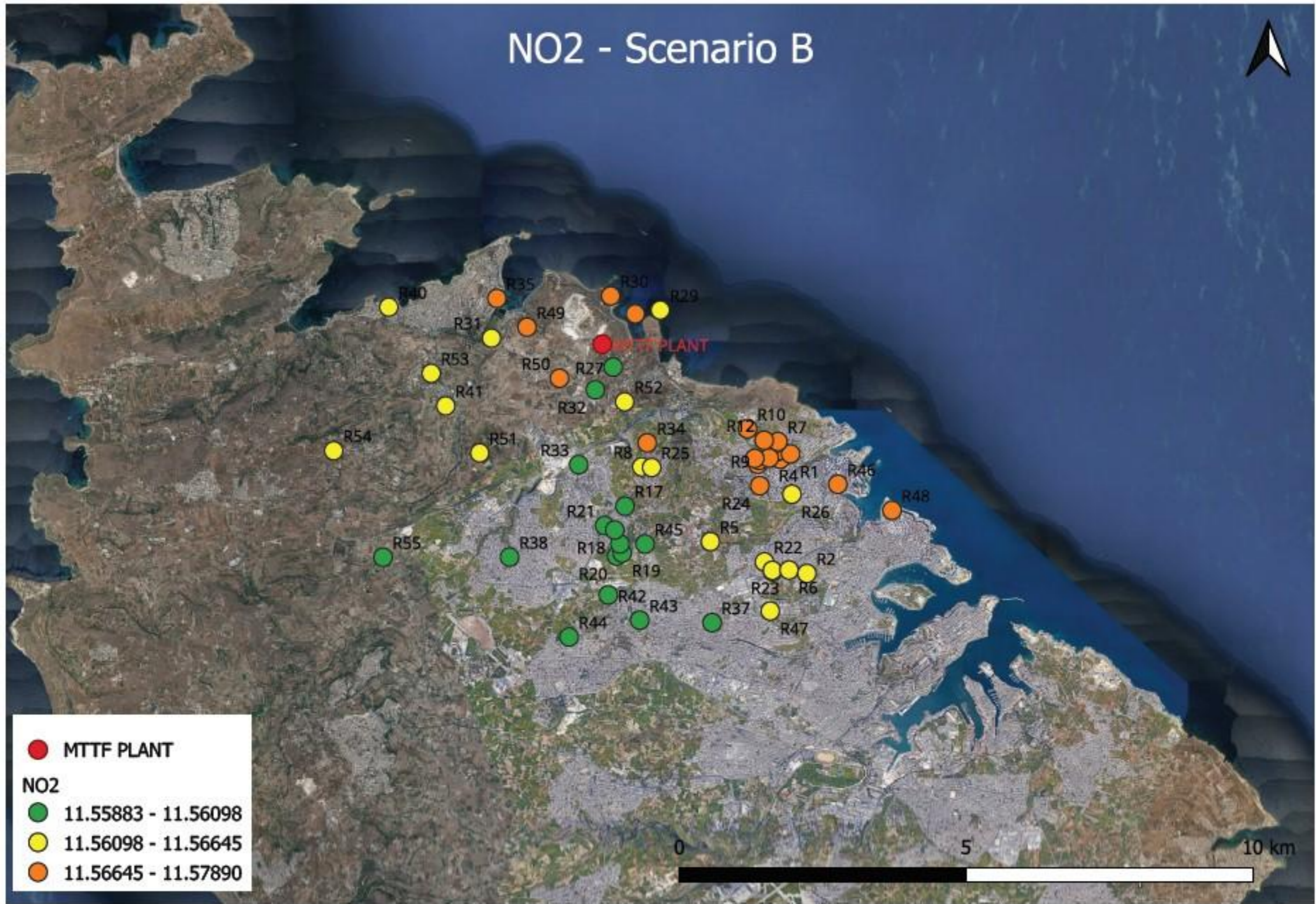


FIGURE 27: RESULTS NO<sub>2</sub> – SCENARIO B

TABLE 21: IMPACT ASSESSMENT – SCENARIO C

RECEPTOR NO.	BASELINE PM <sub>10</sub> (CAA)	PREDICTED PM <sub>10</sub>	CHANGE PM <sub>10</sub> (DAA)	IMPACT <sup>1</sup>	BASELINE NO <sub>2</sub> (CAA)	PREDICTED NO <sub>2</sub>	CHANGE NO <sub>2</sub> (DAA)	IMPACT <sup>1</sup>
	µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>		µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>	
R1 to R55	36.53	36.530 - 36551	0.00044 - 0.0218	N/S	11.56	11.558 - 11578	0.000435 - 0.0205	N/S

<sup>1</sup> Not Significant (N/S), Minor (MI), Moderate (MO), Major (MA)

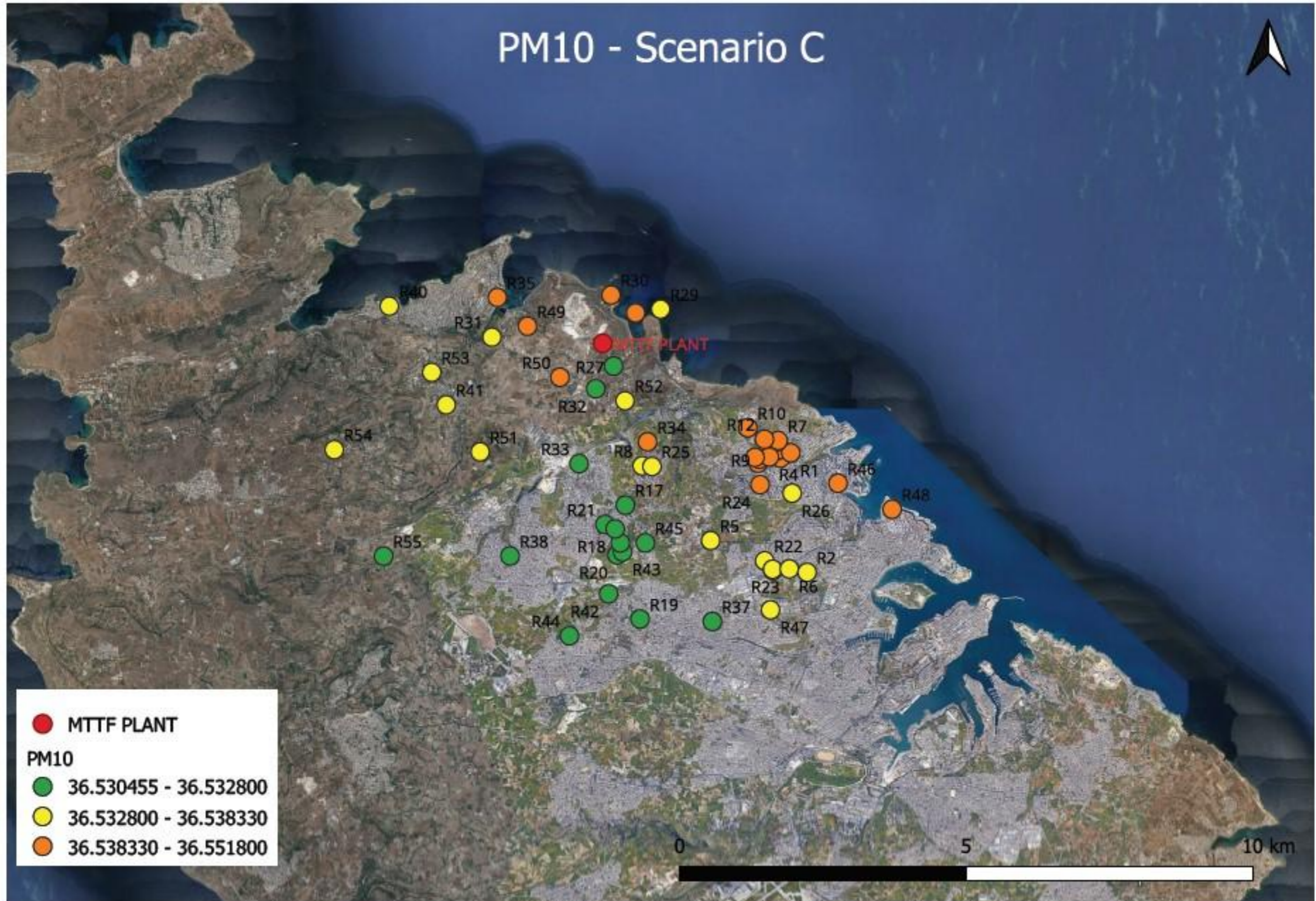


FIGURE 28: PM10 RESULTS – SCENARIO C

3.8.1 Summary of Impact table

TABLE 22: SUMMARY OF IMPACTS TABLE

IMPACT TYPE AND SOURCE			IMPACT RECEPTOR		EFFECT & SCALE								PROBABILITY OF IMPACT	OVERALL IMPACT SIGNIFICANCE	PROPOSED MITIGATION MEASURES	RESIDUAL IMPACT SIGNIFICANCE	OTHERS REQUIREMENTS
IMPACT TYPE	SPECIFIC INTERVENTION LEADING TO IMPACT	PROJECT PHASE (CONSTRUCTION/ OPERATION/ DECOMMISSIONING)	RECEPTOR TYPE	SENSITIVITY & RESILIENCE TOWARD IMPACT	DIRECT/ INDIRECT/ CUMULATIVE	BENEFICIAL/ ADVERSE	SEVERITY	PHYSICAL/ GEOGRAPHIC EXTENT OF IMPACT	SHORT-/ MEDIUM-/ LONG-TERM	TEMPORARY (INDICATE DURATION)/ PERMANENT	REVERSIBLE (INDICATE EASE OF REVERSIBILITY)/ IRREVERSIBLE						
Emissions from stack	Hazardous waste incineration plant	Operation	Residential areas, Agricultural land and disturbed ground Natura2000 Sites of Community Importance (SCI) Natura2000 Special Protection Area (SPA) Natura2000 SPA and SCI Tree Protected Areas	High	Direct	Adverse	High	Immediate surroundings	Long-term	Temporary combustion phases	Reversible with some difficulty	Remote	Not significant	Monitoring of the pollutants levels around the Scheme to ensure that they are within limits, and periodic monitoring and maintenance of the abatement technologies	Not significant	N/A	

The impact assessment for the three simulation scenarios (Scenarios A, B and C), corresponding to three different plant operations, all achieved a not significant adverse impact when evaluating the MTF in isolation. The differences in emissions that are likely to arise across the three Scenarios are negligible in concentration and thus do not lead to a discernable adverse impact on air quality.



### 3.9 CUMULATIVE IMPACT

The cumulative impacts of the project were assessed with those of other existing and/or approved projects and other waste management plants identified within the Waste Management Plan Waste (2021 -2030). This assessment takes into account existing environmental problems, areas of particular environmental importance that may be affected and the use of natural resources. Specifically, the cumulative impact was assessed between the Marsa Thermal Treatment Facility built (MTTF) plant project with the Maghtab Waste to Energy Facility (WtE).

The results obtained show that the cumulative impact of the project and the Waste to Energy facility can be considered for:

- Scenario A
  - **Not Significant** for NO<sub>2</sub>;
  - **Not Significant** for PM<sub>10</sub>, except in the R27 receptor where the change in the annual PM<sub>10</sub> (dAA) levels due to scheme is equal to 0,4 µg/m<sup>3</sup> and the Impact result is **Minor**.
  
- Scenario B
  - **Not Significant** for NO<sub>2</sub>;
  - **Not Significant** for PM<sub>10</sub>, except in the R27 receptor where the change in the annual PM<sub>10</sub> (dAA) levels due to scheme is equal to 0,4 µg/m<sup>3</sup> and the Impact result is **Minor**;
  
- Scenario C
  - **Not Significant** for NO<sub>2</sub>;
  - **Not Significant** for PM<sub>10</sub>, except at R27 receptor where the change in the annual PM<sub>10</sub> (dAA) levels due to scheme is equal to 0,4 µg/m<sup>3</sup> and the Impact result is **Minor**;

The overlap of the emissions from two production plants (WtE and MTFF) does not show a substantial variation in the fallout calculated at the sensitive receptors identified in the investigated areas, compared to what was obtained only from the MTTF.

The results obtained show that the operation of the MTTF plant adjacent to the WtE plant, does not produce a significant worsening of the atmospheric impact on the identified receptors.

The results obtained show for NO<sub>2</sub> and PM<sub>10</sub> concentrations higher than 0.3 µg/m<sup>3</sup> occurred up to a distance of approximately 1.35 km from the chimney in a north-east and north-west direction, specifically at the R27 - R28 - R29 - R30 - R49 - R50 - R52 receptors, but the value is significantly lower than the 40.0 µg/m<sup>3</sup> limit (ALV), thus contributing to a negligible adverse impact.

TABLE 23: CUMULATIVE IMPACT – SCENARIO A

RECEPTOR	BASELINE PM <sub>10</sub> (CAA)	PREDICTED PM <sub>10</sub>	CHANGE PM10 (DAA) MTTF+WTE	IMPACT <sup>1</sup>	BASELINE NO <sub>2</sub> (CAA)	PREDICTED NO <sub>2</sub>	CHANGE NO <sub>2</sub> (DAA) MTTF+WTE	IMPACT <sup>1</sup>
	µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>		µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>	
R1 to R26	36.53	36.57 - 36.69	0.04 - 0.16	N/S	11.56	11.60 - 11.73	0.04 - 0.17	N/S
R27		37.000	0.470	Minor (MI)		12.281	0.721	N/S
R28		36.880	0.350	N/S		12.105	0.545	N/S
R29		36.850	0.320	N/S		12.065	0.505	N/S
R30		36.880	0.350	N/S		12.106	0.546	N/S
R31 to R48		36.58 - 36.78	0.05 - 0.25	N/S		11.60 - 11.81	0.04 - 0.255	N/S
R49		36.840	0.310	N/S		12.049	0.489	N/S
R50		36.890	0.360	N/S		12.126	0.566	N/S
R51		36.640	0.110	N/S		11.673	0.113	N/S
R52		36.840	0.310	N/S		12.042	0.482	N/S
R53 to R55		36.60 - 36.66	0.07 - 0.130	N/S		11.63 - 11.69	0.07 - 0.133	N/S

<sup>1</sup> Not Significant (N/S), Minor (MI), Moderate (MO), Major (MA)

TABLE 24: CUMULATIVE IMPACT – SCENARIO B

RECEPTOR	BASELINE PM <sub>10</sub> (CAA)	PREDICTED PM <sub>10</sub>	CHANGE PM10 (DAA) MTTF+WTE	IMPACT <sup>1</sup>	BASELINE NO <sub>2</sub> (CAA)	PREDICTED NO <sub>2</sub>	CHANGE NO <sub>2</sub> (DAA) MTTF+WTE	IMPACT <sup>1</sup>
	µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>		µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>	
R1 to R26	36.53	36.57 - 36.69	0.04 - 0.16	N/S	11.56	11.60 - 11.74	0.04 - 0.18	N/S
R27		37.000	0.470	Minor (MI)		12.281	0.721	N/S
R28		36.880	0.350	N/S		12.108	0.548	N/S
R29		36.850	0.320	N/S		12.066	0.508	N/S
R30		36.880	0.350	N/S		12.110	0.550	N/S
R31 to R48		36.57 - 36.78	0.04 - 0.25	N/S		11.60 - 11.81	0.04 - 0.259	N/S
R49		36.840	0.310	N/S		12.055	0.495	N/S
R50		36.890	0.360	N/S		12.130	0.570	N/S
R51		36.640	0.110	N/S		11.674	0.114	N/S
R52		36.840	0.310	N/S		12.044	0.484	N/S
R53 to R55		36.60 - 36.66	0.07 - 0.130	N/S		11.63 - 11.69	0.07 - 0.135	N/S

<sup>1</sup> Not Significant (N/S), Minor (MI), Moderate (MO), Major (MA)

TABLE 25: CUMULATIVE IMPACT – SCENARIO C

RECEPTOR	BASELINE PM <sub>10</sub> (CAA)	PREDICTED PM <sub>10</sub>	CHANGE PM10 (DAA) MTTF+WTE	IMPACT <sup>1</sup>	BASELINE NO <sub>2</sub> (CAA)	PREDICTED NO <sub>2</sub>	CHANGE NO <sub>2</sub> (DAA) MTTF+WTE	IMPACT <sup>1</sup>
	µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>		µG/M <sup>3</sup>	µG/M <sup>3</sup>	µG/M <sup>3</sup>	
R1 to R26	36.53	36.57 - 36.71	0.04 - 0.18	N/S	11.56	11.60 - 11.74	0.04 - 0.185	N/S
R27		37.000	0.471	Minor (MI)		12.281	0.721	N/S
R28		36.888	0.358	N/S		12.108	0.548	N/S
R29		36.858	0.328	N/S		12.068	0.508	N/S
R30		36.891	0.361	N/S		12.110	0.550	N/S
R31 to R48		36.57 - 36.78	0.04 - 0.25	N/S		11.60 - 11.81	0.04 - 0.259	N/S
R49		36.840	0.325	N/S		12.055	0.495	N/S
R50		36.890	0.370	N/S		12.130	0.570	N/S
R51		36.640	0.114	N/S		11.674	0.114	N/S
R52		36.840	0.314	N/S		12.044	0.484	N/S
R53 to R55		36.60 - 36.66	0.07 - 0.130	N/S		11.63 - 11.69	0.07 - 0.133	N/S

<sup>1</sup> Not Significant (N/S), Minor (MI), Moderate (MO), Major (MA)

## 4 EMISSIONS IN TONS

The annual emission loads in tons have been estimated assuming that the incinerator complies with the daily limit values in Table 3 of EIA TOR (Appendix 4B). The limit values in the TORs are expressed as dry gas at 273.15 K, 101.3 kPa, and 11% oxygen.

TABLE 26 – DAILY LIMIT VALUE OF TABLE 3 OF EIA TORs

POLLUTANTS	LIMIT VALUE 1 [mg/Nm <sup>3</sup> ]	LIMIT VALUE 2 [mg/Nm <sup>3</sup> ]	LIMIT VALUE 3[mg/Nm <sup>3</sup> ]
Dust	1	5	10
SO <sub>2</sub>	1	40	50
NO <sub>x</sub>	30	100	200
TOC	1	10	-
NH <sub>3</sub>	1	10	-

The annual emission loads in tons have been estimated multiplying the values in the TORs, relating to LIMIT VALUE 1, with the mass flow of:

- *Scenario A* equal to 2.29 Nm<sup>3</sup>/s;
- *Scenario B* and *Scenario C* equal to 3.83 Nm<sup>3</sup>/s.

TABLE 27 – ANNUAL EMISSION LOADS IN TONS ESTIMATED MULTIPLYING THE LIMIT VALUE 1 WITH THE MASS FLOW OF SCENARIO A

POLLUTANTS	LIMIT VALUE 1 [TON/YEAR]
Dust	0.072112
SO <sub>2</sub>	0.072112
NO <sub>x</sub>	2.163370
TOC	0.072112
NH <sub>3</sub>	0.072112

TABLE 28 – ANNUAL EMISSION LOADS IN TONS ESTIMATED MULTIPLYING THE LIMIT VALUE 1 WITH THE MASS FLOW OF SCENARIO B/C

POLLUTANTS	LIMIT VALUE 1 [TON/YEAR]
Dust	0.120884
SO <sub>2</sub>	0.120884
NO <sub>x</sub>	3.626509
TOC	0.120884
NH <sub>3</sub>	0.120884

The EIA TOR of 08/05/2024 also specifies the need to estimate the annual emission loads in tons based on the daily emission contribution foreseen by the TTF for dust, SO<sub>2</sub>, NO<sub>x</sub>, TVOC and NH<sub>3</sub>.

The annual emission loads in tons were estimated on the basis of the daily emission contribution foreseen by the TTF for dust (PM<sub>2.5</sub> and PM<sub>10</sub>), SO<sub>2</sub>, NO<sub>x</sub>, TVOC and NH<sub>3</sub>). The maximum concentration values present in the calculation domain were considered and subsequently multiplied by the mass flow rate.

TABLE 29 – THE ANNUAL MISSION LOADS IN TONS ESTIMATED ON TTF'S DOMAIN OF SCENARIO A

POLLUTANTS	[TON/YEAR]
PM <sub>2.5</sub>	0.0000091261
PM <sub>10</sub>	0.0000400335
SO <sub>2</sub>	0.0003216177
NO <sub>x</sub>	0.0012864708
TOC	0.0001072059
NH <sub>3</sub>	0.0001072059

TABLE 30 – THE ANNUAL MISSION LOADS IN TONS ESTIMATED ON TTF'S DOMAIN OF SCENARIO B

POLLUTANTS	[TON/YEAR]
PM <sub>2.5</sub>	0.0000256450
PM <sub>10</sub>	0.0001124967
SO <sub>2</sub>	0.0009037657
NO <sub>x</sub>	0.0036150633
TOC	0.0003012553
NH <sub>3</sub>	0.0003012553

TABLE 31 – THE ANNUAL MISSION LOADS IN TONS ESTIMATED ON TTF'S DOMAIN OF SCENARIO C

POLLUTANTS	[TON/YEAR]
PM <sub>2.5</sub>	0.0007693475
PM <sub>10</sub>	0.0033748978
SO <sub>2</sub>	0.0009037657
NO <sub>x</sub>	0.0036150633
TOC	0.0003012553
NH <sub>3</sub>	0.0003012553

## 5 CONCLUSIONS

A 6-week air quality monitoring campaign was developed which made it possible to know the average daily concentrations of PM<sub>10</sub>. Similarly, a 6-week air quality monitoring campaign was developed which made it possible to know the average daily concentrations of NO<sub>2</sub>.

The concentration values obtained formed the basis for evaluating the possible interferences between the sensitive receptors identified in the survey area and the repercussions due to the new Maghtab Thermal Treatment Facility.

A significance criteria table was used to determine the significance of the impact at all sensitive receptors and at any point within the investigated area, the results obtained made it possible to reach the following conclusions:

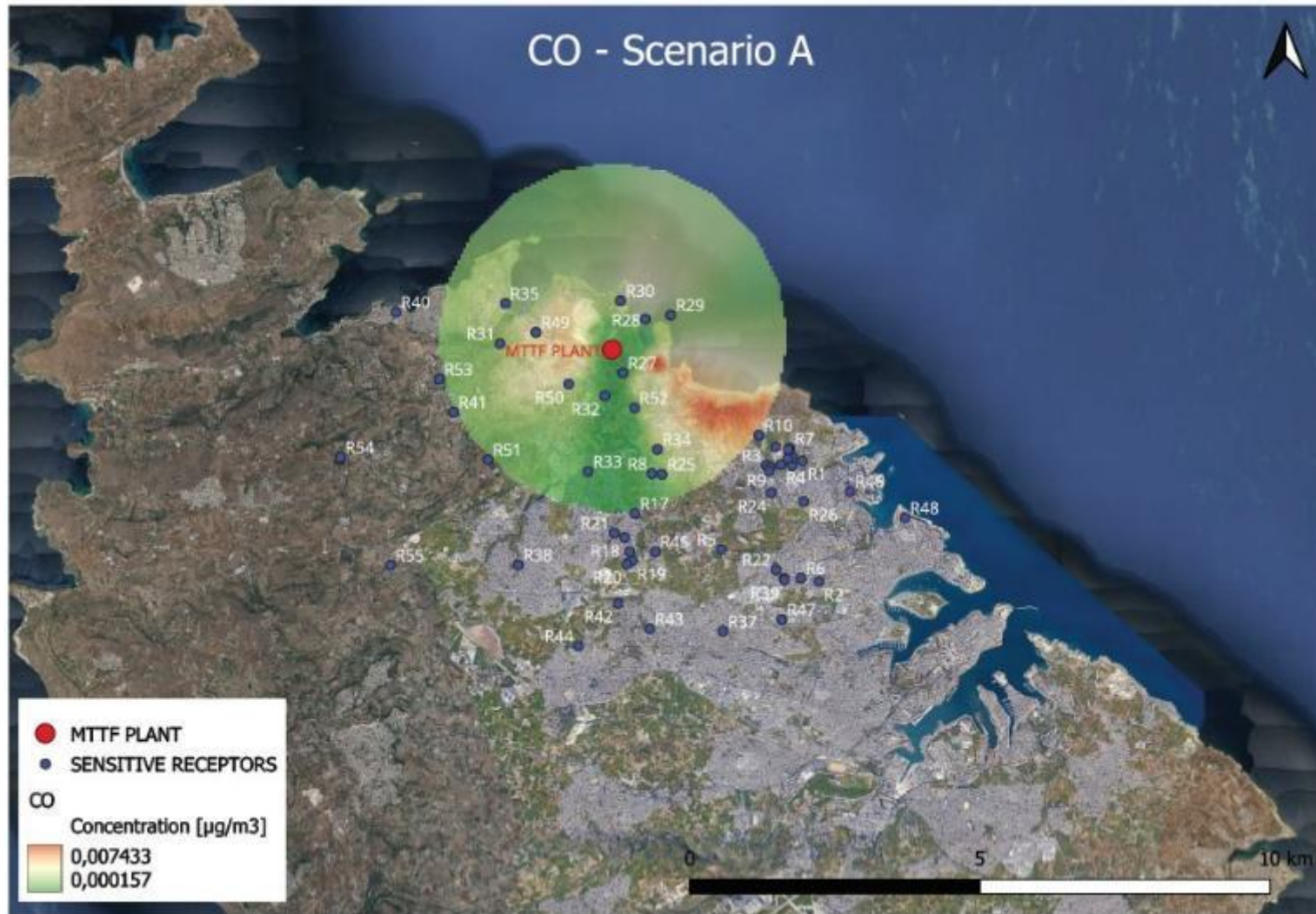
For PM<sub>10</sub>, the annualization factor 0.85 achieved a CAA value equal to 36.53 µg/m<sup>3</sup>. This value is significantly lower than the Annual Limit Value ALV (40 µg/m<sup>3</sup>) of PM<sub>10</sub> therefore contributing to a non-significant impact for each Scenario simulated at each sensitive receptor considered.

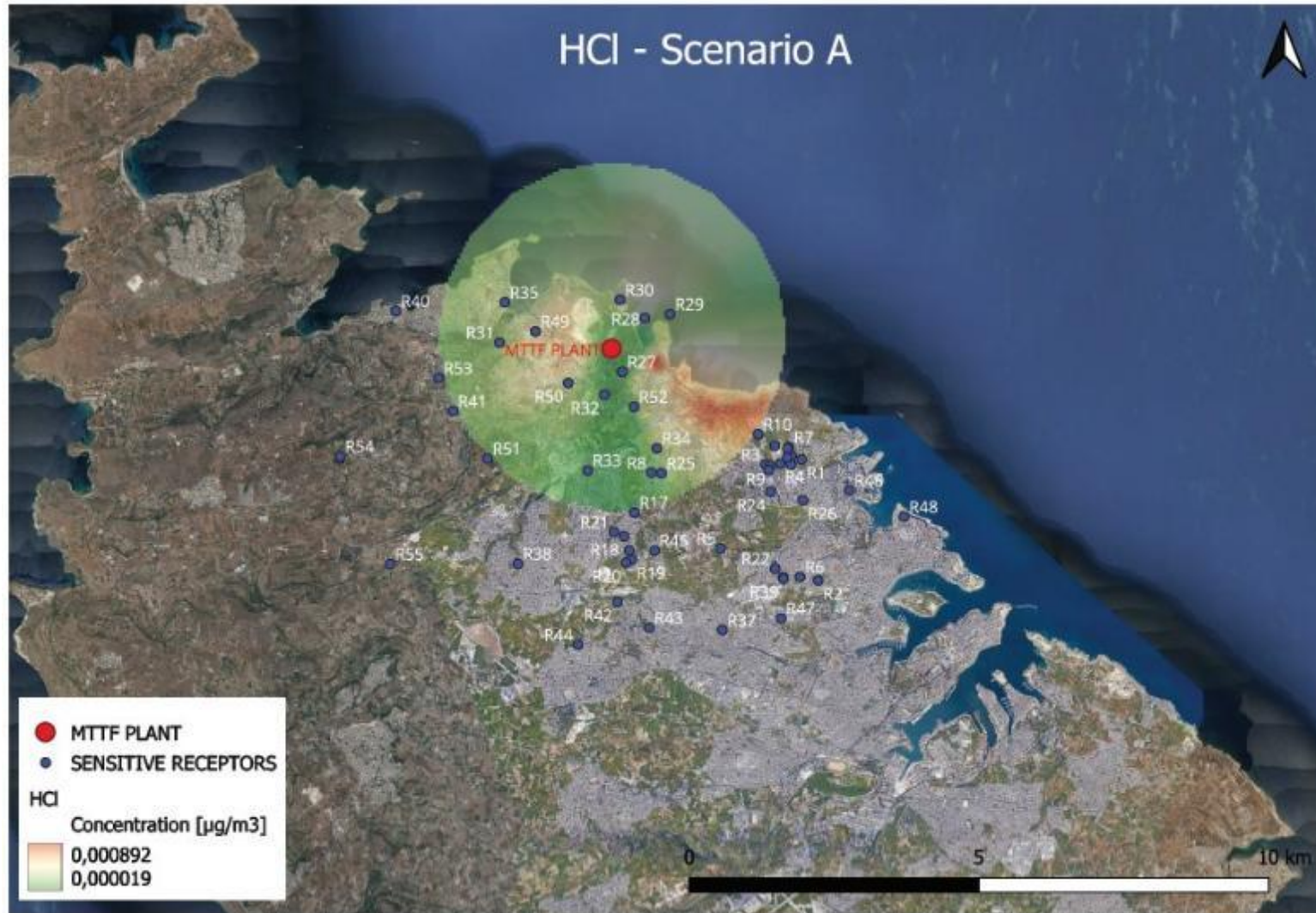
For NO<sub>2</sub>, the annualization factor 0.96 achieved a CAA value equal to 11.56 µg/m<sup>3</sup>. This value is significantly lower than the Annual Limit Value ALV 40 µg/m<sup>3</sup> of NO<sub>2</sub> therefore contributing to a non-significant impact for each Scenario simulated at each sensitive receptor considered.

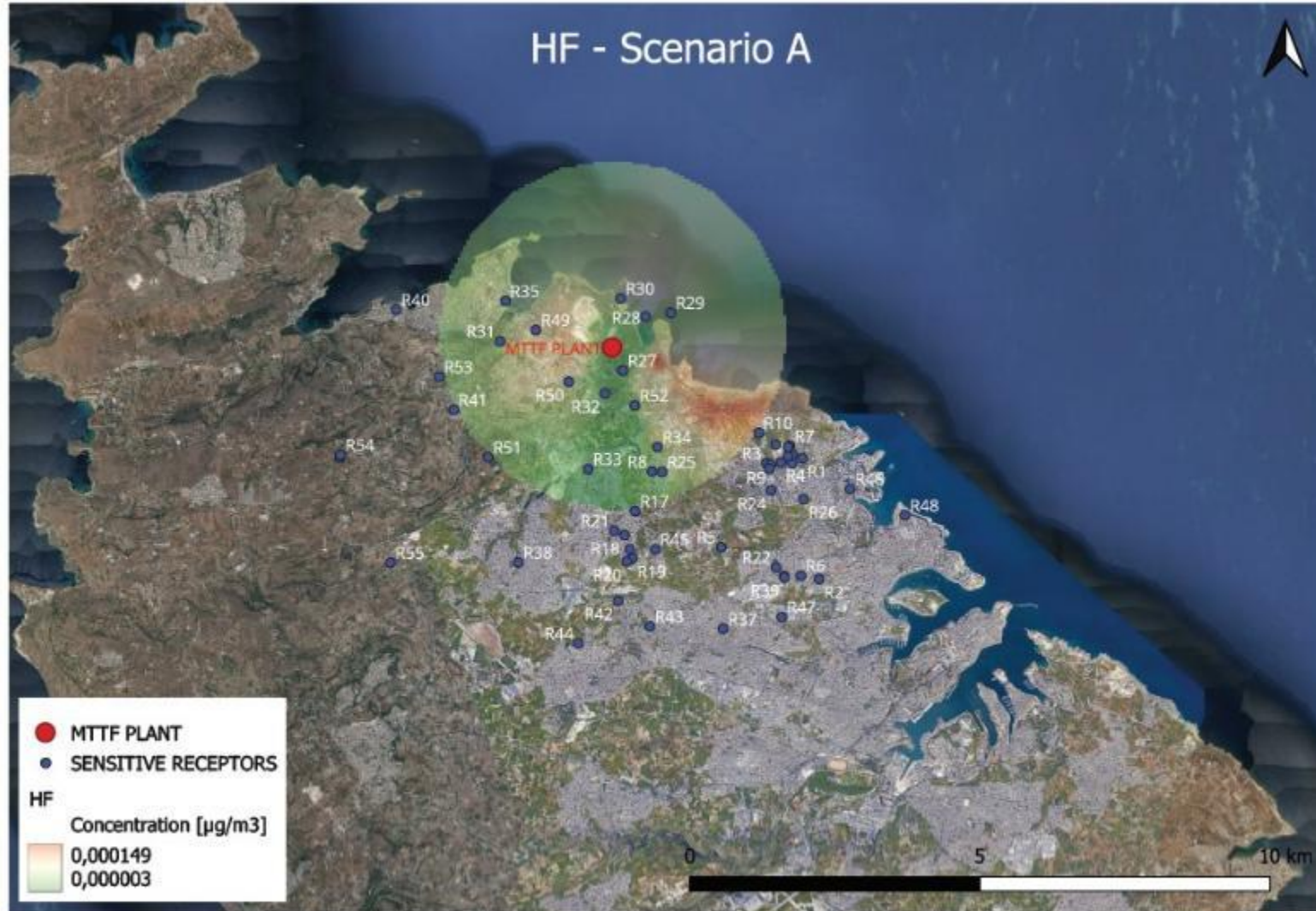
The development of the deposition fallout model carried out across the three scenarios at a stack height of 25m shows that there are no significant variations in the impacts on air quality.

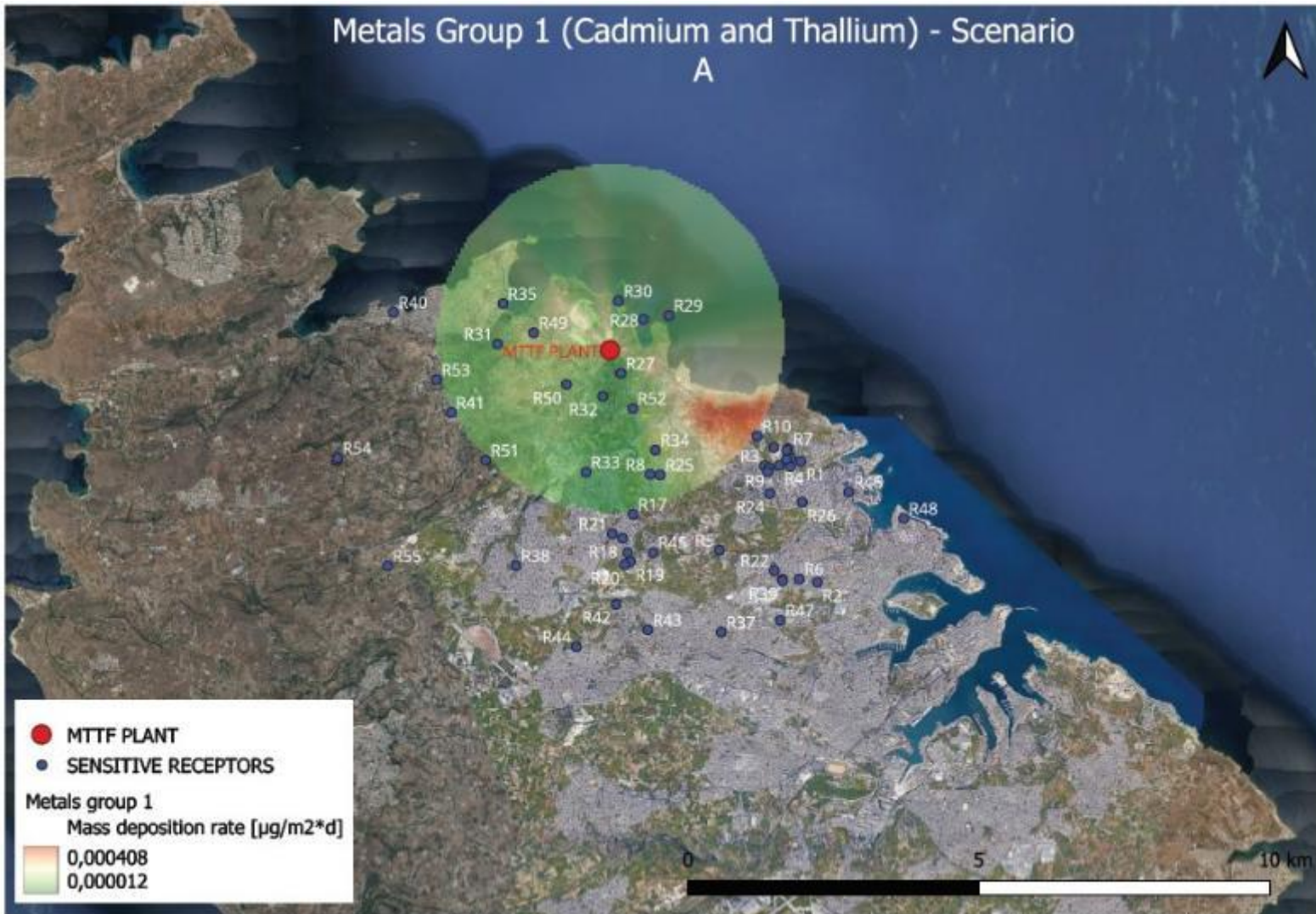
A minor adverse impact is predicted at R27 located 0.43km away from the chimney stack at all three Scenario when considering the cumulative impact of the simultaneous operation of the MTTF and the adjacent WtE facility.

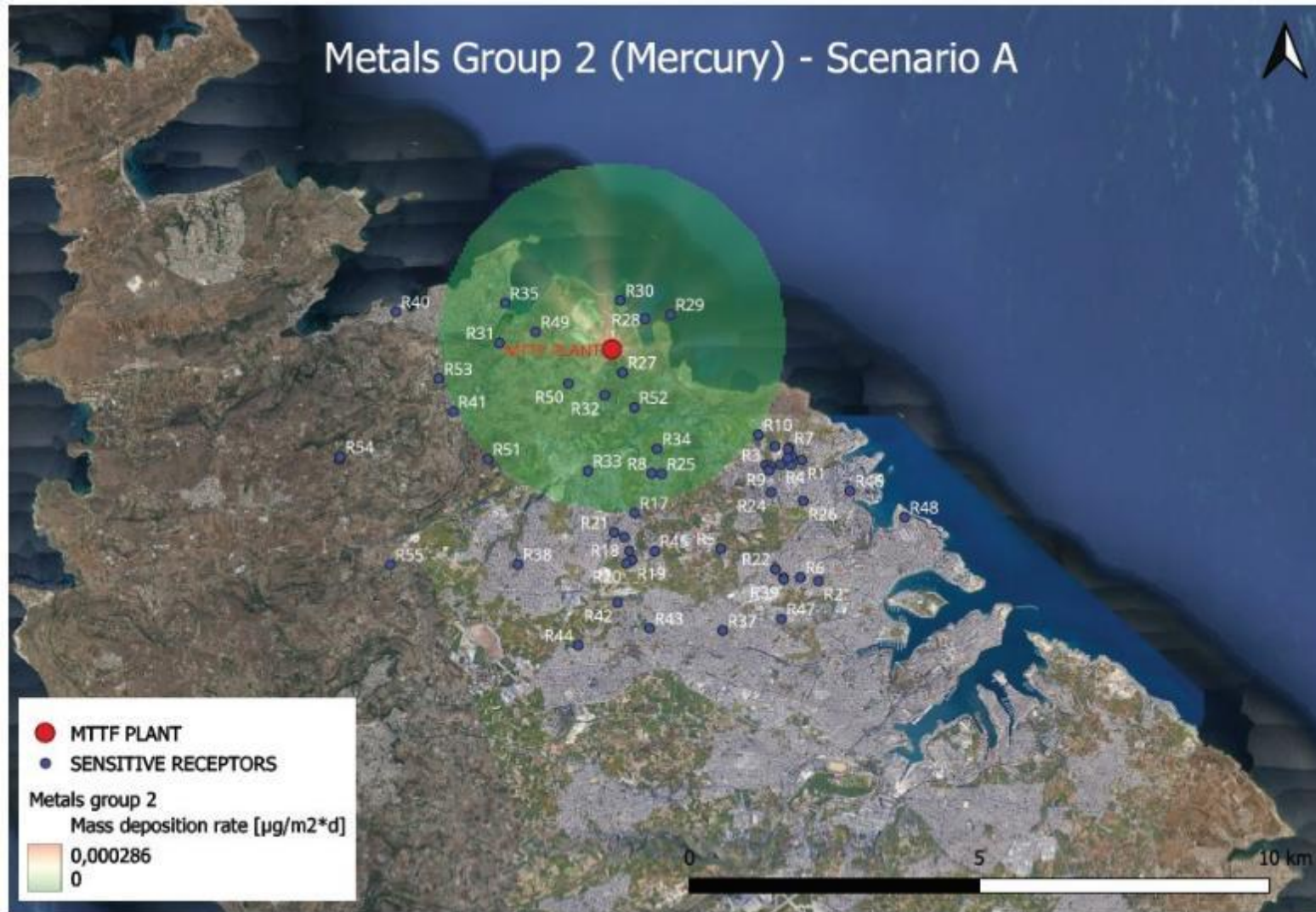
## APPENDIX 1 - MODEL OUTPUTS

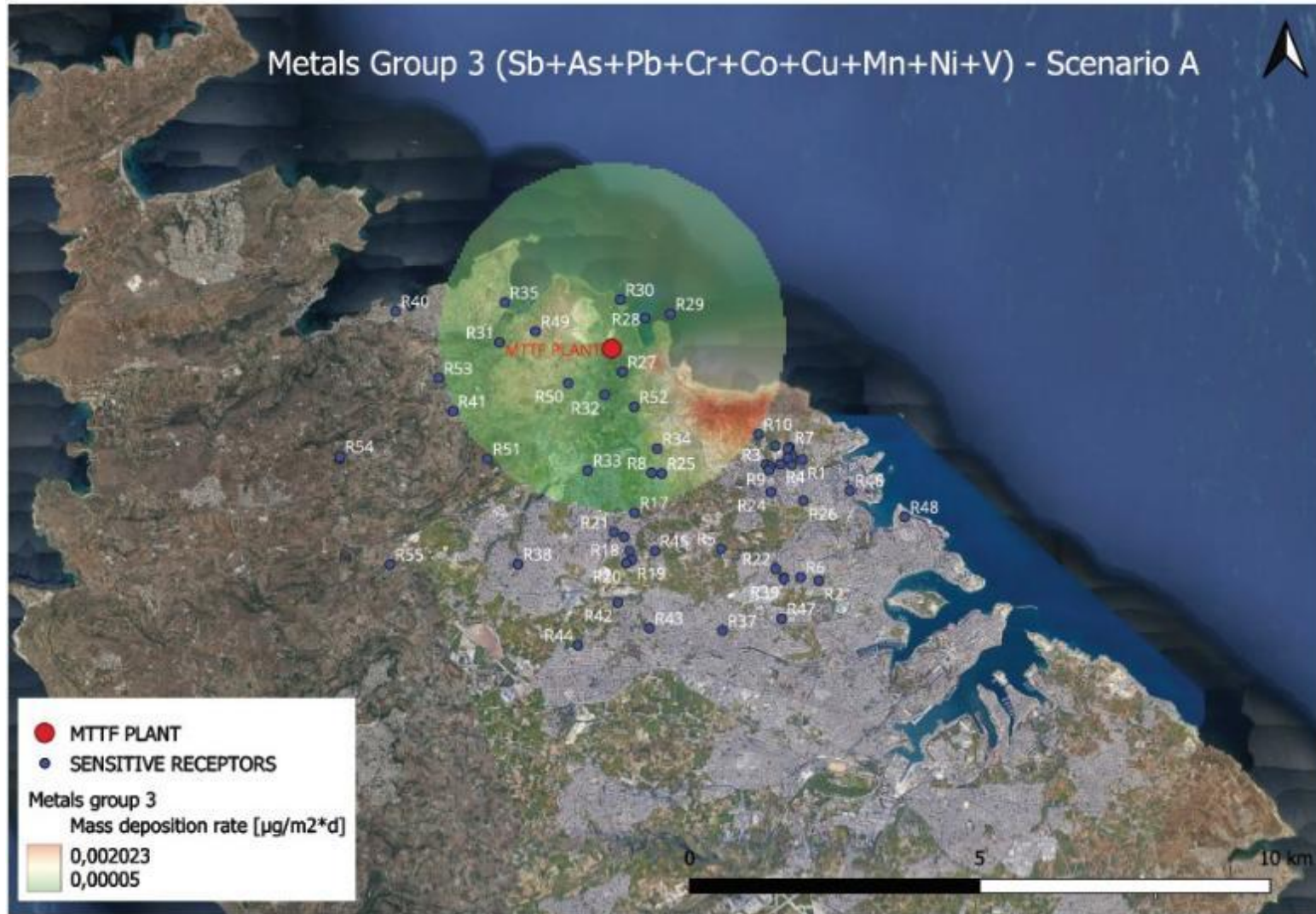


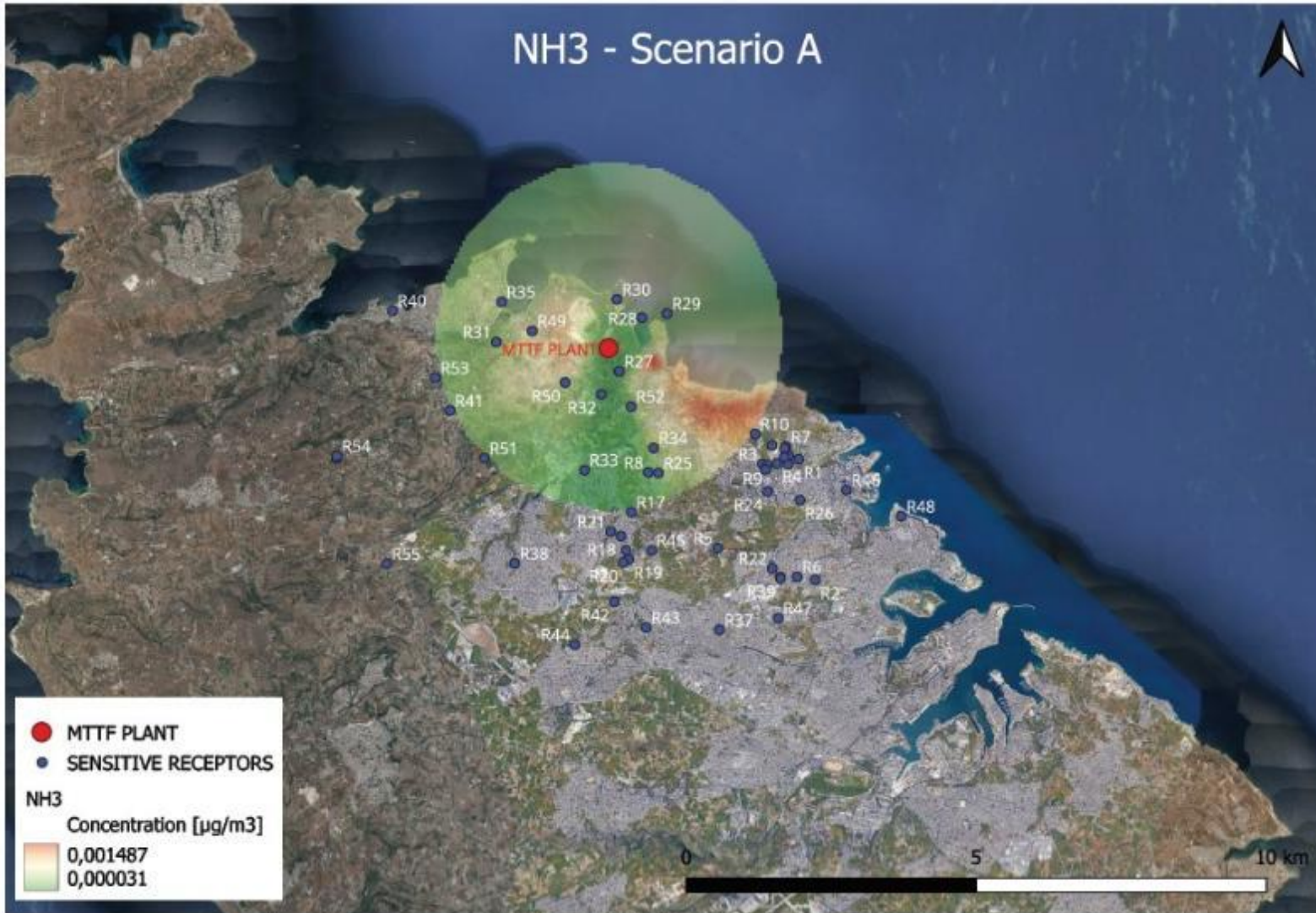


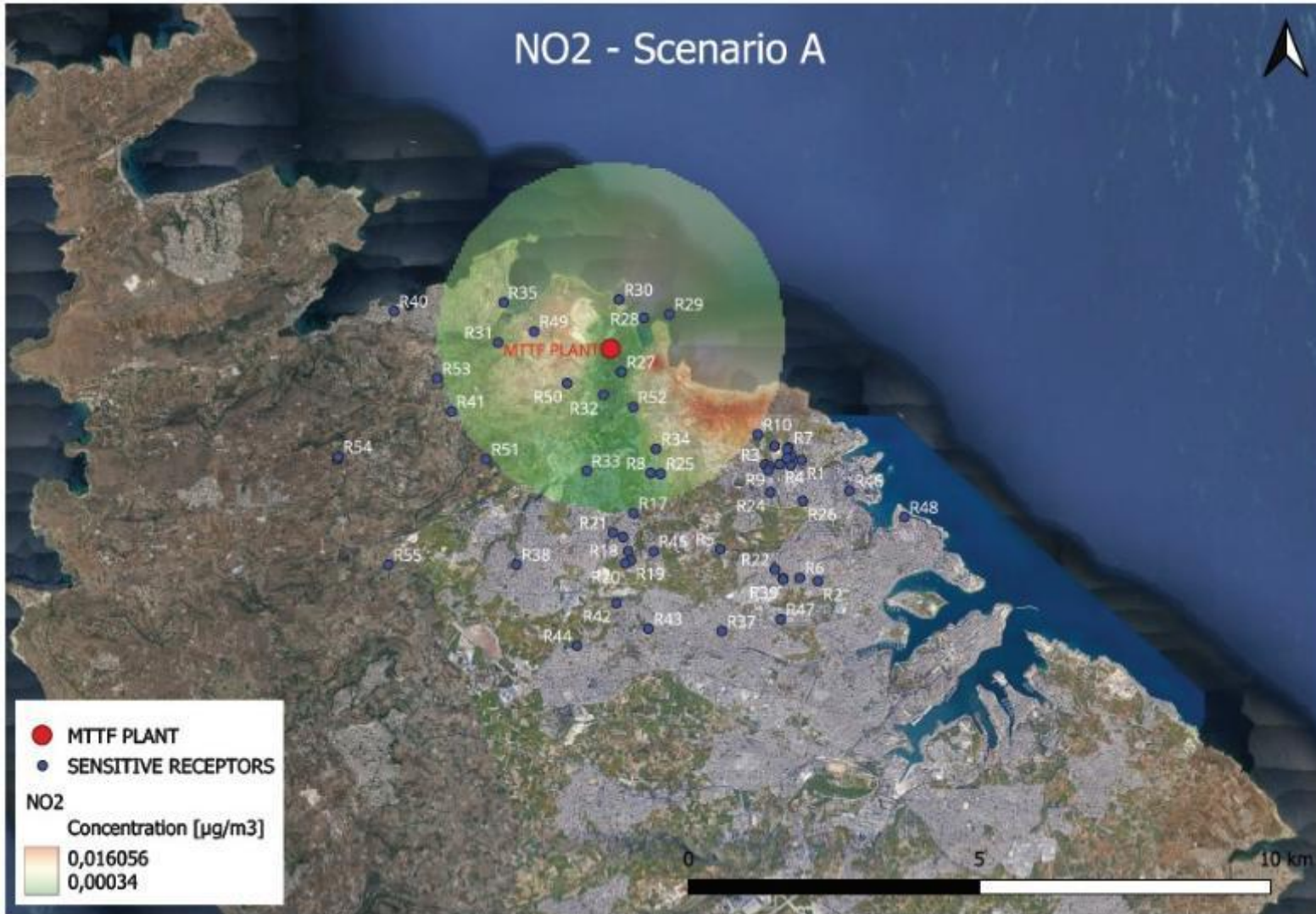


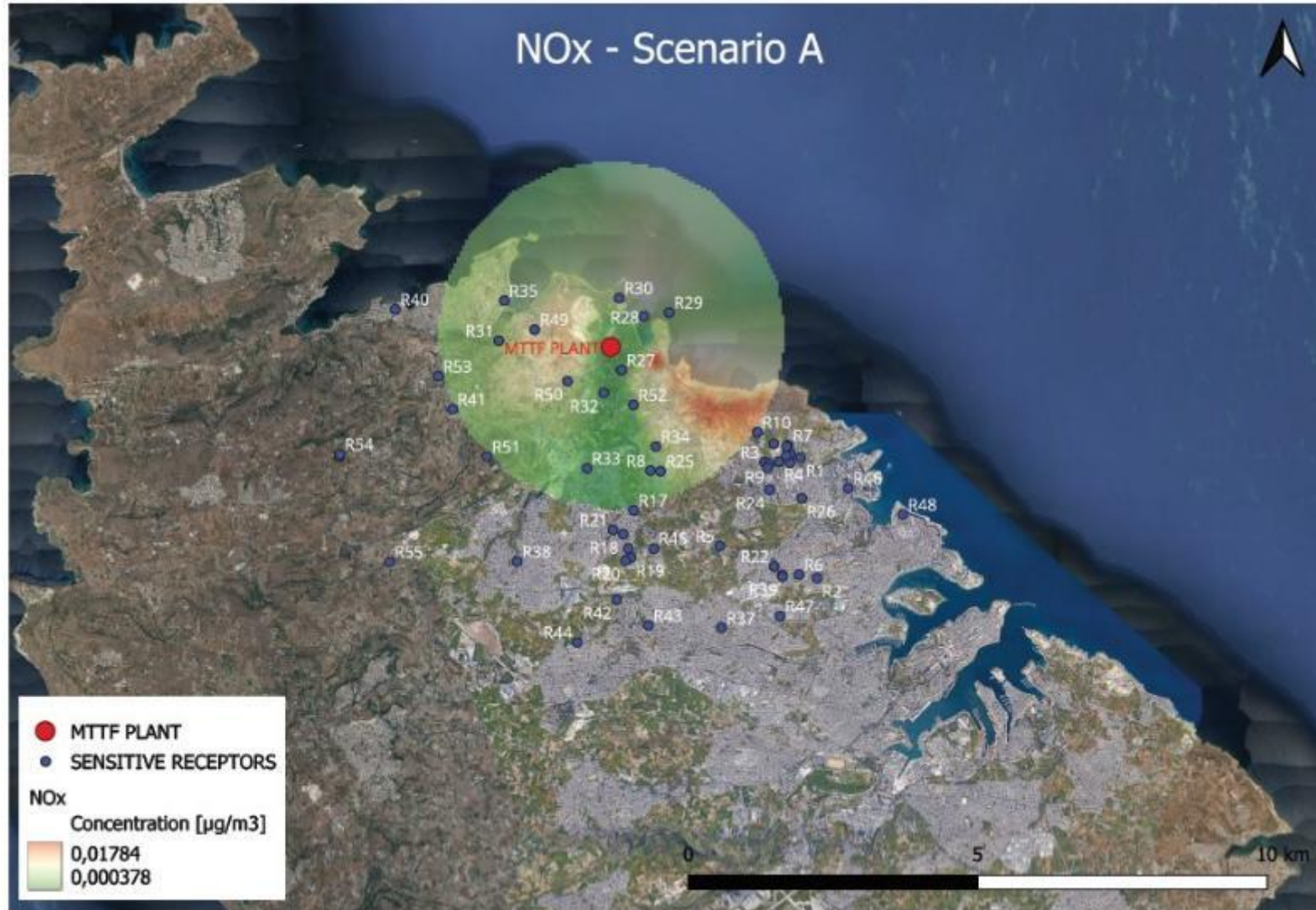


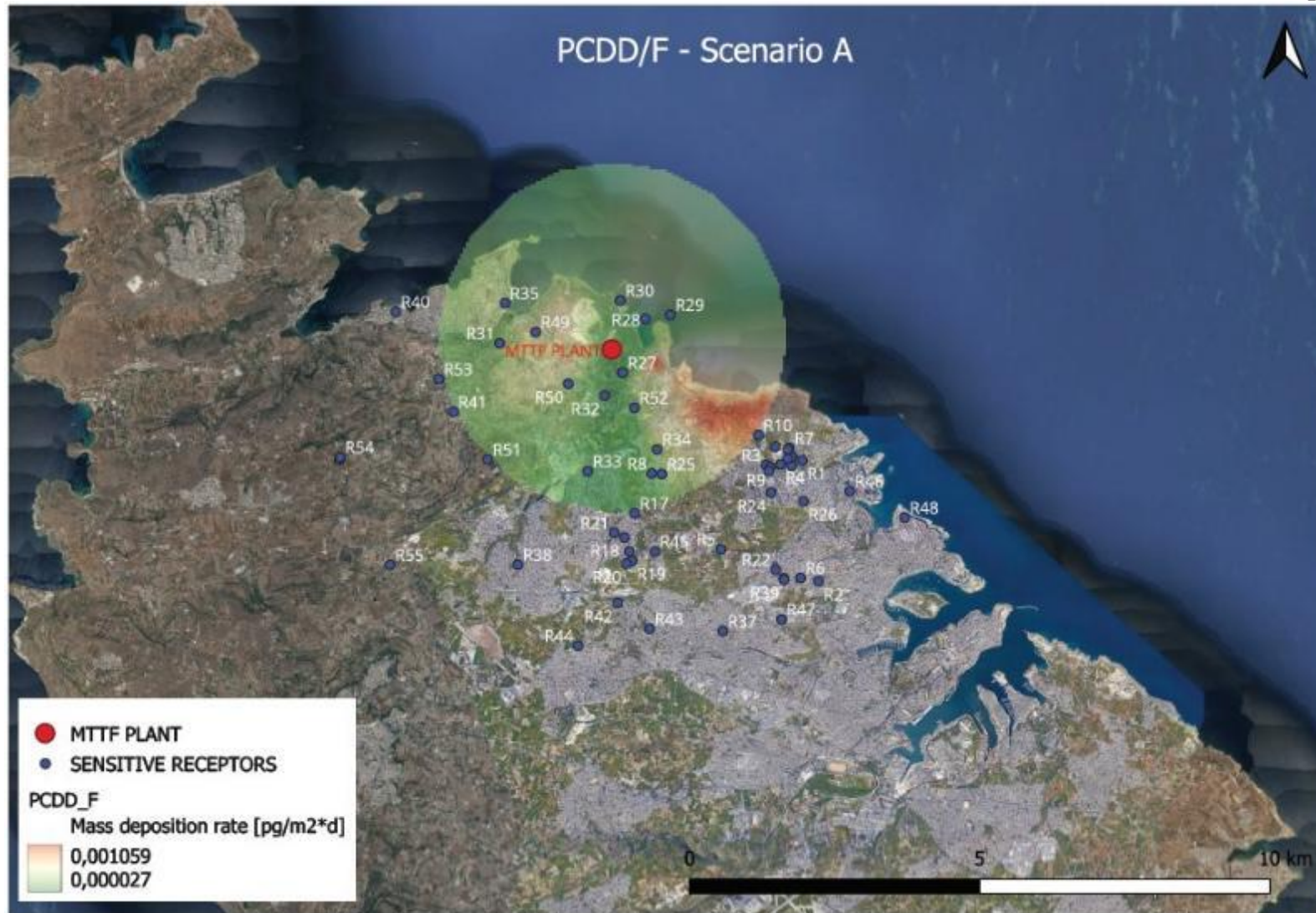


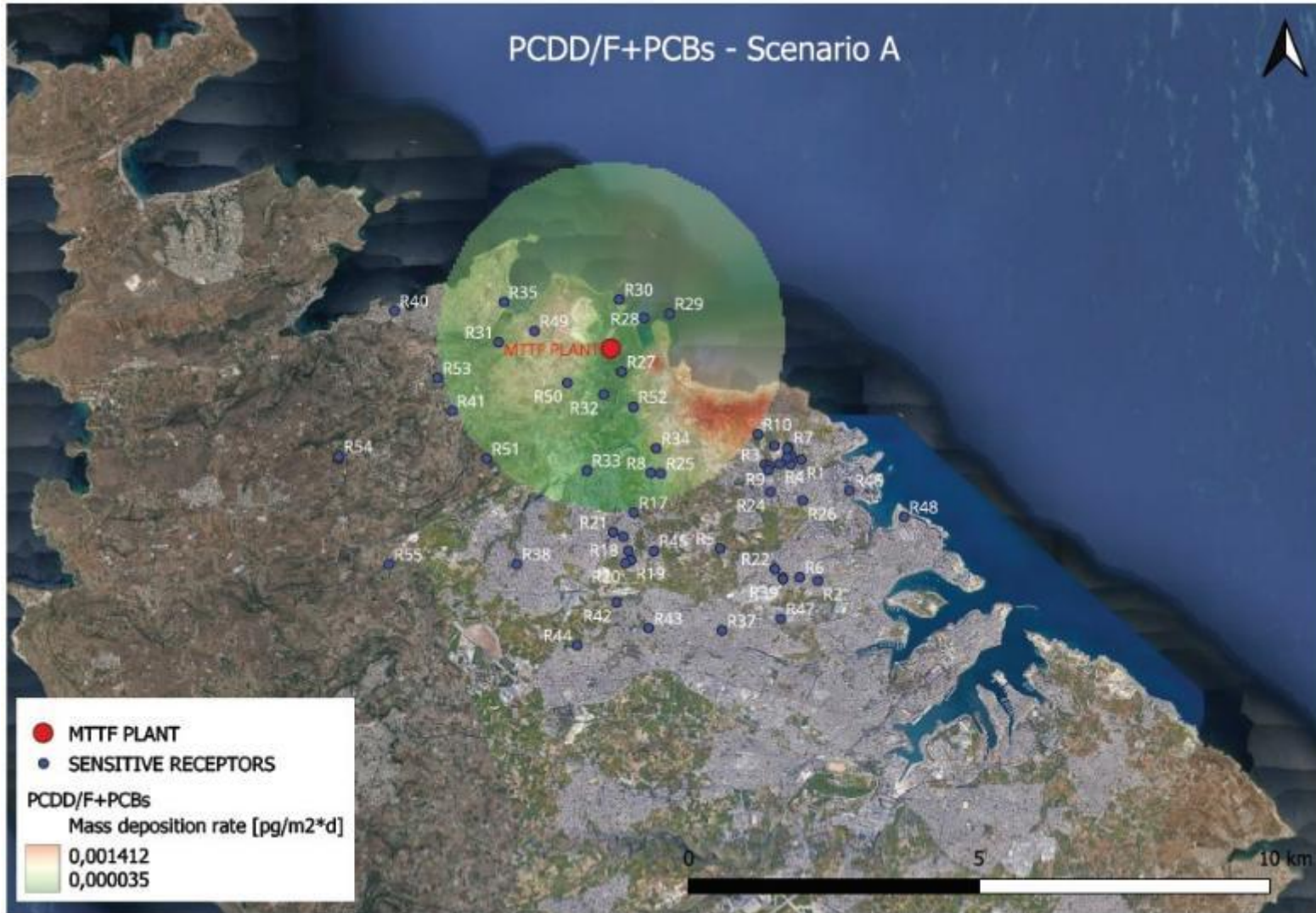


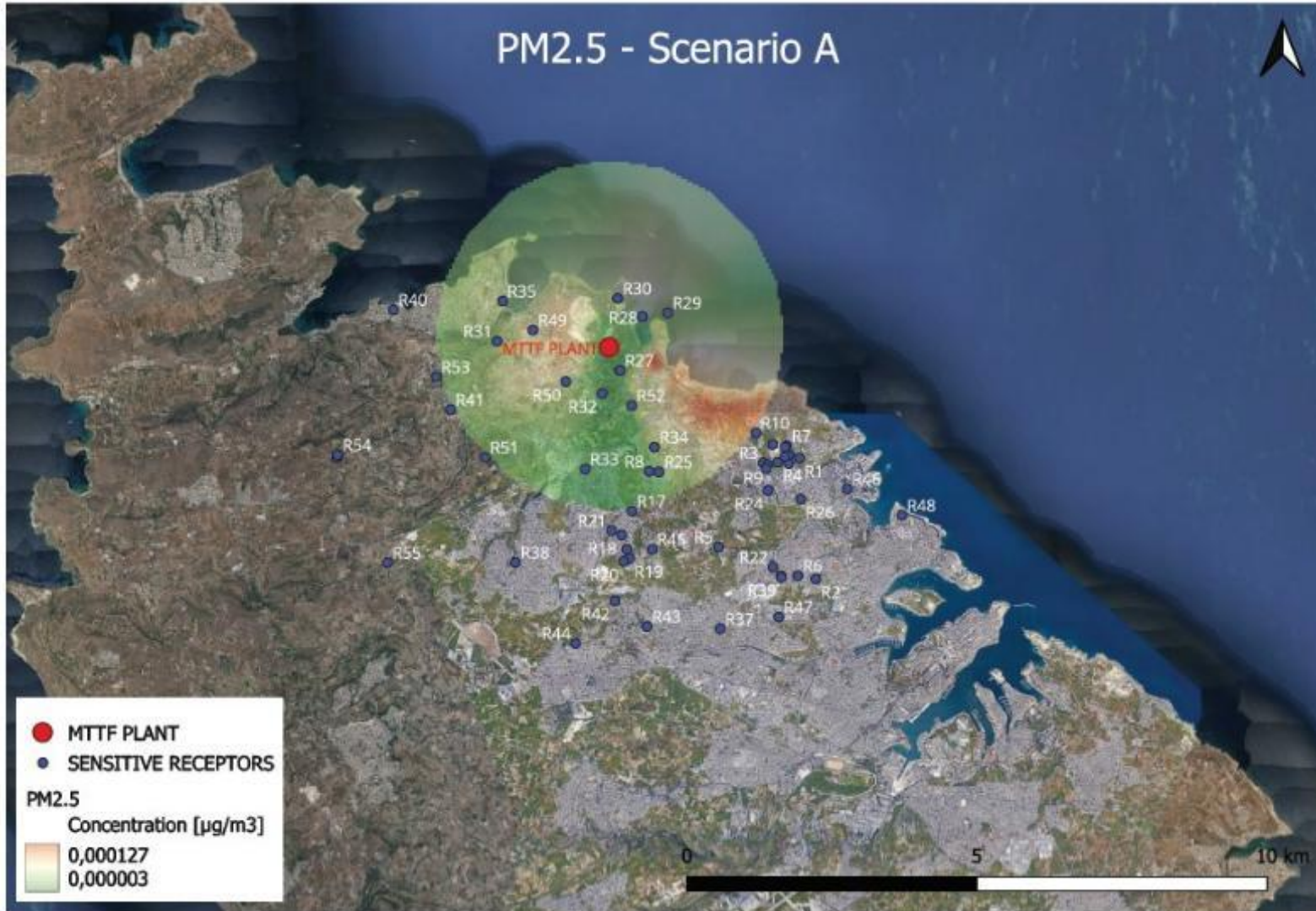


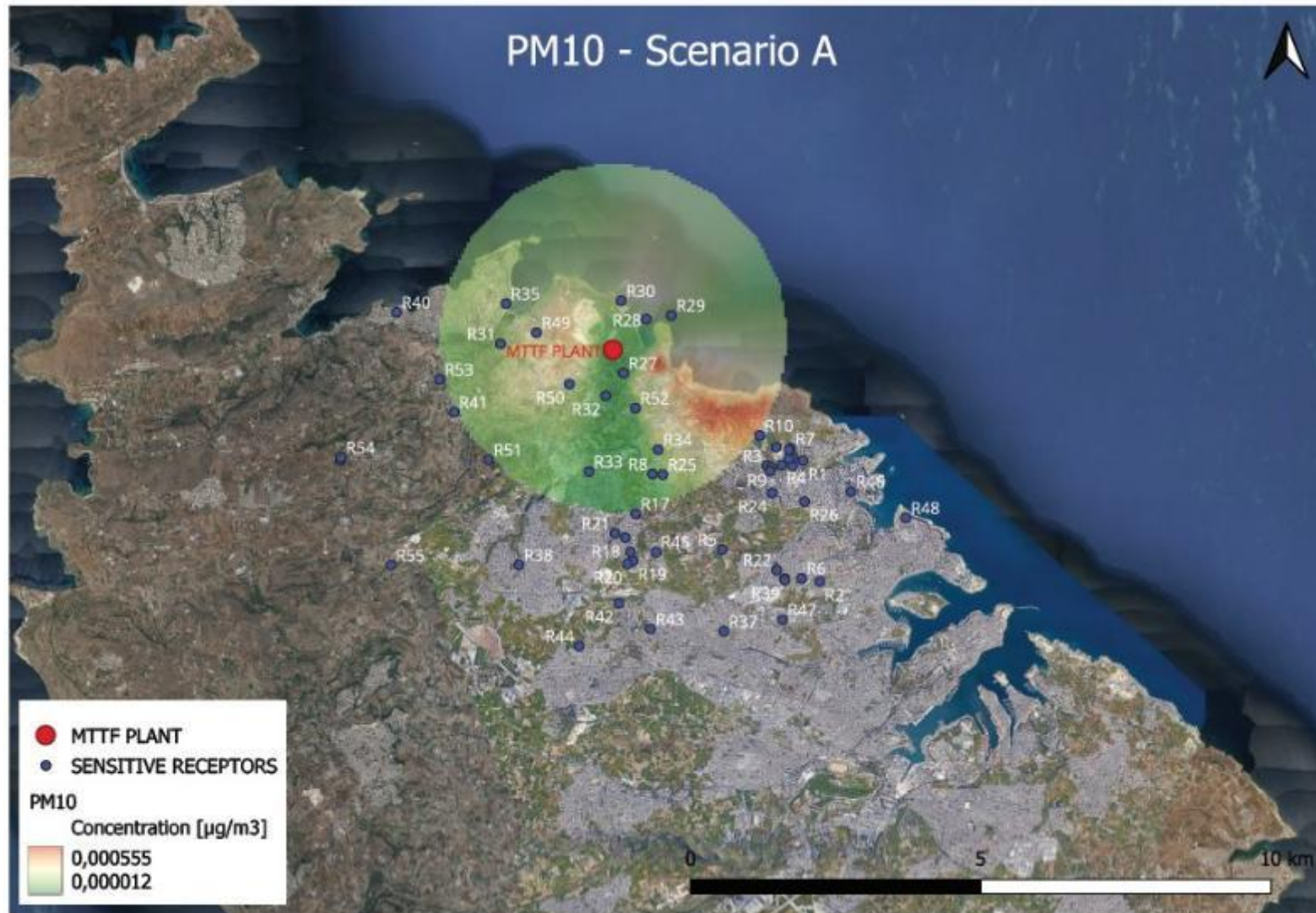


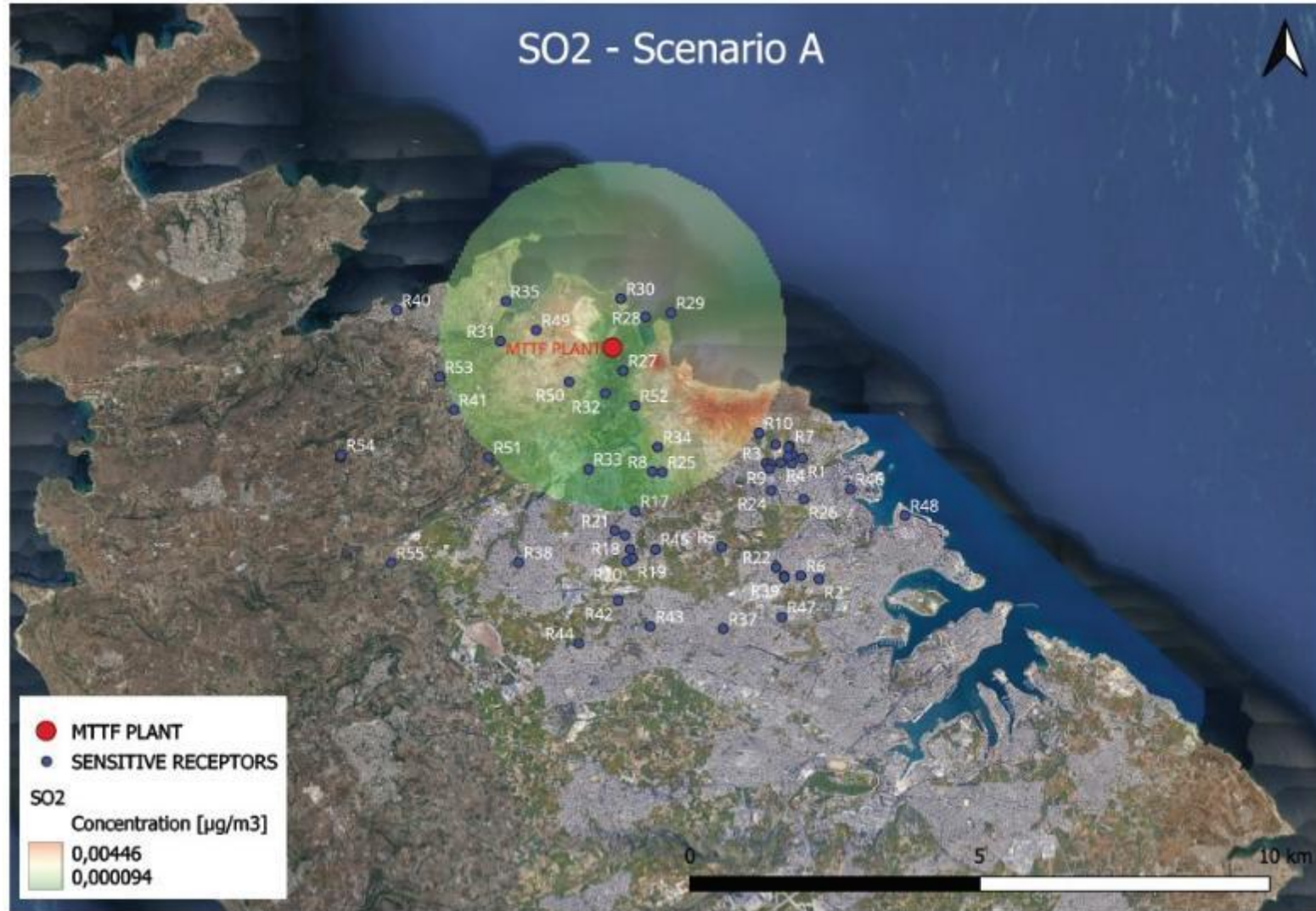


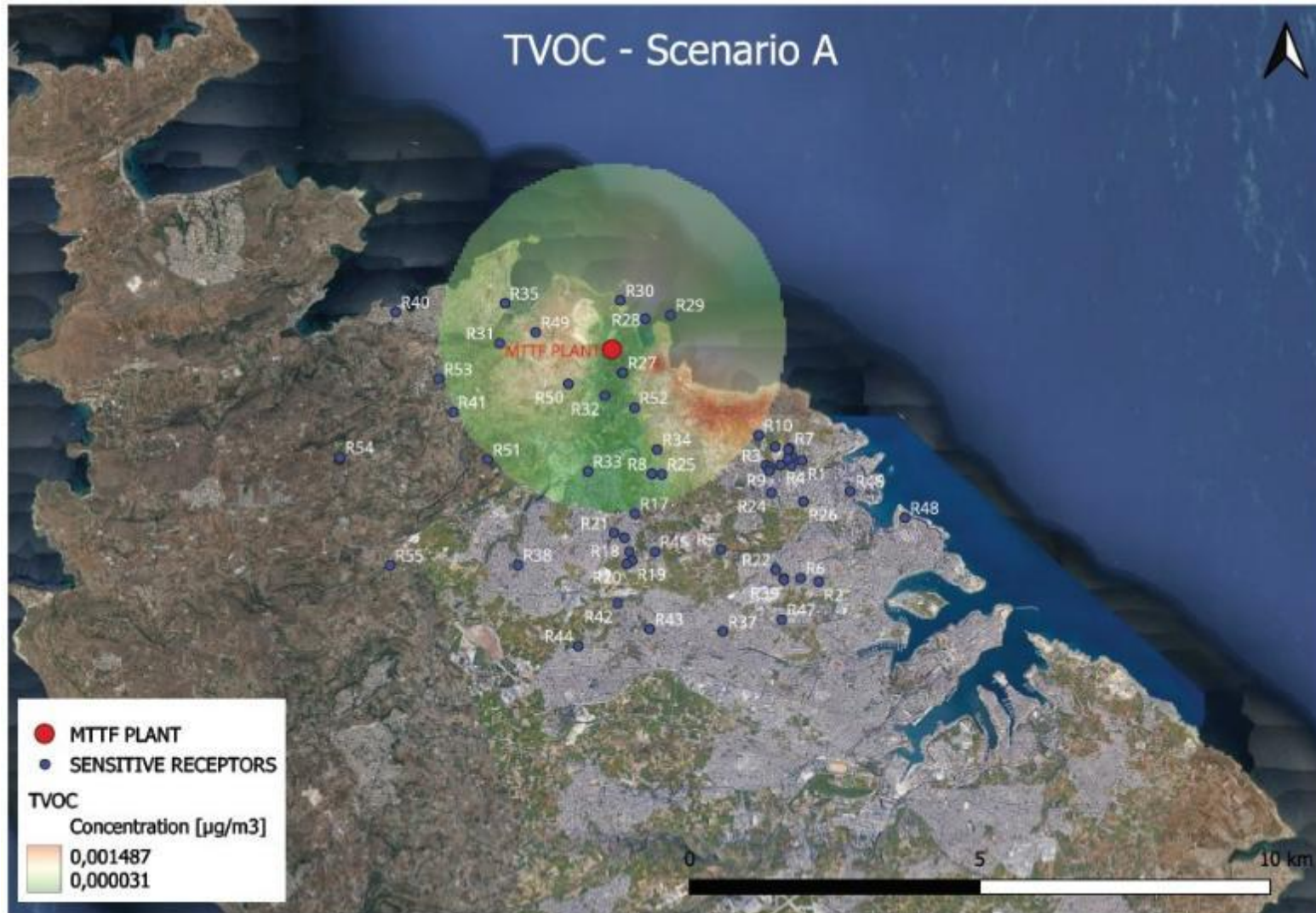


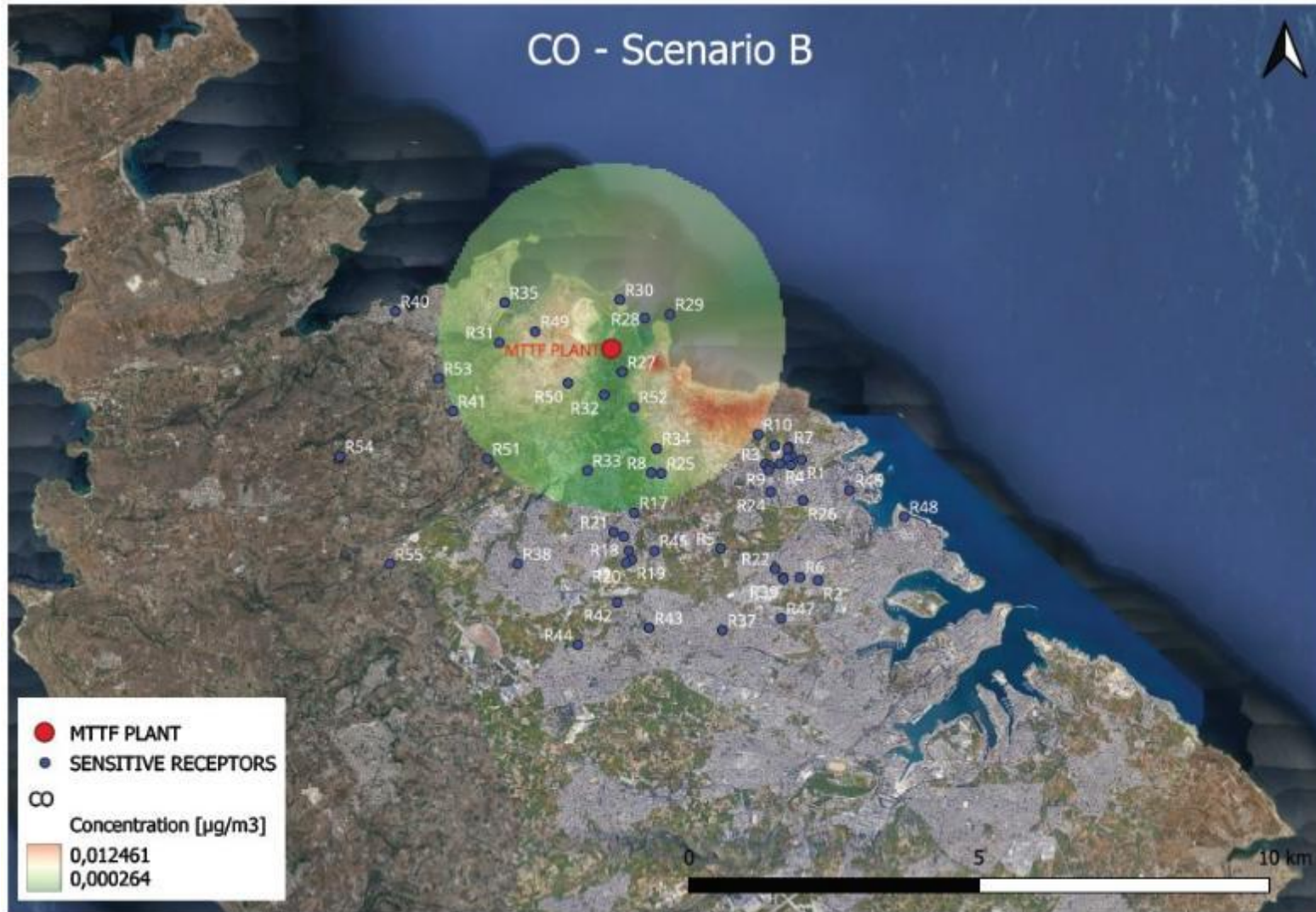


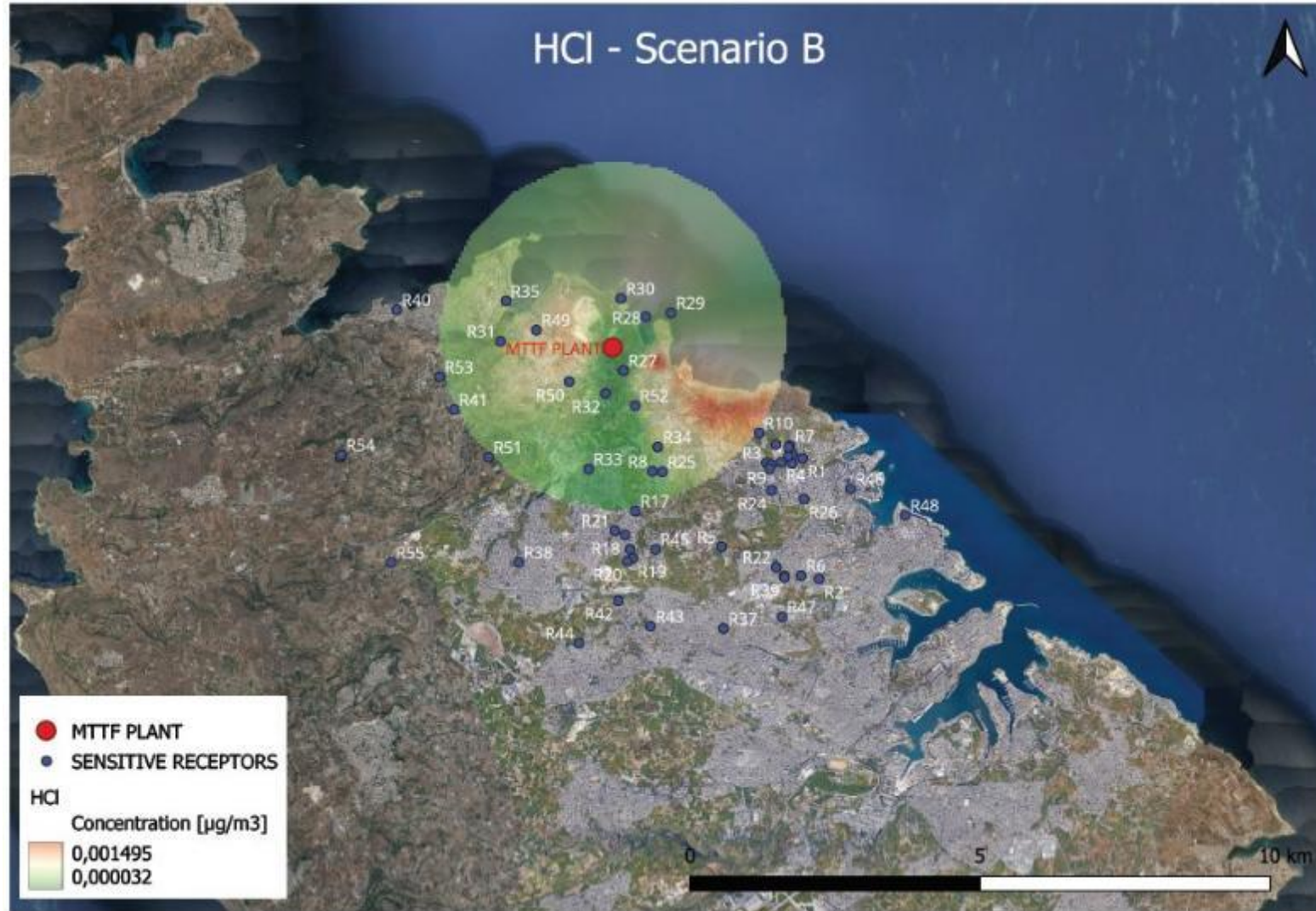


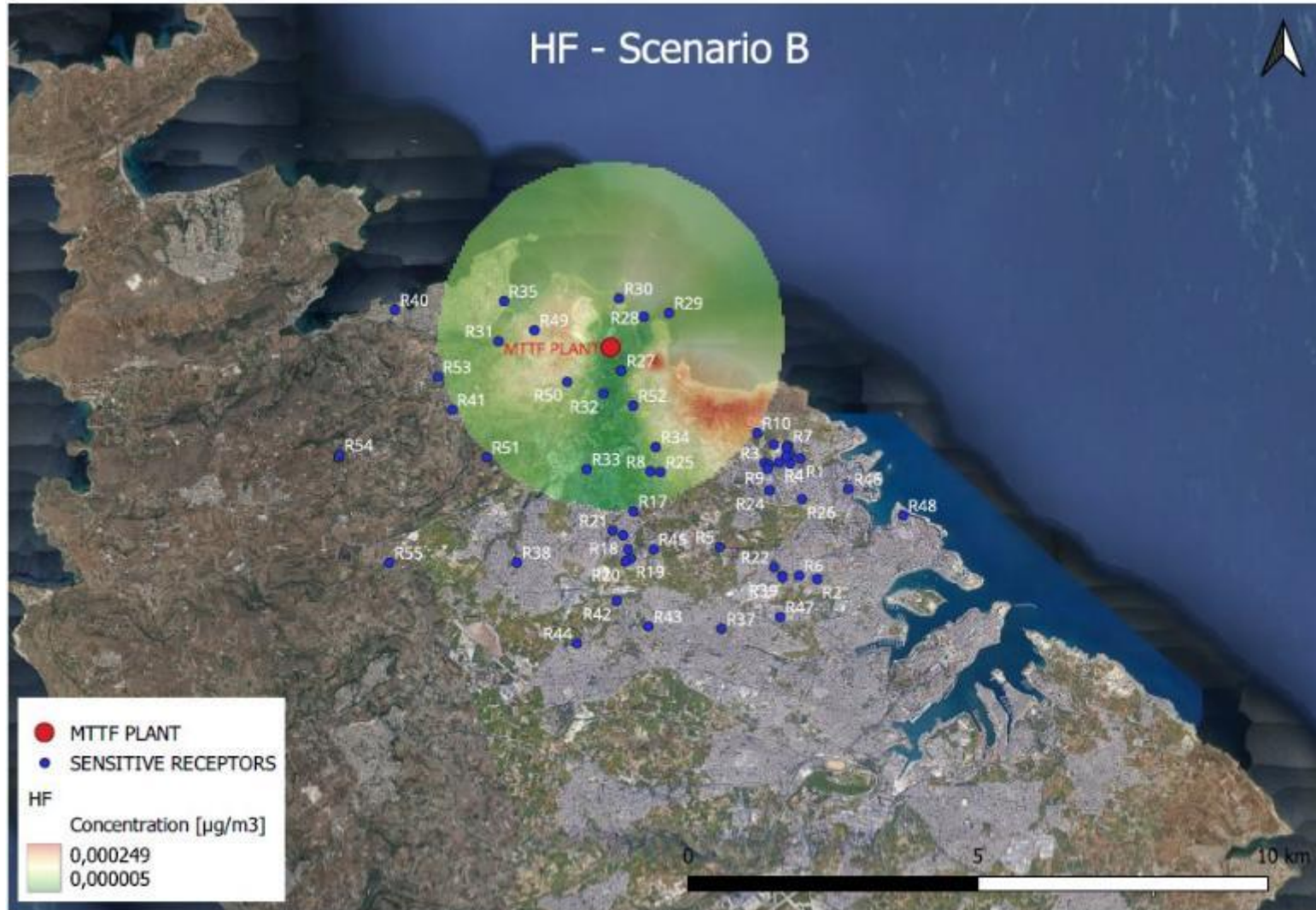


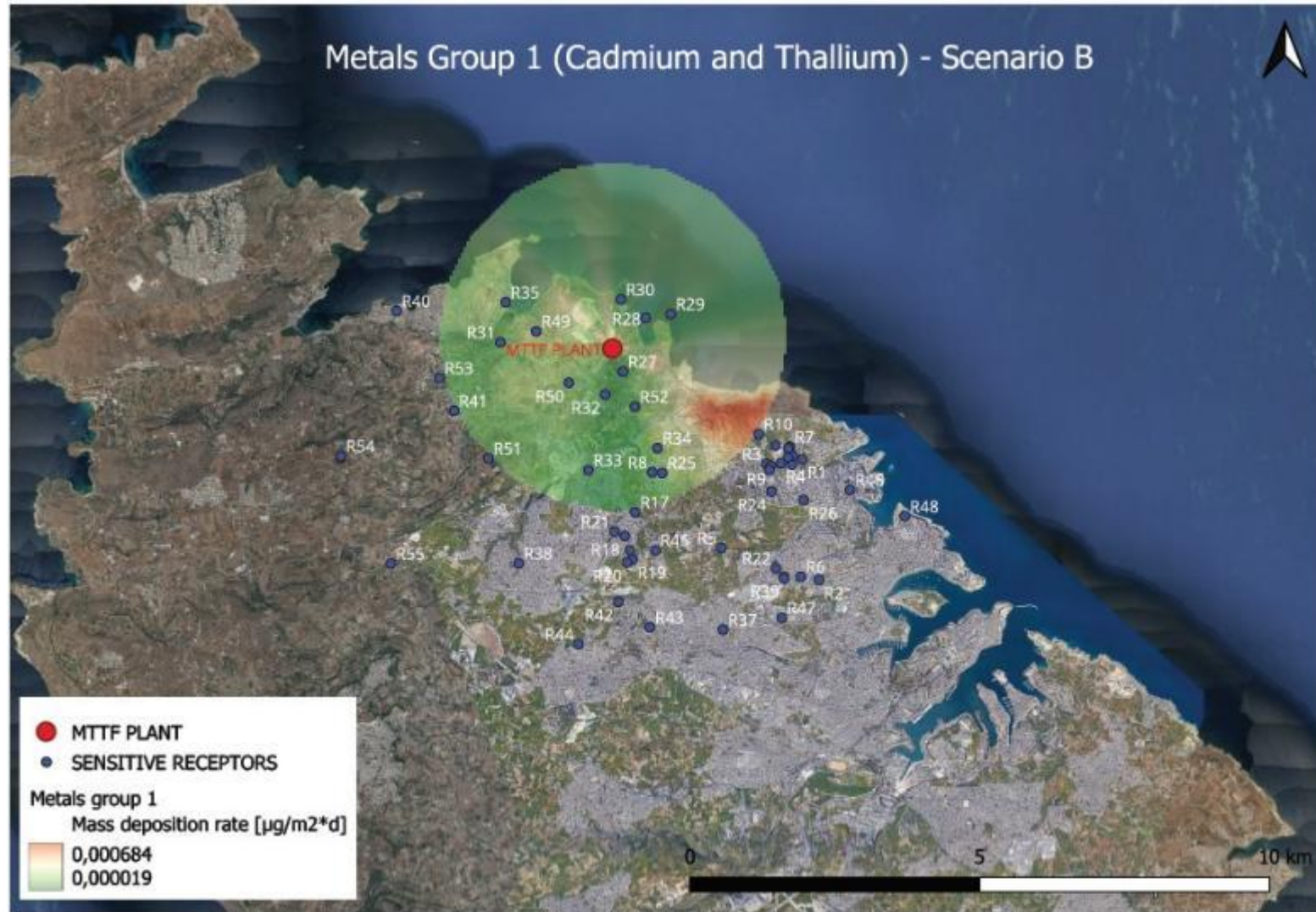


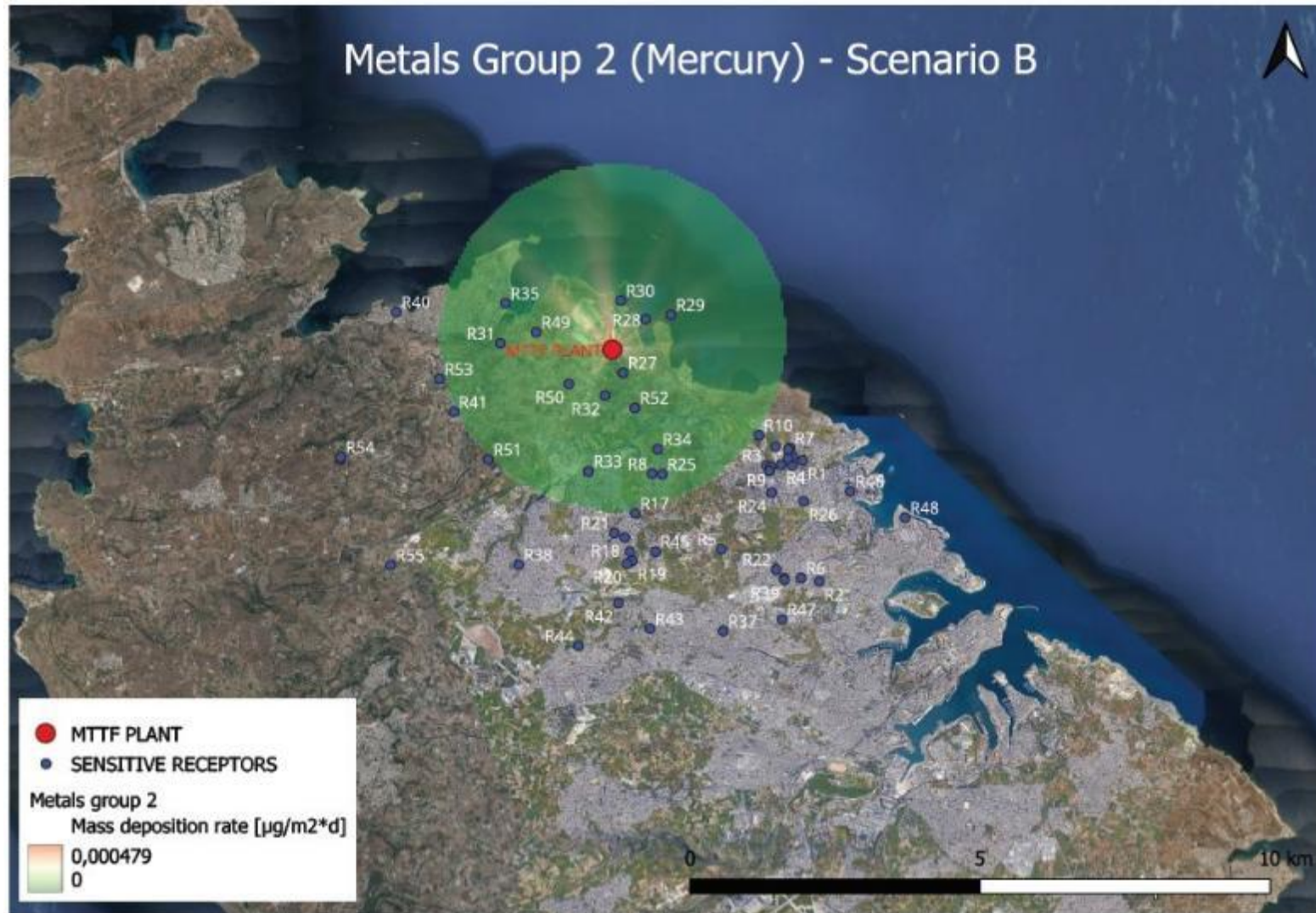


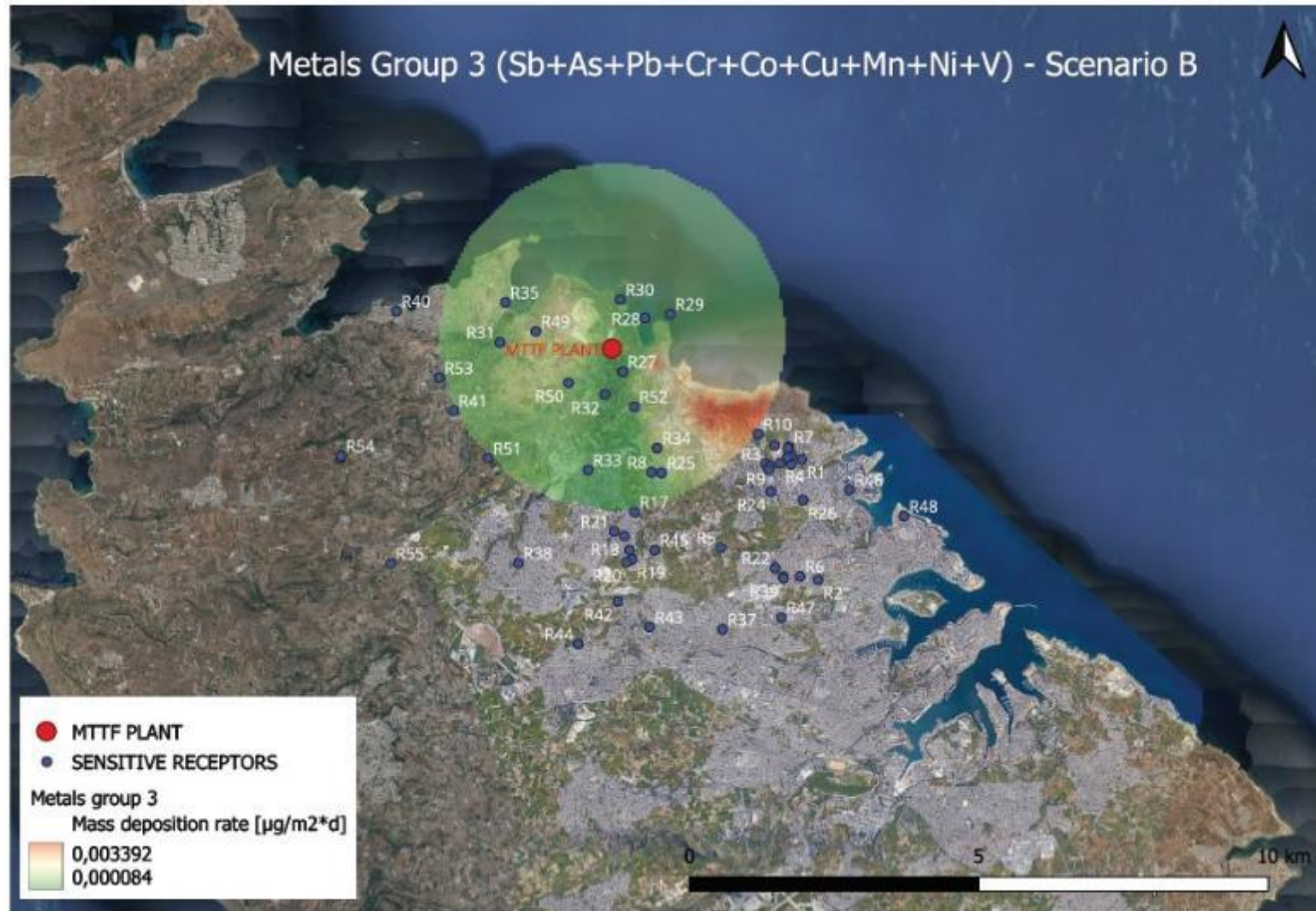


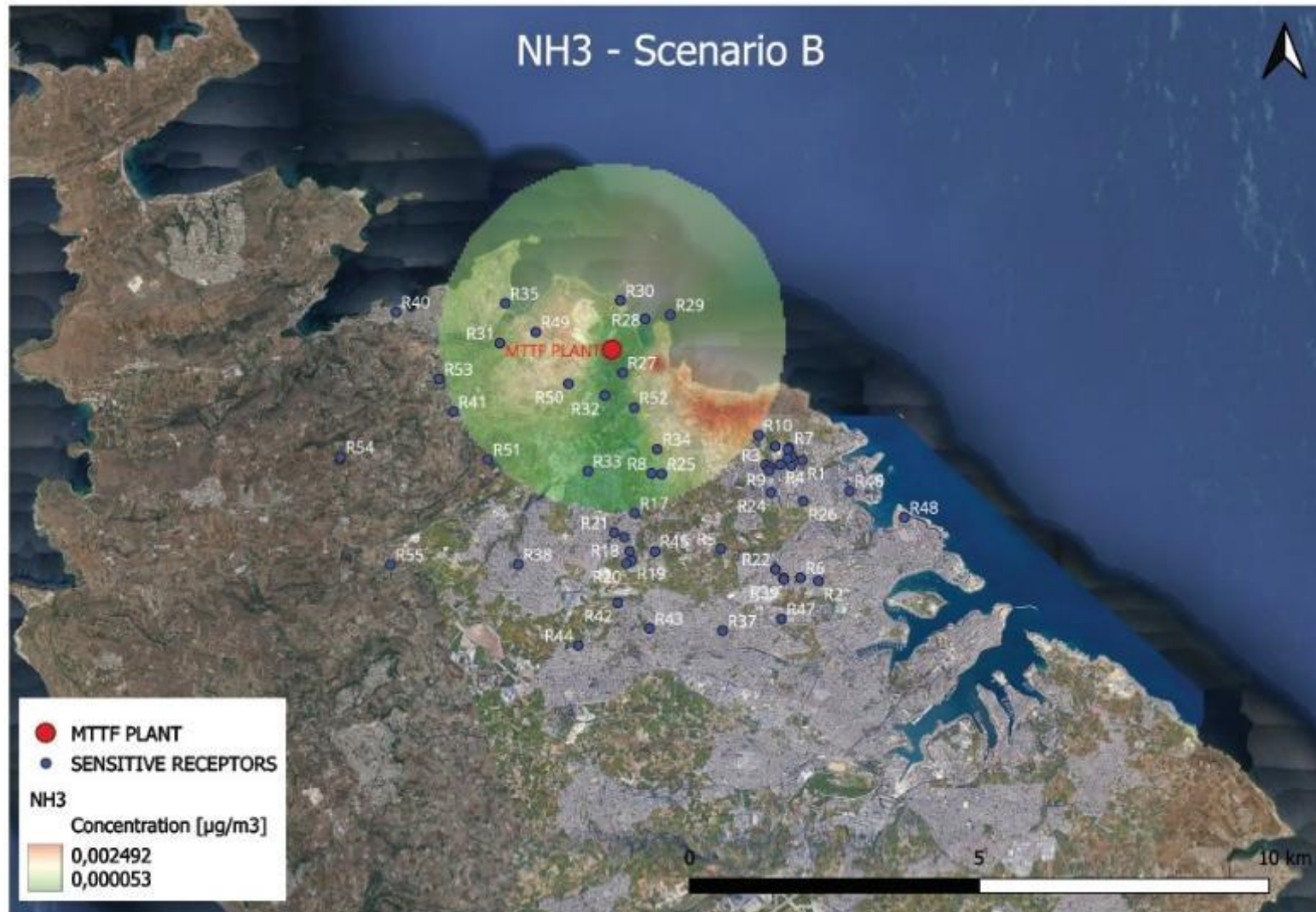


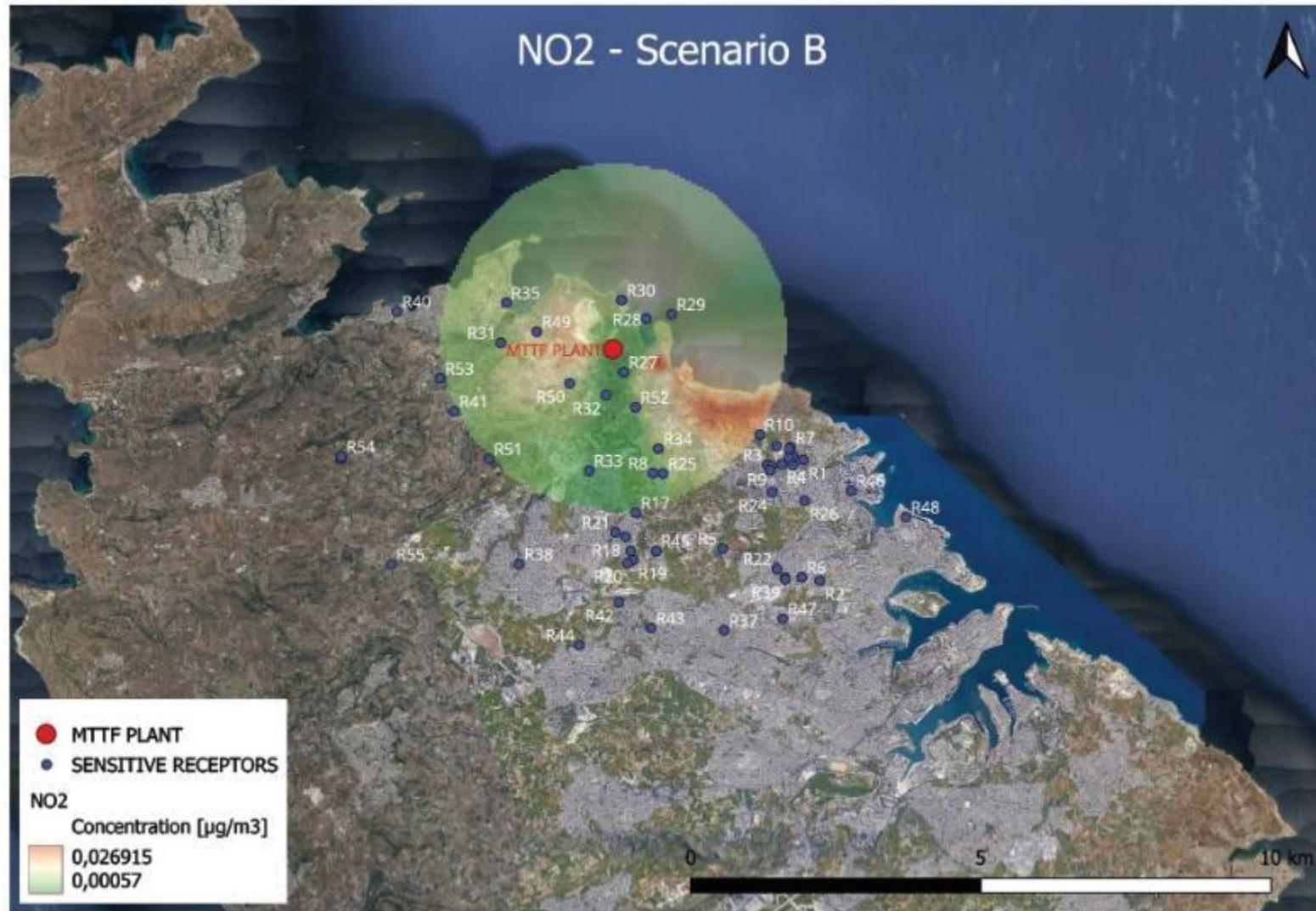


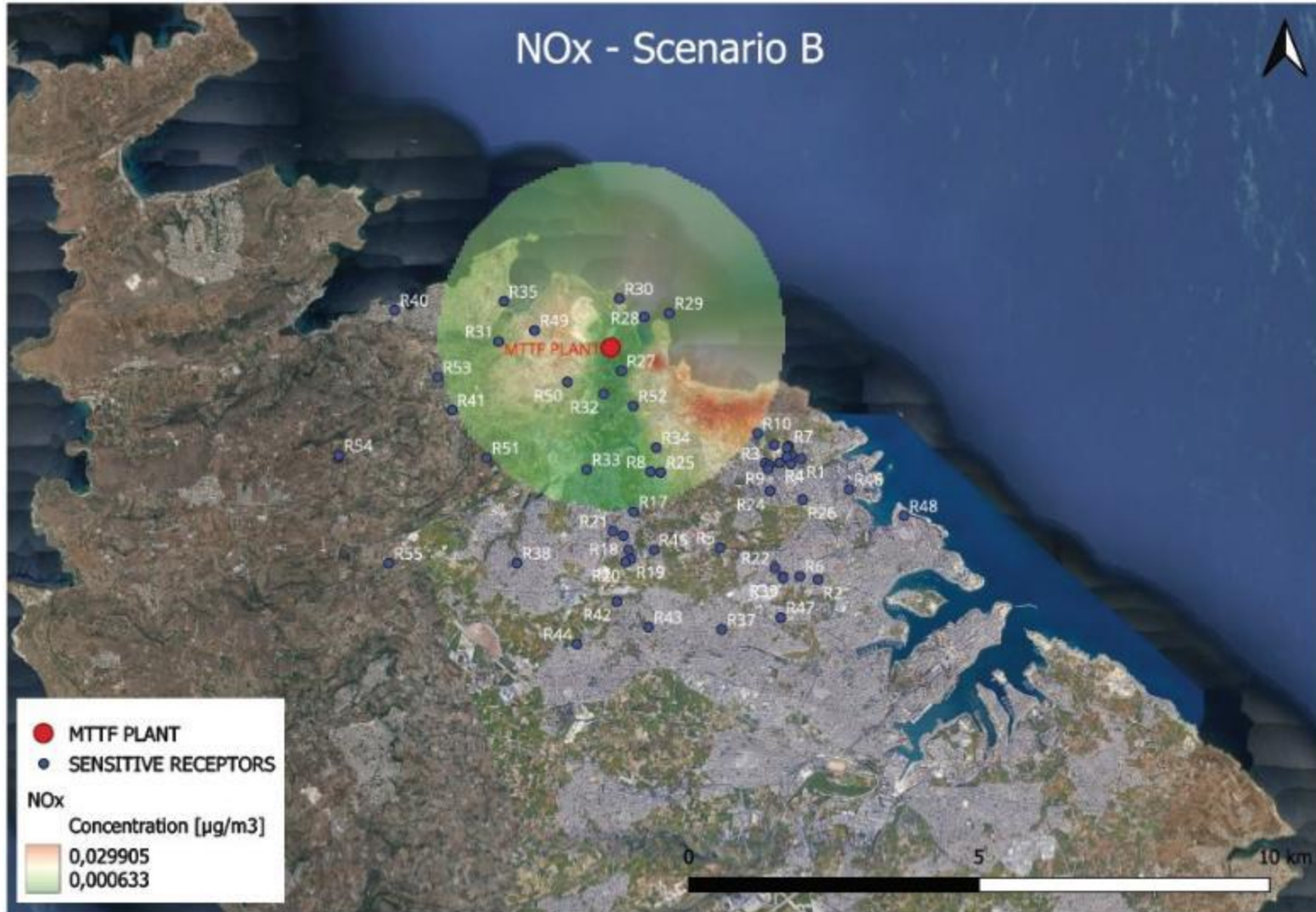


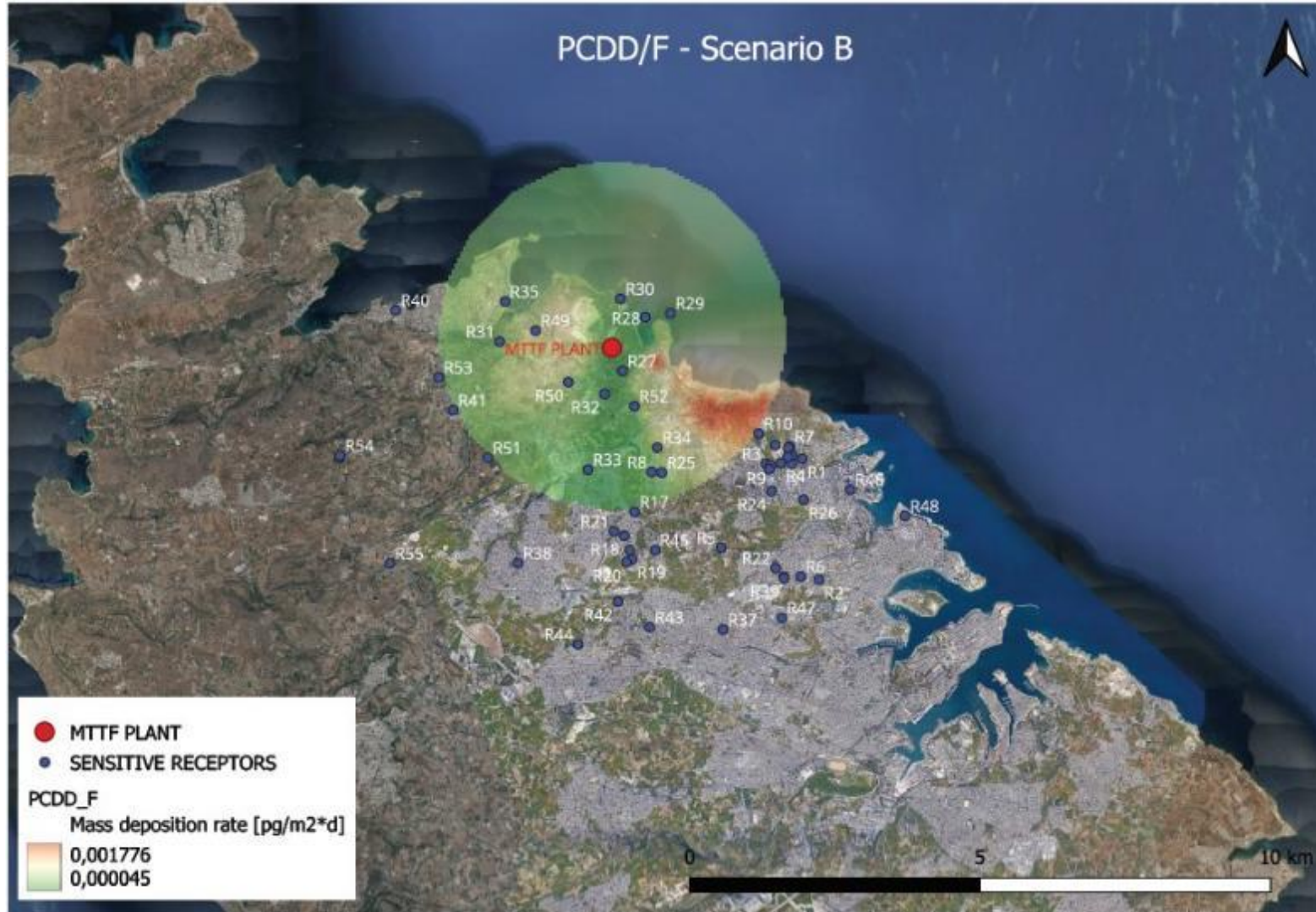


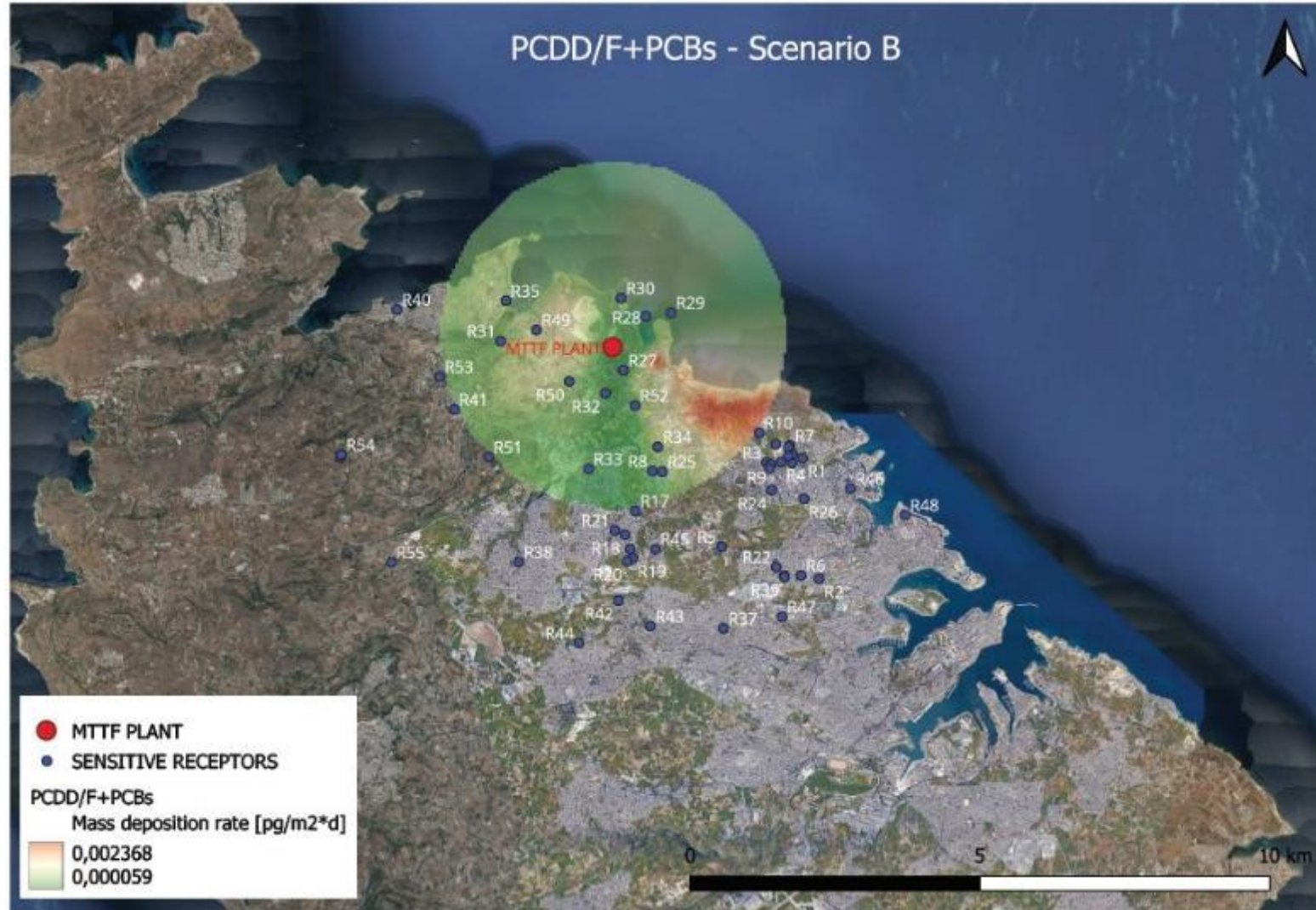


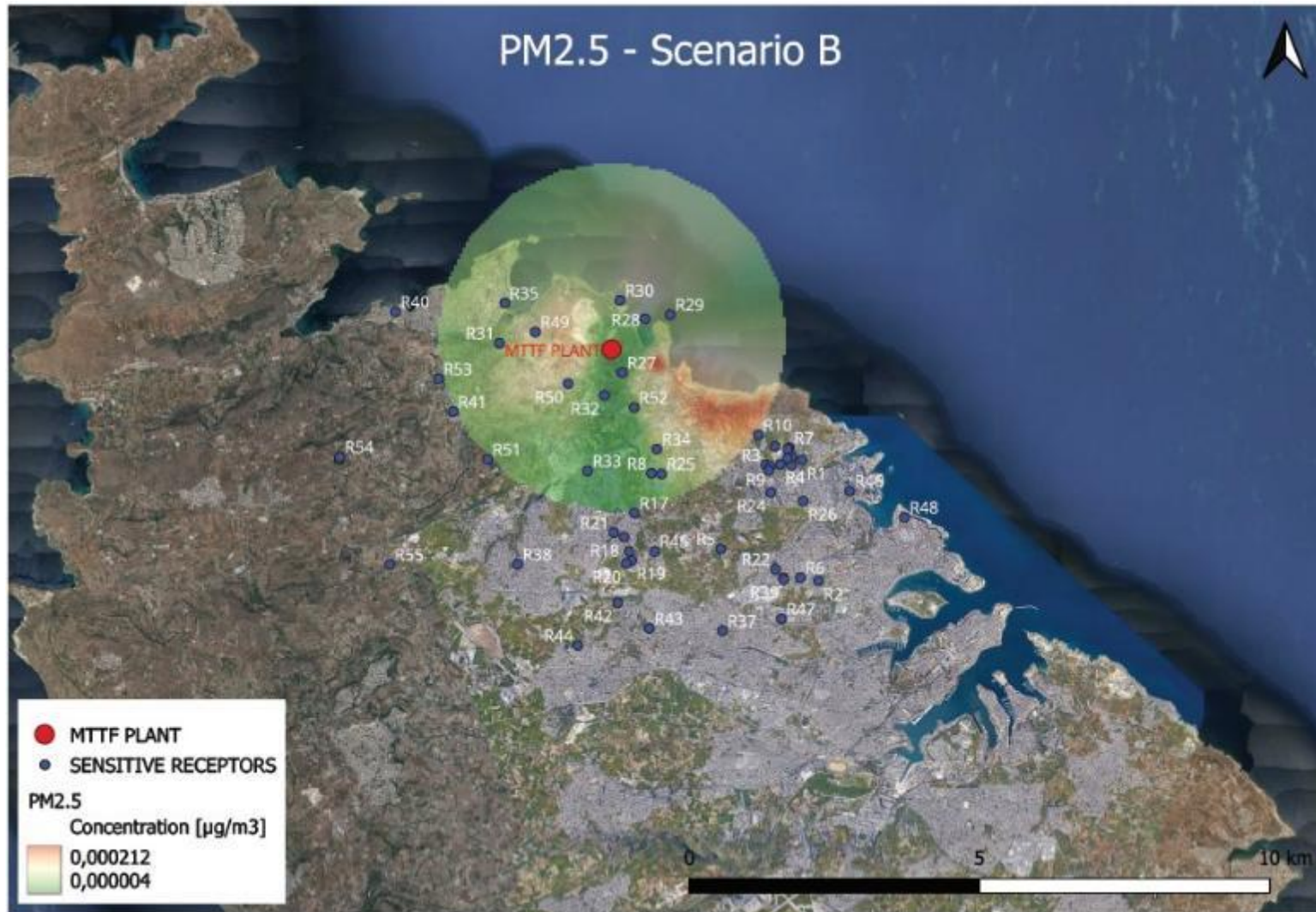


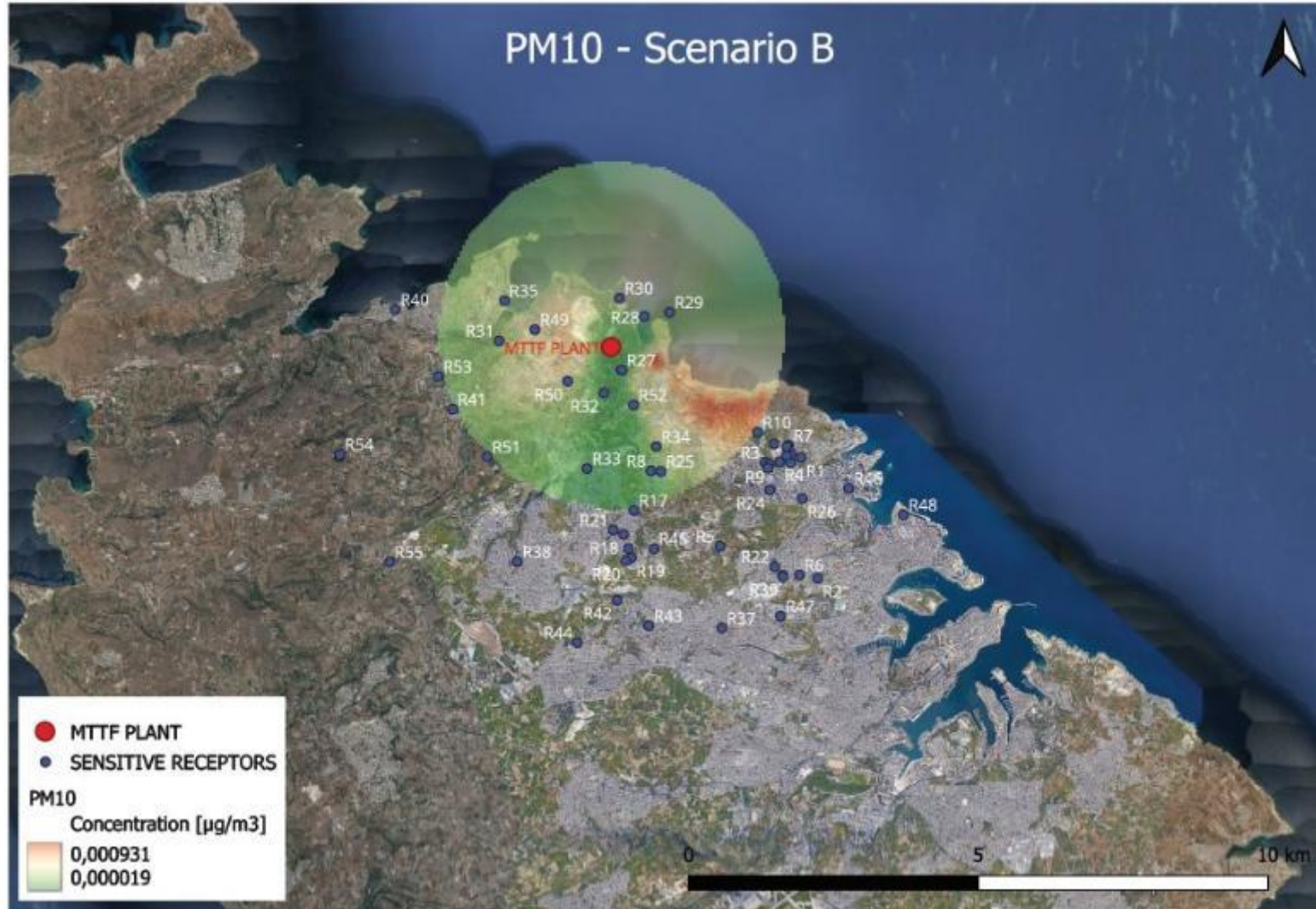


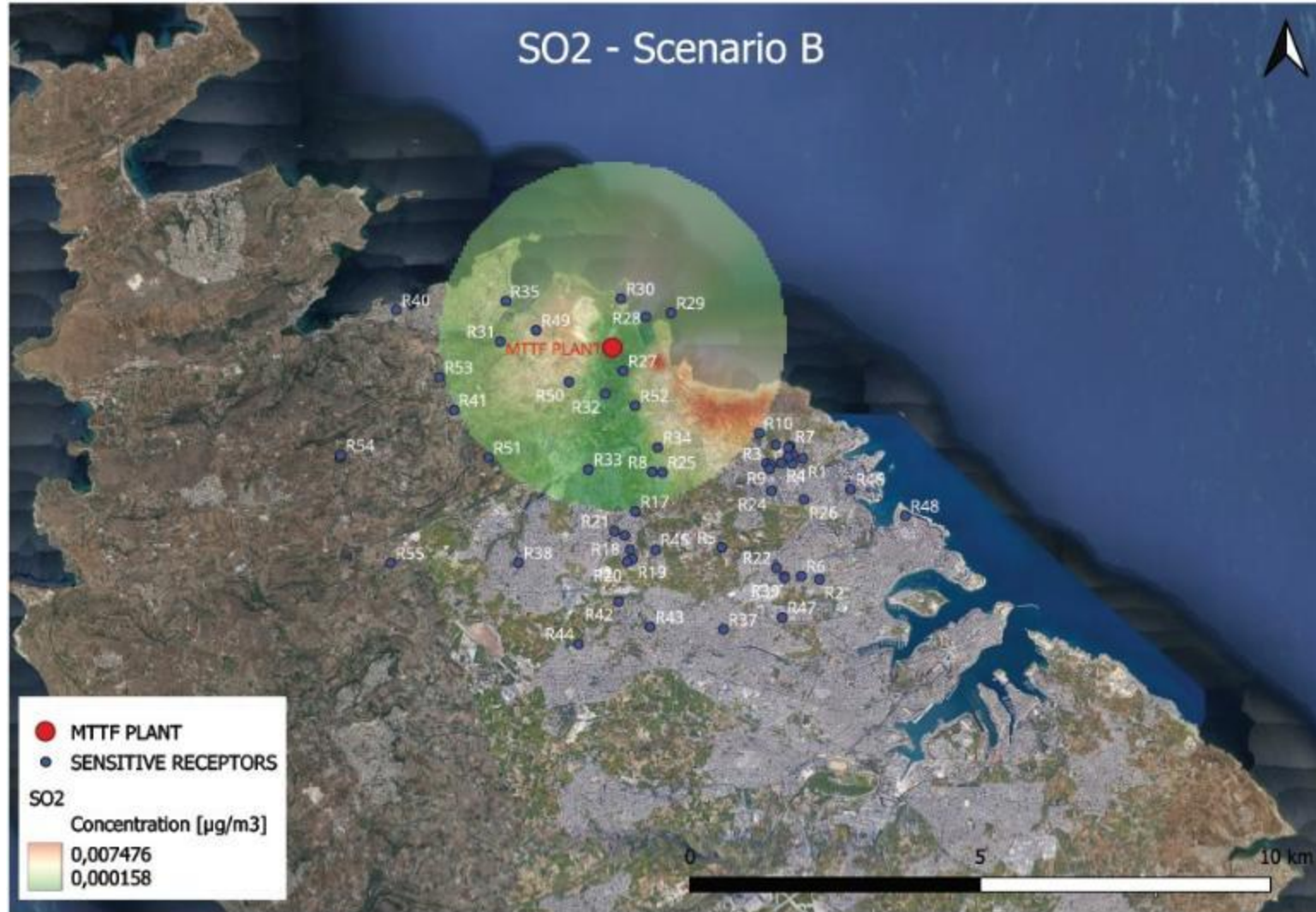


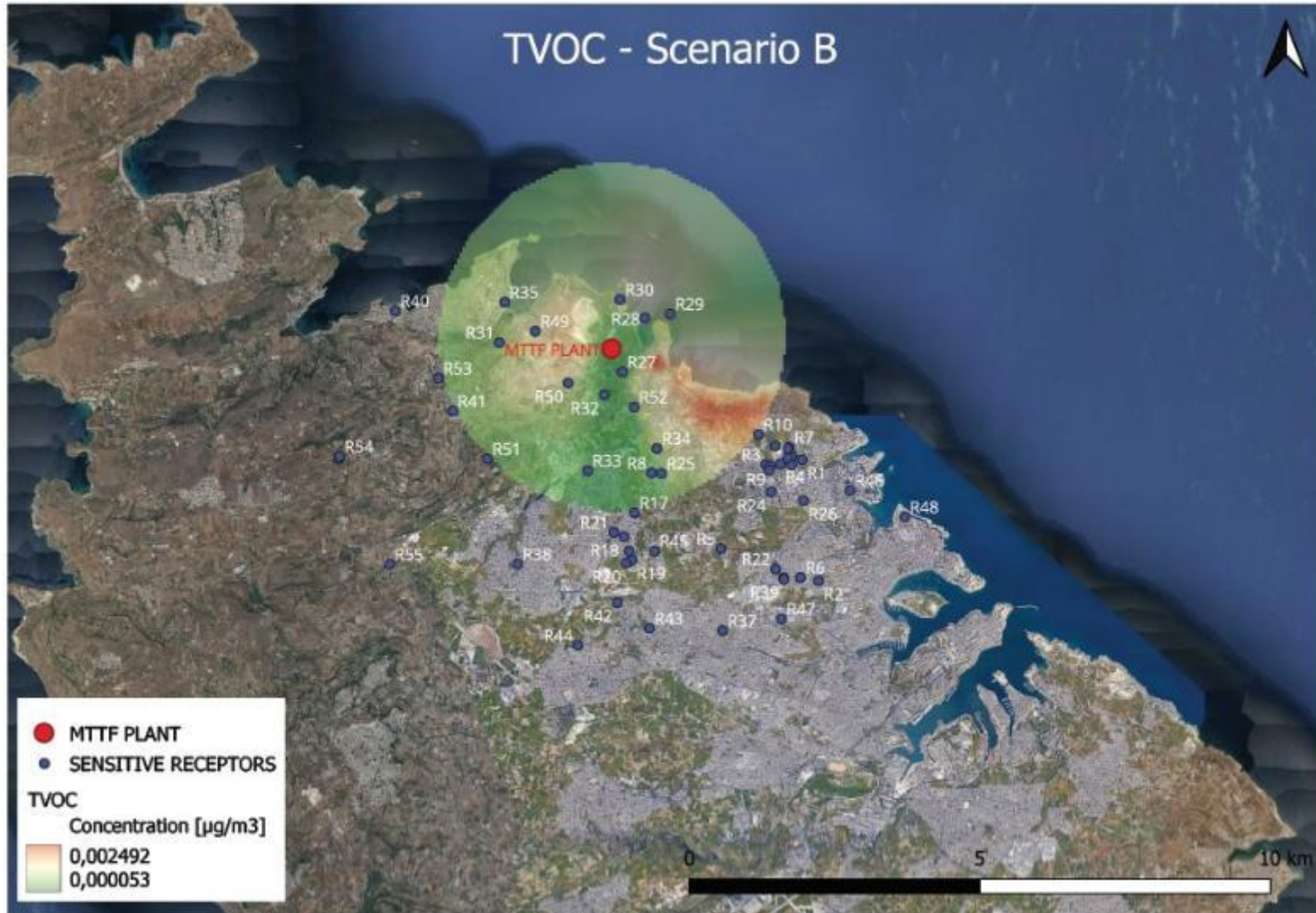


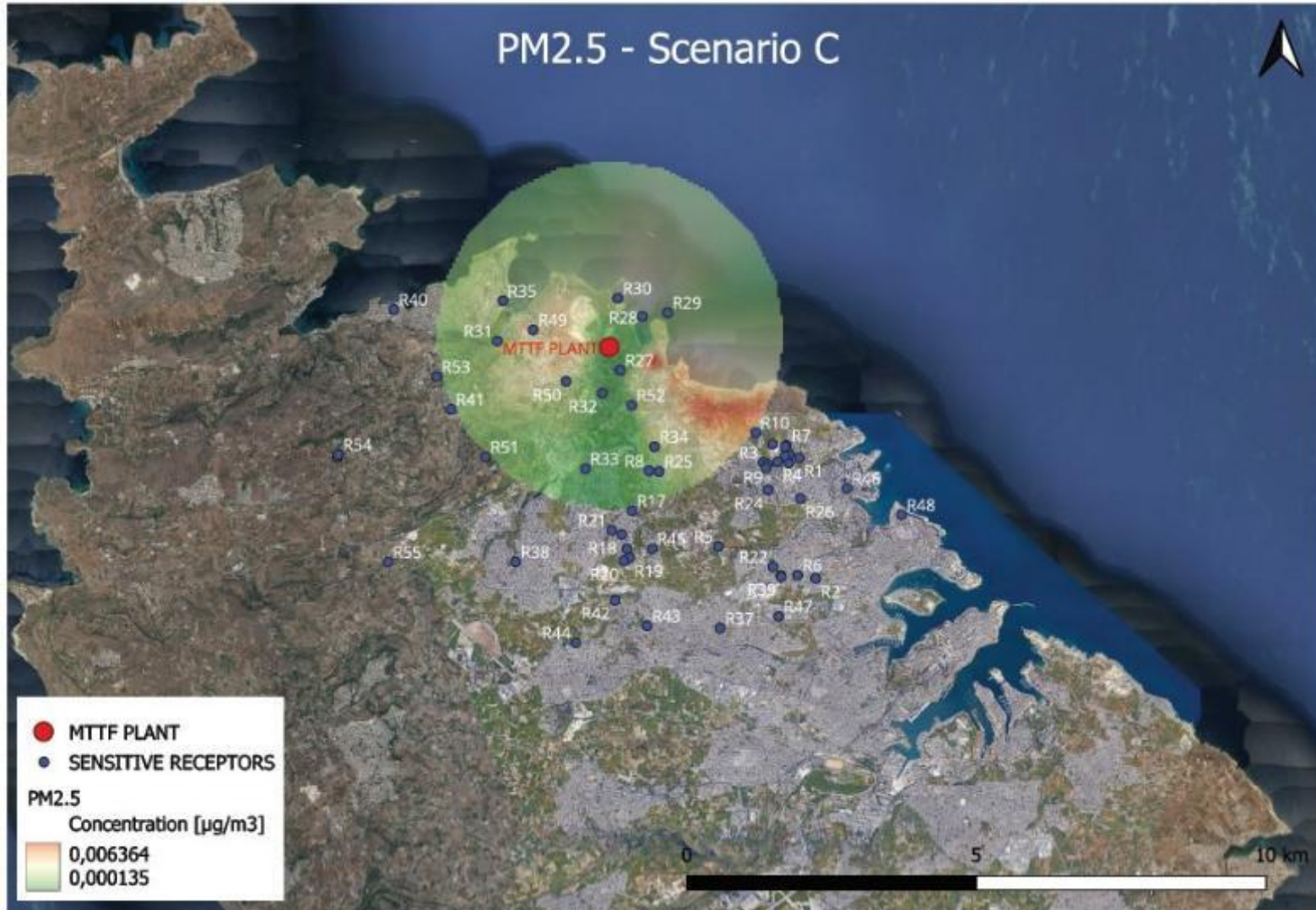


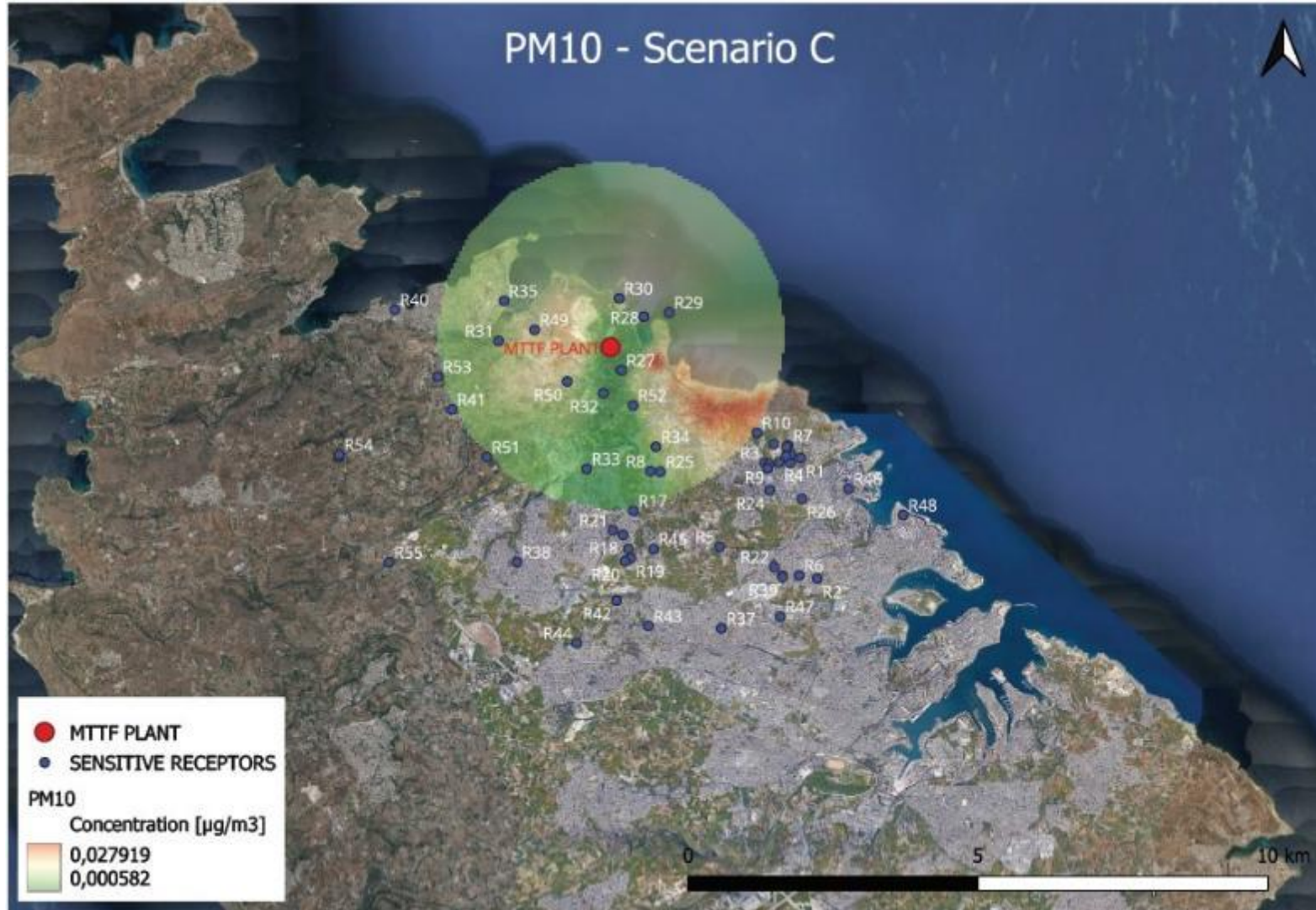












## APPENDIX 2 - TORs



***FINAL***

**Terms of Reference for the preparation of an  
*ENVIRONMENTAL IMPACT ASSESSMENT***

**PA 6096/23  
EA/00020/22:**

**Proposed Thermal Treatment Facility in the ECOHIVE  
Complex, including plant building, storage building,  
administration building, waste water treatment, tank  
farm and cisterns.**

**Site at: ECOHIVE Complex, Magħtab, Naxxar**

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10/06/2024

- Note 1:** The Environment and Resources Authority (ERA) reserves the right to modify these Terms of Reference according to any relevant environmental and planning considerations that may emerge at any relevant stage of the EIA or the permit application process, as well as in the event of any changes or updates to the proposed development. ERA also reserves the right to request additional or amended studies should the findings of the EIA be insufficient to adequately inform the decision-making process or if the EIA identifies matters which should be subject to further investigation.
- Note 2:** Unless otherwise agreed with ERA, all requirements set out in these Terms of Reference are to be complied with. If there are any aspects that the consultants deem irrelevant to this study, or if at any stage the consultants discover any environmentally-relevant aspect (not included in these TORs) that needs to be studied, the consultants shall inform ERA immediately, justifying their reasoning.
- Note 3:** Difficulties, including technical difficulties and lack of information, encountered by the consultants in compiling the required information shall be made clear in the EIA. All references to published works and sources of information shall be duly acknowledged in a manner that enables tracing of the information source and verification. No material may be incorporated by reference unless it is reasonably available for inspection by potentially interested persons within the consultation period and thereafter, and for record-keeping and unhindered perusal by ERA. Any material which is based on unavailable proprietary data shall not be incorporated by reference.
- Note 4:** Any requirement for confidentiality of any section or detail of the EIA must be strongly justified and a formal request in this regard must be submitted to ERA. Should ERA grant confidentiality, alternative material that is still adequate for proper assessment, public consultation and decision-making must be provided.
- Note 5:** Agreement on method statements, and ancillary liaison with ERA, is not mandatory but is recommended. Nevertheless, ERA reserves the right to disagree with the methodology proposed, including proposed areas of influence, and with the EIA submissions in general, and to factor such disagreement in its critique of the EIA.
- Note 6:** During review of the EIA, ERA will submit comments for the consultants' consideration, as relevant. Following the consultants' response to ERA satisfaction, a revised version of the EIA, addressing the comments, will normally be required. This may take the form of a complete resubmission or of an Addendum detailing the revisions to the previous submissions, as deemed most expedient by ERA, taking into account continuity and traceability of the information, and overall user-friendliness vis-à-vis subsequent review, presentation, public consultation, record-keeping and decision-making. A complete resubmission will generally be required if changes are numerous or complex, whereas an Addendum may be preferred if changes are more limited.
- Note 7:** The consultants are not exonerated from obtaining any formal authorisation from ERA, and from other relevant entities, vis-à-vis any activity ancillary to the EIA (e.g. collection, sampling, capture, or waiver of access restrictions) wherever such authorisation is legally required.
- Note 8:** These Terms of Reference, and all ancillary correspondence, are issued without prejudice to ERA's position on the project. Accordingly, their issuing (even when customised to address specific project details) should not be construed as evidence in favour or against the project or any component thereof, unless the contrary is clearly stated.
- Note 9:** Wherever relevant, references to land also include the sea, and ancillary terms such as land-take, ground cover, landscape, vehicles, access roads, etc. should be interpreted accordingly.
- Note 10:** Wherever any baseline studies required by these Terms of Reference is covered by already-existing data, such data should be used in preference to unnecessary duplication of baseline studies, unless the consultants or ERA or both are of the opinion that the existing data is unavailable, incorrect, outdated, unreliable, insufficient, or otherwise inadequate for the purpose of the EIA.

An Environmental Impact Assessment (EIA) Report is to be prepared as required by the Schedule I, Category I, Section 5.0.1.1 of the Environmental Impact Assessment Regulations (S.L. 549.46). The required components of the EIA are:

- i. A **Coordinated Assessment Report**, in conformity with the following Sections of these Terms of Reference. This report should assess the project in its totality;  
*[Note: The coordinated assessment should seek to analyse and integrate the main considerations emerging from the technical reports, rather than just reproducing excerpts from the reports].*
- ii. A separate **Appendix (or Appendices)** containing all technical studies and original survey reports as prepared by the individual specialist consultants for specific topics;  
*[Note: Experts contributing to the EIA should be specifically asked to consider impact interactions and cross-cutting issues, and to communicate information between each other accordingly].*
- iii. A separate **Non-Technical Summary** of the EIA, in both the Maltese and English languages. This should have enough details for the public to understand the project and the related environmental considerations, and should be written in reader-friendly language (e.g. avoiding unnecessary technical jargon);
- iv. A **declaration of conformity** with regards to conflict of interest, in accordance with sub-regulations 17(3) of the EIA Regulations (refer to Appendix 1 to these Terms of Reference); and
- v. An addendum detailing the **feedback received from stakeholders, from the public, and from ERA** during the relevant consultation stages of the EIA, and how they were addressed.

Wherever relevant and appropriate, all components of the EIA should include tables and figures (e.g. maps, plans, photographs, photomontages, charts, graphs, diagrams, cross-sections) and quantifications.

The complete EIA Report (including all the above components) should be submitted as a printable digital copy (in .pdf format, with copying fully enabled throughout) and as a printed copy. Likewise, in case further revisions are to be made to the EIA Report, both a printable digital copy (in .pdf format, with copying enabled throughout) and a printed copy of the revised EIA Report, or an Addendum, is to be submitted to ERA.

Any other assessments, including Appropriate Assessment [as required by the Flora, Fauna and Natural Habitats Regulations (S.L. 549.44)] are to be submitted separately from the EIA. Cross-referencing between the EIA and any such assessment should be clear and reasonably limited, such that both of the following considerations are duly satisfied:

1. Alerting the reader to the fact that the aspect in question is also being addressed in another parallel assessment; and
2. Enabling the reader to easily follow both the EIA and the other assessments as stand-alone documents.

Any other technical studies/ reports which are of direct environmental relevance to the project or are cross-referred to in the EIA report, should be submitted together with the EIA, and made available to the public. Should these documents not be made available upon submission of the EIA report, ERA reserves the right to re-open the public consultation for an additional 30-days, over and above the timeframe stipulated in Regulation 19(1), as deemed fit.

More detailed specifications are identified in the following pages.

## **1.0 DESCRIPTION OF THE PROPOSED DEVELOPMENT AND ITS CONTEXT**

The description of the proposal is to include the aspects outlined below, and should take into account the entire proposal and any ancillary facilities and infrastructure connected with, or arising due to, the project.

### **1.1 Justification for the Proposal**

#### **1.1.1 Objectives**

The purpose and objectives of the development and whether these are related to current legal obligations, policies or plans.

#### **1.1.2 Demand**

The current and expected requirement or demand for the proposed land uses, also explaining how the proposal will address the requirement/demand.

### **1.2 Description of the Physical Characteristics of the Whole Project and the Land Use Requirements during the Construction, Operational and Decommissioning Phases**

The following aspects should be addressed for all phases of the project, clearly distinguishing between aspects relating to construction phase, operational phase, decommissioning phase, or more than one phase. References to the construction phase and decommissioning phase also include ancillary site preparation, clearing, excavation, demolition/dismantling, and site reinstatement works, as relevant.

#### **1.2.1 General characteristics**

Description of the proposed development including size, area, height, volume, configuration/layout, general design, location and proposed elevations of buildings/structures/installations, hard and soft landscaping, access arrangements, boundary demarcation arrangements, land use requirements, and land take of ancillary facilities (including infrastructure, storage, servicing, security etc.). The description is to be consistent with the details submitted in the relevant permit applications, throughout both the EIA process and the development permission application process.

#### **1.2.2 Construction, Operational and production processes**

The relevant construction, operational and production processes and their main characteristics, including:

- The nature and quantity of materials used or generated;
- The source, type, quantity, composition and concentration of residues and emissions including water, air, soil pollution, noise, vibration, light, heat, radiation etc. resulting from the proposed project; the parameters to be reported should be in line with relevant EU policy; and
- The expected annual and total emissions, including Greenhouse Gases (GHG), and the contribution to total national GHG emission on an annual basis.

#### **1.2.3 Project management**

An indicative framework outlining the key parameters and site management arrangements during construction, operation and decommissioning phases, including:

- Works methodology, including any mineral processing plants such as batching plants within the construction site;
- Expected duration of all phases, as well as season, frequency and duration of interventions;
- Depths and volumes of excavation, type and fate of material to be excavated; and
- Types and quantities of raw materials and primary resources to be consumed, including water, energy, stone and other resources, and measures to reduce such consumption.

#### **1.2.4 Access, transportation and related infrastructure**

1. A forecast of the type, quantity and size of vehicles (and/or vessels) envisaged during each phase and their respective frequency of use, as well as an identification of the routes that vehicles will use to/from and within the site. The required arrangements should also be compared with the relevant existing situation (in terms of structural considerations, stability and state of roads, road width and gradient, turning circles and junctions, type of surfacing, and other physical or environmental constraints, etc). Interventions that would need to be carried out to accommodate the required vehicles (e.g. new or altered access roads), and sites/buildings/structures/features likely to be affected as a result, should be identified accordingly.
2. Facilities for the storage, parking, on-site servicing, loading/unloading of equipment, vehicles and other machinery.

#### **1.2.5 Water, sewerage, runoff management, energy, telecommunications, and ancillary infrastructure**

1. Estimates of water management specifications of the development and the identification of the sources of water to be used, including the following:
  - The features and processes of the proposed development and its ancillary facilities which consume water, including estimates of water consumption and runoff/effluent generation during operation;
  - The sources of water (e.g. second-class water, public potable water mains, on-site production) envisaged to meet the projected demand;
  - The water-saving measures, where applicable, that are envisaged (e.g. use of low-flow fittings, reuse of harvested storm water runoff and rainwater, treatment and reuse of grey water/sewage), and details as to how such water will be used/managed; and
  - The facilities and structures to be installed in connection with the above (e.g. water production, purification, collection, storage, distribution and saving) including estimates of the sizing of pipelines, reservoirs and equipment.
2. Estimates of the energy-related specifications, including:
  - The features and processes of the proposed development and its ancillary facilities which consume energy, including estimates of consumption during operation. The analysis should consider, as relevant, the connected load (in MW or MVA), the overall power factor, the annual MWh split in terms of end-use (lighting, climate cooling/heating/ventilation, plant etc.) which reflects the expected use of the facilities;
  - The energy sources envisaged to meet the projected demand;
  - The facilities and structures to be installed in connection with the above (e.g. energy production, storage, distribution and saving) including estimates of the sizing of cables, buildings and equipment; and
  - The expected energy performance of the proposal, including building orientation, natural ventilation, construction materials, integration of low/zero-carbon technologies to meet energy needs; avoidance of features which increase energy consumption; and energy efficiency measures in the finishing and operation of the development.
3. Infrastructural services and utilities related to water and power supplies, sewerage, telecommunications and runoff management, and ancillary works (e.g. trenches, tunnels, culverts, switching/transformer stations, pump houses, inspection chambers).
4. The extent to which the project can realistically be self-sufficient with regard to its energy and water needs, through appropriate measures such as the efficient use of energy and water, collection of rain and storm water for reuse, reuse of treated wastewater/sewage, technologies that reduce energy consumption, and the integration of alternative energy sources. Alternatives in terms of design, fabric and orientation of the buildings should also be explored and assessed.

### 1.2.6 Waste management

1. A sufficiently detailed indication of the waste management implications likely to arise from the project, including wastes generated by ancillary facilities and wastes which may arise from accidental spillages and leakages and from repair works. Wastes should be subdivided according to the relevant project phases.
2. The following information is to be provided for each waste stream, as relevant to each phase:
  - Identification of processes or activities that would result in waste generation;
  - European Waste Catalogue Codes for each waste stream, as per relevant legislation;
  - The projected quantities and rate of generation for each type of waste;
  - Information on waste handling and storage, on site as well as off site;
  - The method of transportation and frequency; and
  - The method of characterizing the chemical composition of dredged waste; where applicable.

This information should be presented in table format as follows, and should also include cross-references to the relevant regulations, particularly The Waste Regulations (S.L. 549.63):

Phase	Type of waste	EWC Code	H-Code	Activity (e.g. sanding, scraping, power washing etc.)	Estimated quantities	Final permitted disposal location

3. The envisaged waste management arrangements using the Best Practicable Environmental Options (BPEO) available, and the envisaged efforts to minimise waste generation and to divert waste to reuse or recycling rather than disposal.
4. Layout plans (to scale) clearly showing all relevant waste management infrastructure and related facilities (e.g. bunded areas for storage of waste fuels, wheel-wash facilities, etc.), clearly distinguishing between temporary and permanent structures for each phase.

### 1.2.7 Longer-term developments

Additional future developments, land uses and other commitments that are ancillary or consequent to the project or are likely to arise in relation to the same project or its expansion, as well as longer-term needs of the proposal, including: ancillary infrastructure not accounted for in the previous sections; any consequent interventions/arrangements required to accommodate the development; any foreseeable extensions or updates to the proposal; any displacement of existing uses; and decommissioning.

**Note:** Details in relation to the maturation area and areas that might be required during the construction phase are to be included in the EIA Report.

## 2.0 ASSESSMENT OF ALTERNATIVES

An outline of the main alternatives studied and an indication of the main reasons for this choice, taking into account the relevant environmental effects and their prevention (or optimisation) at source. The following alternatives need to be duly considered, as relevant to the development itself (or to one or more phases thereof) and its requirements and constraints:

- 2.1 Alternative sites
- 2.2 Alternative technologies including BAT and any relevant abatement measures<sup>1</sup>
- 2.3 Alternative layouts (including building heights, where relevant)
- 2.4 Downscaling of the project, or elimination of project components
- 2.5 Zero option (do-nothing scenario) - *i.e.* an assessment of the way the site would develop in the absence of the proposed project.  
*[Note: The zero option should be considered in sufficient detail as a plausible scenario in the EIA, wherever relevant, and not discarded upfront without proper discussion of its implications.]*
- 2.6 Hybrids/combinations of the above

The findings of the assessment of alternatives should be summarised in a table format for ease of comparison.

## 3.0 A DESCRIPTION OF THE SITE AND ITS SURROUNDINGS (I.E. ENVIRONMENTAL BASELINE)

The existing environmental features, characteristics and conditions, in and around the proposed development site as well as in all locations likely to be affected by the development or by ancillary interventions and operations, are to be identified and described in sufficient detail, with particular attention to the aspects elaborated further in the next sections.

The consultants should also identify (and justify) wherever relevant:

1. The geographic area (e.g. viewshed or other area of influence) that needs to be covered by each study;
2. The relevant sensitive receptors vis-à-vis the environmental parameter under consideration (e.g. residential communities, other users, natural ecosystems, specific populations of particular species, or individual physical features);
3. The location of the reference points or stations (e.g. viewpoints, monitoring stations, or sampling points (including depth of multiple sampling points at a single sampling point in the case of water media and sediment, where applicable) to be used in the study; and
4. Other methodological parameters of relevance, also noting that the assessment will normally require both desk-top studies and on-site investigations (including visual observations and sampling, as relevant).

*Note: It is recommended that these details are discussed in advance with the ERA prior to commencement of the relevant parts of the studies, in order to pre-empt (as much as possible) later-stage issues.*

Wherever relevant to the environmental aspects under discussion, reference to legislation, policies, plans (including programmes and strategies) standards and targets, should also be made, such that the compatibility (or otherwise) of the proposal therewith is also factored into the assessment required by **Section 4** below. The discussion should cover the following aspects, in the appropriate level of detail:

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<sup>1</sup> The technology employed and any infrastructure requirements are to be catered for at the design stage and is to be in line with *all applicable Best Available Techniques (Best available techniques in the slaughterhouses and animal by-products industries & Best available techniques waste incineration)*. Other horizontal BREFs may be applicable (emissions from storage/ energy efficiency/ industrial cooling systems).

- Supra-national (e.g. European Union; United Nations; or other international or regional) legislation, directives, policies, conventions, protocols, treaties, charters, plans and obligations;
- National legislation, policies and plans (e.g. Structure Plan; National Environment Policy); and
- Sub-national legislation, policies and plans (e.g. local plans, site-specific regulations, action plans, management plans, and protective designations such as scheduling or Natura 2000).

**Note:** In addition to already in-force legislation, policies and plans, the discussion should also cover any foreseeable future updates (or new legislation, policies and plans) likely to be fulfilled, affected or compromised by the proposed project. Furthermore, it should be noted that some cross-cutting legal/policy instruments (e.g. Water Framework Directive and Marine Strategy Framework Directive) may need to be factored into more than one aspect of the discussion.

### **3.1 Land Cover and Land/Sea Uses**

A description of the land cover and land uses (and/or sea uses, as relevant) within the area of influence of the project, including roads, footpaths and public access routes. Details including nature, magnitude, proximity to site, etc. should be included.

### **3.2 Landscape Character and Visual Amenity**

#### **3.2.1 Landscape Character**

The study should describe the landscape-related area of influence and landscape setting of the proposed site, identifying the component character areas and local landscape tracts, and the landscape elements, characteristics and degree of sensitivity thereof, so as to enable the prediction and assessment of:

- The changes to the landscape attributable (in full or in part) to the proposed development;
- The implications of such changes on the quality and perception of the landscape and its elements, in each of the identified landscape character areas and local landscape tracts; and
- The effects of such changes on relevant receptors (the receptors should also be duly identified and their degree of sensitivity should also be indicated and justified).

Reference should also be made to the 'Draft Landscape Assessment Study, 2004,' and to the *Guidelines for Landscape and Visual Impact Assessment (The Landscape Institute & IEMA)*, as relevant.

#### **3.2.2 Visual Amenity**

The following need to be identified and submitted for prior ERA approval:

- The Zone of Theoretical Visibility (ZTV; also known as Zone of Visual Influence) of the site and the development under consideration; and
- Assessment viewpoints representative of short-, medium- and long-distance views towards the site. A baseline photograph taken from each proposed viewpoint is also required. The submission should cover all the important views of the site, whilst avoiding the inclusion of superfluous or inappropriate viewpoints (e.g. positions from which the site is not visible, or where the view is obstructed or dominated by physical obstacles in the foreground).

Thereafter, for each approved viewpoint, the projected situation and appearance of the site (*i.e.* as it would look with the proposed development in place) should be compared to the current baseline situation (*i.e.* without the proposed development). The following should be predicted and assessed accordingly:

- The expected changes to visual amenity as a result of the proposed development;
- The effects of such changes on the quality of the visual amenity of the site; and
- The effects of such changes on relevant receptors. (The receptors should also be duly identified and their degree of sensitivity should also be indicated and justified).

**Note:** The baseline photographs and the photomontages should, unless otherwise directed by ERA, satisfy the following:

- (a) The location of each viewpoint should be shown on a map that also depicts the viewshed for the proposed site as described above. The visual angle of the photograph should also be indicated and should not be greater than 50°. Stitched photos that illustrate the field of vision towards the site from each viewpoint are acceptable as long as they are additional to the 50-degree photograph.
- (b) The photographs and photomontages submitted should:
- Be at least A3 in size. Strips which are A3 in width but not in length are not appropriate except as supplementary illustrative material;
  - Include the date and time at which the photo was taken;
  - Be of good quality, with faithful reproduction approximating as much as reasonably possible what would normally be visible to the naked eye. The photos should be taken in good weather, and should be taken at least 2 hours after sunrise and 2 hours before sunset. Colours should not be digitally or otherwise manipulated. As a guideline, the image should have a printing density of 200 dots per inch or better. In some instances, digital images having a resolution of 1024 x 728 or better may be required for multimedia presentation purposes;
  - Be taken in such a manner that near-field objects do not overpower or dominate features near the image plane passing through the project area;
  - Be taken from a height above ground level that is representative of the eye level of the viewer, and such height should be duly documented; and
  - Ensure that all additional/replacement structures and features depicted in the photomontages have a scale which proportionately tallies with the existing nearby features.
- (c) Wherever relevant, the photomontage(s) should cover the following scenarios:
- The development without the proposed landscaping scheme, representing the worst-case scenario;
  - The development complete with the proposed landscaping scheme as it is expected to look when the trees reach maturity, also providing an indicative timeframe as to when such maturity is expected to be attained; and
  - (where relevant in relation to impact of nocturnal lighting) the development and its ancillary lighting as it would appear during night-time.

### 3.3 Geology, Geomorphology, Hydrogeology, and Soils

A comprehensive investigation of:

1. The geology and geomorphology of the site and its surroundings, including:
  - (i) existing geology, stratigraphy, structure, lithology, physiography and geomorphology features;
  - (ii) palaeontological features;
  - (iii) hydrogeological features; and
  - (iv) soil types.

Each feature shall be listed in a table, together with a short description and if any of the features are absent, this shall be stated. A scaled map, clearly depicting the feature occurrence within the area of influence, shall also be provided.

2. The geo-technical properties and considerations relevant to the site and its area of influence, including:
  - (i) land stability;
  - (ii) mechanical, erosional and structural properties of the terrain and land mass;
  - (iii) any relevant fissures, faults, hollows, or weak points;
  - (iv) the vulnerability of the site to natural forces such as wave action, erosive elements, landslides and mass movements; and
  - (v) any other considerations affecting the implications and risks posed by the proposed development or by any of its ancillary interventions such as site clearance, earth-moving, and excavations.

Each of the above shall be listed in a table along with a short description and if any of the features are absent, this shall be stated. A scaled map, clearly depicting the feature occurrence within the area of influence, shall also be provided.

3. The quality of the material that will be excavated (including soil, rock/mineral resource, and any existing fill material) and its potential for reuse.

4. Sampling and testing should comply with the relevant standards (unless otherwise agreed, BS standards or other recognised equivalents should be used), and should extend to a sufficient depth below the deepest level of the proposed development (taking into consideration all proposed excavations and underground structures). Wherever the study involves the drilling of core samples, the number, depth and location thereof should also be submitted for ERA approval prior to carrying out of any *in situ* tests.
5. A method statement for land and groundwater testing in line with the ERA's 'Terms Of Reference for site clearance and land contamination investigations' in Appendix 2 shall be submitted.

The method statement is part of the baseline report pursuant to the Industrial Emissions (Integrated Pollution Prevention and Control) Regulations and in accordance with the European Commission Guidance concerning baseline reports under Article 22(2) of Directive 2010/75/EU on industrial emissions 2014/C 136/03 which is to be submitted to ERA. Such a baseline is to be carried out prior to start of operations.

### **3.4 Water bodies (including Terrestrial, Underground and Marine water bodies, as relevant)**

The study should identify the hydrological, hydromorphological and physicochemical characteristics of the water bodies, water resources and aquatic environments in the area under investigation, including (as relevant):

1. The hydrology of the site and its surroundings, including all relevant features and dynamics, such as: aquifers; springs; surface waters; wetlands; watercourses; valley catchments; etc, including a description of any potential linkages between different water bodies (i.e. groundwater linkages to surface waters, coastal water linkages to inland surface waters), also cross-referring to hydrogeological factors (see **Section 3.3** above) as relevant;
2. The type, size and physical characteristics of any aquifers and surface water bodies within the area of influence of the site, including: the nature of the water body (e.g. aquifer, flowing surface water, marine, etc.); whether the water body is ephemeral or permanent; and other characteristics such as depth/bathymetry; type of bottom and topography; prevailing currents and wave exposure; as well as physical and chemical characteristics of the water column which are deemed relevant for determination of hydrological characteristics such as nutrient status, temperature, salinity, dissolved oxygen and pH;
3. Natural and anthropogenic dynamics including groundwater recharge patterns; pumping and abstraction patterns; on-site and off-site drainage patterns; pipe/culvert connectivity between water bodies, run-off patterns; and flood risks;
4. Water quality (salinity, pollutant load, sediment load and characteristics, microbiological load, BOD & COD, transparency, temperature, etc.), with particular reference to any established quality parameters (e.g. legally-established bathing water quality parameters; effluent discharge parameters; objectives and requirements of the Water Framework Directive, Marine Strategy Framework Directive and related instruments); and
5. The study should provide a sufficiently detailed baseline to enable assessment of the effects of the proposal on the quality of the water body (terrestrial, underground and marine), the extent of area affected by hydrographical changes (terrestrial and marine), the nature of the changes (whether temporary or permanent) and effects of such changes on the ecological features and functions as described in line with Section 3.5. Such assessment should be undertaken in line with indicators used/established by relevant EU policy.

### **3.5 Ecology (including Terrestrial Ecology & Avifauna, as relevant)**

The assessment should include:

1. An investigation of the ecology of the site and its surroundings (including, as relevant: flora, fauna, avifauna, and their habitats and ecosystems), duly covering the relevant seasons (e.g. wet and dry seasons, in the case of terrestrial ecology) to ensure adequate coverage of all relevant species and ecosystem components;
2. A reporting of the conservation status and ecological condition of the area and the state of health of its habitats, species and ecological features;

3. A reporting of all protected, endangered, rare, unique, endemic, high-quality, keystone, invasive/deleterious, or otherwise important species, habitats, ecological assemblages, and ecological conditions found in the area under study; and
4. A prediction of the potential impacts of the proposed project on the ecology of the site and its surroundings, including loss, damage or alteration of habitats and species populations (including potential increases in ambient noise levels in the marine environment) including alteration in the habitats and species' condition/state of health as measured through indicators used/specified for assessment of status in relevant EU policy.

In particular, the study should identify all relevant species and assemblages (e.g. protected species or habitats, key species relevant to habitat characterisation, and monitoring indicators), and assess their abundance and distribution patterns as well as the species' ecological niches. The findings should be supported by adequate maps and photographs. Classification of habitat types and species should be conducted in accordance with recognised classification systems (e.g. EUNIS and Palaeartic), to ERA's satisfaction.

**Note 1:** A stand-alone Appropriate Assessment in terms of the Flora, Fauna and Natural Habitats Protection Regulations (S.L. 549,46) is required, for which separate Terms of Reference are issued.

**Note 2:** Where the area of influence encompasses both marine and terrestrial environments, one or more of the sections indicated in these specimen TORs may need to be restructured accordingly to reflect the specific circumstances (e.g. separate reports for marine and terrestrial ecology).

### 3.6 Agricultural land

The study should identify any agricultural land within the area of influence of the development, and should provide a clear and reasonably detailed indication of:

1. The physical quality and productivity of the land, justifying the indicators used in this regard. Soil depths, textures, and properties should also be described in the relevant level of detail;
2. Whether the land is dry land, irrigated land, recently reclaimed land, long-abandoned land with an established trend toward regeneration of natural vegetation, or otherwise;
3. The main crops and trees cultivated in the surrounding area, as a meaningful indicator of longer-term quality and potential of the cultivable fields. In this regard, emphasis is to be laid on appropriate and representative indicator crops, avoiding overly precise but superficial field-by-field snapshots of all crops that happen to be under cultivation at a given point in time. For similar reasons, superficial indicators based on transitory factors (e.g. fallow land, currently abandoned land; or underutilised land) are insufficient and potentially distortive, and for a more representative baseline the investigation needs to look more deeply into how the land was used over the past years;
4. Any agroecosystems and related interactions including the living and non-living components (e.g. dry-stone rubble walls, associated natural and man-made habitats etc) that are currently coexisting with established agricultural activity or are being maintained in connection with such activity;
5. All relevant ancillary aspects (e.g. irrigation water sources, access routes, land drainage patterns, exposure and microclimate, holding sizes and configurations) that may be lost, displaced or otherwise affected by the proposed development; and
6. Any baseline environmental pressures and exceedances (e.g. pollution) resulting from agricultural activity, that may be directly or indirectly relevant to the proposed development, particularly any aspects that will be displaced, abated or compounded as a result of the development.

### 3.7 Architectural, Archaeological, Historical & Cultural Heritage and related Material Assets

Refer to Appendix 3.

### 3.8 Air Quality

This study should clearly establish the current background levels of pollution (including dust, chemical emissions such as VOCs, and odours) and should include a clear comparison to the relevant reference and limit values as specified in the relevant legislation as well as in any other relevant guidance documents. Details on prevailing wind and climate conditions should also be included, amongst other relevant parameters.

The methodology to be used should be submitted for ERA's evaluation prior to commencement of the studies. The Air Quality Study shall be conducted in accordance with the terms of reference in Appendix 4.

### **3.9 Noise, Vibrations and Exterior Lighting**

A qualitative statement providing sufficiently detailed information from noise generating equipment, vibration and nocturnal lighting (as relevant). This should also take into account other relevant factors such as:

- Sensitive receptors (e.g. residents, recreational areas, fauna and avifauna, natural ecosystems); and
- The potential for attenuation or exacerbation by 'environmental' factors (e.g. topography, vegetation, physical barriers etc.), and for mitigation (e.g. shielding, muffling/soundproofing, reduced lighting, etc.).

*Note 1: In the case of light pollution, the study needs to consider, among others, glare (e.g. the blinding light which is a danger to motorists/pedestrians and to fauna), light trespass (light straying into an area where it is not desired or required) and sky glow ('wasted' light directed upwards), together with any other relevant variables which are relevant to the determination of impact on the surrounding receptors.*

*Note 2: ERA's request for a qualitative study does not need to include baseline monitoring. The study should consist in a desk study outlining the qualitative impact from the operations of the plant on the nearby receptors.*

### **3.10 Infrastructure and Utilities**

The assessment should investigate the currently available infrastructural services (including water supply, energy supply, sewerage, telecommunications infrastructure, access roads, parking, etc.), including details about their carrying capacity, physical condition and other relevant practical considerations. It should also compare this information to the infrastructural demands of the project as identified in **Section 1** above, so as to clearly indicate:

1. whether the current utilities are adequate to meet the demand arising from the proposed development;
2. whether any significant loading, congestion or damaging of the infrastructural or transport network is envisaged; and
3. whether any new or upgraded services/arrangements will be rendered necessary, both in the short-term and in the longer-term. If any requirement for new infrastructure (or upgrading, alteration or extension of the existing infrastructure) is envisaged, the relevant details including associated works and their environmental implications should also be indicated.

The assessment should also identify any existing or projected infrastructural services located within the area of influence of the development (even if not related to the demands of the development) that might be affected by the development or which may need to be displaced or diverted as a consequence of the development or its ancillary operations and interventions.

### **3.11 Other relevant environmental aspects and features**

Other relevant environmental features or considerations not identified in the preceding sections should also be identified and described, as relevant.

## **4.0 ASSESSMENT OF ENVIRONMENTAL IMPACTS AND ENVIRONMENTAL RISKS**

All likely significant effects and risks posed by the proposed project on the environment during all relevant phases (including construction/excavation/demolition, operation and decommissioning) should be assessed in detail, taking into account the information emerging from Sections 1, 2 and 3 above. Apart from considering the project on its own merits (*i.e.* if

taken in isolation), the assessment should also take into account the wider surrounding context and should consider the limitations and effects that the surrounding environmental constraints, features and dynamics may exert on the proposed development, thereby identifying any incompatibilities, conflicts, interferences or other relevant implications that may arise if the project is implemented.

In this regard, the assessment should address the following aspects, as applicable for any category of effects or for the overall evaluation of environmental impact, addressing the worst-case scenario wherever relevant:

1. An exhaustive identification and description of the envisaged impacts;
2. The magnitude, severity and significance of the impacts;
3. The geographical extent/range and physical distribution of the impacts, in relation to: site coverage; the features located in the site surroundings; whether the impacts are short-, medium- or long-range; and any transboundary impacts (*i.e.* impacts affecting other countries);
4. The timing and duration of the impacts (whether the impact is temporary or permanent; short-, medium- or long-term; and reasonable quantification of timeframes);
5. Whether the impacts are reversible or irreversible (including the degree of reversibility in practice and a clear identification of any conditions, assumptions and pre-requisites for reversibility);
6. A comprehensive coverage of direct, indirect, secondary and cumulative impacts, including:
  - interactions (*e.g.* summative, synergistic, antagonistic, and vicious-cycle effects) between impacts;
  - interactions or interference with natural or anthropogenic processes and dynamics;
  - cumulation of the project and its effects with other past, present or reasonably foreseeable developments, activities and land uses and with other relevant baseline situations; and
  - wider impacts and environmental implications arising from consequent demands, implications and commitments associated with the project (including: displacement of existing uses; new or increased pressures on the environment in the surroundings of the project, including pressures which may be exacerbated by the proposal but of which effects may go beyond the area of influence; and impacts of any additional interventions likely to be triggered or necessitated by situations created, induced or exacerbated by the project);
7. Whether the impacts are adverse, neutral or beneficial;
8. The sensitivity and resilience of resources, environmental features and receptors vis-à-vis the impacts;
9. Implications and conflicts vis-à-vis environmentally-relevant plans, policies and regulations;
10. The probability of the impacts occurring; and
11. The techniques, methods, calculations and assumptions used in the analyses and predictions, and the confidence level/limits and uncertainties vis-à-vis impact prediction.

The impacts that need to be addressed are detailed further in the sub-sections below.

#### **4.1 Effects on the environmental aspects identified in Section 3**

The assessment should thoroughly identify and evaluate the impacts and implications of the project on all the relevant environmental aspects identified in Section 3 above, also taking into account the various considerations outlined in the respective sections.

With regards to Section 3.4 and 3.5 above, the ecological status of the area in question is to be evaluated, taking into consideration the definition of status by relevant EU Policy, and assessing the extent to which the project will cause deterioration in status or compromise the achievement of good status in line with Article 4(7) of the EU Water Framework Directive.

#### **4.2 Impacts related to Climate Change and Climate Change Adaptation**

The assessment should address the following aspects, as relevant:

1. The contribution of the project to greenhouse gas (GHG) emissions and climate change, including:

- (i) The direct, indirect and off-site GHG emissions and related impacts during all relevant phases of the project, including those arising as a result of the electrical power demand of the project;
  - (ii) Any massive GHG emissions that may occur as a consequence of accidents or malfunctions;
  - (iii) The impacts of the proposal on carbon sinks (e.g. wooded/afforested areas, agricultural soils, landfills, wetlands, and marine environments);
  - (iv) The components of the project that are expected to contribute to renewable energy generation on site or to a reduction in GHG emissions through substitution of current generation facilities, including a quantification and critique of their reliability and actual net contribution to climate change mitigation as well as an identification of the impacts of such components on other aspects of the environment (e.g. landscape, land take, avifauna); and
  - (v) The implications of the project and its operations and ancillary demands on National GHG emission targets.
2. The implications of climate change on the proposal, including:
- (i) The aspects/elements of the project that are likely to be affected by changes or variability in climate-related parameters (e.g. temperature, humidity, weather patterns, sea level, etc.);
  - (ii) The potential impacts that such changes may have on the proposal, including any possible impacts resulting from changes to multiple parameters; and
  - (iii) The adaptability of the project and its components and operations vis-à-vis the relevant climate change parameters and trends.

#### **4.3 Environmental risk**

The assessment should also address, in sufficient detail, any relevant environmental risk (including major-accident scenarios such as contamination, emissions, explosions, blast, flooding, major spillages, etc.) likely to result in environmental damage or deterioration. The range of accident scenarios considered should exhaustively cover, as relevant:

1. one-time risks (e.g. during construction or decommissioning works);
2. recurrent risks during project operation; and
3. risks associated with extreme events (e.g. effect of earthquakes or natural disasters on the project).

The assessment should include, as relevant: a quantification of the risk magnitude and probability; and risk analysis vis-à-vis any hazardous materials stored, handled, or generated on site or transported to/from the site.

**Note:** Should the proposal fall within the scope of the Seveso/COMAH regulations, a stand-alone Risk Assessment may be required, to the satisfaction of the relevant Competent Authority. In such instances, separate Terms of Reference are issued for the Risk Assessment.

#### **4.4 Effects on Human Populations resulting from impacts on the environment**

This assessment should also identify any impacts of the development on the surrounding and visiting population (e.g. effects on public health), that may result from impacts on the environment. In the case of health-related effects, reference should be made to published epidemiological and other studies, as relevant, and the views of the Environmental Health Directorate should be sought.

#### **4.5 Other Environmental Effects**

Any other environmental effects deemed relevant to the project but not fitting within any of the above sections should also be identified and assessed.

##### *Cumulative impacts*

The cumulation of the effects of the project with those of other existing and/or approved projects and other waste management facilities as identified within the Waste Management Plan (2021-2030). This shall take into account existing environmental problems, areas of particular environmental importance likely to be affected, and the use of natural resources.

## **5.0 REQUIRED MEASURES, IDENTIFICATION OF RESIDUAL IMPACTS, AND MONITORING PROGRAMME**

### **5.1 Mitigation Measures**

A clear identification and explanation of the measures envisaged to prevent, eliminate, reduce or offset (as relevant) the identified significant adverse effects of the project during all relevant phases including construction, operation and decommissioning [see **Section 1.2.3** above].

As a general rule, mitigation measures for construction-phase impacts should be packaged as a holistic Works Method Statement (WMS). Whilst the detailed workings of the WMS may need to be devised at a later stage (e.g. after the final design of the project has been approved and/or after a contractor has been appointed), the key parameters that the WMS must adhere to for proper mitigation need to be identified in the EIA. Broadly similar considerations also apply vis-à-vis operational-phase impacts [which may need to be mitigated through an operational permit] and decommissioning-phase impacts [see **Section 5.4** below], where relevant.

Mitigation measures for accident/risk scenarios should be packaged as a holistic plan that includes the integration of failsafe systems into the project design as well as well-defined contingency measures.

The recommended measures should be feasible, realistically implementable to the required standards and in a timely manner, effective and reliable, and reasonably exhaustive. They should not be dependent on factors that are beyond the developer's and ERA's control or which would be difficult to monitor, implement or enforce. The actual scope for, and feasibility of, effective prevention or mitigation should also be clearly indicated, also identifying all potentially important pre-requisites, conditionalities and side-effects.

### **5.2 Residual Impacts**

Any residual impacts [*i.e.* impacts that cannot be effectively mitigated, or can only be partly mitigated, or which are expected to remain or recur again following exhaustive implementation of mitigation measures] should also be clearly identified.

### **5.3 Additional Measures**

Compensatory measures (*i.e.* measures intended to offset, in whole or in part, the residual impacts) should also be identified, as reasonably relevant. Such measures should be not considered as an acceptable substitute to impact avoidance or mitigation.

If the assessment also identifies beneficial impacts on the environment, measures to maximise the environmental benefit should also be identified.

In both instances, the same practical considerations as indicated vis-à-vis mitigation measures should also apply.

### **5.4 Decommissioning Plan**

A decommissioning plan (DP) should also be proposed to address the following circumstances, as relevant:

1. Removal of any temporary or defined-lifetime development (or of any structures, infrastructure or land use required temporarily in connection with it) upon the expiry of their permitted duration; and
2. Removal of the development (or of any secondary developments, infrastructure or land use ancillary to it) in the event of redundancy, cessation of operations, serious default from critical mitigation measures, or other overriding situations that may emerge in future.

The DP should also include, as relevant, a phasing-out plan, proposals for site remediation or decontamination, and methodological guidance on site reinstatement or appropriate after-use.

### **5.5 Monitoring Programme**

A realistic and enforceable programme for effective monitoring of those works envisaged to have an adverse or uncertain impact. The monitoring programme should include:

1. Details regarding type and frequency of monitoring and reporting, including spot checks;
2. The parameters that will be monitored, their units of measurement, the monitoring indicators to be used; and standard analytical methods in line with relevant EU policy;
3. An effective indication of the required action to address any exceedances, risks, mitigation failures or non-compliances for each monitoring parameter;
4. An evaluation of forecasts, predictions and measures identified in the EIA; and
5. An indication of the nature and extent of any additional investigations (including EIAs or ad hoc detailed investigations, if relevant) that may be required in the event of any contingencies, unanticipated impacts, or impacts of larger magnitude or extent than predicted.

The programme should address all relevant stages, as follows:

- (a) Where relevant, monitoring of preliminary on-site investigations that may entail significant disturbance or damage to site features (e.g. archaeological excavations, geological sampling, or any works that require prior site clearance or any significant destructive sampling);  
*[Note: Official written consent from the competent authorities (e.g. Superintendence of Cultural Heritage) may also be required for such interventions.]*
- (b) Monitoring of the construction phase, including the situation before initiation of works (including site clearance), during appropriate stages of progress, and after completion of works;
- (c) Monitoring of the operational phase, except where otherwise directed by ERA (e.g. where monitoring would be more appropriately integrated into an operating permit); and
- (d) Where relevant, monitoring of the decommissioning phase, including the situation before initiation of works, during appropriate stages of progress, and after completion of works.

## **5.6 Identification of required authorisations**

The assessment should also identify all environmentally-relevant permits, licences, clearances and authorisations (other than the development permit to which this EIA is ancillary) which must be obtained by the applicant in order to effectively implement the project if development permission is granted. Any uncertainty, as to whether any of these pre-requisites is applicable to the project, should be clearly stated.

### **Note on Sections 5.1 to 5.6 above:**

The expected effects, the proposed measures, the residual impacts, the proposed monitoring etc. should also be summarised in a user-friendly itemised table that enables the reader to easily relate the various aspects to each other. An indicative specimen table is attached in **Appendix 5**.

**Signed Declaration: Conflict of interest**

**Signed declaration in accordance with sub-regulation 17(3):**

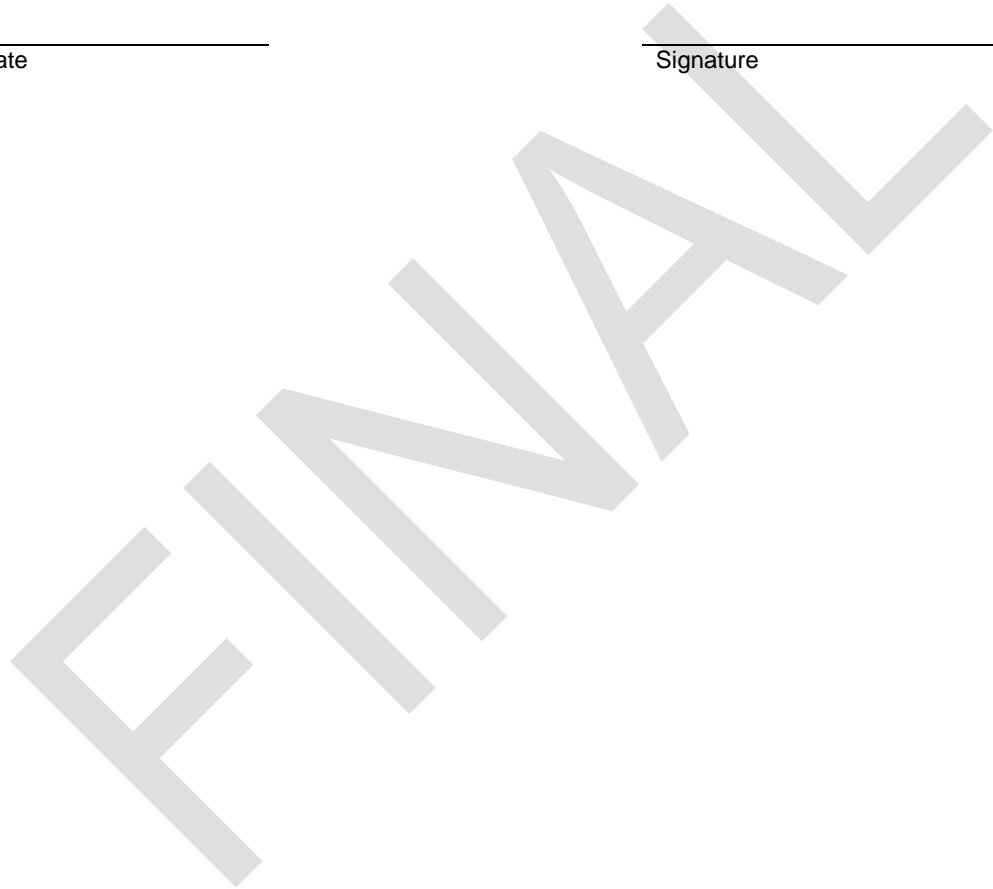
This declaration is to be submitted with each environmental survey report forming part of the EIA.

Attn: Director Regulatory Affairs (ERA).

I, \_\_\_\_\_, hereby declare that, I have no personal or financial interest in the proposed development. Moreover, I declare that I am not in any way associated with any individual, company, association or grouping that has any direct or indirect, personal, professional or financial interest in the proposed development.

\_\_\_\_\_  
Date

\_\_\_\_\_  
Signature



## TERMS OF REFERENCE FOR SITE CLEARANCE AND LAND CONTAMINATION INVESTIGATIONS (VERSION 6; NOVEMBER 2021)

The following terms of reference have been compiled on the basis of BS 10175:2011+A2:2017

In view of the current state of the site and activities carried out to date which could potentially have led to land and groundwater contamination, clearance of the site and preliminary investigations for contamination are required. The documents detailed in the terms of reference below are to be approved by ERA prior to the commencement of any works on site. Malta Resources Authority (MRA) and Energy and Water Agency (EWA) shall also be notified of the activities on site so they will be able to take any action from their end that they may deem necessary. Should the site bear any legal restrictions / protections, consultation should be carried out with the relevant authorities.

### **1. Land and groundwater investigations**

A proposal for land and groundwater investigations is to be submitted, prepared by experts in the field upon consultation with MRA and EWA (in relation to groundwater), which should include a chemist and/or a hydro geologist, with at least three years' experience in designing land and groundwater monitoring proposals and assessing land and groundwater contamination. Collection of samples should also be carried out by suitably qualified / certified persons familiar with the required methods.

CVs of the persons involved in developing and carrying out the land contamination survey, including assessment of the results, are to be submitted for approval by ERA prior to development of the proposal detailed below.

The proposal for land and groundwater investigations is to include the following:

- a. An overview of the site history including details on the activities carried out (such as illegal dumping and incineration of wastes) and the type of wastes that have been deposited on site and that could have led to land contamination. If information is not available, expert judgment should be used regarding assumptions on the type of activities and wastes associated with such sites and directly associated contaminants.
- b. A conceptual site model (CSM) is to be developed indicating:
  - i. Which areas have been used for the different activities (known / assumed);
  - ii. Which areas could have been potentially contaminated by said activities (clearly indicating the sources of contamination identified through the site history, related information and/or assumptions on activities and materials handled / deposited / incinerated), and
  - iii. The extent of areas that could have been affected through the different potential pathways of contamination identified; this needs to take into consideration sub-surface soils, groundwater and surface waters, potentially contaminated through direct exposure, leaching and run off, within and outside the site.
  - iv. The ecology, geology, hydrogeology and topography of the site and surrounding area shall be taken into account during the development of the CSM.
  - v. The proximity of the site to other potential sources of contamination that could have an impact on the site.
- c. A risk assessment evaluating the environmental setting of the site and identifying any sensitive receptors that may be impacted by potential contamination present within the site.
- d. Provide rationale / justification for the area of influence proposed for the preliminary investigation, and the number, location and depths of sampling points, making reference to the CSM. It should be noted that the number of sampling points should be statistically representative for the area under investigation, and ensure adequate coverage of the site as well as the greater area of influence (in line with requirements in Table 1 below). In view that groundwater could potentially have been contaminated; sampling of

groundwater also needs to be included, preferably making use of existing boreholes<sup>2</sup>. Consultation with the MRA and EWA is required in this regard.

- e. Based on the CSM developed, sampling locations shall be set to target locations being of a known or suspected source of contamination (ex. existing tanks, waste storage areas etc.) or observed environmental impact. Sampling locations may be set to target potential migration routes of mobile contaminants from such sources. The authority may instruct the person to carry out sampling from specific points in the case where reasonable suspicion persists on potential land contamination.

Should defined sources of contamination as described above not be identified by the CSM, the sampling locations proposed are to be evenly distributed to cover the entirety of the site.

- f. The following table is an indication of the expected sampling effort. Sampling locations shall not be set at a distance greater than 50m from each other. This may require modification based upon the CSM developed.

**TABLE 1: SAMPLING REQUIREMENTS PER AREA OF INVESTIGATION.**

SITE (square m <sup>2</sup> )	LAND	GROUNDWATER	
	DRILLING/ TRENCHES	DRILLING WELLS	SAMPLING
< 5,000	At least 2 points	At least 1 point	n. 1 samples per point
5,000 - 10,000	At least 5 points	At least 3 points	n. 1 samples per point
10,000-50,000	From 5 to 15 points	From 4 to 6 points	n. 1 samples per point
50,000-250,000	From 15 to 60 points	From 6 to 10 points (subject to a risk analysis ) <sup>3</sup>	n. 1 samples per point

- g. Samples from various depths are to be taken from each sampling location identified<sup>4</sup>. The first sample is to be within 0.5m from the surface, subsequent sampling depths are to be set at intervals of 1m. The extent of investigation for each sampling location is to be:
- i. A minimum depth of 4m  
OR
  - ii. until the target depth has been reached if this extends beyond the boundaries set in (i) above.  
OR
  - iii. until proposed excavation depth is reached  
OR
  - iv. a different geological stratum has been encountered.

<sup>2</sup> To note that drilling of any borehole requires authorization from the Competent Authority, and drilling works must comply with the provisions of S.L. 423.32; drilling rigs must also be registered with the Competent Authority as per S.L. 545.06.

<sup>3</sup> If such plants are located inland, the drilling of 6 to 10 monitoring points per plant is considered to increase the pollution potential of the plants and acceptability would need to be assessed on a case by case basis.

<sup>4</sup> The Authority may amend sampling depths on a case-by-case basis.

- h. Provide information on sampling procedure to be followed including:
- i. The drilling/coring equipment to be used;
  - ii. Any *in-situ* testing that may be required (ex. PIF / FID)
  - iii. Methods to be followed during sampling to ensure cross-contamination does not occur and that samples are handled/stored appropriately until delivery to the lab for testing;
  - iv. Proposed method for backfilling of voids left by extraction of cores including the use of appropriate impermeable compounds such as bentonite.

It should be noted that dry-drilling is recommended to avoid flushing and dispersion of the contaminants which may be present

- i. Provide rationale / justification for contaminants selected for analysis of land and groundwater samples based on the site history and CSM developed. Consultants are to provide a list of contaminants to be investigated in this regards. Proposed omission of analytes is to be duly justified.

The assessment should consider analysis for:

- Heavy metals
- Total organic carbon (TOC)
- Hydrocarbons
- BTEX
- Dioxins & furans
- Cyanide
- Fluoride
- MTBE
- PAHs<sup>5</sup>
- PCBs
- Chlorinated aliphatic hydrocarbons
- Halogenated aliphatic hydrocarbons
- Asbestos

ERA may request testing for additional contaminants other than those proposed depending on the results obtained during the works on site as well as following consultation with MRA and EWA.

- j. EPA, ISO, EN or equivalent standards to be used to test for the different contaminants shall be provided, together with the detection limits. Certification of the laboratory/ies chosen for testing is to be provided; Laboratory is to be accredited to at least EN ISO 17025:2005/Cor 1:2006 and accredited for each and every analysis<sup>6</sup>.
- k. Sample containers are to be sealable and of the appropriate material so as not to cause contamination of the sample, absorb any sample components nor allow losses of volatile compounds. Routinely, wide-mouth amber glass containers are used for analyses of non-volatile organic compounds and PET containers for water-soluble analyses. Containers with a pierceable-septum screw cap can be used to allow for head space analysis for VOCs as required. Any container pretreatment is to be specified. The use of appropriate containers is to be determined in conjunction with the instructions provided by the analyzing lab.
- l. Collected samples are to be maintained at 4°C - 8°C and retained in darkness at all times up to delivery to the analyzing lab. Samples collected from land are to be maintained under such conditions upon immediate retrieval from the ground and dispatched for analysis at the earliest. Samples to be kept for long-term storage pending further testing shall be maintained at -20°C.
- m. Drilling logs and photographs are to be taken of the collected cores in their entirety and presented in the final report.
- n. Locations of core samples are to be confirmed with the Authority on-site prior to initiation of works.

<sup>5</sup> 16 PAHs: Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k) fluoranthene, Benzo(g, h,i) perylene, Chrysene, Naphthalene, Anthracene, Phenantrene, Fluoranthene, Dibenzo(a, h)anthracene, Indeno (1,2,3 – c,d) pyrene, Pyrene, Acenaphthylene, Acenaphthene, Fluorene

<sup>6</sup> Unless substantiated that accreditation is not technically feasible for certain analytes.

- o. The results of the investigation and their interpretation are to be presented in a report which includes:
  - i. Description of ground conditions encountered at the site, including groundwater regime and surface water features
  - ii. Cross-sections showing site strata and shallow and deep groundwater levels
  - iii. Summary tables of chemical analyses and site monitoring
  - iv. Description of type, nature and spatial distribution of contamination, with plans where appropriate
  - v. Statistical analysis of the data set and derivation of representative concentrations for individual contaminants to a suitable level of statistical significance
  - vi. Evaluation of site investigation results against the outline conceptual model
  
- p. Further to (o), presentation of the raw data is to be included as an Annex to the report including:
  - i. Plans showing monitoring and sample point locations including the GPS coordinates
  - ii. Description of site works and on-site observations
  - iii. Exploratory borehole (where applicable), core or drilling logs including the GPS coordinates (UTM WGS 84).
  - iv. Details of response zone and other construction details of borehole monitoring installations
  - v. Monitoring results
  - vi. Description of samples submitted for analysis
  - vii. Relevant Quality Assurance/Quality Control (QA/QC) data – this may include accreditations of staff, calibration certificates of equipment, laboratory accreditations (national and international standards)
  - viii. Laboratory analytical reports, completed in accordance with the relevant QA/QC data, including relevant
  - ix. international analytical or test method standards

## **2. Clearance of the site**

Method Statement is to be submitted outlining how clearance of the site shall be carried out, including:

- a. Details of when site is planned to be cleared.
- b. How all wastes shall be identified and separated according to the different waste streams as per European Waste Catalogue (EWC) codes defined in Commission Decision 2000/532/EC. A list of these wastes and projected quantities is to be included.
- c. How all wastes shall be characterised according to the hazard properties (HP) codes as per The Waste Regulations - S.L. 549.63, Schedule 3.
- d. Indicate disposal facilities for all wastes stream identified on site. In this regard it should be noted that:
  - i. All wastes leaving the site after storage and/or processing must only be sent to facilities licensed to accept the individual waste stream, either locally or abroad.
  - ii. Only registered waste carriers as per activity 38 of Schedule 1 in S.L. 549.45 - Waste Management (Activity Registration) Regulations, 2007 are allowed to transport waste to and from this site.
  - iii. The applicant shall keep records for every consignment of wastes removed from the site indicating the EWC Code, description, quantities, date of removal, contractor name (including for transport), consignment note number (where applicable) and manner and place of final disposal/recovery. Such records will need to be submitted as part of the final report submitted to ERA for approval documenting the site clearance.
  - iv. Contaminated excavated material are to be managed and disposed of as waste.
  - v. Wastes identified as inert are to be tested if suspected to be contaminated by other deposited material.
  - vi. Should any of the excavated material from the contaminated land be destined for disposal in a landfill, in addition to the abovementioned characterisation analysis, leaching tests should be carried out according to the Waste Acceptance Criteria

set out in Council Decision 2003/33/EC.

- vii. Should any of the excavated material from the contaminated land be destined for disposal at sea, testing for additional parameters may be requested in addition to the abovementioned characterisation analysis, in line with ERA's [Terms of Reference for the Management and Disposal of Dredged Material](#).

**Aspects indicated in Parts 3 and 4 below will need to be included in the final report submitted to ERA (post survey/analysis), which should include the results of the investigation and assessment thereof.**

### **3. Way Forward following site clearance and land/groundwater investigations**

Action may be required by ERA depending on the levels and location of contamination found. The requirement for remediation will depend on the eventual associated risk to human health and the environment from any contamination of land and groundwater, which would need to be assessed following a preliminary screening of the results obtained from the preliminary investigations.

The engagement of experts for further investigations/assessments and proposals for land decontamination and remediation may be required following the preliminary assessment of contamination. Consultation with MRA will also be required in the event of risks to groundwater.

### **4. Documents to be submitted**

- a. List of consultants to be commissioned for approval by ERA
- b. Land investigation proposal for approval by ERA
- c. Method Statement for site clearance for approval by ERA
- d. Site clearance report following works
- e. Land investigation report.

Further assessment may be required depending on the results obtained.

## **APPENDIX 3: TERMS OF REFERENCE FOR A CULTURAL HERITAGE ASSESSMENT (AS PROVIDED BY THE SUPERINTENDENCE OF CULTURAL HERITAGE, AS REVISED IN OCTOBER 2013)**

### **1.0 Preamble**

The proposed project would involve development over an extensive area and may lead to intensification of activity over a larger area. Potential impacts may occur within the footprint of the project, in the immediate environs, and along access routes to the site. Potential impacts may include direct and immediate material impacts, as well as subsequent impacts that might arise from the modification of the existing situation.

### **2.0 Scope and Definitions of the EIA**

For the purposes of this document, cultural heritage is defined by Article 2 of the Cultural Heritage Act (2019). This includes movable or immovable objects of artistic, architectural, historical, archaeological, ethnographic, palaeontological and geological importance.

2.1 The study area shall include the total footprint of the proposed development.

2.2 In the context of this particular application, cultural heritage considerations may include:

- Features of archaeological value and potential;
- Military or civil architecture from the Knights period to British period;
- Vernacular structures; and
- Field systems and agricultural features such as irrigation systems.

The above cultural heritage definitions and considerations are not to be considered as exhaustive. The EIA must consider all other forms of cultural heritage, both known and unknown.

2.3 The Environmental Impact assessment will:

- Describe the Cultural Heritage assets within the study area;
- Analyse the cultural heritage features within the context of the cultural landscape;
- Assess the physical, spatial and visual impacts of the proposed development on the cultural heritage assets; and
- Propose corrective measures for the protection of the cultural resources.

### **3.0 Methodology**

In quantifying the cultural heritage assets within the study area, and assessing the impacts of the proposed development, the EIA will undertake:

- Description and assessment of the property;
- Desktop and archival research limited to the study area;
- Fieldwork and research, including "field walking", topographic survey and remote sensing as may be necessary within the site. All fieldwork has to be authorised by the Superintendence of Cultural Heritage as defined below under point 4;
- Consultations with any relevant bodies, including the Superintendence of Cultural Heritage, Heritage Malta, the University of Malta, NGOs and Local Councils;
- Compilation of an inventory of the cultural heritage assets identified within the study area. The features of cultural heritage are to be described and plotted with grid references, on Data Capture Sheets, the design of which should be approved in advance by the Superintendence of Cultural Heritage. The Data Capture Sheets will be presented as an appendix to the EIS. The analysis of the features will be included in the main report; and
- A cultural heritage Risk Assessment Map examining the various impacts of the proposed project is to be included in the EIA.

### **4.0 Authorisation by the Superintendence of Cultural Heritage**

As per Cultural Heritage Act 2019, any form of investigation or prospection required for the identification of cultural heritage (including excavation, field walking, topographic survey and remote sensing) may only be undertaken by the Superintendence of Cultural Heritage or with its written approval.

PROTECTIVE INVENTORY OF THE MALTESE CULTURAL HERITAGE HERITAGE DATA CAPTURE SHEET						Ref. No.
Location	Category	Type	Site Location ( Address )			
Eastings	Northings	Feature	Period - Year			
S.S. No. 1	S.S. No. 2	Description				
S.S. No. 3	S.S. No. 4					
Date						
Negative No.	Film No.					
Present Utilization						
Existing Legal Protection		GN. Number	GN. Date			
Comments						
Buffer Zone	A	B	C	D	E	Others
Eastings						
Northings						
Site Map						
Scale 1 : 2500						

Archaeological Characteristics – Sketch/Scaled drawings:	
Condition:	Degree of Protection (Structure Plan policies UCO7 or ARC 2):
State of Security:	Proposed Utilization:
Basic Bibliography:	
Compiled by:	Revised by:
Checked by:	Checked by:
Date:	Date:

## **APPENDIX 4: TERMS OF REFERENCE FOR THE DISPERSION MODELLING OF INCINERATOR EMISSIONS**

### **Part A. Stack height and effect of stack emissions on deposition rates and emissions loads**

#### **A.1 SCOPE**

To use dispersion modelling suites, in order to assess for the likelihood of significant effects on ambient air quality (including exceedances of the ambient limit values in SL.549.59) as well as on the deposition levels of particular components, due to the operation of a Thermal Treatment facility. The analysis should focus on the area of influence of the facility, and should include the sensitive receptors in this area. For the deposition levels, the sensitive receptors shall include ALL farms within this area.

The study shall be repeated at predetermined intervals and using in-stack emissions data from the plant.

#### **A.2 DEFINITION**

The “area of influence - AOI” means the contour around the plant in which the contribution of the plant to the annual ambient levels of NO<sub>2</sub>, PM<sub>10</sub> or PM<sub>2.5</sub> is 0.3 µg/m<sup>3</sup> for NO<sub>2</sub> or 0.3 µg/m<sup>3</sup> for PM<sub>10</sub> or 0.19 µg/m<sup>3</sup> for PM<sub>2.5</sub>, whichever results in the largest AOI. If the area of the AOI is < 113 km<sup>2</sup> then the AOI shall be assumed to be a circle of radius 6 km centred on the chimney.

#### **A.3 TECHNICAL SPECIFICATIONS**

##### **A.3.1 Point source modelling**

The modelling suite used throughout this exercise shall be capable of incorporating all the substances included in these terms of reference. Any emission factors used shall be European emission factors preferably based on plants similar (same manufacturer and operating conditions) to the one under study. The model must be capable of predicating the dispersion and deposition of pollutants under variable meteorological conditions ranging from the most favourable to the least favourable.

The modelling suite shall model annual levels of the required parameters.

A few examples of acceptable dispersion models are ADMS, AERMOD, and IMMIS. Other dispersion models may be accepted provided that the requirements in this document are met. The spatial resolution achievable by the model shall be 5 × 5 m<sup>2</sup>, to enable the identification of impacts at sensitive receptors.

The model shall include a meteorological processor and a terrain processor (i.e. capable of modelling dispersion over a complex terrain).

Rather than using the Pasquill-Gifford stability classes, the model shall rely on the use of the Monin-Obukov lengths.

The model shall be capable of modelling the effect of the interaction of the pollutant(s) from the plant with natural or man-made structures (e.g. aerodynamic downwash, cavity and wake effects, amongst others).

The consultants shall provide documentation that the chosen model has been utilised in any one of the 27 EU member states, for regulatory applications involving the local scale effects of point sources on air quality.

For particulate matter, both primary and secondary particulate shall be modelled.

In addition, the total deposition of certain pollutants shall be modelled.

The consultants shall be obliged to follow industry best practice standards in respect of quality assurance requirements of the dispersion model and in order to ensure that the final report satisfies its intended objectives in respect of resolution, accuracy and reliability.

The dispersion modelling study shall assume that the incinerator<sup>7</sup> always operates at full capacity assumed to be operating at the maximum input load, 24 hours/day over the course of a full year, and the reference conditions are 273.15 K, 101.3 kPa, 0% water and 11% oxygen.

### A.3.2 Specific requirements

The dispersion modelling study shall establish the AOI.

The dispersion modelling study shall establish the combination of chimney height and abatement measures required in order to ensure that the contribution of the plant to annual levels of PM<sub>2.5</sub>, PM<sub>10</sub>, NO<sub>2</sub> and benzo(a)pyrene in PM<sub>10</sub> within the AOI is nowhere higher than the value indicated in

Table 2 below. These values represent 3% of the respective annual limit or target values, where these are available.

The model shall also be used in order to determine the likelihood of exceedances of the limit values for PM<sub>10</sub>, PM<sub>2.5</sub> and NO<sub>2</sub> at the sensitive receptors within the AOI, due to the operation of the plant. In this context, the consultants will be required to carry out at their own expense any baseline monitoring studies for these pollutants. The sites used for these studies as well as the monitoring methods are to be agreed upon with ERA. For PM<sub>10</sub>, the consultants shall also estimate the 90.4<sup>th</sup> percentile of the daily readings using the following equation:

$$P = (1.46 \times A) + 0.03$$

Whereby P is the 90.4<sup>th</sup> percentile of the daily readings and A is the annual average of the daily readings.

In addition, the dispersion model shall establish chimney height and abatement measures required in order to ensure that ambient levels of dioxins and furans within the AOI are kept below the level indicated in

Table 2.

Furthermore, the dispersion model shall establish the chimney height and abatement measures required to ensure that annual bulk deposition rate for dioxins and furans as well as for the metals, particularly in any nearby farms and these shall be below the limit in Table 4.

The dispersion model shall establish the points at which the annual averaged daily bulk deposition rates are the highest.

The model shall determine the appropriate in-stack limit values, which would enable the achievement of the limits in

Table 2 and Table 4 below and those set out in

Table 3 which are based on Schedule 2 of S.L.549.81 - The Industrial Emissions (Waste Incineration) Regulations, and Commission Implementing Decision (EU) 2019/2010 of 12 November 2019 establishing the best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for waste incineration, whichever is the strictest. The proposed technology should strive to achieve the strictest achievable level within the BAT-AEL range (or lower). These concentrations shall be expressed at the reference conditions mentioned above.

Emissions from the site shall be assessed initially considering typical operations, which shall be determined by the expected throughput of the facility. Secondly, they shall be assessed under maximum operating conditions. Lastly, emissions shall be assessed under abnormal operating conditions as detailed in footnote 3.

---

<sup>7</sup> Task 6 – Basic Design report for Maghtab Hazardous waste incineration facility, May 2023’ - A common stack shall be installed. The stack shall be with three separate flue gas ducts.

**TABLE 2<sup>8</sup>: LIMIT VALUES TO BE COMPLIED TO AND WHICH REFER TO 3% OF THE LIMIT VALUES OR TARGET VALUES ESTABLISHED IN DIRECTIVE 2008/50/EC ON AMBIENT AIR QUALITY AND CLEANER AIR FOR EUROPE**

Pollutant	Limit
Fine particulate matter (PM <sub>2.5</sub> )	0.6 µg/m <sup>3</sup>
Coarse particulate matter (PM <sub>10</sub> )	1.2 µg/m <sup>3</sup>
Nitrogen dioxide (NO <sub>2</sub> )	1.2 µg/m <sup>3</sup>
Benzo(a)pyrene (B[a]P) in PM <sub>10</sub>	0.36 pg/m <sup>3</sup>
Lead (Pb) in PM <sub>10</sub>	15 ng/m <sup>3</sup>
Cadmium (Cd) in PM <sub>10</sub>	0.15 ng/m <sup>3</sup>
Arsenic (As) in PM <sub>10</sub>	0.18 ng/m <sup>3</sup>
Nickel (Ni) in PM <sub>10</sub>	0.60 ng/m <sup>3</sup>
Chromium (Cr) in PM <sub>10</sub>	0.50 ng/m <sup>3</sup>
Hexavalent chromium (Cr (VI)) in PM <sub>10</sub>	51 pg/m <sup>3</sup>
Mercury (Hg) total	1.5 ng/m <sup>3</sup>
Polychlorinated dibenzo-p-dioxins/ polychlorinated dibenzofurans (PCDD/F)	70 fg WHO-TE/m <sup>3</sup>

**TABLE 3: TENTATIVE LIMIT VALUES UNDER NORMAL OPERATING CONDITIONS BASED ON BAT AND IED**

Daily Average Values	Limit	
Total dust	5 mg/Nm <sup>3</sup>	
Total volatile organic carbon (TVOC)	10 mg/Nm <sup>3</sup>	
Hydrochloric acid (HCl)	6 mg/Nm <sup>3</sup>	
Hydrogen fluoride (HF)	1 mg/Nm <sup>3</sup>	
Sulphur dioxide (SO <sub>2</sub> )	30 mg/Nm <sup>3</sup>	
Nitrogen oxides (NO <sub>x</sub> expressed as NO <sub>2</sub> )	120 mg/Nm <sup>3</sup>	
Ammonia (NH <sub>3</sub> )	10 mg/Nm <sup>3</sup>	
Half-hourly Averages Values	Limit	
	(100%)	(97%)
Total Dust <sup>9</sup>	30 mg/Nm <sup>3</sup>	10 mg/Nm <sup>3</sup>
Total volatile organic carbon (TVOC)	20 mg/Nm <sup>3</sup>	10 mg/Nm <sup>3</sup>
Hydrochloric acid (HCl)	60 mg/Nm <sup>3</sup>	10 mg/Nm <sup>3</sup>
Hydrogen fluoride (HF)	4 mg/Nm <sup>3</sup>	2 mg/Nm <sup>3</sup>
Sulphur dioxide (SO <sub>2</sub> )	200 mg/Nm <sup>3</sup>	50 mg/Nm <sup>3</sup>
Nitrogen oxides (NO <sub>x</sub> expressed as NO <sub>2</sub> )	400 mg/Nm <sup>3</sup>	200 mg/Nm <sup>3</sup>
Average value over 30 min to 8 hours <sup>10</sup>	Limit	
Cadmium and Thallium and their compounds, expressed as Cadmium (Cd) and Thallium (Tl)	Total: 0.02 mg/Nm <sup>3</sup>	
Total Metals and their compounds, expressed as their native elements (As, Cr, Co, Cu, Mn, Pb, Sb, V & Ni)	Total: 0.03 mg/Nm <sup>3</sup>	

<sup>8</sup> It is to be noted that, the Ambient Air Quality Directive is currently under revision. The ambient air quality limit values indicated in such are subject to change and will become stricter as of 2030.

<sup>9</sup> Total dust emissions may not exceed 150 mg/m<sup>3</sup> as a half-hourly average under any circumstance.

<sup>10</sup> These average values cover also the gaseous and the vapour forms of the relevant heavy metal emissions as well as their compounds.

Mercury and its compounds, expressed as Mercury (Hg)	0.02 mg/Nm <sup>3(11)</sup>	
<b>Average value over 6 to 8 hours<sup>12</sup></b>	<b>Limit</b>	
Polychlorinated dibenzo-p-dioxins/ polychlorinated dibenzofurans (PCDD/F)	< 0.06 ng I-TEQ/Nm <sup>3</sup>	
Polychlorinated dibenzo-p-dioxins/ polychlorinated dibenzofurans (PCDD/F) + dioxin-like polychlorinated biphenyls (PCBs)	< 0.08 ng WHO-TEQ/Nm <sup>3</sup>	
<b>Average value</b>	<b>Limit</b>	
	<b>Daily</b>	<b>30 min</b>
Carbon monoxide (CO)	50 mg/Nm <sup>3</sup>	100 mg/Nm <sup>3</sup>

**TABLE 4: LIMIT VALUES FOR BULK DEPOSITION**

<b>Pollutant</b>	<b>Limit</b>
Polychlorinated dibenzo-p-dioxins/ polychlorinated dibenzofurans (PCDD/F)	4 pg WHO-TE/m <sup>2</sup> ·day (bulk deposition)
Cadmium (Cd)	2 µg/m <sup>2</sup> day (bulk deposition)
Arsenic (As)	4 µg/m <sup>2</sup> day (bulk deposition)
Mercury (Hg)	1 µg/m <sup>2</sup> day (bulk deposition)
Nickel (Ni)	15 µg/m <sup>2</sup> day (bulk deposition)
Lead (Pb)	100 µg/m <sup>2</sup> day (bulk deposition)
Thallium (Tl)	2 µg/m <sup>2</sup> day (bulk deposition)

The model used shall incorporate terrain, land coverage and wind speed and wind direction (at least a year's data) ideally from the site. However, if this is not possible data should be sourced from a weather station nearby.

Various meteorological conditions, ranging from most frequently occurring to the most adverse, shall be modelled for both ambient air quality and deposition levels.

### **A.3.3 Emissions in tons**

The consultants shall also estimate the annual emission loads in tons based on the envisaged daily emission contribution of the TTF for Dust, SO<sub>2</sub>, NO<sub>x</sub>, TVOC and NH<sub>3</sub>.

The emission loads will assist ERA in setting a cap on the emission loads of PM<sub>2.5</sub>, SO<sub>2</sub>, NO<sub>x</sub>, NMVOC and NH<sub>3</sub> from the incinerator in order to ensure compliance with Malta's 2025 and 2030 obligations under both European and International environmental law.

### **A.3.4 Submission of report**

The final report shall as a minimum contain the following sections:

1. Non-technical summary
2. Introduction
3. Scope of work
4. Site description
5. Methodology
6. Identification of sensitive receptors
7. Dispersion models
8. Comparison with limits in legislation
9. Limitations of study
10. Conclusions and recommendations
11. Appendices.

<sup>11</sup> Daily average or average over the sampling period. Continuous monitoring may be imposed, half-hourly averages 35µg/Nm<sup>3</sup>

<sup>12</sup> Either the limit for PCDD/F or PCDD/F+ dioxin-like PCBs applies

The consultants may also be required to present the methodology and results of these studies to *inter alia* members of the public, the ERA Board Members, etc.

### **Part B. Effect of stack on compliance with the air quality limit values**

This part of the study should be carried out once the AOI for emissions from the stack has been determined. The total effect of all stacks within the ECOHIVE complex, including the Waste-to-Energy facility, must be computed based on the assumption that they operate at maximum input load 24 hours a day for an entire year. Once this is completed, the consultants should revert to ERA for direction.

### **Part C. Qualifications of the person carrying out the Dispersion study**

At least an MQF Level 7 in Atmospheric Physics/Chemistry, Environmental Engineering, Air Quality Modelling or similar with experience in modelling for regulatory applications. Should have a demonstrable knowledge of the requirements of Directives 2008/50/EC and Directive 2010/75/EU (Chapter IV).

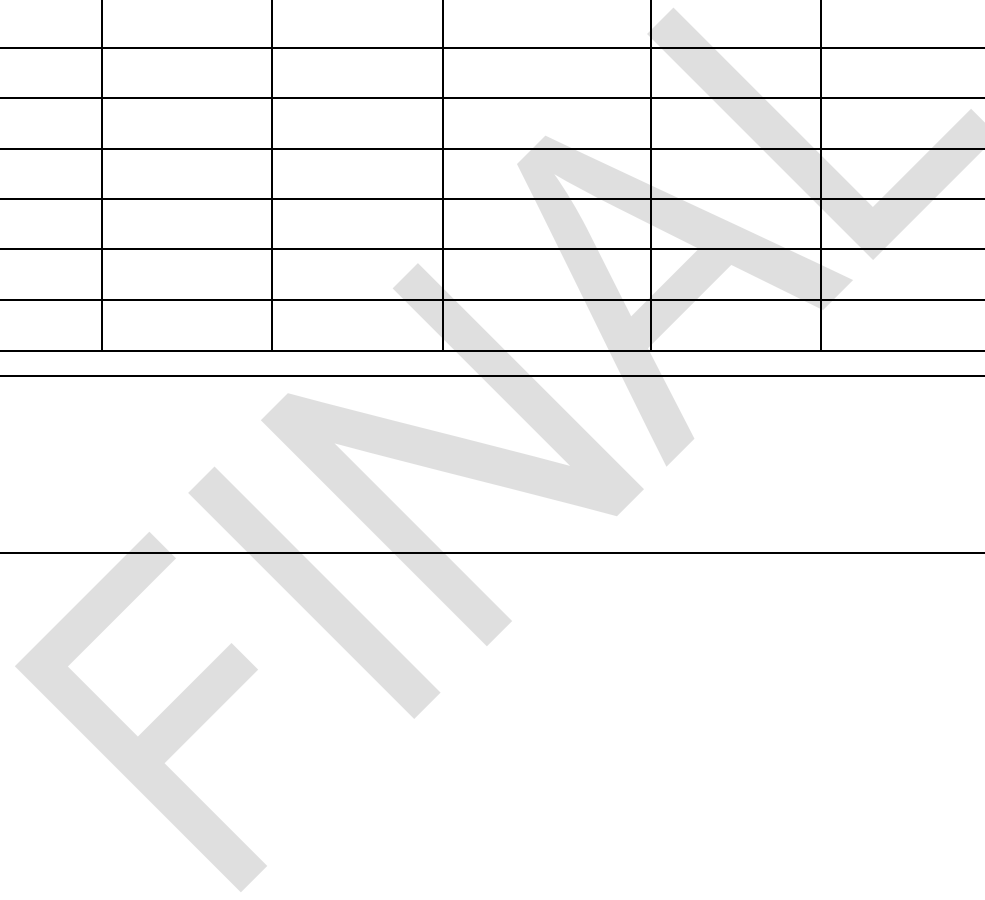
Modelling experience to be specifically related to the modelling of the effect of large combustion sources on air quality and on deposition rates and should be accompanied by a list of completed projects.

ENVIRONMENTAL

**APPENDIX 5: SPECIMEN IMPACT TABLE**

Impact type and source			Impact receptor		Effect & scale							Probability of impact occurring (Inevitable, Likely, Unlikely, Remote, Uncertain)	Overall impact significance	Proposed mitigation measures	Residual impact significance	Other requirements (monitoring, authorisations, etc)
Impact type	Specific intervention leading to impact	Project phase (construction/operation/decommissioning)	Receptor type	Sensitivity toward impact	Direct/Indirect/Cumulative	Beneficial/Adverse	Severity	Physical / geographic extent of impact	Short-/medium-/long-term	Temporary (indicate duration)/Permanent	Reversible (indicate ease of reversibility) / Irreversible					

*[Insert definition of relevant criteria used to describe the impacts]*

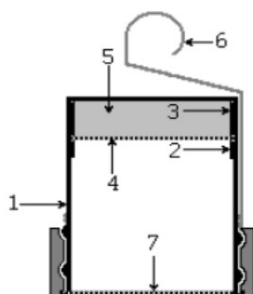


## APPENDIX 3 - ARTICLE



# Review of the application of diffusive samplers in the European Union for the monitoring of nitrogen dioxide in ambient air

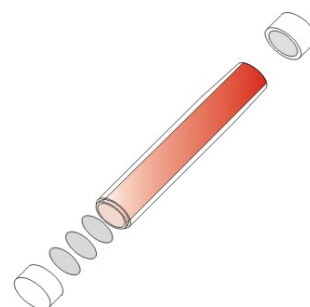
T. Hafkenschied, A. Fromage-Mariette, E. Goelen, M. Hangartner, U. Pfeffer, H. Plaisance, F. de Santis, K. Saunders, W. Swaans, Y.S. Tang, J. Targa, C. van Hoek and M. Gerboles



Analyst



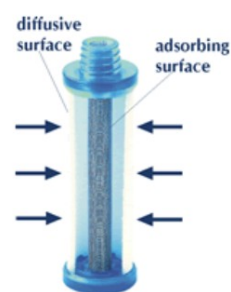
Ogawa



Palmes tube



Passam



Radiello

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## Executive summary

A number of diffusive samplers that are used for long-term monitoring of nitrogen dioxide in the European Union were subjected to a review of their use and performance characteristics. The information collected was used:

- To draft conclusions about the feasibility of using the samplers for the long-term monitoring of nitrogen dioxide, with the particular aim of checking compliance with the European Union annual limit value of  $40 \mu\text{g}\cdot\text{m}^{-3}$  (at  $20^\circ\text{C}$  and  $101,2 \text{ kPa}$ );
- To draft a proposal method for monitoring nitrogen dioxide using diffusive samplers that could be later used by the CEN Technical Committee 264 “Air Quality” Working Group 11 “Diffusive Samplers” to prepare a CEN standard devoted to the measurement of nitrogen dioxide in ambient air.

The main criteria for assessing sampler feasibility for both purposes were:

- Validation level of the samplers based either on application of EN 13528 part 2 or the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods, including information about the uncertainty of results obtained using the samplers;
- Potential to meet European Air Quality Directive data quality objectives for indicative and/or fixed measurements;
- Extent or lack of information available to underpin the validity of results obtained using the different samplers;
- Number of different sources providing the above information;
- Differences in performance depending on site type (tube type): traffic, urban, rural;
- Possibility for users to analyse the samplers, e.g., based on procedures specified by manufacturers;
- Their current use throughout the European Union for measuring ambient air quality related to concentrations of nitrogen dioxide.

Of the samplers investigated, two tube-type samplers and a radial sampler were found to be used throughout the European Union for monitoring nitrogen dioxide in ambient air. Other samplers exist that are used mainly for other purposes. In addition, the tube-type samplers are used in monitoring networks for supplementary measurements to the fixed measurements at the level of an indicative method.

Based on the findings of the review, the samplers used in the European Union for ambient air quality monitoring purposes should be of the tube-type design with triethanolamine as sorbent. Sufficient information was available to underpin its potential for meeting European Union data quality objectives, at least for indicative measurements of nitrogen dioxide in ambient air. For other samplers, more supporting information would be needed to draw a similar conclusion.

In conclusion, it is recommended that the proposed method for monitoring nitrogen dioxide using diffusive samplers should be based on the tube-type sampler. If more information becomes available on the performance of the radial sampler, then this sampler could also be included in the standard.

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# 1 Introduction

Ambient air quality problems associated with levels of nitrogen dioxide (NO<sub>2</sub>) are largely due to exceedances of annual limit values. Short-term limit values are only occasionally exceeded in the EU. Diffusive sampling would be an ideal technique for the assessment of compliance with long-term (i.e., annual) limit values for NO<sub>2</sub>.

Recent developments indicate that earlier fundamental problems associated with diffusive sampling of NO<sub>2</sub> may have been overcome. Due to modifications in the design of the samplers, potential variations in sampler performance have been eliminated [1,2].

These developments should support the application of diffusive sampling for the assessment of NO<sub>2</sub> in ambient air. Already networks are in operation for routine measurements in many European countries (including Belgium, France, Germany, Switzerland and United Kingdom).

An additional stimulus for applying diffusive sampling is a provision in the ambient air quality directive 2008/50/EC [3] that the number of fixed monitoring sites may be reduced by up to 50 % in zones and agglomerations where supplementary methods for assessment such as modelling and indicative measurements are used. Prerequisites are that:

- The supplementary methods provide sufficient information for air quality assessment;
- The number of sampling points to be installed and the spatial resolution are sufficient to meet the relevant data-quality objectives.

Diffusive sampling methods should be capable of meeting these requirements.

However, the full validation of diffusive sampling methods e.g. according to EN 13528-2, and/or the demonstration of their equivalence with the reference method for NO<sub>2</sub> requires special facilities that are only available to well-equipped institutes/laboratories.

Other smaller institutes and monitoring networks wishing to apply diffusive sampling have to rely on external assistance from commercial/public laboratories. Although small-scale validation experiments and comparisons of diffusive samplers can be performed, it is not clear what the quality and comparability of the results produced by these laboratories could be.

In addition, suppliers of samplers may require that analysis of samplers provided is performed only by themselves. Although perhaps justifiable from a viewpoint of the experience required to correctly perform such analysis, this requirement imposes severe restrictions on the potential application of diffusive sampling.

The availability of a properly validated standard method for the measurement of NO<sub>2</sub> by diffusive sampling would permit the unrestricted use of diffusive samplers by all interested parties.

In August 2006, a New Work Item describing the standardization of a method for the measurement of NO<sub>2</sub> using diffusive sampling methods was submitted to CEN Technical Committee 264 "Air Quality". The proposed New Work Item was accepted.

In order to facilitate the drafting of a future CEN standard, the European Commission made available funding for a group of experts to draft a proposal method for monitoring NO<sub>2</sub> in ambient air with diffusive samplers. The group of experts carried out a literature review of existing information about NO<sub>2</sub> diffusive samplers, to be used as a basis for the subsequent development of the proposal method.

This report summarizes the findings of the literature review. Several different types of diffusive samplers in general use were identified. They may be classified as samplers based on sorption of NO<sub>2</sub> on triethanolamine (TEA), and "other" samplers.

In the chapter devoted to TEA-based samplers, four different samplers are described separately: two tube-type samplers, a badge-type sampler, and a radial-type sampler. In the chapter devoted to other samplers, one badge-type sampler is described.

Other samplers are known to exist, but are not described in this report due to a lack of information. A comprehensive list of samplers may be found in [4].

This report is not intended to specify the various applications of diffusive samplers. Relevant information may be found, e.g., in references [5] and [6].

## References

- [1] M. Gerboles, D. Buzica, L. Amantini. Modification of the Palmes diffusion tube and semi-empirical modeling of the uptake rate for monitoring nitrogen dioxide. *Atmos. Environ*, 39 (2005) 2579-2592.
- [2] U. Pfeffer, R. Beier, T. Zang. Measurements of nitrogen dioxide with diffusive samplers at traffic sites in North-Rhine Westphalia (Germany). *Gefahrstoffe – Reinhaltung der Luft*, 66 (2006) 38-44.
- [3] 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, *Official Journal of the European Union* L 152/1, 2008.
- [4] C. Yu, M. Morandi, C. Weisel. Passive dosimeters for nitrogen dioxide in personal/ indoor air sampling: A review. *J. Exposure Sci. Environ. Epidemiol.* 18 (2008) 441–451.
- [5] European Environment Agency. Guidance report on preliminary assessment under EC air quality directives. EEA Technical Report 11, 1998.
- [6] EN 13528 part 3. Ambient air quality - Diffusive samplers for the determination of concentrations of gases and vapours – Guide for selection, use and maintenance. CEN, Brussels, 2003.

## 2 Samplers based on sorption by triethanolamine

### 2.1 Introduction

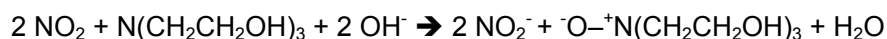
Since their introduction in 1976 for measuring personal exposure to nitrogen dioxide (NO<sub>2</sub>) [1], diffusive samplers employing triethanolamine (TEA) as sorbent have been used. Diffusive samplers are an inexpensive method for measuring NO<sub>2</sub> in air over periods from one day to several weeks.

The characteristics of these samplers will be described in separate sections of this report. This section gives an overview of the general properties of TEA-based samplers.

### 2.2 The sorbent: triethanolamine

Triethanolamine (2,2',2''-nitrilotriethanol (C<sub>2</sub>H<sub>4</sub>O)<sub>3</sub>N, TEA) is a hygroscopic pale yellow liquid with a melting point of 21,6 °C. It has been used as a sorbent for sampling NO<sub>2</sub> since the 1970s, initially in solution in a bubbler or impinger, or in the solid phase on molecular sieve [2]. Its capacity to remove NO<sub>2</sub> from the sampled air is high (90-100 %), as demonstrated using sequential sampling.

The proposed reaction pathway is the following [3].



The collected NO<sub>2</sub> is extracted as nitrite using water. The resulting extract may be analyzed by:

- Colorimetry after derivatization of the nitrite, using the Griess-Saltzman method [4];
- Ion chromatography with conductivity detection [5].

The stoichiometry of the above reaction is dictated to a large extent by the presence of water in the sampled air [3, 6]. The sudden decrease in sampling efficiency below -8 °C [7] suggests that a minimum of around 3 g H<sub>2</sub>O m<sup>-3</sup> is required for TEA to be effective as a sorbent in diffusive samplers.

### 2.3 Interferences

In addition to its reaction with NO<sub>2</sub>, TEA also traps and reacts with other molecules to produce NO<sub>2</sub><sup>-</sup> ions on extraction into aqueous solution. The two most important potential positive interferences, apart from the reaction of NO with O<sub>3</sub> during sampling, are from peroxyacetyl nitrate (PAN) and nitrous acid (HONO). Dosing of TEA absorbent with NO<sub>3</sub><sup>-</sup> ions does not produce interference [8]. There is a negligible effect of exposure to O<sub>3</sub> alone in the short term; an atmosphere of 200 ppb of O<sub>3</sub> for 12 h converted less than 10 % of trapped (reacted) NO<sub>2</sub> to NO<sub>3</sub><sup>-</sup> [9]; active co-sampling of 130 ppb O<sub>3</sub> and 10 ppb NO<sub>2</sub> using TEA on a filter at a relative humidity (RH) of 50 % produced no interference [10].

Interference from PAN is important in that PAN is quantitatively converted to NO<sub>2</sub><sup>-</sup> on (naturally alkaline) TEA [11]. For tube-type samplers, interference from PAN was lower than 5 % (ppb:ppb) [12]. In practice, interference from PAN is likely to be very small under most exposure conditions, particularly in northern Europe [13]. However, it could be a significant interference in regions with high levels of photochemistry [14].

HONO gives 100 % interference, producing NO<sub>2</sub><sup>-</sup> on reaction with TEA [10]. However, HONO concentrations in the EU air are likely to be small; even in cities they account for only a few percents of NO<sub>2</sub> concentrations [15].

Not unimportantly, both PAN and HONO would also be measured quantitatively as positive interference by a chemiluminescence NO<sub>x</sub> analyzer using thermal conversion of NO<sub>2</sub> (also PAN and HONO) to NO, and would not lead to positive interferences when diffusive samplers are compared with continuous automatic samplers.

Ozone has been reported to interfere through reacting with nitrogen monoxide in the diffusion path of tube-type samplers [16]. However, this finding has not been confirmed by other studies [27].

Sulfur dioxide was found not to interfere with the measurement of NO<sub>2</sub> using tube-type samplers [17].

## 2.4 Effects of meteorological conditions

### 2.4.1 Temperature

One of the earliest tests of tube-type samplers showed a 15 % decrease in uptake rate between 27 °C and 15 °C, compared with a theoretical change of less than 2 %. This was attributed to a phase change from solid to liquid of TEA at 21 °C [18]. However, the role of the melting point of TEA was challenged by a later study [19], which showed that TEA solutions did not freeze, but formed a gel even at temperatures as low as -10 °C.

The effectiveness of TEA as a sorbent appears to be dependent on humidity. Some of the reported effects of temperature on uptake rate may be confounded by simultaneous changes in absolute humidity [20], leading to low effective uptake rates at low temperatures that are caused by a lack of water vapour rather than low temperatures *per se* [10, 21, 22]

One laboratory study (designed to evaluate tube-type samplers for use in Greenland) showed almost constant uptake rates from 20 °C down to -8 °C, then a linear decrease to around 30 % of the constant rate, at -28 °C [7]. Another laboratory study found no temperature dependence between 5 and 45 °C [20], while another study found an effect of extremes of temperature and relative humidity on uptake rates, and low uptake rates in the field in winter (by comparison with an automatic monitor) [24].

For short-path 'badge' type samplers the effectiveness of the absorbent may be limited by the rate of diffusion in the liquid phase [25], but this is unlikely to be an issue for the tube type, which has much slower uptake rates. Comparisons of a short path sampler with an active sampler suggest a dependence on temperature of around 1 % per °C [26]. Different designs of sampler have different temperature responses, which must be characterised before they can be used [27].

### 2.4.2 Relative humidity

The effect of humidity on uptake rate appears to be related to the use of TEA as a sorbent for NO<sub>2</sub>, rather than any effect on the diffusion process. Most laboratory studies have used relative humidity (RH) as a measure of water vapour concentration, rather than absolute humidity, which may be more important. Early studies showed no effect of RH between 20 % and 60 % on a short path sampler at room temperature [28]. This was confirmed by subsequent studies with RH higher than 20 % at ambient temperatures [23, 29]. Studies with tube-type samplers between 5 % and 85 % RH at room temperatures (above 22 °C) showed a weak linear dependence of the uptake rate equivalent to an 18 % change in uptake rate between 20 % and 80 % RH [30].

Recent studies demonstrated a dependence on absolute humidity, expressed in terms of the uptake rate for a membrane-capped tube [27], equivalent to a 23 % change in uptake rate between 20 % and 80 % RH at 20 °C.

The effects of variations in absolute humidity on a short path sampler were also reported, with significant reductions in uptake at low RH at low temperature [20, 22].

Effects of humidity on tube-type sampler performance in the field were noted [31], with uptake changing by 17 % between 20 % and 80 % RH at 20 °C with wind velocity of 1 m.s<sup>-1</sup>. If the uptake rate is dependent on absolute humidity, the above figures may not present a true picture of the dependence on temperature and relative humidity, because RH is a function of water vapour concentration (absolute humidity) and temperature.

However, in comparing results from diffusive samplers with those from automatic analyzers, it is important to note that automatic NO<sub>2</sub> analyzers also have a dependence on humidity, which may not

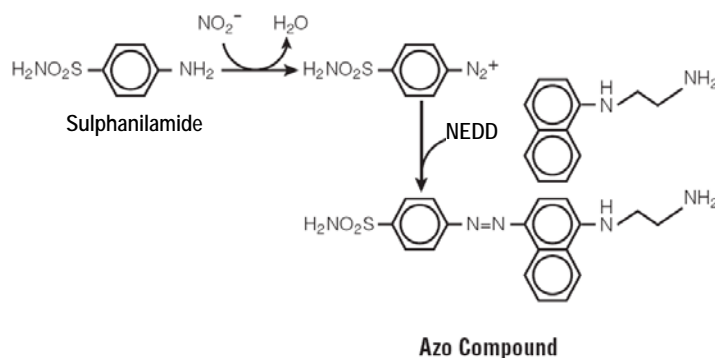
have been allowed for in comparing the response of diffusion tubes relative to automatic methods. The response of a chemiluminescence analyzer typically decreases by 0,5 % per  $\text{g}/\text{m}^3$  of water vapour [32]. This is equivalent to a change of 5 % between 20 % and 80 % RH at 20 °C.

### 2.4.3 Air velocity

The effects of air velocity are highly dependent on the sampler design and will be discussed in the sampler-specific sections of the report.

## 2.5 Analysis of TEA-based samplers

The original method used by Palmes [1] for measurement of the trapped  $\text{NO}_2$  relied on the colorimetric determination of  $\text{NO}_2^-$  using the diazotisation reaction with acidified sulphanilamide and N-(1-naphthyl)-ethylene diamine dihydrochloride (NEDD, sometimes also referred to as NEDA), with detection and quantification of the pink colour produced using photometric absorption spectroscopy at 537 - 542 nm. This colour reagent, or 'Saltzman reagent' has long been used for the quantification of  $\text{NO}_2^-$  in solution.



However, several authors used ion chromatography (IC) to quantify  $\text{NO}_2$  uptake. The benefit of using IC was recognised over 20 years ago, in terms of a greatly improved limit of detection using tube-type samplers, compared with colorimetric analysis [5]. Using gradient elution IC, the limit of detection for tube-type samplers was measured as 4 ppb.hour, compared with 33 ppb.hour for a colorimetric method [12]. Other authors have shown a 14-fold decrease in the limit of detection [33].

## 2.6 Conclusions

Diffusive sampling of  $\text{NO}_2$  using TEA-based samplers dates back 35 years. Meanwhile, a substantial number of studies have been devoted to investigating the behaviour of TEA-based diffusive samplers and their dependence on environmental conditions (presence of interferents, temperature, humidity).

Humidity is probably the most important environmental variable that affects the performance of diffusive samplers using TEA as absorbent. TEA does not perform quantitatively at low humidity. The data of Hansen et al. [7] suggest a loss of efficiency below -8 °C, equivalent to an air concentration of water vapour of about  $3 \text{ g}/\text{m}^3$ , or 35 % RH at 5 °C. At any given temperature, the effect of a change in relative humidity between 20 % and 80 % is to change uptake rates by about  $\pm 15$  % relative to the values at 50 % RH. In practice, the dependence on humidity has rarely been tested in the field, and the interaction between humidity and the reaction of TEA with  $\text{NO}_2$  has not been investigated systematically.

The dependence of uptake rate on temperature is small and predictable, except in cold dry air. This deviation from theory is related to the use of TEA as the sorbent and appears to be caused by a lack of sufficient water vapour to ensure quantitative conversion of trapped  $\text{NO}_2$  to  $\text{NO}_2^-$  ions. The availability of water is crucial to the way in which TEA reacts with  $\text{NO}_2$ . As noted above, the sudden decrease in sampling efficiency below -8 °C suggests that a minimum of around  $3 \text{ g H}_2\text{O}/\text{m}^3$  is required for TEA to be effective as the sorbent in diffusive samplers. This is unlikely to be a problem under most EU conditions, except for very cold, dry weather.

A number of compounds, particularly PAN and HONO are known to produce positive biases when co-sampled with NO<sub>2</sub>. However, under typical EU conditions the biases are expected to be small.

Moreover, the current reference method for the measurement of NO<sub>2</sub> in ambient air which is based on thermal conversion of NO<sub>2</sub> to NO with detection of chemiluminescence, suffers from similar biases. Consequently, when comparing TEA diffusive samplers with this reference method, the effects of the interference cannot be quantified.

## 2.7 References

- [1] E. Palmes, A. Gunnison, J. DiMattio, C. Tomczyk. Personal Sampler for Nitrogen Dioxide. *Am. Ind. Hyg. Assoc. J.* 37 (1976) 570-577.
- [2] J. Blacker. Triethanolamine for collecting nitrogen dioxide in the TLV range. *Am. Ind. Hyg. Assoc. J.*, 34 (1973) 390-395.
- [3] M. Glasius, M. Carlsen, T. Hansen, C. Lohse. Measurements of nitrogen dioxide on Funen using diffusion tubes. *Atmospheric Environment* 33 (1999) 1177-1185.
- [4] 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.
- [5] D. Miller. Ion chromatographic analysis of Palmes tubes for nitrite. *Atmos. Environ.* 18 (1984) 891-892.
- [6] E. Palmes, E. Johnson. Explanation of Pressure Effects on a Nitrogen-Dioxide (NO<sub>2</sub>) Sampler. *Am. Ind. Hyg. Assoc. J.* 48 (1987) 73-76.
- [7] T. Hansen, M. Kruse, H. Nissen, M. Glasius, C. Lohse. Measurements of nitrogen dioxide in Greenland using Palmes diffusion tubes. *J. Environ. Monit.* 3 (2001) 139-145.
- [8] U. Haue-Pedersen, C. Hansen, K. Knudsen, H. Skov, C. Lohse. Measurements of NO<sub>2</sub> by passive sampling. In: G. Angeletti and G. Restelli (Eds), *Physico-chemical behaviour of atmospheric pollutants*. European Commission, 1993, pp. 737-743.
- [9] F. de Santis, I. Allegrini, M. Fazio, D. Pasella, R. Piredda. Development of a passive sampling technique for the determination of nitrogen dioxide and sulphur dioxide in ambient air. *Anal. Chim. Acta*, 346 (1997) 127-134.
- [10] J. Sickles. Development of a method for the sampling and analysis of sulfur dioxide and nitrogen dioxide from ambient air. *Anal. Chem.* 62 (1990) 338-346.
- [11] M. Hisham, D. Grosjean. Sampling of atmospheric nitrogen dioxide using triethanolamine: Interference from peroxyacetyl nitrate. *Atmos. Environ. Part A.* 24 (1990) 2523-2525.
- [12] A. Gair, S. Penkett, P. Oyola. Development of a simple passive technique for the determination of nitrogen dioxide in remote continental locations. *Atmos. Environ. Part A*, 25 (1991) 1927-1939.
- [13] G. McFadyen, J. Cape. Peroxyacetyl nitrate in eastern Scotland. *Sci. Tot. Environ.* 337(2005) 213-222.
- [14] D. Grosjean. Ambient PAN and PPN in southern California from 1960 to the SCOS97-NARSTO. *Atmos. Environ.* 37 (2003) S221-S238.

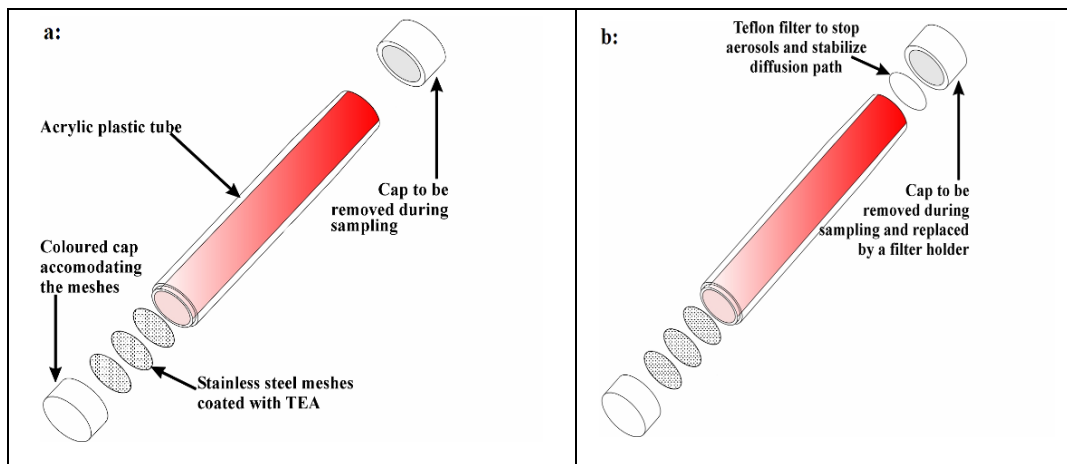
- [15] G. Martinez-Villa, K. Clemitshaw, A. Marsh. Observations of nitrous acid at a kerb side site in central London, Workshop on Traffic Emissions, Roadway and Tunnel Studies, Vienna University of Technology, 2000.
- [16] T. Bush, M. Jenkin, J. Banham, A. Loader. Investigation of NO<sub>2</sub> diffusion tube over-read resulting from reduced photolysis by UV light. AEA Technology Report AEAT/ENV/R/0562, 2001.
- [17] P. Burri. Passivsammler für die Messung von Stickstoffdioxid und Schwefeldioxid Immissionen. PhD Thesis, ETH Zürich, 1989.
- [18] Girman, J., A. Hodgson, B. Robison, G. Traynor. Laboratory studies of the temperature dependence of the Palmes NO<sub>2</sub> passive sampler. LBL-16302, Lawrence Berkely Laboratory, Berkely, 1983.
- [19] C. Kirby, M. Fox, J. Waterhouse, T. Drye. Influence of environmental parameters on the accuracy of nitrogen dioxide passive diffusion tubes for ambient measurement. *J. Environ. Monit.* 3 (2001) 150-158.
- [20] D. Moschandreas, S. Relwani, K. Taylor, J. Mulik. A laboratory evaluation of a nitrogen dioxide personal sampling device. *Atmos. Environ.. Part A.*, 24 (1990) 2807-2811.
- [21] H. Moriske, M. Schondube, G. Menk, B. Seifert. Measurements of NO<sub>2</sub> concentrations in the air using passive Palmes samplers. 1. Laboratory studies and quality design. *Gefahrstoffe Reinhaltung der Luft*, 56 (1996) 129-132.
- [22] H. Tang, T. Lau, B. Brassard, W. Cool. A new all-season passive sampling system for monitoring NO<sub>2</sub> in air. *Field Anal. Chem. Technol.* 3 (1999) 338-345.
- [23] M. Hangartner. Influence of meteorological factors on the performance of diffusive samplers. In: R.H. Brown, T.L. Hafkenscheid, K.J. Saunders, A. Borowiak and E. De Saeger (Eds), *Proceedings of the International Conference Measuring Air Pollutants by Diffusive Sampling*, Montpellier, France, 2001, pp. 78-83.
- [24] D. Buzica, M. Gerboles, L. Amantini. Laboratory and Field Inter-comparisons of NO<sub>2</sub> Diffusive Samplers. Report EUR 20860 EN, JRC-IES, 2003.
- [25] D. Krochmal, L. Górski, L. Determination of nitrogen dioxide in ambient air by use of passive sampling technique and triethanolamine as absorbent. *Environ. Sci. Technol.* 25 (1991) 531-535.
- [26] E. Yamada, M. Kimura, K. Tomozawa, Y. Fuse. Simple analysis of atmospheric NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub> in mountains by using passive samplers. *Environ. Sci. Technol.* 33 (1999): 4141-4145.
- [27] M. Gerboles, D. Buzica, L. Amantini. Modification of the Palmes diffusion tube and semi-empirical modelling of the uptake rate for monitoring nitrogen dioxide. *Atmos. Environ.* 39 (2005) 2579-2592.
- [28] B. Cadoff, J. Hodgeson. Passive sampler for ambient levels of nitrogen dioxide. *Anal. Chem.* 55 (1983) 2083-2085.
- [29] A. Hagenbjörk-Gustafsson, R. Lindahl, J. Levin, D. Karlsson. Validation of a diffusive sampler for NO<sub>2</sub>. *J. Environ. Monit.* 1 (1999) 349-352.
- [30] J. Boleij, E. Lebret, F. Hoek, D. Noy, B. Brunekreef. The use of Palmes diffusion tubes for measuring NO<sub>2</sub> in homes. *Atmos. Environ.* 20 (1986) 597-600.

- [31] D. Buzica, M. Gerboles, L. Amantini, P. Ballesta, E. De Saeger. Modelling of the uptake rate of the nitrogen dioxide Palmes diffusive sampler based on the effect of environmental factors. *J. Environ. Monit.* 7 (2005) 169-174.
- [32] H. Plaisance. Response of a Palmes tube at various fluctuations of concentration in ambient air. *Atmos. Environ.* 38 (2004) 6115-6120.
- [33] H. Plaisance, A. Piechocki-Minguy, S. Garcia-Fouque, J. Galloo. Influence of meteorological factors on the NO<sub>2</sub> measurements by passive diffusion tube. *Atmos. Environ.* 38 (2004) 573-580.

### 3 The Palmes tube

#### 3.1 Sampler design

The traditional NO<sub>2</sub> Palmes tube consists of an acrylic tube (of 71,16 +/- 0,20 mm long and 10,91 +/- 0,15 mm internal diameter) open at one end and two or three stainless steel mesh discs coated with a solution containing triethanolamine (TEA) at the closed end (see figure 3.1, a). A removable cap is used to close the open end of the tube after exposure. The NO<sub>2</sub> molecules diffuse through the air into the tube, following the concentration gradient and are trapped as nitrite ion on TEA. In a recent study, Gerboles et al. [1] proposed a modification of the traditional Palmes diffusion tube by fitting a Teflon membrane at the open end of the tube (see figure 3.1, b). This membrane was used to obtain a sampler free of wind speed effect. In the United Kingdom, a Teflon mesh is used instead of a membrane [2]. All ready-to-use Palmes tube components are commercially available.



**Figure 3.1.a: The traditional Palmes diffusion tube, b: The membrane-closed Palmes tube proposed by Gerboles et al. [1].**

The coloured cap needs to be completely opaque and without cracks [2].

Samplers are mounted vertically, with the cap containing the coated discs uppermost. Positions allowing unrestricted movement of air around the sampler are selected. Diffusion tube samplers are fixed by spring clips to the supports (pylons or posts) using supports or spacers of different types. The samplers are, as far as practicable attached at 3-4 meter above the ground in order to avoid vandalism. To attenuate the effect of wind turbulence and improve the precision of measurements by Palmes tubes, it is recommended to use a protective device as for example, shown in Figure 3.2.



**Figure 3.2: Cylindrical protective box**

The decision to use a protective device should come first (before using a spacer). Criteria to use the protective box may be:

- To prevent exposure to direct sunlight;
- To prevent turbulence in the tube entrance (but at least  $0,2 \text{ m}\cdot\text{s}^{-1}$  should be ensured);
- To avoid ingress of rain.

In the case of the membrane-closed Palmes tube proposed by Gerboles et al. [1], the protective box is not necessary since the membrane introduced at the open end of tube is intended for isolating the molecular diffusion path from air movements.

### **3.2 Sampler preparation**

The Palmes tube described here needs to be assembled from individual parts. The tube, Teflon membrane and caps are cleaned in a glass container filled with ultra high purity water under magnetic stirring and changing the water every half an hour for 3 h. All components are then placed in an oven at  $45^\circ\text{C}$  until they are completely dry. The stainless-steel mesh discs are cleaned in an ultrasonic bath at  $60^\circ\text{C}$  for 5 h, with the water changed every half an hour. They are then placed in an oven and flushed with nitrogen at  $125^\circ\text{C}$  until they are completely dry. Three clean and dry discs are placed in the coloured cap with tweezers. Then, a tube is placed onto the coloured cap [1].

In practice, this procedure may be quite tedious. Less stringent procedures are described in [3] and [4].

In addition, the coating of the sampling substrate needs to be performed by the user itself. Different procedures for preparation are described [e.g. 5]. Methods of proven validity are:

- 50 % solution of TEA in acetone, grids dipped into solution and dried before assembly;
- 20 % solution of TEA in deionised water, 50  $\mu\text{l}$  of solution pipetted onto grids already placed in end cap;

- 10 % solution of TEA in deionised water with 0,3 % of wetting agent (e.g. Brij-35), 40 µl of solution pipetted onto grids already placed in end cap.

### 3.3 Extraction and analysis

To determine the quantity of nitrite sampled by the Palmes tube, the Griess-Saltzman method is generally used. The Saltzman reagent consists of a solution of sulphanilamide (2 % w/v) and N-(naphthyl-1) ethylene diamine dihydrochloride (0,007 % w/v) in 5 % v/v ortho-phosphoric acid. A known volume of colorimetric reagent solution is introduced into the tube, and extraction is effected either by:

- Vortex shaking for a minimum of 15 s;
- Vibrating for a minimum of 10 min at 750 rpm.

Nitrite reacts in the phosphoric acid solution with sulphanilamide to give a diazonium salt that couples with naphthalene derivative to form an azo dye. It is recommended to allow the colour to develop at ambient temperature in the dark for a minimum time of 1 h. The absorbance of the azo dye is measured at 542 nm [4].

### 3.4 Expression of the NO<sub>2</sub> concentration

To calculate the airborne NO<sub>2</sub> concentration, the equation 3.1 is generally applied.

$$C_{NO_2} = \frac{(m_s - m_b)}{v \times t \times 10^{-6}} \quad (\text{eq. 3.1})$$

where

$C_{NO_2}$  = NO<sub>2</sub> concentration in µg.m<sup>-3</sup> at actual average temperature and pressure during the exposure;

$m_s$  = mass of nitrite measured in the exposed sampler in µg;

$m_b$  = mass of nitrite in the blank in µg;

$v$  = uptake rate in cm<sup>3</sup>.min<sup>-1</sup>;

$t$  = sampling time in min.

Several authors also prefer to use equation 3.2 for the calculation of NO<sub>2</sub> concentration, with the uptake rate expressed in ng.ppb<sup>-1</sup>.min<sup>-1</sup>.

$$C_{NO_2} = 1,91 \frac{(m_s - m_b)}{u \times t} \quad (\text{eq. 3.2})$$

where

$C_{NO_2}$  = NO<sub>2</sub> concentration in µg.m<sup>-3</sup> at 20 °C and 101,3 kPa;

$m_s$  = mass of nitrite measured in the exposed sampler in ng;

$m_b$  = mass of nitrite in the blank in ng;

$u$  = uptake rate in ng.ppb<sup>-1</sup>.min<sup>-1</sup>;

$t$  = sampling time in min.

The coefficient 1,91 is used to convert ppb to µg.m<sup>-3</sup> at 20 °C and 101,3 kPa.

### 3.5 Application range and conditions

The Palmes tube may be exposed for 1 to 5 weeks sampling periods according to results of field validation tests obtained from many sites across Europe [1, 2, 6-9]. Some users have exposed tubes for up to 8 weeks [10].

Results of validation studies described below suggest that the Palmes tube sampler, when properly prepared and exposed with sufficient protection from adverse influences, may be used over a temperature range from -5 °C to 40 °C, and a relative humidity range from 30% to 95%.

Detection limits for a one-week sampling period were found to be 1,4 [1] and 1,9  $\mu\text{g}\cdot\text{m}^{-3}$  [3], depending on the preparation procedure (see section 3.2). In a field experiment, the upper limit for  $\text{NO}_2$  that was found in practice to lead to valid results for 5-week sampling was 150  $\mu\text{g}\cdot\text{m}^{-3}$  [2].

When stored in a clean refrigerator at 4°C before exposure, an unexposed tube may be stable for up to 1 year [11].

Stability tests of Palmes tubes after exposure were performed by Gerboles et al. [11] in a feasibility study of the preparation and certification of a reference material for  $\text{NO}_2$  in diffusive samplers. The Palmes tubes were stored under two different conditions: at room temperature (22°C) in the dark and at 4°C in a refrigerator. It was demonstrated that the samples may be stable for at least one year under both conditions of storage. The results were in agreement with those obtained previously by Palmes et al. [12], where the samplers were found to be stable for at least 6 months.

### 3.6 Uptake rate

For the traditional Palmes diffusion tube without membrane, the theoretical uptake rate (72,8  $\text{cm}^3\cdot\text{h}^{-1}$ ) calculated using the diffusion coefficient of  $\text{NO}_2$  in air and the dimensions of the sampler is currently the most common value. It has also been confirmed by test results in exposure chambers under standard conditions ( $T=20^\circ\text{C}$ ,  $\text{RH}=50\%$  and wind speeds between 0,1 and 0,3  $\text{m}\cdot\text{s}^{-1}$ ) [8].

The uptake rate is dependent on the air temperature and pressure during exposure. In appendix 2 of reference [2], a correction for the uptake rate is proposed (equation 3.3). Temperature correction raised to the power 1,5 instead of 1,81 have been proposed by other authors [4]. In most cases, the pressure correction may be neglected.

$$v_{T,P} = v_{ref} \left( \frac{273,2 + T}{273,2 + T_{ref}} \right)^{1,81} \frac{P_{ref}}{P} \quad (\text{eq. 3.3})$$

where

$v_{T,P}$  = uptake rate in  $\text{cm}^3\cdot\text{min}^{-1}$  at temperature  $T$  and pressure  $P$  during sampling;

$v_{ref}$  = uptake rate in  $\text{cm}^3\cdot\text{min}^{-1}$  at the reference temperature and pressure;

$T$  = actual temperature during sampling in °C;

$T_{ref}$  = reference temperature in °C at which  $v_{ref}$  rate is given (for example if  $v_{ref}$  was calculated using a value of 0,154  $\text{cm}^2\cdot\text{s}^{-1}$  for the diffusion coefficient of  $\text{NO}_2$  in air, the reference temperature is 21,1 °C);

$P$  = actual pressure during sampling in kPa;

$P_{ref}$  = reference pressure in kPa at which  $v_{ref}$  is given, in general 101,3 kPa.

To improve the accuracy of measurements by Palmes tubes, some authors established empirical equations to estimate the uptake rate as a function of influential environmental parameters. These equations were defined from the results of complete programs of tests in exposure chamber.

Plaisance et al. [8] proposed a first equation which allows the effects of temperature and humidity to be taken into account on the uptake rate of the open Palmes tube exposed in cylindrical box for 2-week sampling:

$$v = 72,8 \times (2,85 \times 10^{-3} \times [T] - 1,62 \times 10^{-4} \times [RH] + 4,96 \times 10^{-5} \times [T] \times [RH] + 0,9) \quad (\text{eq. 3.4})$$

where

$v$  = uptake rate in  $\text{cm}^3\cdot\text{h}^{-1}$ ;

$T$  = temperature in °C.

Buzica et al. [9] provided another model-predicted uptake rate. It was deduced from tests in exposure chamber carried out by applying a fractional factorial plan of experiments with 5 factors at two levels

(wind speed, temperature, humidity, NO<sub>2</sub> concentration level and sampling time). The equation predicts the uptake rate of the Palmes tube without membrane exposed from 1 to 2 weeks:

$$v = 7,4 \times 10^{-4} + 2,72 \times 10^{-5} \times T + 1,43 \times 10^{-5} \times RH + 5,81 \times 10^{-4} \times w \quad (\text{eq. 3.5})$$

where

$v$  = uptake rate in ng.ppb<sup>-1</sup>.min<sup>-1</sup>;  
 $T$  = temperature in °C;  
 $RH$  = relative humidity in %;  
 $w$  = wind speed in m.s<sup>-1</sup>.

For the Palmes tube equipped with a Teflon membrane proposed by Gerboles et al. [1], the membrane introduced a resistance to molecular diffusion. Therefore the uptake rate of the sampler could not be determined using the first Fick's law, but was instead estimated by laboratory experiments in exposure chamber. Gerboles et al. carried out the same program of tests as described in [9] and derived a model-predicted uptake rate for the membrane-closed Palmes tube exposed from 3 to 14 days:

$$v = \frac{1}{2} (134 + 0,86RH - 0,00130 t + 1,28T + 3,18w) 10^{-5} \times \left( 1 + \sqrt{1 - \frac{0,64 \cdot 10^{-5} m}{t ((134 + 0,86RH - 0,00130 t + 1,28T + 3,18w) 10^{-5})^2}} \right) \quad (\text{eq. 3.6})$$

where

$v$  = uptake rate in ng.ppb<sup>-1</sup>.min<sup>-1</sup>;  
 $T$  = temperature in °C;  
 $RH$  = relative humidity in %;  
 $w$  = wind speed in m.s<sup>-1</sup>;  
 $m$  = mass of nitrite in ng;  
 $t$  = exposure time in min.

### 3.7 Environmental effects

#### 3.7.1 Air velocity

Some studies [8, 9, and 13] reported that the greatest effect on the uptake rate of a traditional open Palmes tube may be attributed to wind velocity. An increase in uptake rate was observed with increasing air velocities usually following a logarithmic trend [8, 13]. The effect starts from very low wind velocities (between 0,1 m.s<sup>-1</sup> and 0,2 m.s<sup>-1</sup>).

The magnitude of the uptake increase was found to be about 60 % over the wind velocity range of 0 m.s<sup>-1</sup> to 7 m.s<sup>-1</sup> [13]. Other authors [8, 9] confirmed that the increase rate was high, about 40 % from 1 m.s<sup>-1</sup> to 2.8 m.s<sup>-1</sup>. An effective and practical way for reducing the effect of air turbulence was demonstrated by the use of a cylindrical protective box (figure 3.2).

Buzica et al. [9] observed that for the open Palmes tube the effect of the wind speed was ±25 % of the average uptake rate, while the effects of the relative humidity and temperature were smaller, at ±10 % and ±7 %, respectively.

Gerboles et al. [1] proposed the addition of a porous membrane at the open end of the Palmes tube. It removes the high influence of wind speed and wind direction on uptake rate. With the addition of the membrane, the wind becomes a minor influencing factor.

#### 3.7.2 Temperature and relative humidity

Temperature and humidity were found to have a smaller influence on the response of the sampler (see above) with the uptake rate increasing linearly by 0,3 %·°C<sup>-1</sup>, in agreement with the theoretical dependence of the diffusion coefficient of NO<sub>2</sub> on temperature.

A maximum bias in the uptake rate of nearly +10 % was observed under particularly extreme conditions (temperature higher than 30 °C and relative humidity higher than 80 %) [8].

### 3.7.3 Interferences

Potential interferences from nitrous acid (HONO) and peroxyacetyl nitrate (PAN) which give rise to nitrite ion must be recognised. However, neither compound is likely to be present at sufficient concentrations or over sufficiently long periods to cause serious interferences in most situations. Gair et al. [14] found only a positive interference lower than 6 % which they considered non-significant.

Heal et al. [15] and Jenkins [16] showed that the chemical reaction between O<sub>3</sub> and NO within diffusion tubes may lead to an overestimation of the measured NO<sub>2</sub> concentration. The light transmission characteristics of the acrylic tube used for sampling showed some attenuation in the photochemically important region, possibly leading to changes in the photochemical equilibrium in the air actually inside the sampler.

This information, together with ozone data, was used to model the system for typical conditions of exposure of urban and rural areas. The model showed an increase in NO<sub>2</sub> of about 11 % in rural and 6 % in urban areas. The photochemical reaction is only of importance during daylight and even in the more sensitive rural areas the effect would be difficult to detect.

In field tests carried out by Atkins et al. [17] and Bush et al. [18], no differences were found in the performance of the diffusion tube at rural and urban locations. Likewise, the laboratory experiments in an exposure chamber [1] revealed no bias of O<sub>3</sub> on the NO<sub>2</sub> measurements by Palmes tubes.

## 3.8 Validation of sampler performance

### 3.8.1 Comparisons with reference methods

Palmes tubes were validated for outdoor use in several studies. The first extended outdoor evaluation was carried out by Atkins et al. [17] at two sites (rural and urban locations) using the Palmes tubes (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) and the theoretical uptake rate.

Precision was found to be satisfactory with coefficients of variation for batches of 10 Palmes tubes between 5 % and 8 % for NO<sub>2</sub> concentrations above 5 ppb, which appeared to be independent of NO<sub>2</sub> level and sampling duration (1 week or 4 weeks). Parallel measurements using chemiluminescence analysers and diffusion tubes revealed a good agreement between the two methods. Regression analysis on 42 paired measurements produced a line with a slope not significantly different to 1 and a correlation coefficient above 0,98, over a range of concentrations of 3 ppb to 60 ppb. There was no difference in the performance of the Palmes tube at the rural (NO<sub>2</sub> lower than 30 ppb) and urban (NO<sub>2</sub> higher than 30 ppb) locations.

Gladius et al. [6] confirmed the good agreement between NO<sub>2</sub> measurements carried out with Palmes tube and co-located chemiluminescence analysers at three sites in Denmark and Italy. However, samplers (33 % TEA/acetone solution) at sheltered locations slightly overestimated NO<sub>2</sub> (less than 10 % of overestimation) at concentration levels above 15 ppb. An opposite trend was found at concentrations lower than 15 ppb.

Heal et al. [15] observed overestimations of NO<sub>2</sub> measured by Palmes tubes (50 % TEA/acetone solution) against co-located chemiluminescence analyser at an urban site in Edinburgh (UK). The average ratios of Palmes tube to analyser NO<sub>2</sub> were 1,27 (n=22), 1,16 (n=34) and 1,11 (n=7) for exposures of 1, 2 and 4-weeks, respectively. Based on further modelling of the diffusion, the authors concluded that the overestimation of NO<sub>2</sub> by Palmes tubes could be explained by the generation of excess NO<sub>2</sub> due to the reaction of NO with O<sub>3</sub> inside the tube.

Bush et al. [18] co-located Palmes tubes (50 % TEA/acetone solution) with chemiluminescence analysers at 17 urban monitoring stations in the UK for a one year period. Highly significant correlations (above 0,95) were found between all Palmes tube exposure types (sampling time of 2

and 4 weeks with sheltered and unsheltered samplers) and co-located chemiluminescence analysers. The uncertainty calculated from the overall differences between Palmes tube measurements and the chemiluminescence measurements of NO<sub>2</sub> was estimated to be between ±24 % and 38 % for individual Palmes tube measurements, but reduced between ±10 % and 18 % for annual averages. Differences due to the exposure period and exposure procedure were found, but these were not large.

Tang et al. [10] compared measurement results obtained with Palmes tubes (both open and equipped with a membrane, using protective shelters consisting of a sheet of curved stainless steel painted black, open to the air on 3 sides) with those from chemiluminescence reference analyzers. Comparative measurements were performed at 5 sites: 3 urban sites and 2 rural sites.

Exposure periods were 1, 2, 4 and 8 weeks. In general, it was found that open tubes overestimated NO<sub>2</sub> concentrations at urban sites (average levels around 20 ppb) by almost 30 % to 35 % on average. At the rural site (average levels around 4 ppb) the results agreed much better (ratios between 0,98 and 1,03).

Results obtained with membrane tubes were 10 % lower on average than the reference values for the 4-week sampling period, but were in excellent agreement with those obtained over an 8-week exposure period. At the rural site, the membrane tubes yielded levels that were about 75 % of those of the reference analyzers.

During 2001-2002, CEN/TC264 WG11 (Diffusive sampling) performed a small-scale pilot study at two locations in which 6 replicate samplers of different types of diffusion samplers were exposed for two weeks, in parallel with measurements from a chemiluminescence analyser. These results have not been published and were provided by CEN for the purpose of the present report. Samplers were analysed by the suppliers. The results for two Palmes tube samplers are reported in table 3.1.

**Table 3.1: Results of CEN pilot study for Palmes tube samplers**

<b>Willebroek</b>	<b>NO<sub>2</sub> (µg.m<sup>-3</sup>)</b>	<b>Ratio Palmes/reference</b>
<i>Reference</i>	40,8	
Palmes 1	52,8	1,30
Palmes 2	57,1	1,40
<b>Teddington</b>	<b>NO<sub>2</sub> (µg.m<sup>-3</sup>)</b>	<b>Ratio Palmes/reference</b>
<i>Reference</i>	13,8	
Palmes 1	17,6	1,28
Palmes 2	18,7	1,36

Both Palmes tubes were found to overestimate NO<sub>2</sub> concentrations.

Buzica et al. [19] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler was exposed in replicate (6) for a period of 14 days, except in the laboratory trial “high” (see table 3.2).

**Table 3.2: Laboratory conditions (intercomparison of Buzica et al.)**

<b>Parameter</b>	<b>High</b>	<b>Low</b>
Exposure time (d)	7	14
Concentration (µg.m <sup>-3</sup> )	80	40
Air velocity (m.s <sup>-1</sup> )	2,5	1,0
Temperature (°C)	25	5
Relative humidity (%)	75	30

Five laboratories participated with different implementations of the Palmes tube (with and without shelter; with membrane). The results obtained for the samplers are presented in table 3.3.

**Table 3.3: Results field tests, (intercomparison of Buzica *et al.*)**

<b>Lab high</b>	<b>NO<sub>2</sub> (µg.m<sup>-3</sup>)</b>	<b>Ratio Palmes/reference</b>
<i>Chemiluminescence</i>	76,8	
Palmes open 1	125,8	1,64
Palmes open 2	138,5	1,80
Palmes sheltered 1	96,5	1,26
Palmes sheltered 2	97,0	1,26
Palmes membrane	71,5	0,93
<b>Lab low</b>	<b>NO<sub>2</sub> (µg.m<sup>-3</sup>)</b>	<b>Ratio Palmes/reference</b>
<i>Chemiluminescence</i>	43,5	
Palmes open 1	46,0	1,06
Palmes open 2	37,2	0,86
Palmes sheltered 1	32,6	0,75
Palmes sheltered 2	35,8	0,82
Palmes membrane	40,4	0,93
<b>Genevilliers</b>	<b>NO<sub>2</sub> (µg.m<sup>-3</sup>)</b>	<b>Ratio Palmes/reference</b>
<i>Chemiluminescence</i>	41,6	
Palmes open 1	45,2	1,09
Palmes open 2	42,5	1,02
Palmes sheltered 1	47,2	1,14
Palmes sheltered 2	40,5	0,97
Palmes membrane	40,5	0,97
<b>Fontainebleau</b>	<b>NO<sub>2</sub> (µg.m<sup>-3</sup>)</b>	<b>Ratio Palmes/reference</b>
<i>Chemiluminescence</i>	14,1	
Palmes open 1	13,1	0,93
Palmes open 2	12,4	0,88
Palmes sheltered 1	11,6	0,82
Palmes sheltered 2	11,8	0,83
Palmes membrane	12,4	0,88

Apart from the results of the laboratory trial “high”, the results are comparable with those of the reference method (chemiluminescence, CLS).

The precision of the replicate measurements ranged from 3 % to 9 %, except for the laboratory trial “high”, where some values exceeded 10 %.

Plaisance *et al.* [8] produced a large series of comparison data (n = 52) between diffusion tubes (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) with and without protection device (cylindrical box) and the chemiluminescence analyser carried out at four French urban monitoring stations for ten months. No systematic differences in measurements were observed between the two techniques, using both the theoretical uptake rate and model-predicted uptake rate (see section 3.6).

A lower scattering of points around the regression line (the slope was not significantly different from 1) was found for Palmes tubes set in the protective device and with the model-predicted uptake rate, revealing a significant improvement in the precision of measurements.

The ISO 13752 standard (1998) was used to evaluate the expanded uncertainty of the Palmes tubes under field conditions. Using the model-predicted uptake rate and the protective device, the expanded uncertainty is reduced to < 25%, implying that this diffusion sampler fulfils the uncertainty requirement for indicative measurements of EU Directive 2008/50/EC.

Buzica et al. [9] investigated the performance of Palmes tube (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) at one background location in comparison with the chemiluminescence analyser. The use of the theoretical uptake rate gave a high coefficient of correlation ( $r^2 = 0,97$ ) between the measurements of two methods, but resulted in a substantial underestimation (slope 0,75) of the NO<sub>2</sub> concentration measured by the Palmes tube. By applying the model-predicted uptake rate established in this study (see section 3.6), this bias was corrected. For individual measurements, the Palmes tube was shown to comply with the 25% uncertainty requirement.

Gerboles et al. [1] carried out the field tests of the membrane-closed Palmes tube (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) at the EMEP station in Ispra (I). Forty pairs of data (passive samplers vs chemiluminescence) were collected over a range of concentrations from 8 to 45 µg.m<sup>-3</sup>. Data were analysed to evaluate the equivalence of this sampler to the reference method for NO<sub>2</sub> (chemiluminescence method) in accordance to the Guide to the Demonstration of Equivalence of ambient air monitoring methods [20]. The relative between sampler uncertainty was found to be 3,7%, a value that satisfies the requirement for NO<sub>2</sub> (≤5%) defined in the Guide.

The regression line obtained by applying the method of ISO 6143 (2001) for the reference results of the chemiluminescence analyzer versus those of the membrane-closed Palmes tube revealed no systematic bias in measurements (a slope of  $1,05 \pm 0,045$  and an intercept of  $-0,24 \pm 0,93$ ).

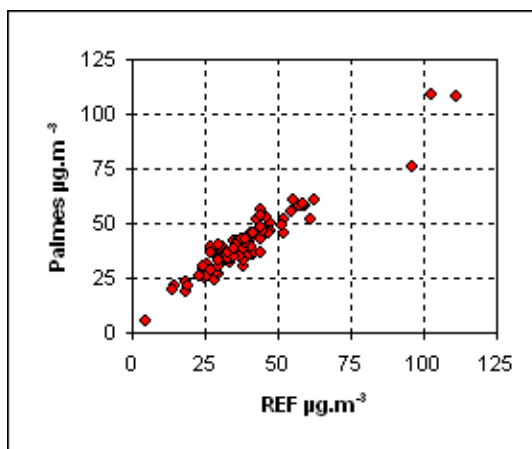
To determine the NO<sub>2</sub> concentrations measured by the membrane-closed Palmes tube, the model-predicted uptake rate was used (see section 3.6). From the results of these field tests and in accordance with the Guide of Demonstration of Equivalence, the expanded uncertainty was calculated to be 17% for an individual sampler measurement when the NO<sub>2</sub> concentrations were higher than 20 µg m<sup>-3</sup>. For the estimation of annual average concentrations, the relative expanded uncertainty was found to be 12% at the limit value of 40 µg.m<sup>-3</sup>, satisfying the data quality objective for indicative measurements (25%). According to these experiments, the membrane-closed Palmes tube for NO<sub>2</sub> could become equivalent to the reference method even for fixed measurements [21].

Through AEA Technology (United Kingdom), annual average data for a large number of monitoring sites for both Palmes tube samplers and reference monitors [22] were provided. In summary, two methods were used for the preparation of the sampler substrates:

- 50 % solution of TEA in acetone, grids dipped into solution and dried before assembly;
- 20 % solution of TEA in deionised water, 50 µl of solution pipetted onto grids already placed in end cap.

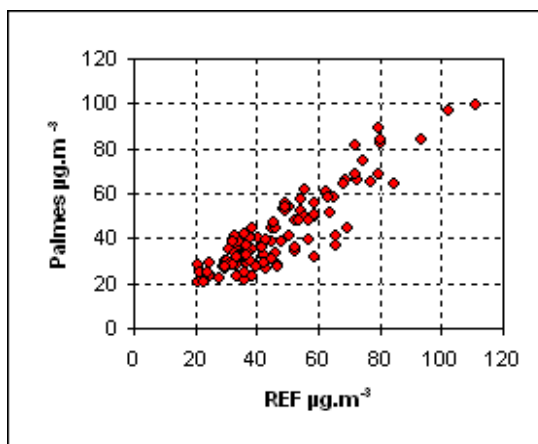
The two datasets derived from different preparation methods were evaluated according to the methodology of the Guide for the Demonstration of Equivalence [20]. By applying an orthogonal regression forced through the origin (0,0), the results given in the figures 3 and 4 were obtained. One may notice that using an orthogonal regression forced through the origin, the intercept is still be slightly different from (0,0).

<i>REGRESSION OUTPUT</i>	
slope, b	1,023
uncertainty of b	0,014
intercept, a	0,6
uncertainty of a	0,59
number of data pairs	83
<i>EQUIVALENCE TEST RESULTS</i>	
random term	5,2 $\mu\text{g.m}^{-3}$
bias at LV	1,5 $\mu\text{g.m}^{-3}$
combined uncertainty	5,4 $\mu\text{g.m}^{-3}$
relative uncertainty	13,6%
reference uncertainty	1,0 $\mu\text{g.m}^{-3}$
limit value	40 $\mu\text{g.m}^{-3}$



**Figure 3.3: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Palmes substrate 20 % TEA in water vs chemiluminescence analyser**

<i>REGRESSION OUTPUT</i>	
slope, b	0,906
uncertainty of b	0,014
intercept, a	-0,3
uncertainty of a	0,71
number of data pairs	116
<i>EQUIVALENCE TEST RESULTS</i>	
random term	7,6 $\mu\text{g.m}^{-3}$
bias at LV	-4,1 $\mu\text{g.m}^{-3}$
combined uncertainty	8,6 $\mu\text{g.m}^{-3}$
relative uncertainty	21,6%
reference uncertainty	1,0 $\mu\text{g.m}^{-3}$
limit value	40 $\mu\text{g.m}^{-3}$



**Figure 3.4: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Palmes substrate 50 % TEA in acetone vs chemiluminescence analyser**

The results suggest that preparation of the sampling substrate using 20 % TEA in water leads to a better comparability with reference data.

Currently, a comparison is ongoing in the United Kingdom in which Palmes tube samplers and Radiello samplers are exposed at a traffic site in London. Results of this comparison were not available at the time of the drafting of this report.

### 3.9 Measurement uncertainty

#### 3.9.1 GUM approach

A French Guide [24] is fully devoted to the assessment of measurement uncertainty from the application of the Palmes tube for measurement of  $\text{NO}_2$ . In a fully worked example based on practical data, the relative expanded uncertainty at  $\text{NO}_2$  concentration of  $37 \mu\text{g.m}^{-3}$  was calculated to be 32 % for a single measurement of 2 weeks duration.

The main contribution to this uncertainty (around two thirds of total uncertainty) was from the uptake rate. The uncertainty of the uptake rate was assessed from tests performed by JRC using Palmes

tubes with a cylindrical protective box in an exposure chamber, under two extreme environmental conditions, yielding low and high values of uptake rate [19] which represented worst case scenarios. Hence, the 32 % represents a worst-case estimate. Practical values are expected to be lower.

### 3.9.2 Direct approach

From the comparisons described above, estimates of the uncertainty associated with NO<sub>2</sub> measurements performed with Palmes tubes were made.

Based on a series of 52 comparison data using an ISO 13752 approach, Plaisance et al. [8] estimated the expanded uncertainty to be < 25 % for a sampler in protective box, using a model-predicted uptake rate.

This finding was confirmed by Gerboles et al. [1], and by Buzica et al. [21], again when using a modelled uptake rate. For the membrane tube, the relative expanded uncertainty of individual measurement results at the level of the annual limit value (40 µg.m<sup>-3</sup>) was estimated to be 17 %.

When aggregating individual results to form an annual average, the relative expanded uncertainty reduced to 12 %. To reach this level of uncertainty, knowledge of average temperature, pressure and relative humidity and wind speed during exposure is a prerequisite.

### 3.10 Application in EU monitoring networks

Palmes tube samplers are extensively used e.g. in Denmark, France, the Netherlands, Spain and the United Kingdom for supplementary measurements to fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

### 3.11 Conclusions

The Palmes tube-type diffusive sampler is suitable for long-term monitoring of NO<sub>2</sub> in ambient air. Exposure periods of 1 to 8 weeks are feasible. The lower detection limit for a 1-week sampling period varied with the meticulousness of the sampler preparation procedure, and generally was between 1,4 µg.m<sup>-3</sup> and 2 µg.m<sup>-3</sup>. The upper limit for a 5-week exposure period was at least 150 µg.m<sup>-3</sup>.

Information about the precision of the sampler showed that it is usually better than 5 % when using a barrier or shelter to reduce effects of wind-induced turbulence. Without these, the precision was generally higher.

Comparisons of sampler results with those obtained from reference monitors (chemiluminescence) gave varying results; however, the results are generally consistent within the uncertainties of the methods. At urban sites, where unprotected open tubes were used, a tendency was observed towards overestimation of NO<sub>2</sub> concentrations.

When using membrane-capped tubes in combination with model equations describing the uptake rate as a function of temperature, humidity, wind speed etc. the comparability improved.

When the uncertainty associated with the measurement results was evaluated according to the Guide to the Expression of Uncertainty in Measurement, the relative expanded uncertainty of individual results was estimated to be 32 % for worst-case conditions (when using a single value for the uptake rate independent of environmental conditions). When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO<sub>2</sub>, better results were obtained (generally < 25 %).

These findings suggest that the Palmes tube is at least suitable for performing long-term measurements of NO<sub>2</sub> for indicative purposes, and possibly even for fixed measurements.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

### 3.12 References

- [1] M. Gerboles, D. Buzica, L. Amantini. Modification of the Palmes diffusion tube and semi-empirical modeling of the uptake rate for monitoring nitrogen dioxide. *Atmos. Environ*, 39 (2005) 2579-2592.
- [2] Diffusion tubes for NO<sub>2</sub> monitoring: Practical guidance. AEA Technology Report AEAT/ENV/R/2504 - Issue 1a, 2008.
- [3] D. Atkins, I. Quirino. A survey of nitrogen dioxide in Paris. Report of Commission of the European Communities EUR 13369 EN, Bruxelles, 1992.
- [4] Échantillonneurs passifs pour le dioxyde d'azote. Passive Samplers for nitrogen dioxide. ADEME Éditions, Paris, 2002. Réf. : 4414.
- [5] C. Kirby, M. Fox, J. Waterhouse. Reliability of nitrogen dioxide passive diffusion tubes for ambient measurement: *in situ* properties of the triethanolamine absorbent. *J. Environ. Monit.*, 2000, 2, 307-312.
- [6] M. Glasius, M. Carlsen, T. Hansen, C. Lohse. Measurements of nitrogen dioxide on Funen using diffusion tubes. *Atmos. Environ*, 33 (1999) 1177-1185.
- [7] T. Bush, S. Smith, K. Stevenson, S. Moorcroft. Validation of nitrogen dioxide diffusion tube methodology in the UK. *Atmos. Environ.*, 35 (2001) 289-296.
- [8] H. Plaisance, A. Piechocki-Minguy, S. Garcia-Fouque, J-C. Galloo. Influence of meteorological factors on the NO<sub>2</sub> measurements by passive diffusion tube. *Atmos. Environ*, 38 (2004) 573-580.
- [9] D. Buzica, M. Gerboles, P. Perez-Ballesta, E. De Saeger. Modeling of the uptake rate of the nitrogen dioxide Palmes diffusive samplers based on the effect of the environmental factors. *J. Environ. Monit.*, 7 (2005) 169-174.
- [10] Y.S. Tang, N van Dijk N, J.N. Cape, L Love, R Storeton-West & M.A. Sutton. Test and validation of passive diffusion sampling methods for long-term ambient monitoring of NO<sub>2</sub> and NH<sub>3</sub> concentrations as part of the BIOROVER project. Centre for Ecology and Hydrology (CEH) Project Report to SEERAD, 2002.
- [11] M. Gerboles, D. Buzica, L. Amantini, F. Lagler, T. Hafkenschied. Feasibility study of preparation and certification of reference materials for nitrogen dioxide and sulfur dioxide in diffusive samplers. *J. Environ. Monit.*, 8 (2006) 174-182.
- [12] E. Palmes, A. Gunnison, J. Dimattio, C. Tomczyk. Personal sampler for nitrogen dioxide. *Am. Industr. Hyg. Assoc. J.* 37 (1975) 570-577.
- [13] Y. Yanagisawa, C. Hemphill, J. Spengler, P.B. Ryan. Wind effect on absorption rate of NO<sub>2</sub> passive sampler, Palmes tube and filter badge. 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, Minnesota, June 22-27, 1986.
- [14] A. Gair, S. Penkett and P. Oyola. Development of a simple passive technique for the determination of nitrogen dioxide in remote continental locations. *Atmos. Environ.* 25A (1991) 1927-1939.

- [15] M. Heal, C. Kirby, J. Cape. Systematic biases in measurement of urban nitrogen dioxide using passive diffusion samplers. *Environ. Monit. Assess.* 62 (2000) 39-54.
- [16] T. Bush, M. Jenkin, J. Banham, A. Loader. Investigation of NO<sub>2</sub> diffusion tube over-read resulting from reduced photolysis by UV light. AEA Technology Report AEAT/ENV/R/0562, 2001.
- [17] D. Atkins, J. Sandalls, D. Law, A. Hough, K. Stevenson. The measurement of nitrogen dioxide in the outdoor environment using passive tube samplers. Report AERE R. 12133 Environmental and medical Sciences Division, Harwell Laboratory, Oxfordshire, United Kingdom, 1986.
- [18] T. Bush, S. Smith, K. Stevenson, S. Moorcroft. Validation of nitrogen dioxide diffusion tube methodology in the UK. *Atmos. Environ.* 35 (2001) 289-296.
- [19] M. Gerboles, D. Busica, L. Amantini, F. Lagler. Laboratory and field comparison of measurements obtained using the available diffusive samplers for ozone and nitrogen dioxide in ambient air. *J. Environ. Monit.* 8 (2003) 112-119.
- [20] 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.
- [21] D. Buzica, M. Gerboles, H. Plaisance. The equivalence of diffusive samplers to reference methods for monitoring O<sub>3</sub>, benzene and NO<sub>2</sub> in ambient air. *J. Environ. Monit.* 10 (2008) 1052-1059.
- [22] Available from <http://www.uwe.ac.uk/aqm/review/index.html>.
- [23] J. Visser, GGD Amsterdam. Personal communication.
- [24] Guide pratique d'utilisation pour l'estimation de l'incertitude de mesure des concentrations en polluants dans l'air ambiant. Partie 4: Estimation des incertitudes sur les mesurages de dioxyde d'azote réalisés sur site par tube à diffusion suivis d'une analyse spectrophotométrique en laboratoire.

## 4 The Passam sampler

### 4.1 Sampler design

The Passam sampler, which is based on the Palmes tube design, is shown in figure 4.1 and consists of an opaque polypropylene tube. The tube is slightly conical. The dimensions of the tube have been measured by Ecole de Mines de Douai [1, p. 46] (see figure 4.1).

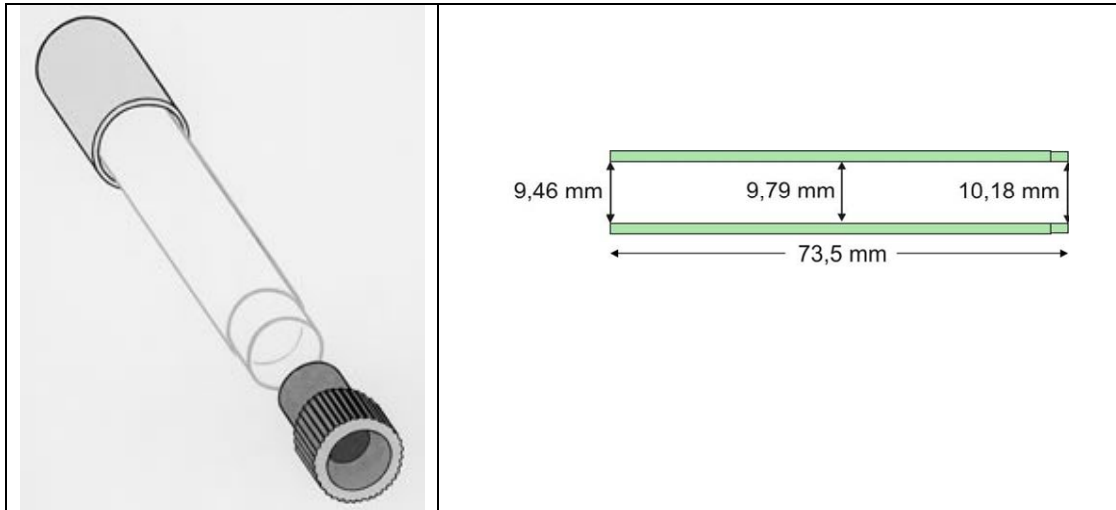


Figure 4.1: Passam tube design

At the narrow end, 3 stainless steel screens are mounted, which are coated by dipping into a solution of TEA - acetone 1:7. Shelf life of the sampling substrate of up to 2 years has been found [2]. Passam tubes are exposed in specific shelters [3]. These shelters are designed to protect the samplers from environmental factors such as rain, excessive radiation and wind. The shelters are an integral component of the measurement method (see figure 4.2).



Figure 4.2: Passam protective shelter

In order to reduce the effect of wind-induced turbulence the sampler may be equipped with a membrane or a glass frit [4].

## 4.2 Extraction and analysis

The manufacturer describes the determination of the collected NO<sub>2</sub> by colorimetry, after reaction with sulphanic acid and N-1-naphthylethylenediamine [3].

## 4.3 Application range and conditions

Information on application ranges and conditions given in table 4.1 was provided by the manufacturer [3].

**Table 4.1: Application ranges and conditions**

Parameter		Application ranges/Conditions
Sampling time		1 – 4 weeks
Working range		1 – 200 µg.m <sup>-3</sup>
Detection limit		0,8 µg.m <sup>-3</sup> for 1-week exposure 0,4 µg.m <sup>-3</sup> for 2-week exposure
External influences	Wind speed	Influence of wind speed < 10 % up to 4,5 m.s <sup>-1</sup> when using protective shelter
	Turbulence at kerb sites	Use of membrane recommended because of potential increase of uptake rate
	Temperature	No effect between 5 and 40 °C
	Humidity	No effect between 20 and 80 % RH
Storage	Before use	12 months
	After exposure	4 months
Cross sensitivity		Nitric oxide and sulfur dioxide do not interfere
		Presence of PAN will lead to high results

Field studies showed that exposure periods of up to 6 weeks are feasible without introducing differences [4].

## 4.4 Uptake rate

The uptake rate of the Passam tube was determined in a series of laboratory experiments [5] designed as prescribed in EN 13528 part 2. In addition, the results of a series of comparisons performed by Buzica *et al.* [6] were used to validate these earlier results.

The manufacturer reported a nominal uptake rate of 0,85 cm<sup>3</sup>.min<sup>-1</sup> ± 11 % for a reference temperature of 9 °C and a reference pressure of 950 mbar.

When applying Fick's first law of diffusion, an uptake rate of 0,947 cm<sup>3</sup>.min<sup>-1</sup> was calculated at a temperature of 21 °C and pressure of 101,3 kPa [1, p. 47].

For practical purposes, users may correct the uptake rate to actual conditions of temperature and pressure by applying equation 3.3. In most cases, the pressure correction may be neglected. Other authors proposed e.g. 4.1 with a temperature correction raised to the power of 1.5 instead of 1.81 ([1], page 74):

$$v_{T,P} = v_{ref} \left( \frac{273,2 + T}{273,2 + T_{ref}} \right)^{1,5} \frac{P_{ref}}{P} \quad (\text{eq. 4.1})$$

where

- $v_{T,P}$  = uptake rate in cm<sup>3</sup>.min<sup>-1</sup> with temperature T and Pressure P during sampling;
- $v_{ref}$  = uptake rate in cm<sup>3</sup>.min<sup>-1</sup> at reference temperature and pressure;
- $T$  = actual temperature during sampling in °C;
- $T_{ref}$  = reference temperature in °C at which  $v_{ref}$  rate is given;
- $P$  = actual pressure during sampling in kPa

$P_{ref}$  = reference pressure in kPa at which  $v_{ref}$  is given.

When applying a glass frit [4] to reduce effects of wind-induced turbulence, the uptake rate reduces to  $0,827 \text{ cm}^3 \cdot \text{min}^{-1}$ .

## 4.5 Environmental effects

### 4.5.1 Air velocity

The migration of  $\text{NO}_2$  molecules to the absorption layer at the lower end of the diffusive sampler is determined by the length of the diffusion path. Eddies created by wind turbulence can shorten the diffusion path, thereby increasing the uptake rate and producing higher results. This phenomenon can be eliminated in one of two ways:

- by using protective shelters;
- by equipping the sampler inlet with a membrane.

#### Protective shelters

Protective shelters reduce the wind velocity at the sampler openings (the sampler and the shelter are an integral system):  $0,5 \text{ m} \cdot \text{s}^{-1}$  outside corresponds to about  $0,1 \text{ m} \cdot \text{s}^{-1}$  inside the shelter [3, 6] (see figure 4.3).

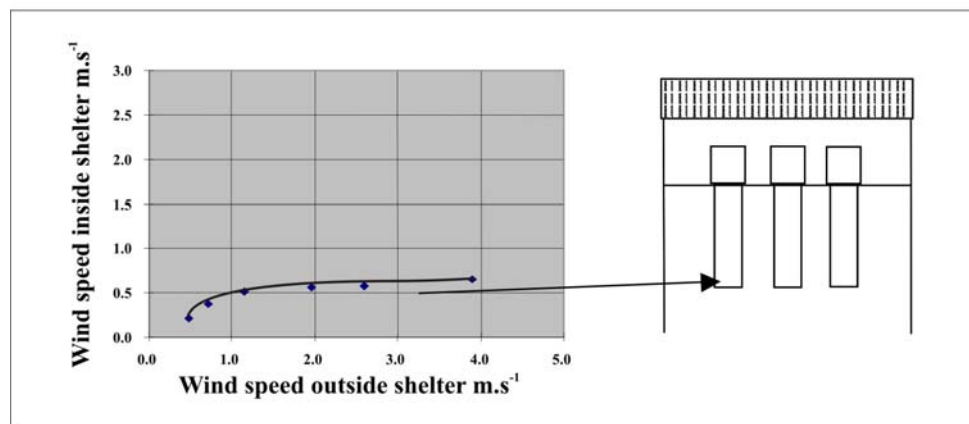


Figure 4.3: Effect of protective shelter on wind velocity inside the shelter

#### Effect of diffusion barrier like membranes or glass frit

The effect of using a polyethylene membrane on the relative uptake rate is illustrated in the figure 4.4.

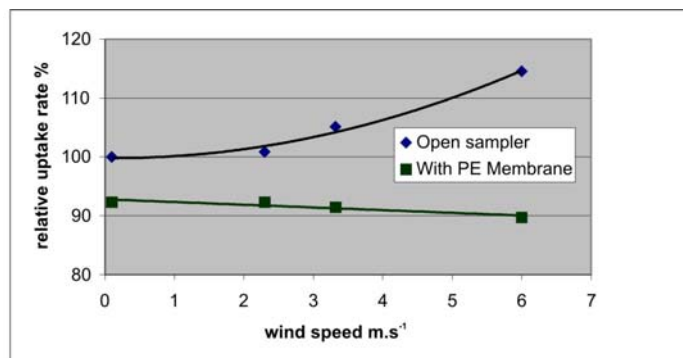


Figure 4.4: Relative uptake rate with and without membrane.

However, membranes affect the uptake rate of a diffusive sampler. The tested membranes (Fluoropore  $1 \mu\text{m}$ , Glass fibre EPM 2000 and Polyethylene  $15\text{-}45 \mu\text{m}$ ) produced a decrease around

10% ± 4%. The results of the tests with different membranes are reported in table 4.2. The tests were conducted in a glass chamber with concentrations of 50 and 100 µg.m<sup>-3</sup> and wind speeds of 0,01 and 0,5 m.s<sup>-1</sup>. By using membranes, an additional resistance to the diffusion of NO<sub>2</sub> towards the absorbent is introduced (see section 3.7.1). This resistance tends to change with sampling conditions and creates another source of uncertainty. However, this uncertainty was found to be lower than the effect of wind velocities above 2 – 3 m.s<sup>-1</sup> for open tubes without protective shelters.

**Table 4.2: Uptake rate for membrane closed Passam samplers relative to open tube**

Membrane type	50 µg.m <sup>-3</sup> 0,5 m.s <sup>-1</sup>	100 µg.m <sup>-3</sup> 0,01 m.s <sup>-1</sup>	100 µg.m <sup>-3</sup> 0,5 m.s <sup>-1</sup>
Fluoropore 1 µm	90 %	95 %	94 %
Glass fibre EPM 2000	91 %	93 %	94 %
Polyethylene 14-45 µm	87 %	90 %	89 %

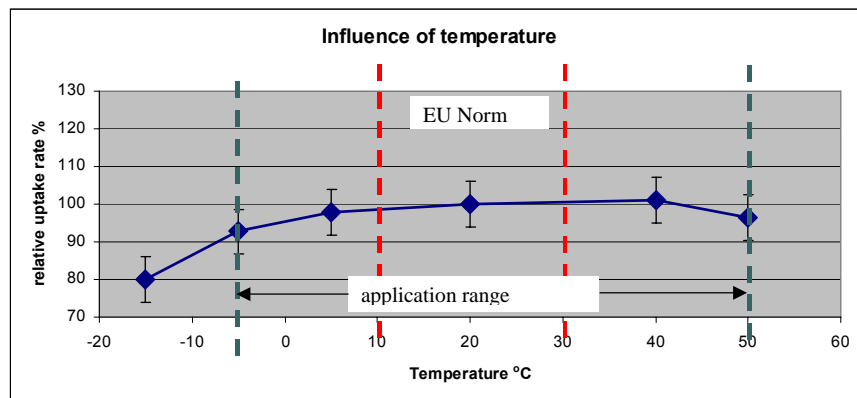
#### 4.5.2 Relative humidity

No influence of relative humidity between 20 and 80% was observed [8]. No data are available for extreme conditions such as dry desert areas and wet tropic areas.

Under European climatic conditions, no humidity effects were reported [9].

#### 4.5.3 Temperature

To investigate the influence of temperature, two glass chambers were set up in series. Six laboratory tests were performed. One chamber was always set at a controlled temperature of 20°C, while the second one was set at different temperatures between -15 and 50 °C (see figure 4.5). For each test, paired uptake rates (one at 20 °C and one at the temperature under test) were determined by exposure and analysis of several samplers in the chambers. For each paired uptake rate, a relative difference with reference to the uptake rate at 20 °C was calculated. Figure 4.5 shows that in the range of 5 to 40 °C, the uptake remained nearly constant and that it does not need any correction [8] according to temperature during exposure.



**Figure 4.5: Effect of temperature on uptake rate, error bars represent the standard deviation of the relative uptake rates**

In a year-long study conducted in Switzerland at 3 monitoring sites, where meteorological data were collected, comparisons between measurements by Passam samplers and chemiluminescence analysers were carried out [8]. A correlation analysis was performed between the meteorological factors and the ratios of NO<sub>2</sub> concentrations measured by the analysers to the diffusive sampler values. In total, 78 2-week pairs of measurements were available. All samplers were equipped with protective shelters. No influence of wind velocity and radiation was observed (see table 4.3). There was a slight correlation with temperature and humidity, although the median test was negative in all cases.

**Table 4.3: Correlation coefficients of meteorological parameters with the ratios of NO<sub>2</sub> measurements carried out with chemiluminescence analyses out of diffusive samplers**

	Temperature	Humidity	Wind speed	Radiation
Unit	°C	% rel.	m/sec	Watt/m <sup>3</sup>
Correlation r	0.136**	0.113**	0.021	-0.019
Range <sub>min</sub>	-0.7	42	0.7	15
Range <sub>max</sub>	23	85	2.6	273
Median	11.2	67	1.4	112
Median test	n.s.	n.s.	n.s.	n.s.

\*\* = 99% significance level.

In a Swiss alpine Valley 1800 m above sea level, a measurement comparison between a chemiluminescence monitor and the Passam samplers was performed. The mean temperature in the coldest season was -4,1 °C. No differences in results of the two methods were observed for temperatures above - 5 °C [3].

#### 4.5.4 Pressure

A pressure effect of 0,5 % decrease in uptake rate with an increase in ambient air pressure of 10 mbars has been observed [8].

#### 4.5.5 Interferences

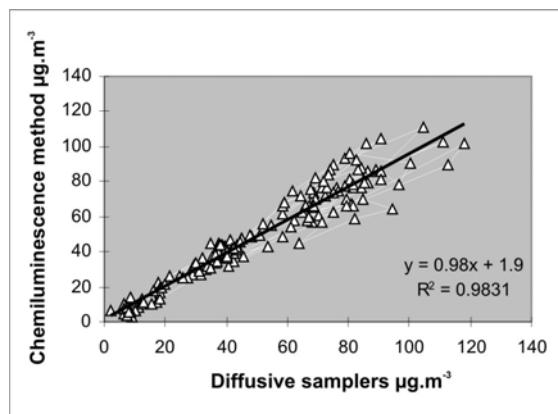
Burri has studied the interferences of NO, SO<sub>2</sub> and ozone. No effects could be shown when single substances were applied [10].

### 4.6 Validation of sampler performance

#### 4.6.1 Comparisons with reference methods

##### Basic validation studies 1986 – 1988

To validate the diffusive sampling system, comparisons with continuous monitors were performed [10]. The comparisons were made at 5 different monitoring sites over one year. 184 weekly monitoring pairs were collected. The concentration values of the monitors were standardized to 9 °C and 950 mbar. The results are compiled in figure 4.6.



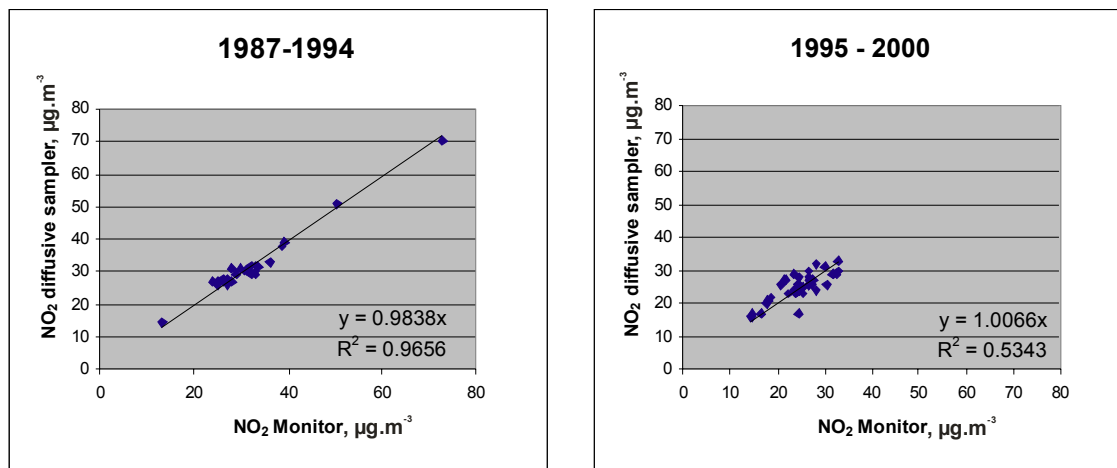
**Figure 4.6. Relationship between results of Passam and chemiluminescence monitors**

### Reports from cantons of Switzerland

#### Comparisons of yearly means

In figure 4.7, the results of comparisons of annual  $\text{NO}_2$  averages are shown. Each point is characterized by 50 to 70 diffusive sampler measurements over one year and a complete data set of chemiluminescence analyser results. The exposure period was two weeks. Under these conditions, varying meteorological factors such as humidity, wind, temperature etc. were automatically considered.

The 95 % confidence interval was calculated to be  $\pm 4 \mu\text{g.m}^{-3}$  at the level of the Swiss long-term limit value of  $30 \mu\text{g.m}^{-3}$ . This figure is valid for the investigations conducted from 1987 to 1994. Figure 4.7 shows that the uptake rate of the sampler remained constant from 1987 to 1994 and from 1995 to 2000. The ratio of  $\text{NO}_2$  measured by samplers vs monitors was 0,98 from 1987 to 1994. The same ratio (1,01), was not significantly different from 1995 to 2000. The difference in  $R^2$  values may be explained by the larger range of  $\text{NO}_2$  concentrations measured between 1987 and 1994.



**Figure 4.7. Relationship between results of Passam and chemiluminescence monitors**

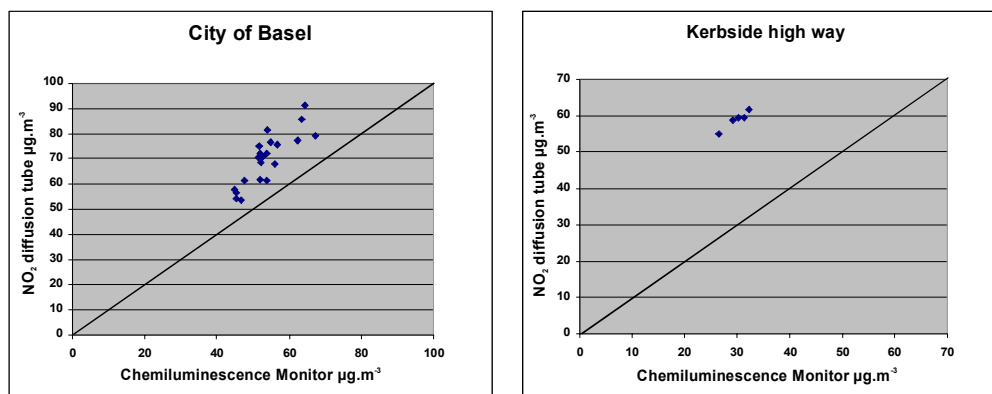
#### Comparisons of single pairs

Table 4 gives a regression analysis for individual  $\text{NO}_2$  concentrations measured using Passam samplers and chemiluminescence analysers. The data were communicated by the Environmental Agencies of the cantons of Grison, Basel and Bern (CH). For each sampling site, the slope/intercept of the regression line, the percentage of variation expressed by the regression line ( $R^2$ ) and the number of samples are given. Samplers were exposed for 2 weeks.

**Table 4.4: Comparisons of individual NO<sub>2</sub> measurements by Passam samplers and chemiluminescence analyser at field sites. Results of environmental agencies in Grison, Basel and Bern (CH)**

Canton	Type of site	Year	Slope	Intercept	R <sup>2</sup>	n
Bern	city background	2005	1,15	-3,4	0,939	26
		2006	0,96	-0,91	0,975	26
		2007	0,94	-0,03	0,928	26
	agglomeration, highway	2005	1,49	-25	0,780	26
		2006	1,12	-9,1	0,889	26
		2007	1,22	-12,7	0,889	26
Basel	city	2001/02	1,15		0,954	124
Grison	industrial	2001-2003	0,94	-6,8	0,700	166
	traffic		0,94	-3,1	0,840	54
	rural		0,9	-1,1	0,890	113
	mountain city,suburb		1,09	-0,9	0,850	128
	mountain city, traffic		1,08	-7,3	0,860	41
	traffic		1,12	-11,4	0,570	25
	mountain		1,16	-11,1	0,750	24
	highway		0,97	-1,2	0,740	231
	mountain village		1,26	-5,8	0,930	15
highway	0,26	16,4	0,130	58		
Neuchatel	city	2005	1,13	0	0,927	27

Near highways and in cities, site-specific discrepancies were sometimes observed (see figure 4.8). In general, an overestimation of the concentration of NO<sub>2</sub> in the vicinity of highly trafficked streets was observed [11]. The deviations are most likely due to traffic-induced vertical air turbulence.



**Figure 4.8. Examples of relationships between results of Passam and chemiluminescence monitors for specific city and highway conditions**

#### Reports from outside Switzerland

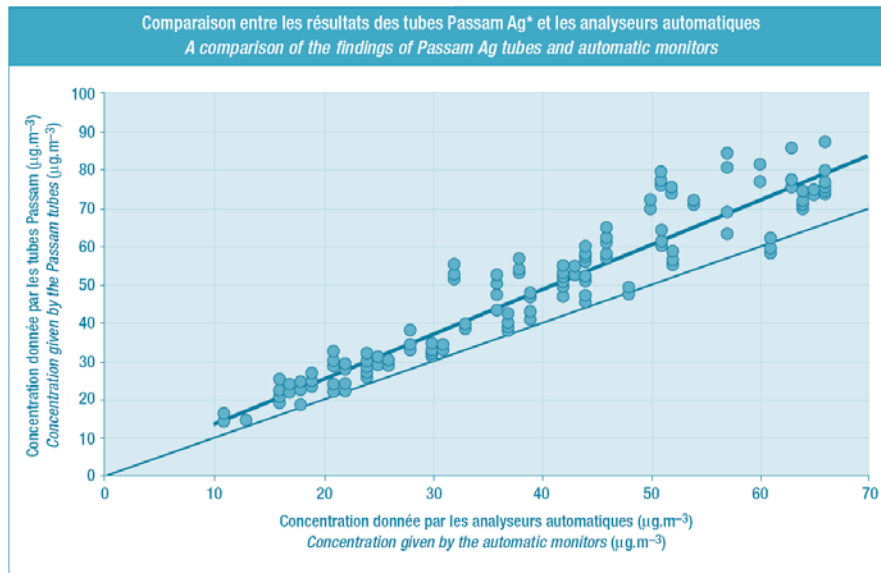
In 2001-2002, CEN/TC264 WG11 performed a small-scale pilot study at two locations in the UK. At each location, 6 replicate samplers of different NO<sub>2</sub> passive samplers were exposed for two weeks, in parallel with measurements from a reference chemiluminescence analyser. Samplers were provided and analysed by the suppliers. The unpublished results for the exposed Passam samplers are reported in table 4.5.

**Table 4.5: Results of CEN pilot study for Passam samplers**

Willebroek	NO <sub>2</sub> (µg.m <sup>-3</sup> )	Ratio Passam/reference
Reference	40,8	
Passam	55,0	1,35
Teddington	NO <sub>2</sub> (µg.m <sup>-3</sup> )	Ratio Passam/reference
Reference	13,8	
Passam	20,2	1,46

Passam samplers were found to overestimate NO<sub>2</sub> concentrations.

Experiments in France at various sites also concluded that the Passam tubes overestimated NO<sub>2</sub> concentrations, when using the uptake rate of 0,85 cm<sup>3</sup>.min<sup>-1</sup> (see figure 4.9). In order to obtain correct values, a uptake rate of 0,947 (21 °C, 101,3 kPa) should be used, reducing the results of the Passam tubes by about 11 %. [1, p. 47].



**Figure 4.9: Relationship between results of Passam and chemiluminescence monitors**

ASPA (the French air quality Alsace network) reported slopes of linear regressions between results of chemiluminescence monitors and Passam tubes from 0,95 to 1,15 (see table 4.6). The NO<sub>2</sub> concentrations were corrected to 20 °C and 1013 mbar according to equation 4.1. The slope/intercept of the regression line, the percentage of variation expressed by the regression line (R<sup>2</sup>) and the number of samples are given. Samplers were exposed for 2 weeks.

**Table 4.6: Comparisons of individual NO<sub>2</sub> measurements by Passam samplers and chemiluminescence analyser at field site. Results of ASPA in France**

ASPA	Type of site	Year	Slope	Intercept	R <sup>2</sup>	n
1	agglomeration	2005	1,15	-3,42	0,939	25
2	rural	2005	0,964	-0,91	0,975	25
3	agglomeration	2005	0,953	-0,03	0,928	25
4	city centre	2005	1,006	1,29	0,963	25
5	city centre	2005	1,023	2,36	0,989	25

Buzica et al. [6] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days, except in the laboratory trial “high” (see table 4.7).

**Table 4.7: Laboratory conditions (intercomparison of Buzica et al.)**

Parameter	High	Low
Exposure time (d)	7	14
Concentration ( $\mu\text{g.m}^{-3}$ )	80	40
Air velocity ( $\text{m.s}^{-1}$ )	2,5	1,0
Temperature ( $^{\circ}\text{C}$ )	25	5
Relative humidity (%)	75	30

The results obtained for the Passam sampler (implemented by an external laboratory following the Passam protocol), are presented in table 4.8.

**Table 4.8: Results of Passam sampler analysed by an external laboratory (intercomparison of Buzica et al.)**

Location	CLS ( $\mu\text{g.m}^{-3}$ )	Passam ( $\mu\text{g.m}^{-3}$ )	Ratio
Laboratory, high	76,8	97 $\pm$ 5	1,27
Laboratory, low	43,5	39,5 $\pm$ 0,7	0,91
Genevilliers	41,6	53,1 $\pm$ 0,3	1,28
Fontainebleau	14,1	15,7 $\pm$ 0,4	1,11

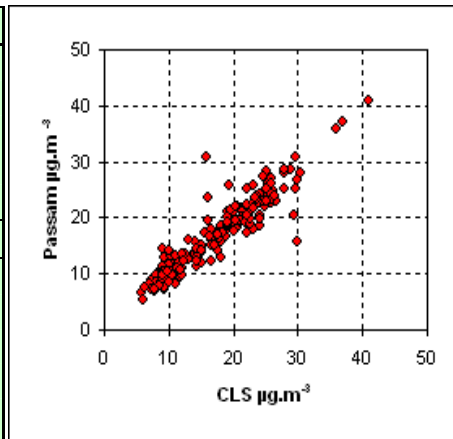
CLS: chemiluminescence method

The Passam tubes were found to overestimate  $\text{NO}_2$  concentrations, confirming the findings reported in [1] (see table 4.8). This was attributed to the use of an uptake rate for reference conditions differing considerably from the exposure conditions.

In 2004-2005, Pfeffer et al. [4] performed an extensive study into the use of Passam tubes. Tubes were exposed for periods from 2 to 6 weeks at 10 different sites in North-Rhine Westphalia in Germany (LANUV network)). In this investigation, a diffusion barrier consisting of a porous glass membrane was fitted at the open end of all samplers. The uptake rate of the tubes, derived from the comparison with reference method according to EN 14211 was  $0,8270 \pm 0,0085 \text{ cm}^3.\text{min}^{-1}$ . When comparing concentrations measured with the reference method and the modified Passam sampler by linear regression, the site-specific slope derived for each monitoring site generally did not differ significantly from the slope calculated from the complete data set at the 95% confidence level. The site-specific slopes varied between 0,93 and 1,11. The between-sampler uncertainty obtained from replicate sampling was  $1,2 \mu\text{g.m}^{-3}$ . The tubes were subsequently used in the LANUV monitoring network. They were further investigated for consistency with the reference method. No deviations were observed when comparing 789 data pairs of results [12].

In France, Passam samplers were extensively compared to the chemiluminescence reference method [13]. During the years 2005, 2007 and 2008 samplers were exposed side-by-side with the reference method at 6 locations (5 in 2005) with exposure periods of 4 weeks, resulting in a total of 181 valid data pairs. From the results reported, it was observed that the data capture of the Passam samplers (100%) was higher than that of the reference method (95,5%). Further, when subjecting the data to the evaluation of equivalence [14], the results presented in figure 4.10 were found. The evaluation revealed excellent agreement between the results of both methods. The resulting uncertainty, 13 % for a 95 % confidence level, fulfils the 15 % uncertainty requirement for fixed measurements of  $\text{NO}_2$ . The ratio of the overall means of diffusive sampling results and reference results was 0,98.

<i>REGRESSION OUTPUT</i>		
slope b	0,975	
uncertainty of b	0,010	significant
intercept a	0,1	
uncertainty of a	0,19	
number of data pairs	181	
<i>EQUIVALENCE TEST RESULTS</i>		
random term	2,4	$\mu\text{g}\cdot\text{m}^{-3}$
bias at LV	-0,9	$\mu\text{g}\cdot\text{m}^{-3}$
combined uncertainty	2,6	$\mu\text{g}\cdot\text{m}^{-3}$
relative uncertainty	6,4%	pass
reference uncertainty	1,0	$\mu\text{g}\cdot\text{m}^{-3}$
limit value	40	$\mu\text{g}\cdot\text{m}^{-3}$



**Figure 4.10: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Passam sampler vs chemiluminescence analyser**

## 4.7 Measurement uncertainty

### 4.7.1 GUM approach

Passam applied the (indirect) GUM approach for the evaluation of the uncertainty associated with the measurement of  $\text{NO}_2$  using the Passam tube [15]. The uncertainty assessment was based on the following measurement equation:

$$C_{\text{NO}_2} = \frac{(m_d - m_b) \cdot 10^6}{v \cdot t} \quad (\text{eq 4.2})$$

where

- $C_{\text{NO}_2}$  = ambient concentration in  $\mu\text{g}\cdot\text{m}^{-3}$ ;
- $m_d$  = mass of desorbed analyte in  $\mu\text{g}$ ;
- $m_b$  = blank of analyte in  $\mu\text{g}$ ;
- $v$  = diffusive uptake rate in  $\text{cm}^3\cdot\text{min}^{-1}$ ;
- $t$  = exposure time in min.

The input quantities and their uncertainties are defined as follows:

- $u_{md}$  : Uncertainty of the mass of measured nitrite. The standard uncertainty is characterised by the standard deviation of the calibration function;
- $u_{mb}$  : Blank values: the variation of blank value has to be added to  $u_{md}$  in absolute terms;
- $u_v$  : Uncertainty of uptake rate. The variation of this term is given by the standard deviation of repeated verification experiments in standard atmospheres;
- $u_t$  : Exposure time. This term is in general negligible at exposure times of more than one week.

An additional term is introduced, which covers the uncertainties associated with between-sampler precision, micro-environmental factors, variations in the geometry of samplers etc.

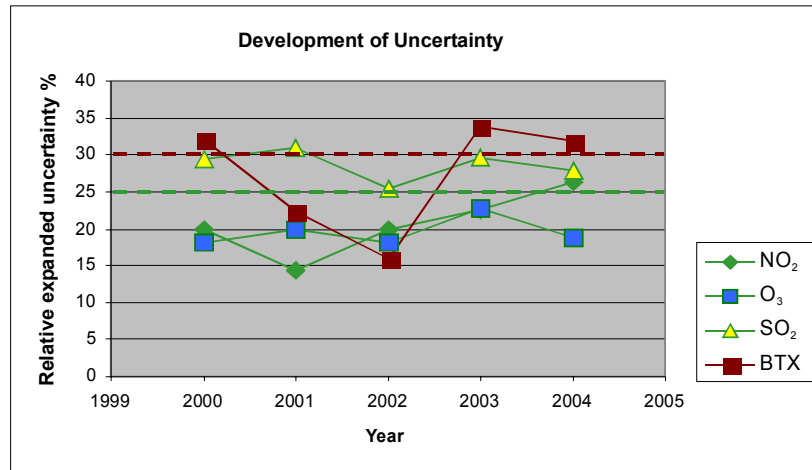
- $u_p$  : Variation of multiple samples at the same site. The size of this term is estimated by the median of triplicate samplers in the field.
- $u_{ext}$  : External influences such as temperature, wind speed, humidity. This term has to be taken into account, if the samplers are used in extreme conditions. This term has to be estimated.

The combined uncertainty  $u_c$  is calculated using equation 4.3.

$$u_c^2 = u_v^2 + u_{md}^2 + u_{mb}^2 + u_p^2 + u_t^2 + u_{ext}^2 \quad (\text{eq. 4.3})$$

The expanded uncertainty is calculated by using a coverage factor of 2. Detailed figures for  $u_v$ ,  $u_p$  and  $u_{mb}$  are given in [16]. The coefficient of variation of replicates is reported in [17] to be 1,7 %. The uncertainty figures are re-evaluated every year [16].

The expanded uncertainty calculated in the above manner varies between 20 % and 25 % (see figure 4.11). The data quality objective of EU Directive 2008/50/EC for indicative measurements is generally fulfilled.



**Figure 4.11: Relative expanded uncertainty of Passam results from 2000 to 2004 as monitored by the manufacturer**

#### 4.7.2 Direct approach

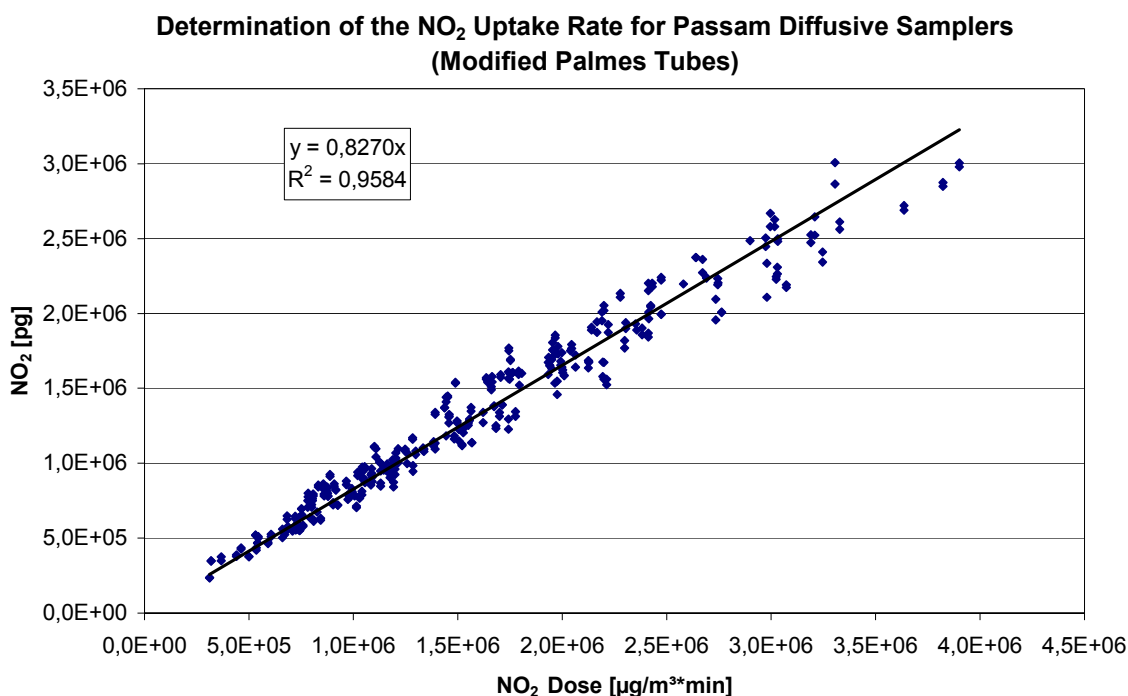
A comprehensive uncertainty evaluation using a direct approach was performed by Pfeffer et al. [4]. At 10 monitoring sites, parallel measurements were performed with Passam samplers and the EU reference method (EN 14211) for more than one year. A modified Passam tube equipped with a porous glass membrane was used.

From the comparisons with reference values obtained from the chemiluminescence monitors, a relative expanded uncertainty for single results between 21 % and 25 % at  $40 \mu\text{g}\cdot\text{m}^{-3}$  was calculated for exposure periods of 2 to 6 weeks. Calculation according to the guide to demonstration of equivalence for 4-weeks exposure resulted in an expanded uncertainty of 22 %. In this calculation, the uncertainty of the reference method results was set to zero. Consequently, the uncertainty represents the worst case [18].

It is unlikely that these results were biased, since the estimation of the uptake rate was based on NO<sub>2</sub> values measured using the reference method (EN 14211). The estimation of the uptake rate was performed using measurements at 10 different monitoring sites and over 14 months (as the slope of the mass uptake versus sampled dose, see figure 4.12). With all these different sampling conditions, the influencing parameters (either chemical or meteorological) encompassed a large range of possible values. It is therefore likely that most of the sources contributing to the uncertainty of the reference method and of the diffusive sampling method were randomised. For this reason, it seemed to be justified to divide the uncertainty of single values by the square root of 12 when calculating annual averages from 12 monthly values. Consequently, the uncertainty of annual averages based on monthly measurements should be less than 10 %. This means that the EU data quality objective of 15 % is safely met for annual means.

In 2004/2005, the uptake rate was evaluated by parallel measurements with chemiluminescence analysers. It was found to be  $0.827 \text{ cm}^3\cdot\text{min}^{-1}$  (see figure 4.12). At this time, the monitors in the

monitoring network were logically not type approved according to the new CEN standard EN 14211 published in 2005.



**Figure 4.12: Relationship between mass of NO<sub>2</sub> obtained by analysis and NO<sub>2</sub> dose sampled**

The uptake rate found in the validation experiments was continuously checked by ongoing parallel measurements with the chemiluminescence method from 2006 to 2008 at six to eight stations. Results for 2006 showed an excellent congruence of the annual averages measured by the chemiluminescence method and with the diffusive samplers [12, 18].

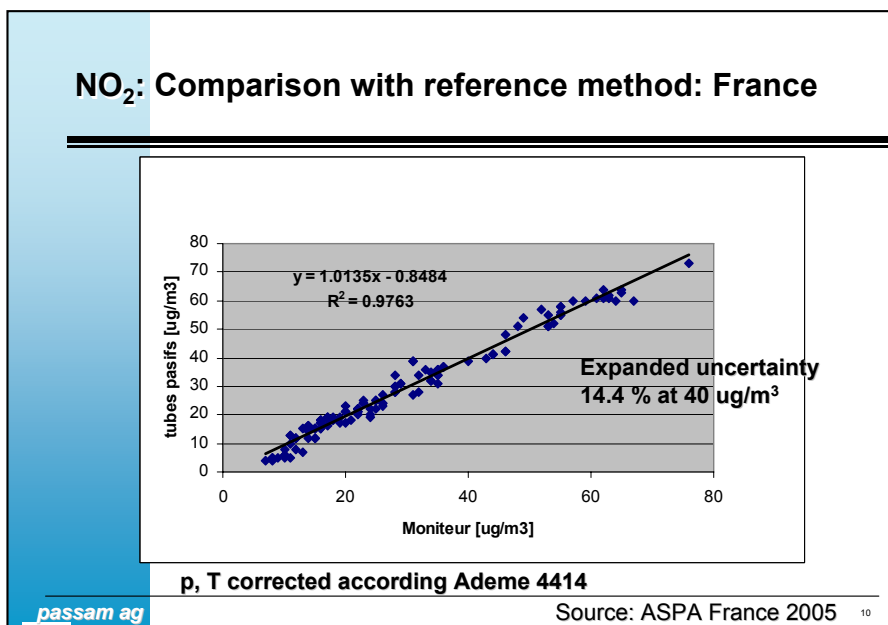
In 2007 and 2008, slight and increasing differences were found at various stations showing higher values of the continuous measurements compared with the diffusive samplers [12].

Comprehensive investigations were performed to find technical reasons for this phenomenon. It was shown that all handling details of the diffusive sampler technique remained unchanged over the years. But in the network of continuous analysers, old instruments were replaced stepwise by new monitors that were type approved according to EN 14211 in order to meet the requirements of Annex VI D of the new European directive 2008/50/EC. The new generation of instruments therefore appears to give higher results for NO<sub>2</sub> in some situations, especially in high ambient humidity conditions. Similar effects were found during inter-laboratory comparisons in the German networks [19].

When sufficient data of parallel measurements are available, it may be necessary to adjust the uptake rate of the diffusive samplers accordingly.

ASPA performed parallel measurements with Passam samplers and the EU reference method (EN 14211) at 5 monitoring sites (rural to city sites) for 1 year using two-week exposure periods [1] (see figure 4.13). The raw data of diffusive samplers, delivered by Passam, were corrected for temperature and pressure according to equation 4.1. Applying the direct approach described in EN-ISO 20988, an expanded uncertainty of 14,4 % at 40 µg.m<sup>-3</sup> was obtained. This figure is similar to the results obtained when evaluating uncertainty for the 3-year data set of monthly measurement results provided by Lig'air [13].

This shows that the uncertainty tends to meet the data quality objective of EU Directive 2008/50/EC for fixed measurements.



**Figure 4.13: Relationship between results of Passam tubes and chemiluminescence monitors, Field site in France (ASPA)**

#### 4.8 Application in EU monitoring networks

Passam tube samplers are used e.g. in Cyprus, France, Germany, Italy, Lithuania and Romania for supplementary measurements to the fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

#### 4.9 Conclusions

The Passam tube-type diffusive sampler is suitable for long-term monitoring of NO<sub>2</sub> in ambient air. Exposure periods of 1 to 6 weeks are feasible. The lower detection limit for a 2-week sampling period is reported to be 0,4 µg.m<sup>-3</sup>.

Information about the precision of the sampler indicates that this is usually better than 5 %.

The comparability of sampler results with those obtained from continuous reference monitors (chemiluminescence) vary somewhat, with ratios of average results generally ranging from 0,9 to 1,3. This variability may be reduced, when :

- Uptake rates are converted to actual conditions of temperature and pressure;
- Membranes are introduced into the sampler inlet, particularly for traffic-related sites.

When the uncertainty associated with the measurement results is evaluated according to the Guide to the Expression of Uncertainty in Measurement, relative expanded uncertainties of individual results were between 20 and 25 %. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO<sub>2</sub>, similar and even better results were obtained.

These findings suggest that the Passam tube is at least suitable for performing long-term measurements of NO<sub>2</sub> for indicative purposes and possibly even for fixed measurements.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

#### 4.10 References

- [1] Échantillonneurs passifs pour le dioxyde d'azote. Passive Samplers for nitrogen dioxide. ADEME Éditions, Paris, 2002. Réf. : 4414.
- [2] C. Kirby, M. Fox, J. Waterhouse. Reliability of nitrogen dioxide passive diffusion tubes for ambient measurement: *in situ* properties of the triethanolamine absorbent. J. Environ. Monit., 2000, 2, 307-312.
- [3] Manufacturer's information: [www.Passam.ch](http://www.Passam.ch).
- [4] U. Pfeffer, R. Beier, T. Zang. Measurements of nitrogen dioxide with diffusive samplers at traffic sites in North-Rhine Westphalia (Germany). Gefahrstoffe – Reinhaltung der Luft, 66 (2006) 38-44.
- [5] Passam validation report (internal).
- [6] D. Buzica, M. Gerboles, L. Amantini. Laboratory and field inter-comparisons of NO<sub>2</sub> diffusive samplers. EUR report 20860, 2003.
- [7] Passam internal Report RBL019901. Windgeschwindigkeit: Einfluss von Schutzboxen und Membranen, 1999.
- [8] M. Hangartner. Diffusive methods for sampling NO, NO<sub>2</sub> and ozone. Presented at Particles and Photo-oxidants in Europe, Prague, 2007.
- [9] M. Hangartner. Influence of meteorological factors on the performance of diffusive samplers. Proceedings of the International Conference on Measuring Air Pollutants by Diffusive Sampling. Montpellier, 2001.
- [10] P. Burri. Passivsammler für die Messung von Stickstoffdioxid und Schwefeldioxid Immissionen. PhD Thesis, ETH Zürich, 1989.
- [11] Versuche mit NO<sub>2</sub>-Passivsammlern an VerVerkehrsexponierten Standorten. Passam Bericht RGC0100\_02, 2000.
- [12] U. Pfeffer. Results presented at 1st Workshop on Nitrogen Dioxide Diffusive Sampling. Ispra, 2-3 October 2008.
- [13] Lig'air, personal communication.
- [14] 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.
- [15] M. Hangartner. Practical approach of uncertainty measurement in ambient monitoring by diffusive samplers. Proceedings of the International Conference on QA/QC in the field of emission and air quality measurements. Prague, 2003.
- [16] M. Hangartner. Ermittlung der Messunsicherheit bei Passivsammlersystemen. Gefahrstoffe – Reinhaltung der Luft, 66 (2006) 58-61.
- [17] S. Garcia-Fouqué, J.-L. Houdret, H. Plaisance. Synthèse de l'expérience acquise par les réseaux sur l'échantillonnage passif du NO<sub>2</sub>. EMD Etude No. 7, 2000.

- [18] U. Pfeffer, T. Zang, R. Beier, E.-M. Douthnik. Experiences with equivalence testing in Germany. EU Report 23216, JRC-IES, 2008, 54-60.
- [19] T. Zang, A. Wagner, U. Pfeffer. Ringversuche der staatlichen Immissionsmessstellen (STIMES), Stickoxide und Ozon, 14. bis 16.11.2006. Fachbericht 10, ISSN: 1864-3930 Fachberichte Landesamt für Natur, Umwelt und Verbraucherschutz NRW, Recklinghausen (2008)

## 5 The Ogawa badge

### 5.1 Sampler design

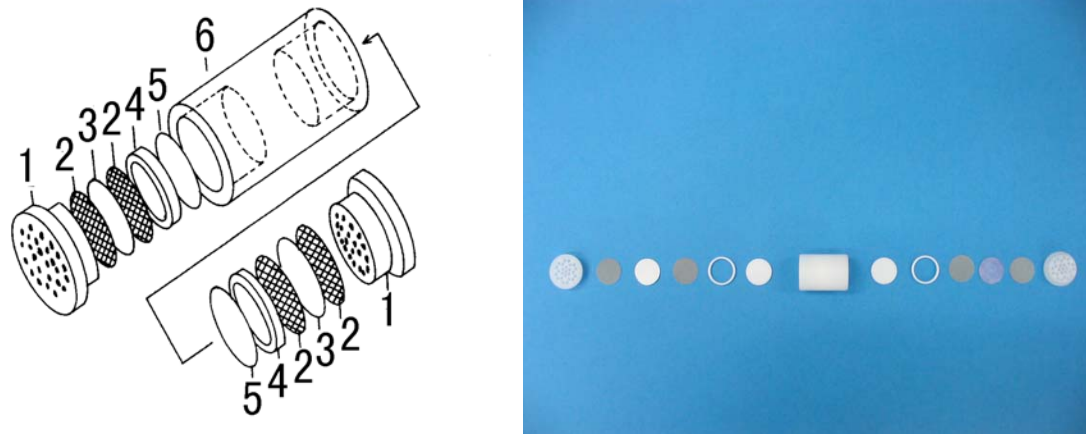


Figure 5.1: Ogawa sampler design

1. Diffuser end cap
2. Stainless steel mesh
3. Sampling filter (14,5 mm  $\phi$ )
4. Teflon ring
5. Teflon disk
6. Body (15 mm ID; 19 mm OD; 6 mm length)

The Ogawa sampler [1] (see figure 5.1) is a badge-type sampler that can be equipped with a sampling filter on either side of the sampler body. Sampling filters consist of cellulose fibre. Both filters can be coated with triethanolamine (TEA) for the sampling of  $\text{NO}_2$  in ambient air. Coated filters may be supplied by the manufacturer. However, literature reveals that filters may also be coated by users themselves [2].

The presence of a second filter permits the simultaneous collection of  $\text{NO}_2$  and nitrogen oxides equal to the concentration of nitrogen monoxide (NO) plus  $\text{NO}_2$ . In this case, the second filter is coated with TEA and 2-phenyl-4,4,5,5-tetramethyl imidazoline-3-oxide-1-oxyl (PTIO), which is a specially prepared reagent for oxidising NO to  $\text{NO}_2$ . This filter then collects both species as  $\text{NO}_2$ . The concentration of NO can be obtained as a difference in  $\text{NO}_2$  concentrations found on the two differently coated filters.

### 5.2 Extraction and analysis

The manufacturer recommends the determination of the collected  $\text{NO}_2$  by colorimetry after reaction with sulphanilamide and N-1-naphthylethylenediamine. However, literature reveals the use of ion chromatography for the measurement of nitrite on the filter [3,4]. In that case, co-sampled sulfur dioxide can also be simultaneously measured.

### 5.3 Application range and conditions

The manufacturer recommends exposure periods from 24 to 168 hours, but indicates that for low concentrations it is possible to sample for up to 30 days. In practice, samplers have been exposed for up to 4 weeks [4].

Although not explicitly stated in [1], the information provided suggests that the samplers may be used over a temperature range from  $-10\text{ }^\circ\text{C}$  to  $40\text{ }^\circ\text{C}$ , and a relative humidity range from 50 % to 80 %.

The sampler should always be exposed with a shelter as provided by the manufacturer.

Detection limits given by the manufacturer are 2,3 ppb for 24-hour sampling, and 0,32 ppb for 1-week sampling. The upper limit for 1-week sampling is reported to be 3600 ppb.

The manufacturer specifies the following conditions for storage of coated filters, samplers and sampled filters upon refrigeration:

- Coated filters sealed in original glass vial with aluminium pouch : 90 days
- Sampler loaded with coated filter(s) placed in bag in sealed brown vial : 60 days
- Exposed sampler placed in bag in sealed brown vial : 14 days\*
- Filter extract in sealed amber glass vial : 90 days.

\* Filters should be analyzed as soon as possible after exposure.

#### 5.4 Uptake rate and environmental effects

The Ogawa Protocol [1] provides information about the uptake rate of the sampler in the form of a coefficient  $\alpha$ , which is a function of temperature and relative humidity. After analysis of an Ogawa sampler,  $\text{NO}_2$  is calculated using equation 5.1

$$C_{\text{NO}_2} = \alpha \cdot \frac{m}{t} \quad (\text{eq. 5.1})$$

where

- $C_{\text{NO}_2}$  = concentration of  $\text{NO}_2$  in ppb;
- $\alpha$  = dose according to the uptake mass in  $\text{ppb} \cdot \text{min} \cdot \text{ng}^{-1}$ , (converse of an uptake rate);
- $m$  = mass of nitrite determined by analysis on a single filter in ng;
- $t$  = exposure time in min.

$\alpha$  may be calculated for a given temperature and relative humidity using the semi-empirical equation 5.2.

$$\alpha = \frac{10^4}{0,677 \cdot P \cdot RH + 2,009 \cdot T + 89,8} \quad (\text{eq 5.2})$$

where

- $RH$  = ambient air relative humidity in %;
- $T$  = ambient temperature in °C.

$P$  is calculated using equation 5.3.

$$P = \left[ \frac{2P_n}{P_T + P_n} \right]^{\frac{2}{3}} \quad (\text{eq. 5.3})$$

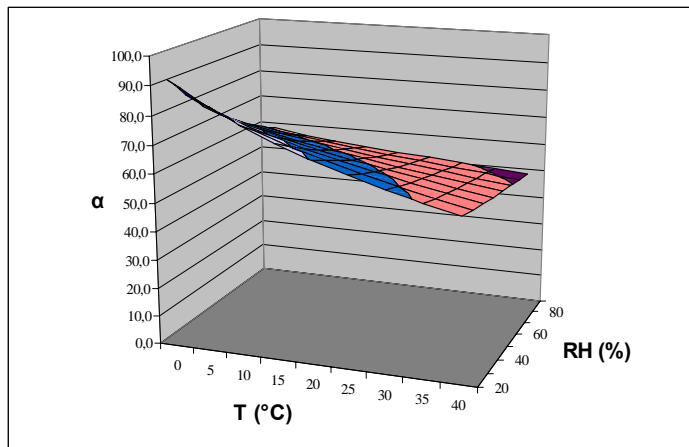
where

- $P_n$  = saturated water vapour pressure at 20 °C in mm of Mercury (Hg) = 17,53
- $P_T$  = saturated water vapour pressure at temperature T in mmHg.

The variation of  $\alpha$  as a function of temperature and relative humidity is presented in table 5.1 and figure 5.2.

**Table 5.1: Variation of  $\alpha$  in ppb.min.ng-1 as a function of temperature and relative humidity**

RH (%) / T (°C)	0	5	10	15	20	25	30	35	40
20	92,4	85,3	79,3	74,2	69,7	65,7	62,2	59,0	56,0
30	85,2	79,4	74,5	70,3	66,5	63,2	60,2	57,4	54,8
40	79,0	74,3	70,3	66,8	63,7	60,9	58,3	55,8	53,5
50	73,6	69,8	66,5	63,6	61,0	58,7	56,5	54,4	52,4
60	68,9	65,8	63,1	60,7	58,6	56,7	54,8	53,0	51,3
70	64,8	62,2	60,0	58,1	56,4	54,8	53,2	51,7	50,2
80	61,2	59,0	57,2	55,7	54,3	53,0	51,8	50,5	49,2
90	57,9	56,1	54,7	53,5	52,4	51,4	50,4	49,3	48,2



**Figure 5.2: Variation of  $\alpha$  in ppb.min.ng-1 according to Temperature (T) and relative humidity (RH)**

In order to calculate a uptake rate in more common units of  $\text{cm}^3 \cdot \text{min}^{-1}$ , equation 5.4 can be used for the conversion.

$$V = \frac{10^3}{\alpha} \cdot \frac{V_{m,air}}{46,0055} \quad (\text{eq. 5.4})$$

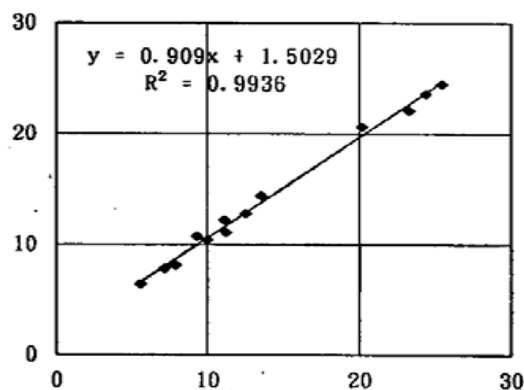
where

$V_{m,air}$  = molar volume of the sampled air.

## 5.5 Validation of sampler performance

### 5.5.1 Comparisons with reference methods

The Ogawa protocol describes a comparison between the results of the sampler and a reference method performed within the frame of the original validation of the sampler (Yokohama City Research Institute of Environmental Science, Yokohama, Japan, Report No. 128, March 1997; see [1]). The results are presented in figure 5.3. The y-axis represents results obtained with the sampler, the x-axis results of the reference method. Unfortunately, the sampling period is unknown.



**Figure 5.3: Comparison between results of the Ogawa sampler with the chemiluminescence method. X and y axis represent the results of the diffusive sampling method and reference method, respectively**

In a further Japanese report supplied by Ogawa USA (no reference available), a comparison was reported between the Ogawa sampler and chemiluminescence monitoring at Funakoshi environmental station. Samplers were exposed during two 5-week periods in July/August 1999 and January/February 2000. Sampling periods of 1, 2, 3, 4 and 5 weeks were used, samplers being exposed in triplicate. The sampler results obtained were internally consistent over the 5-week period. Ratios of results of samplers and chemiluminescence monitors ranged between 0,95 and 1,16, with better comparability observed in the winter period. No information was provided of sampler precision.

Bytnerowicz et al. [5], in a study devoted to the measurement of several air pollutants in Sequoia National Park, measured  $\text{NO}_2$  over the period of May to October 1999 both by the chemiluminescence method and by using the Ogawa sampler. The samplers were exposed in duplicate for consecutive two-week periods. The mean values found by the Ogawa sampler and the chemiluminescence method were 2,6 and 2,0 ppb, respectively. The precision of mean value determined by the Ogawa sampler was 5,6 %.

Buzica et al. [6] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days, except in the laboratory trial "high" (see table 5.2).

**Table 5.2: Laboratory conditions (intercomparison of Buzica et al.)**

Parameter	High	Low
Exposure time (d)	7	14
Concentration ( $\mu\text{g.m}^{-3}$ )	80	40
Air velocity ( $\text{m.s}^{-1}$ )	2,5	1,0
Temperature ( $^{\circ}\text{C}$ )	25	5
Relative humidity (%)	75	30

The results obtained for the Ogawa sampler operated by Lab L – following the Ogawa protocol – are presented in table 5.3.

**Table 5.3: Results of Ogawa sampler operated by Lab L (intercomparison of Buzica et al.)**

Location	CLS ( $\mu\text{g.m}^{-3}$ )	Ogawa ( $\mu\text{g.m}^{-3}$ )	Ratio
Laboratory, high	76,8	132 $\pm$ 19	1,72
Laboratory, low	43,5	46,4 $\pm$ 2,6	1,07
Genevilliers	41,6	41,4 $\pm$ 0,9	1,00
Fontainebleau	14,1	14,8 $\pm$ 3,1	1,05

CLS: chemiluminescence method

Apart from the results of the laboratory trial “high”, the results were comparable with those of the reference method (chemiluminescence, CLS). An explanation for the aberrant results at high air velocity may be that Lab L did not use a protective cover in the laboratory trials. The laboratory “high” trial yielded large variations in results for all participants, with mean results ranging from 54 to 188  $\mu\text{g}\cdot\text{m}^{-3}$ . The precision of the results was also variable, ranging from 2 % to 20 %.

Singer et al. [7] validated the samplers e.g. by parallel measurements with a chemiluminescence analyser. Samplers were exposed for 1 week. They reported a good correlation, with samplers producing slightly lower results (8 % on average). They reported the precision for the sampler to be better than 5 %. The detection limit for a 1-week sampling period was reported to be 0,2 ppb (analysis performed by colorimetry).

Swaans and Goelen [8] reported the results of field tests in Belgium in which a number of diffusive samplers were compared by parallel measurements with a reference monitor. The exposure period was 14 days; each sampler was exposed in triplicate. The results are presented in table 5.4.

**Table 5.4: Results field tests in Belgium**

Location	CLS ( $\mu\text{g}\cdot\text{m}^{-3}$ )	Ogawa ( $\mu\text{g}\cdot\text{m}^{-3}$ )	Ratio
Borgerhout	44,7	47,3 ± 5,2	1,06
Gent	21,0	22,4 ± 2,1	1,07
Borgerhout	51,4	50,6 ± 0,2	0,98
Gent	27,3	25,6 ± 2,7	0,94

Again, results obtained with the Ogawa sampler were comparable to those obtained with the chemiluminescence method. However, the precision of the triplicate results was rather high for 3 trials ( $\approx 10$  %).

Additional work performed by these authors involved a comparison of analyses by ion chromatography and colorimetry. The colorimetric method was found to give a lower detection limit (factor 3). Otherwise, the results obtained were similar.

Sather et al. [9] compared results of 24- and 96-hour diffusive samplers with those from a chemiluminescence analyser. Correlations were good, improving with prolonged sampling duration. Duplicate samplers yielded mean absolute differences of 1,6 to 1,9 ppb for average levels of 22 ppb to 23 ppb.

Sather et al. [4] performed parallel measurements of Ogawa samplers with the US-EPA Federal Reference Method (FRM: the chemiluminescence method) for one year at 6 locations in El Paso, Texas. The extensive dataset resulting from these comparisons was kindly made available by Dr. Sather of US-EPA. Unfortunately, the results received were rounded which may affect comparability at low levels.

The samplers were exposed for different periods: 2, 3 and 4 weeks. All samplers were exposed in duplicate. The mean average difference found between sampler pairs is 0,3 ppb. All results of the trials are presented in tables 5.5 to 5.7.

**Table 5.5: Measurement by the US Federal Reference Method (FRM) and Ogawa sampler at two monitoring sites. Exposure period: 2 weeks; results in ppb. Bold figures represent averages.**

<b>UTEP</b>			<b>Skyline</b>		
<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>	<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>
25	29	1,16	17	17	1,00
22	23	1,05	12	13	1,08
23	25	1,09	13	12	0,92
23	25	1,09	15	13	0,87
18	19	1,06	9	10	1,11
19	19	1,00	11	11	1,00
14	16	1,14	7	7	1,00
17	18	1,06	8	8	1,00
16	16	1,00	8	7	0,88
15	14	0,93	7	7	1,00
14	14	1,00	6	5	0,83
14	12	0,86	6	6	1,00
12	12	1,00	6	6	1,00
14	13	0,93	7	6	0,86
12	12	1,00	6	5	0,83
15	14	0,93	7	6	0,86
14	14	1,00	8	6	0,75
13	14	1,08	7	6	0,86
20	21	1,05	10	9	0,90
13	15	1,15	7	6	0,86
16	17	1,06	8	9	1,13
17	20	1,18	8	12	1,50
18	20	1,11	8	11	1,38
19	21	1,11	10	12	1,20
23	26	1,13	13	16	1,23
23	25	1,09	14	17	1,21
<b>17,3</b>	<b>18,2</b>	<b>1,06</b>	<b>9,2</b>	<b>9,3</b>	<b>1,02</b>

**Table 5.6: Measurement by the US Federal Reference Method (FRM) and Ogawa sampler at two monitoring sites. Exposure period: 3 weeks; results in ppb. Bold figures represent averages.**

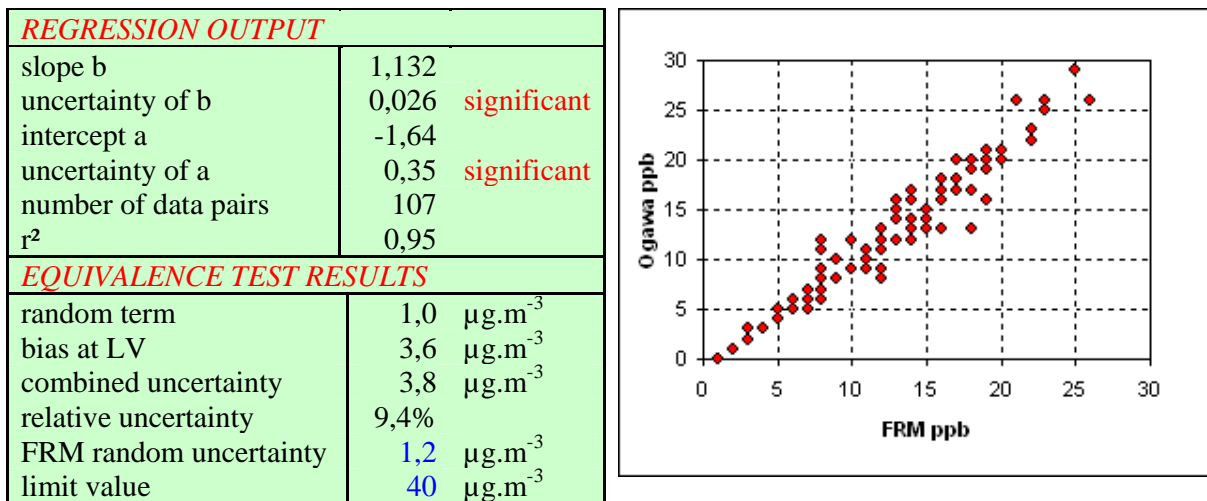
<b>Ascarate</b>			<b>Santa Teresa</b>		
<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>	<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>
21	26	1,24		7	
22	23	1,05	6	6	1,00
22	22	1,00	5	4	0,80
18	19	1,06	5	4	0,80
16	18	1,13	3	3	1,00
19	16	0,84	2	1	0,50
16	13	0,81	1	0	
18	13	0,72	1	0	
13	12	0,92	3	2	0,67
10	9	0,90	3	2	0,67
13	12	0,92	4	3	0,75
15	14	0,93	3	3	1,00
18	17	0,94	5	5	1,00
18	17	0,94	4	3	0,75
19	20	1,05	6	6	1,00
20	20	1,00	6	6	1,00
26	26	1,00	7	7	1,00
<b>17,9</b>	<b>17,5</b>	<b>0,98</b>	<b>4,0</b>	<b>3,6</b>	<b>0,91</b>

**Table 5.7: Measurement by the US Federal Reference Method (FRM) and Ogawa sampler at two monitoring sites. Exposure period: 4 weeks; results in ppb. Bold figures represent averages.**

Socorro			Desert View		
FRM	Ogawa	Ratio	FRM	Ogawa	Ratio
17	20	1,18	14	14	1,00
17	18	1,06	12	11	0,92
14	14	1,00	11	10	0,91
13	12	0,92	7	5	0,71
12	9	0,75	8	6	0,75
12	8	0,67		3	
7	7	1,00		4	
9	8	0,89		6	
10	9	0,90		6	
12	11	0,92	11	9	0,82
14	14	1,00	9	8	0,89
15	15	1,00	12	13	1,08
19	19	1,00	15	15	1,00
<b>13,2</b>	<b>12,6</b>	<b>0,94</b>	<b>11,0</b>	<b>8,5</b>	<b>0,90</b>

By studying the ratios of the mean results obtained by the FRM and the Ogawa sampler, their comparability was evaluated. It was observed that results were comparable for a 2-week exposure period, with the samplers slightly overestimating the reference concentrations. Sampler results for 3- and 4-week periods were generally lower than those of the FRM.

Using this extensive dataset, an attempt to evaluate the equivalence of the sampler with the reference method according to the Guide to the Demonstration of Equivalence [10] was made. The results are presented in figure 5.4.



**Figure 5.4: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Ogawa sampler vs chemiluminescence analyser (FRM)**

The evaluation indicated that, without a recalibration of the uptake rate, keeping the slope and intercept results obtained, this sampler did not meet the data quality objective (DQO) of the EU directive for fixed measurements, as its expanded uncertainty exceeds 15 %, but satisfied the DQO for indicative measurements.

Mosqueron et al. [11] performed a comparison between the sampler and reference method within the frame of quality assurance of an indoor and ambient air exposure study.

The ratio between the means of 49 paired results was 0,97 for an exposure period of 48 hours. When exposing the sampler at both ends, a good correlation was observed between the two results.

Sarnat et al. [12] determined a series of performance characteristics for the sampler when sampling for a period of 24 hours. They found detection limits of 6,4 and 10,8 ppb depending on the sampling season. By measuring with a collocated reference method they determined the precision and accuracy of the sampler to be 17 % and 106 %, respectively.

Van Roosbroeck et al. [13] performed a comparison between the sampler and reference method within the frame of quality assurance of the application of the sampler.

They reported a mean relative difference of 3 %, and a correlation coefficient of 0,96 for an exposure period of 48 hours. The precision of duplicate sampler measurements was reported to be < 5 %.

### **5.5.2 Miscellaneous information about performance characteristics**

A number of publications reported additional information about practical detection limits and precision of the sampler.

Gilbert et al. [3] used samplers to study levels of NO<sub>2</sub> near highways. Employing ion chromatography for analysis, they reported a detection limit for 1-week sampling of 0,7 ppb. The precision of results for duplicate samplers ranged from 6 to 20 %.

Yang et al. [14] used samplers to measure concentrations of NO<sub>2</sub> in indoor air and the penetration of NO<sub>2</sub> from outside to indoor air. Samples were taken over 24-hour periods. Each week duplicate measurements were performed, resulting in an average precision of 8,3 %.

Mukerjee et al. [15] performed a field comparison between samplers and reference monitors. The samplers were exposed for 3, 4 and 7 days for 3 consecutive weeks, with 7-day sampling paralleling 3+4-day sampling. Due to monitor malfunctioning, no definitive conclusions about correlations between results were presented. The study provided information about repeatability and detection limits. Unfortunately, the authors did not report the internal consistency of the 3+4- and 7-day results. The sampler precision was found to be better than 5 %. The detection limit found was lower than 1,3 ppb.

### **5.6 Measurement uncertainty**

No information was found in the literature of (systematic) assessments of measurement uncertainties associated with the use of the Ogawa sampler, e.g., performed according to the Guide to the Expression of Uncertainty in Measurement. When using results from [4] and [6] to make a direct estimation of uncertainties, results found are between 3 % and 23 % expanded relative uncertainty indicating the suitability of the sampler for indicative long-term monitoring of NO<sub>2</sub>. However, further systematically obtained information is needed to substantiate such a claim.

### **5.7 Application in EU monitoring networks**

The Ogawa sampler has been used in Spain. To date, there is no reference found of the sampler being used for ambient air monitoring purposes in the EU. Applications are in the field of indoor air monitoring.

### **5.8 Conclusions**

The Ogawa badge-type diffusive sampler is suitable for long-term monitoring of NO<sub>2</sub> in ambient air. Exposure periods of 2 to 4 weeks are feasible. Lower detection limits reported vary somewhat, but are certainly below 1 µg.m<sup>-3</sup> for a 2-week exposure period.

Information provided about the precision of replicate samples again is variable. Results range from 2 to 20 %. However, frequently precisions better than 5 % are reported.

It is not always clear, though, whether the results of duplicated measurements are based on application of two separate samplers or on analysis of the two filters on either side of the sampler.

When exposed for 14 days or more in the field, the comparability of sampler results to those obtained with continuous reference monitors (chemiluminescence) were good, with ratios of average results ranging from 0,90 to 1,07. The availability of sampler results upon long-term exposure is better than 90 %. Absence of data in comparisons is due to malfunctioning of reference monitors rather than malfunctioning of the sampler.

When using the methodology of the EU Guide to the Demonstration of Equivalence to the results of the US-EPA El Paso study, the sampler is found to pass the uncertainty requirement for indicative measurements. The random uncertainty found for the relation between sampler results and reference method indicate that by correcting the uptake rate the sampler may pass the criterion for fixed measurements. However, the study has been performed in conditions that are atypical of the EU.

No information has been found about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

## 5.9 References

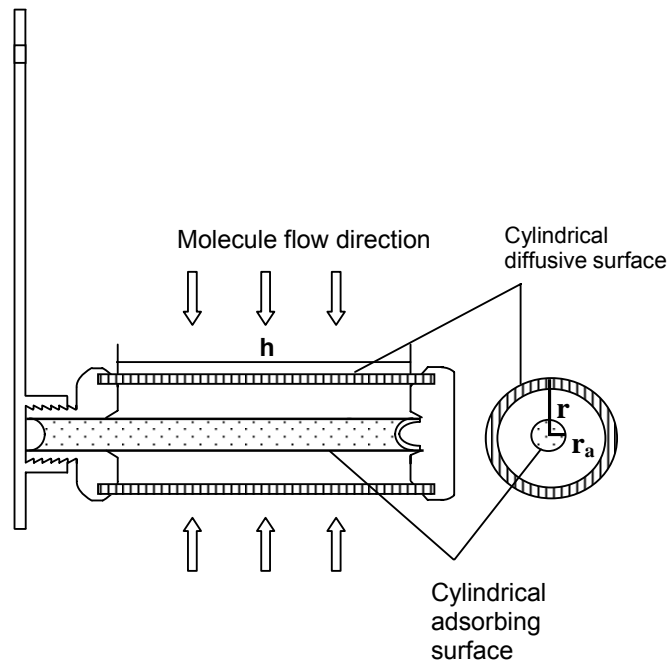
- [1] Ogawa Protocol, version 6, June 2006. Available at [www.ogawa.com](http://www.ogawa.com).
- [2] D. Kim, A. Sass-Kortsak, J.T. Purdham, R.E. Dales, J.R. Brooke. Associations between personal exposures and fixed-site ambient measurements of fine particulate matter, nitrogen dioxide, and carbon monoxide in Toronto, Canada. *Journal of Exposure Science and Environmental Epidemiology* (2006) 16, 172–183.
- [3] N.L. Gilbert, S. Woodhouse, D.M. Stieba, J.R. Brook. Ambient nitrogen dioxide and distance from a major highway. *The Science of the Total Environment* 312 (2003) 43–46.
- [4] M.E. Sather, E.T. Slonecker, J. Mathew, H. Daughtrey, D.D. Williams. Evaluation of Ogawa passive sampling devices as an alternative measurement method for the nitrogen dioxide annual standard in El Paso, Texas. *Environ Monit Assess* (2007) 124:211–221.
- [5] A. Bytnerowicz, M. Tausz, R. Alonso, D. Jones, R. Johnson, N. Grulke. Summer-time distribution of air pollutants in Sequoia National Park, California. *Environmental Pollution* 118 (2002) 187–203.
- [6] D. Buzica, M. Gerboles, L. Amantini. Laboratory and field inter-comparisons of NO<sub>2</sub> diffusive samplers. EUR report 20860, 2003.
- [7] B.C. Singer, A.T. Hodgson, T. Hotchi, J.J. Kim. Passive measurement of nitrogen oxides to assess traffic-related pollutant exposure for the East Bay Children's Respiratory Health Study. *Atmospheric Environment* 38 (2004) 393–403.
- [8] W. Swaans, E. Goelen. Analyse van passieve samplers. Bijkomende NO<sub>2</sub> en SO<sub>2</sub> metingen met verschillende samplers. Rapport 2005/MIM/R/180 (in Dutch).
- [9] M.E. Sather, E.T. Slonecker, K.G. Kronmiller, D.D. Williams, H. Daughtrey, J. Mathew. Evaluation of short-term Ogawa passive, photolytic, and federal reference method sampling devices for nitrogen oxides in El Paso and Houston, Texas. *J. Environ. Monit.*, 2006, 8, 558–563.

- [10] 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.
- [11] L. Mosqueron, I. Momas, Y. Le Moullec. Personal exposure of Paris office workers to nitrogen dioxide and fine particles. *Occup Environ Med* 2002; 59:550–556.
- [12] S.E. Sarnat, B.A. Coull, J. Schwartz, D.R. Gold, H.H. Suh. Factors affecting the association between ambient concentrations and personal exposures to particles and gases. *Environ Health Perspect* 114:649–654 (2006).
- [13] S. van Roosbroeck, J. Jacobs, N.A.H. Janssen, M. Oldenwening, G. Hoek, B. Brunekreef. Long-term personal exposure to PM<sub>2.5</sub>, soot and NO<sub>x</sub> in children attending schools located near busy roads, a validation study. *Atmospheric Environment* 41 (2007) 3381–3394.
- [14] W. Yang, K. Lee, M. Chung. Characterization of indoor air quality using multiple measurements of nitrogen dioxide. *Indoor Air* 2004; 14: 105–111.
- [15] S. Mukerjee, L.A. Smith, G.A. Norris, M.T. Morandi, M. Gonzales, C.A. Noble, L.M. Neas, A.H. Ozkaynak. Field method comparison between passive air samplers and continuous monitors for VOCs and NO<sub>2</sub> in El Paso, Texas. *J. Air & Waste Manage. Assoc.* 54:307–319.

## 6 The Radiello radial sampler

### 6.1 Sampler design

The Radiello sampler is a radial-type diffusive sampler that was developed by Fondazione Salvatore Maugeri in Italy [1]. Its cylindrical outer surface acts as diffusive membrane: the gaseous molecules move axially parallel towards an adsorbent bed which is cylindrical too and coaxial to the diffusive surface [2] (see figure 6.1).



**Figure 6.1: Radiello sampler design**

According to manufacturer's general instructions, exposure for a long time in a wet atmosphere generally does not affect the sampling performances of the Radiello sampler. Nevertheless the sorption of large quantities of water by the cartridges can sometimes affect the sampler performance. Therefore a shelter is important to protect Radiello samplers from rain.

For outdoor exposures, a mountable polypropylene shelter is available (see figure 6.2). It was designed to be mounted easily and without any tool in the field. The shelters are open on three sides. Pylons and posts are recommended as carriers [3]. Once assembled, it ensures the best compromise between protection against rain and wind. It can house up to four samplers and is able to fit a wide range of pole diameters.



**Figure 6.2: Radiello shelter**

The diffusive body can be fitted on a supporting plate either in a vertical or horizontal position as shown in figure 6.3.



**Figure 6.3: Supporting plate for the Radiello sampler**

The adsorbing cartridges are impregnated with a mixture of TEA/water, which also contains traces of ethanol. Further details on the coating and preparation protocol were requested from the manufacturer, but were not provided due to reasons of confidentiality.

The manufacturer recommends and describes the determination of the collected NO<sub>2</sub> by colorimetry after reaction with sulphanilamide and N-1-naphthylethylenediamine [4].

## 6.2 Application range and conditions

According to the manufacturer [4], the uptake rate of NO<sub>2</sub> is constant in the range from 2000 µg.m<sup>-3</sup>.min to 10<sup>7</sup> µg.m<sup>-3</sup>.min (1 ppb to 500 ppb NO<sub>2</sub> for 7-day exposure or 0,5 ppb to 250 ppb for 14-day exposure). The limit of quantification after 7 days exposure is 1 ppb.

The range of meteorological conditions where the use of the Radiello sampler is applicable is given in table 6.1. Exposures up to 15 days are feasible for NO<sub>2</sub>, but if relative humidity is higher than 70 % for the entire sampling duration, the manufacturer recommends a sampling time shorter than or equal to 7 days. Due to the fact that TEA is very hygroscopic, even if water does not actually interfere with sampling or analysis, the excess water adsorbed by the cartridge could cause some loss of adsorbing medium by percolation.

**Table 6.1: Application range of NO<sub>2</sub> Radiello sampler [4]**

Parameter	Range where no effect on uptake rate is observed
Temperature	-10 °C to 40 °C
Relative humidity	15 % to 90 % (maximum RH value 70 % for 14-day exposure); avoid moisture condensation upon the membrane
Wind speed	0,1 m.s <sup>-1</sup> to 10 m.s <sup>-1</sup> The outdoor shelter is required for ambient air measurements
Sampling duration	Up to 15 days If RH>70 %: preferably not longer than 7 days

According to the manufacturer [4], the cartridges are stable for at least 12 months before and 4 months after exposure, if stored in the dark at 4 °C. Expiry date is printed on the plastic bag. At least two cartridges belonging to the same lot should be kept as blanks.

### 6.3 Extraction and analysis

Information on procedures for extraction of sampler cartridges and analysis of sample extracts are available from the manufacturer [4]. The analytical procedures comprise both colorimetry using the Griess-Saltzman method for NO<sub>2</sub> and ion chromatography for SO<sub>2</sub>. An alternative ion chromatographic procedure is available from Swaans et al. [5]. The extraction procedure appears to be a critical factor. During a laboratory and field comparison of NO<sub>2</sub> diffusive samplers by the Joint Research Centre [6], extraction of nitrite from the Radiello cartridge using a vortex shaker for 1 minute at 2500 rpm was found not to be sufficient and needed 1 or 2 repetitions before complete extraction. Another method based on ultrasonic extraction for 25 minutes of the cartridge placed in a glass container with 10 ml of Millipore water gave complete recovery of nitrite.

After tubes were vigorously shaken for two minutes, the contact period between absorption liquid and cartridge was also extended to 1,5 hours by Swaans et al. [5] to ensure complete extraction of nitrite.

### 6.4 Expression of the NO<sub>2</sub> concentration

To calculate the airborne NO<sub>2</sub> concentration, equation 6.1 is generally applied:

$$C_{\text{NO}_2} = 1,91 \frac{(m_s - m_b)}{u \times t} \quad (\text{eq 6.1})$$

where

- $C_{\text{NO}_2}$  = NO<sub>2</sub> concentration in µg m<sup>-3</sup> at 20 °C and 101,3 kPa;
- $m_s$  = mass of nitrite measured in the exposed sampler in ng;
- $m_b$  = mass of nitrite measured in a blank sampler in ng;
- $u$  = uptake rate in ng.ppb<sup>-1</sup>.min<sup>-1</sup>;
- $t$  = sampling time in min.

The coefficient 1,91 is used to convert the NO<sub>2</sub> concentration from ppb in µg m<sup>-3</sup> at 20 °C and 101,3 kPa.

### 6.5 Uptake rate

The uptake rate was determined by the manufacturer as 31,5 cm<sup>3</sup>.min<sup>-1</sup> at 25 °C (corresponding to 0,141 ng.ppb<sup>-1</sup>.min<sup>-1</sup>). The laboratory validation data used for the current model of Radiello NO<sub>2</sub> sampler were supplied by the manufacturer. They are presented in table 6.2. They included the results of two sets of exposure tests at two temperature levels (25 °C and 2 °C) each including three sets of six samples exposed for variable sampling time (approx. 3, 5, 7 days). For one temperature level (9,5 °C), an average value was given while for the other two levels all the individual values were reported.

**Table 6.2: Validation data of the Radiello sampler supplied by the manufacturer**

<b>First test: temperature 25 °C</b>									
<b>Exposure 1</b>									
<i>Camp</i>	$\mu\text{g}$	<i>T</i> (°C)	<i>NO<sub>2</sub></i> (ppb)	<i>Exposure time</i> (min)	<i>NO<sub>2</sub></i> (ppb*min)	$\nu$ (ng/ppb*min)	$\nu$ <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
1°-1	12,90	25,1	22,5	3684	82852	0,156			
1°-2	9,67	25,1	22,5	3684	82852	0,117			
1°-3	11,76	25,1	22,5	3684	82852	0,142			
1°-4	10,24	25,1	22,5	3684	82852	0,124			
1°-5	11,38	25,1	22,5	3684	82852	0,137			
1°-6	7,84	25,1	22,5	3684	82852		0,135	0,015	11,4
<b>Exposure 2</b>									
<i>camp</i>	$\mu\text{g}$	<i>T</i> (°C)	<i>NO<sub>2</sub></i> (ppb)	<i>Exposure time</i> (min)	<i>NO<sub>2</sub></i> (ppb*min)	$\nu$ (ng/ppb*min)	$\nu$ <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
2°-1	20,54	25,1	23,2	6777	157125	0,131			
2°-2	23,89	25,1	23,2	6777	157125	0,152			
2°-3	22,50	25,1	23,2	6777	157125	0,143			
2°-4	18,52	25,1	23,2	6777	157125	0,118			
2°-5	22,69	25,1	23,2	6777	157125	0,144			
2°-6	21,62	25,1	23,2	6777	157125	0,138	0,138	0,012	8,7
<b>Exposure 3</b>									
<i>camp</i>	$\mu\text{g}$	<i>T</i> (°C)	<i>NO<sub>2</sub></i> (ppb)	<i>Exposure time</i> (min)	<i>NO<sub>2</sub></i> (ppb*min)	$\nu$ (ng/ppb*min)	$\nu$ <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
3°-1	30,21	25,0	22,9	9650	220877	0,137			
3°-2	35,78	25,0	22,9	9650	220877	0,162			
3°-3	30,53	25,0	22,9	9650	220877	0,138			
3°-4	32,11	25,0	22,9	9650	220877	0,145			
3°-5	37,48	25,0	22,9	9650	220877	0,170			
3°-6	33,50	25,0	22,9	9650	220877	0,152	0,151	0,013	8,7
						<i><math>\nu</math> overall mean</i>	<b>0,141</b>		
<b>Second test: temperature 2 °C</b>									
<b>Exposure 1</b>									
<i>camp</i>	$\mu\text{g}$	<i>T</i> (°C)	<i>NO<sub>2</sub></i> (ppb)	<i>Exposure time</i> (min)	<i>NO<sub>2</sub></i> (ppb*min)	$\nu$ (ng/ppb*min)	$\nu$ <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
1°-1	8,91	2,2	27,0	3962	107008	0,083			
1°-2	7,21	2,2	27,0	3962	107008	0,067			
1°-3	6,83	2,2	27,0	3962	107008	0,064			
1°-4	7,52	2,2	27,0	3962	107008	0,070			
1°-5	9,04	2,2	27,0	3962	107008	0,084			
1°-6	4,99	2,2	27,0	3962	107008		0,074	0,009	12,8
<b>Exposure 2</b>									
<i>camp</i>	$\mu\text{g}$	<i>T</i> (°C)	<i>NO<sub>2</sub></i> (ppb)	<i>Exposure time</i> (min)	<i>NO<sub>2</sub></i> (ppb*min)	$\nu$ (ng/ppb*min)	$\nu$ <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
2°-1	12,77	2,1	27,0	6900	186166	0,069			
2°-2	15,99	2,1	27,0	6900	186166	0,086			
2°-3	14,41	2,1	27,0	6900	186166	0,077			
2°-4	17,00	2,1	27,0	6900	186166	0,091			
2°-5	14,54	2,1	27,0	6900	186166	0,078			
2°-6	17,19	2,1	27,0	6900	186166	0,092	0,082	0,009	11,2

**Table 6.2: Validation data of the Radiello sampler supplied by the manufacturer (continued)**

<b>Exposure 3</b>									
<i>camp</i>	$\mu\text{g}$	<i>T</i> (°C)	<i>NO</i> <sub>2</sub> (ppb)	<i>Exposure time</i> (min)	<i>NO</i> <sub>2</sub> (ppb*min)	$\nu$ (ng/ppb*min)	$\nu$ <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
3°-1	17,95	2,1	26,9	9688	260828	0,069			
3°-2	21,93	2,1	26,9	9688	260828	0,084			
3°-3	20,29	2,1	26,9	9688	260828	0,078			
3°-4	24,08	2,1	26,9	9688	260828	0,092			
3°-5	23,20	2,1	26,9	9688	260828	0,089			
3°-6	26,80	2,1	26,9	9688	260828		0,082	0,009	11,3
						<i><math>\nu</math> overall mean</i>	<b>0,080</b>		
<b>Third test: temperature 9,5 °C</b>									
<i>T</i> (°C)	<i>NO</i> <sub>2</sub> (ppb)	<i>Exposure time</i> (min)		<i>NO</i> <sub>2</sub> (ppb*min)	$\nu$ (ng/ppb*min)		$\nu$ <i>mean</i>		
9,5	22	10080		221760			<b>0,100</b>		

## 6.6 Environmental effects

### 6.6.1 Air velocity

The uptake rate was reported to be invariant with wind speed between 0,1 m.s<sup>-1</sup> and 10 m.s<sup>-1</sup> [4].

### 6.6.2 Relative humidity and temperature

The uptake rate was reported to be invariant with humidity in the range 15 % to 90 % [4].

However, a significant effect of temperature and relative humidity on uptake rate was observed by Swaans et al. [5]. The temperature effect from 10 °C to 30 °C corresponds to the temperature effect given by the supplier of the samplers (see section 6.7.1). High relative humidity (70 % to 80 %) caused a strong non-reproducible decrease of uptake rate for NO<sub>2</sub> at 24 hour experiments, but this effect was not observed at longer exposures except for the tests at -5 °C. At temperature below zero, in combination with high relative humidity, the sampler showed anomalous behaviour for NO<sub>2</sub>. The possible effect of concentration level and exposure time for NO<sub>2</sub> needs further research.

The NO<sub>2</sub> uptake rate at 25 °C and 101,3 kPa should be corrected so as to reflect the actual sampling conditions. According to the manufacturer's instruction manual [4], the temperature effect for NO<sub>2</sub> on the uptake rate is taken into account using equation 6.2.

$$\nu_T = \nu_{25} \left( \frac{273+T}{273+T_{ref}} \right)^{7,0} \quad (\text{eq. 6.2})$$

where

$\nu_T$  = uptake rate at the temperature T ranging from -10 to 40 °C in ng.pp<sup>b</sup><sup>-1</sup>.min<sup>-1</sup>;

$\nu_{25}$  = reference uptake rate at 25 °C; 0.141 ng.pp<sup>b</sup><sup>-1</sup>.min<sup>-1</sup>;

T = temperature ranging from from -10 to 40°C;

$T_{ref}$  = reference temperature of 25 °C.

The exponential coefficient of 7,0 is derived from the results of the laboratory validation study performed by the manufacturer (see section 6.5).

### 6.6.3 Pressure

The effect of atmospheric pressure (P) on the uptake rate of the Radiello sampler ( $\nu$ ) is usually insignificant. Even though  $\nu$  linearly depends on P, the extent of variation of atmospheric pressure

rarely exceeds 3 kPa about the average value of 101,3 kPa at sea level. An error of  $\pm 3\%$  on uptake rate and usually within  $\pm 1,5\%$  results if no correction for pressure is applied.

## 6.7 Validation of sampler performance

### 6.7.1 Laboratory tests

During the course of year 2002, the NO<sub>2</sub> Radiello sampler was changed by the manufacturer. Since then the cartridges have been made from microporous polyethylene instead of polyester fibre. Afterwards the sampler's manual was also modified a number of times.

Consequently, the results from studies performed using the old type of Radiello cannot be considered in this review. This concerns e.g. results from validation studies performed by the Joint Research Centre Institute for Environment and Sustainability [11], and results from the Resolution project<sup>1</sup>. The validation data presented here relate to the latest version of the Radiello NO<sub>2</sub> diffusive sampler.

In 2005, a validation study of Radiello combined NO<sub>2</sub>-SO<sub>2</sub> diffusive sampler [5] was performed by the Flemish Institute for Technological Research (VITO, Belgium). This was the result of lack of agreement between NO<sub>2</sub> samplers and chemiluminescence analyzers from the VMM automatic network, particularly in case of frost, after changes to the sampler by the supplier. The sampler was first validated under controlled laboratory conditions and subsequently compared with NO<sub>2</sub>-(SO<sub>2</sub>) results of 3 other type of samplers in a field comparison at two locations: Ghent-Mariakerke and Borgerhout in Flanders.

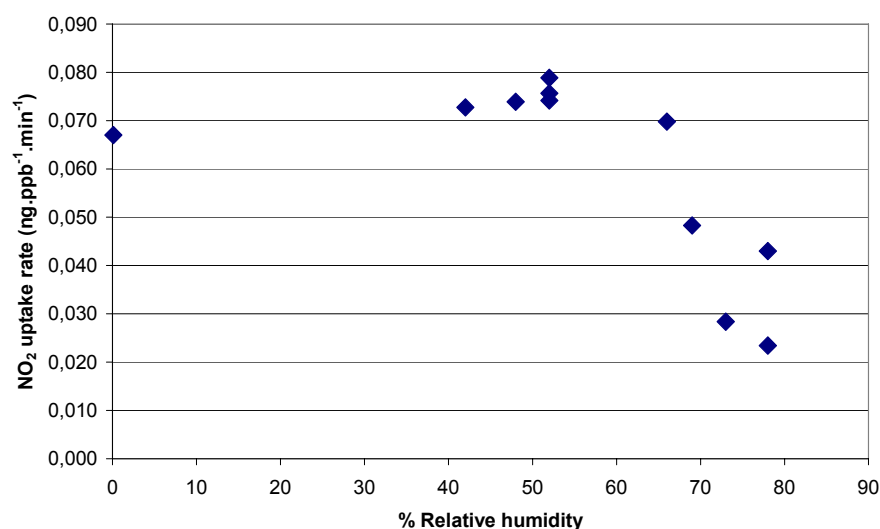
Laboratory exposures at different temperatures (-5, 10 and 30 °C) and relative humidities (0, 50 and 80 % RH) in combination with varying concentration levels and exposure times were carried out, with a focus on extreme conditions (see table 6.4). Typical environmental levels at the monitoring locations of the VMM network for acidic deposition during former campaigns were 10, 20 and 40 µg.m<sup>-3</sup> NO<sub>2</sub>. Under laboratory conditions, exposures were carried out at higher concentrations levels during shorter times within the linear range of 3000–5.10<sup>6</sup> ppb.min according to manufacturer's instructions [4]. By choosing this approach, a better accuracy of the generated higher gas concentrations was achieved. This made it possible to draw better conclusions about the effects on the uptake rate.

**Table 6.4: Laboratory validation set up**

NO <sub>2</sub> (ppb)	Temperature (°C)	Relative humidity (%)	Exposure time
73	-5	80	24 h
18	-5	80	4 days
73	10	0	24 h
73	10	50	24 h
146	10	50	24 h
293	10	50	24 h
73	10	80	24 h
146	10	80	24 h
293	10	80	24 h
11	10	80	14 days (336 h)
73	30	0	24 h
73	30	50	24 h
73	30	80	24 h
18	30	0	4 days
18	30	80	4 days

<sup>1</sup> RESOLUTION Development of a high spatial resolution atmospheric monitoring model to verify the actual emissions reduction of ozone precursors foreseen by Auto-Oil program), LIFE99ENV/IT/081, [http://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=home.createPage&s\\_ref=LIFE96%2520ENV%252FIT%252F000070&area=2&yr=1996&n\\_proj\\_id=1114](http://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=home.createPage&s_ref=LIFE96%2520ENV%252FIT%252F000070&area=2&yr=1996&n_proj_id=1114)

The average uptake rate for NO<sub>2</sub> for 24 hour exposures at 10 °C and 50 % RH and tested concentration levels (73, 146 and 293 ppb NO<sub>2</sub>) was 0,076 ± 0.011 ng ppb<sup>-1</sup> min<sup>-1</sup>. Uptake rates during all experiments were lower than the uptake rate given in the instruction manual of the sampler. As already mentioned in section 6.6.2, a significant effect of temperature and relative humidity on the sampler uptake rate was observed. The temperature effect from 10 to 30 °C corresponds to the temperature effect given by the supplier of the samplers. Exposures to high relative humidity (70 to 80 %) for 24 hours caused a strong non-reproducible decrease of uptake rate for NO<sub>2</sub> (see figure 6.3). However, this effect was not observed for longer exposures, except for the tests at -5 °C. At temperatures below zero in combination with high relative humidity, the sampler showed anomalous behaviour for NO<sub>2</sub>.



**Figure 6.3: NO<sub>2</sub> uptake rate of Radiello sampler at 10 °C versus % relative humidity (24 h exposure)**

### 6.7.2 Comparisons with reference methods

Buzica et al. [6] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days, except in the laboratory trial “high” (see table 6.5).

**Table 6.5: Laboratory conditions (intercomparison of Buzica et al.)**

Parameters	High	High
Exposure time (d)	7	14
Concentration (µg.m <sup>-3</sup> )	80	40
Air velocity (m.s <sup>-1</sup> )	2,5	1,0
Temperature (°C)	25	5
Relative humidity (%)	75	30

The results obtained for the Radiello sampler operated by Lab H, following the manufacturer protocol, are presented in table 6.6.

**Table 6.6: Results of Radiello sampler operated by Lab H (intercomparison of Buzica et al.)**

Location	CLS (µg.m <sup>-3</sup> )	Radiello (µg.m <sup>-3</sup> )	Ratio
Laboratory, high	76,8	54,1 ± 1,5	0,70
Laboratory, low	43,5	30,0 ± 1,0	0,69
Genevilliers	41,6	44,7 ± 1,3	1,075
Fontainebleau	14,1	12,0 ± 0,9	0,85

During the laboratory tests, the samplers were not protected by a shelter, but a holder was used. For the NO<sub>2</sub> laboratory exposures, the uptake rate was calculated using the model equation given in the previous operating manual (2002). By applying the equation of the operational manual version 01/2003 to the laboratory tests (the one given in equation 6.2), the corrected concentrations were in closer agreement with the reference values than with those calculated with the previous model of the uptake rate.

Swaans and Goelen [5] reported the results of field tests in Belgium in which a number of diffusive samplers have been compared by parallel measurements with a reference monitor. The exposure period was 14 days; each sampler was exposed in triplicate. The results are presented in table 6.7. The Radiello samplers were desorbed using a vortex shaking method (a method based on ultrasonic desorption has also been used).

**Table 6.7: Results of field tests in Belgium**

Location	CLS ( $\mu\text{g}\cdot\text{m}^{-3}$ )	Radiello ( $\mu\text{g}\cdot\text{m}^{-3}$ )	Ratio
Borgerhout	55	52,8 ± 8,8	0,96
Gent	37	33,2 ± 7,3	0,92
Borgerhout	44,7	47,4 ± 5,1	1,06
Gent	21,0	16,0 ± 2,1	0,76
Borgerhout	51,4	35,1 ± 3,0	0,68
Gent	27,3	18,2 ± 3,5	0,67

The agreement between measurements performed with Radiello samplers and chemiluminescence analyzer was acceptable, but in some cases the relative standard deviation of the replicates exceeded 30 %. The ratios Radiello samplers/NO<sub>2</sub> analyzer for the different site campaigns ranged from 0,67 to 1,06. In general, the performance of the Radiello sampler was better in the field than during laboratory validation (see table 6.6), although for certain periods samplers gave lower NO<sub>2</sub> concentrations than the continuous analyzer. Conditions were more extreme during the laboratory validation than during the field tests.

Results of comparative measurements between NO<sub>2</sub> Radiello diffusive samplers and chemiluminescence analyzers from 3 French air quality monitoring networks are given in table 6.8.

The results from French studies (personal communication to the authors) confirmed that the Radiello sampler tends to underestimate the concentrations of NO<sub>2</sub> measured by the chemiluminescence analyzers.

Ratios found ranged from 0,57 to 0,99 with one exception (1,42) for concentrations ranging from 22 to 49  $\mu\text{g}\cdot\text{m}^{-3}$ . For a 7-day exposure period the effect appears to be larger than for 14-day exposure.

Other available validation data regarding the NO<sub>2</sub> Radiello sampler exist, but do not apply to the current sampler [7 - 9]. Also the data from the CEN/TC 264 WG11 pilot study date from 2000-2001 and do not apply to the current sampler since the sampler was changed in 2002.

Currently, a comparison is ongoing in the United Kingdom in which Palmes tube samplers and Radiello samplers are exposed at a traffic site in London. Results of this comparison were not available at the time of the drafting of the report.

**Table 6.8: Results of French studies**

Laboratory	Sampling site	Nb of samplers	Sampling time (days)	Start	End	NO2 tube (ppb)	NO2 tube ( $\mu\text{g.m}^{-3}$ )	NO2 chemiluminescence ( $\mu\text{g.m}^{-3}$ )	Ratio Tube / Chemiluminescence	Temperature	Mass of nitrite ( $\mu\text{g}$ )
ATMOSF/AIR Bourgogne		1	7	23/10/07	30/10/07	12,8	20,9	36,9	0,57	8,4	0,171
ATMOSF/AIR Bourgogne		1	7	30/10/07	6/11/07	13,5	21,7	36,6	0,59	6,6	0,168
ATMOSF/AIR Bourgogne		1	7	13/11/07	20/11/07	16,8	25,5	41,2	0,62	1,3	0,158
ATMOSF/AIR Bourgogne		1	7	20/11/07	27/11/07	19,8	31,7	49,0	0,65	6,5	0,168
ATMOSF/AIR Bourgogne		1	7	27/11/07	4/12/07	15,6	24,6	38,1	0,64	4,6	0,164

Laboratory	Site	Nb of samplers	Exposure	Start	End	NO2 $\mu\text{g}/\text{m}^3$ - tube 1	NO2 $\mu\text{g}/\text{m}^3$ - tube 2	NO2 chemiluminescence ( $\mu\text{g.m}^{-3}$ )	Ratio Tube / Chemiluminescence
LIM/AIR	Urban	2	14	10/10/06	24/10/06	37,4	26,1	22,4	1,42

	Site	Nb of samplers	Exposure	Start	End	NO2 $\mu\text{g}/\text{m}^3$ tube 1	NO2 $\mu\text{g}/\text{m}^3$ tube 2	NO2 $\mu\text{g}/\text{m}^3$ - tube 3	NO2 chemiluminescence in $\mu\text{g}/\text{m}^3$	Ratio Tubes mean / Chemiluminescence	Ratio Tube 1 / Chemiluminescence	Ratio Tube 2 / Chemiluminescence	Ratio Tube 3 / Chemiluminescence
	ARLES												
AIRFOBEP	Urban	2	14	2/23/2007	3/9/2007	20,3	25,4		27,4	0,84	0,74	0,93	
AIRFOBEP	Urban	1	14	3/9/2007	3/26/2007	21,3			27,8	0,77	0,77		
AIRFOBEP	Urban	2	14	3/26/2007	4/11/2007	25,9	26,3		31	0,84	0,84	0,85	
AIRFOBEP	Urban	1	14	10/24/2007	11/7/2007		28,3		33	0,86		0,86	
	SALON												
AIRFOBEP	Urban	2	14	2/23/2007	3/9/2007	21,5	18,2		21,7	0,91	0,99	0,84	
AIRFOBEP	Urban	2	14	3/9/2007	3/26/2007	26,4	25,2		28,8	0,9	0,92	0,88	
AIRFOBEP	Urban	2	14	3/26/2007	4/11/2007	31,8	30,4		31,4	0,99	1,01	0,97	
AIRFOBEP	Urban	2	14	10/24/2007	11/7/2007	17,7	15,5		26,4	0,63	0,67	0,59	
	MARIGNANE												
AIRFOBEP	Urban	3	14	2/23/2007	3/9/2007	38	43,4	37,9	42,3	0,94	0,9	1,03	0,9
AIRFOBEP	Urban	3	14	3/9/2007	3/26/2007	27,2	25,7	26,7	32,9	0,81	0,83	0,78	0,81
AIRFOBEP	Urban	2	14	3/26/2007	4/11/2007	38,6	38,4		44,3	0,87	0,87	0,87	
AIRFOBEP	Urban	2	14	10/24/2007	11/7/2007	38,3		39	46,9	0,82	0,82		0,83

## 6.8 Measurement uncertainty

### 6.8.1 GUM approach

The manufacturer in its instruction manual reports an uncertainty of 11,9 % for NO<sub>2</sub> measurements for a probability of 95 % that the true value is within the resulting interval. The method of calculation was requested from the manufacture but was not available.

VITO estimated the NO<sub>2</sub> expanded uncertainty as being 30 % at a 95 % confidence level for the Radiello sampler used to simultaneously determine NO<sub>2</sub> and SO<sub>2</sub> [5]. This uncertainty was estimated using the results of 24-hours laboratory experiments performed in an exposure chamber at 10 °C and 50 % of relative humidity. The estimation was carried out according to the GUM method based on equation 6.3. The contributions of all parameters affecting the uncertainty of measurements are given in table 6.9.

$$C = 1,91 \frac{(m_d - m_b) \cdot 10^6}{v \cdot t} \quad (\text{eq. 6.3})$$

where

- C = ambient concentration in µg.m<sup>-3</sup>;
- m<sub>d</sub> = mass of desorbed analyte in µg;
- m<sub>b</sub> = blank of analyte in µg;
- v = diffusive uptake rate in ng ppb<sup>-1</sup>.min<sup>-1</sup>;
- t = exposure time in min.

**Table 6.9: Uncertainty of NO<sub>2</sub> measurements by Radiello calculated using VITO laboratory experiments**

Uncertainty source	x	u(x)	u(x)/x
nitrite in desorption liquid mg/l	1,3	0,02	0,02
volume of desorption liquid (ml)	6,00	0,08	0,01
absolute amount of nitrite on sampler (µg)	7,62	0,2	0,02
nitrite in desorption liquid from blank sampler (mg/l)	0,09	0,009	0,1
volume of desorption liquid (ml)	6,00	0,08	0,01
absolute amount of nitrite on blank sampler (µg)	0,54	0,05	0,1
<b>nitrite mass after blank-correction (µg)</b>	<b>7,08</b>	<b>0,2</b>	<b>0,03</b>
temperature (T) during measuring period (K)	277,2	1	0.0036
uptake rate (ng ppb <sup>-1</sup> .min <sup>-1</sup> ) at T	0,064	0,010	0,151
sampling duration (min)	20108	10	0,0005
<b>NO<sub>2</sub> Concentration in ambient air (ppb)</b>	<b>5,46</b>	<b>0,8</b>	<b>0,15</b>

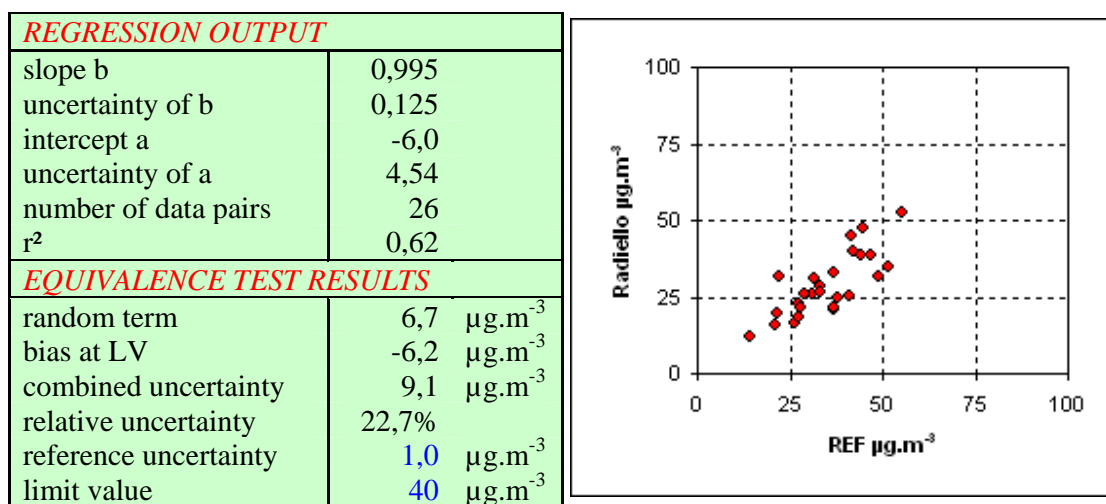
The relative standard uncertainty of the measured NO<sub>2</sub> concentration is 15 %, the expanded uncertainty at a 95 % confidence level (k=2) is then 30 %. This measurement uncertainty is not valid in case of sampling time of 24 hours combined with high relative humidity since a strong decrease of uptake rate may occur under these exposure conditions.

The major source of uncertainty is found to be the uptake rate.

### 6.8.2 Direct approach

When combining data reported in tables 6.6, 6.7 and 6.8 for all field comparisons of Radiello samplers exposed for 14 days with the chemiluminescence reference method, a total of 26 sets of comparison data were available. These were used to make an estimate of the uncertainty of NO<sub>2</sub> concentrations

measured with the Radiello sampler by applying the approach described in the Guide to the Demonstration of Equivalence [10]. The result of this estimation is given in figure 6.4.



**Figure 6.4: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Radiello sampler vs chemiluminescence analyser (REF)**

The relative standard uncertainty calculated in this way was 22,7 %, leading to an expanded uncertainty (95 % confidence) of 45 %. The uncertainty is affected significantly by a systematic underestimation of concentrations by about 6  $\mu\text{g}\cdot\text{m}^{-3}$ .

## 6.9 Application in EU monitoring networks

Radiello samplers are used e.g. in Belgium, France, Italy, Slovakia and Spain for surveys aimed at, e.g. identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

## 6.10 Conclusions

The Radiello radial-type diffusive sampler may be used for long-term monitoring of  $\text{NO}_2$  in ambient air. Exposure periods of 1 day to 2 weeks are feasible. The lower detection limit for a 2-week sampling period was reported to be 0,9  $\mu\text{g}\cdot\text{m}^{-3}$ . Results of a laboratory study in which the sampling period was restricted to one day showed an underestimation of  $\text{NO}_2$  concentrations by a factor of 2 when applying the uptake rate specified by the manufacturer. The reason for this may be a transient period of sorption at the beginning of the sampling period.

Information about the precision of the sampler from field campaigns revealed that the precision relative standard deviation varied around 10 %.

The comparability of sampler results with those obtained with continuous reference monitors (chemiluminescence) varied, with ratios of average results ranging from 0,6 to 1,4. In general, Radiello showed a trend to underestimate concentrations measured by reference monitors. However, the number of field data available was too limited to be conclusive.

When the uncertainty associated with the measurement results for a one-day exposure was evaluated according to the Guide to the Expression of Uncertainty in Measurement, a relative expanded uncertainty of individual results of 31 % was found. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of  $\text{NO}_2$ , similar results were obtained.

These findings suggest that the Radiello sampler did not satisfy the uncertainty data quality objective for indicative measurements of  $\text{NO}_2$ , for which an uncertainty  $\leq 25$  % is required.

When aggregating results to form annual average values, the relative expanded uncertainty was further reduced to levels below 25 % due to the reduction of random effects on uncertainty.

The information collected about the uncertainty of individual measurement results did not correspond with information supplied by the manufacturer stating an expanded measurement uncertainty of 12 %. However, information about the assessment approach used by the manufacturer was (currently) unavailable.

The possible effect of concentration level, high humidity and exposure time for NO<sub>2</sub> needs further research.

## 6.11 References

- [1] V. Cocheo, C. Boaretta, P. Sacco. High uptake rate radial diffusive sampler suitable for both solvent and thermal desorption. *Am. Ind. Hyg. Assoc. J.* 57 (1996) 897-904.
- [2] General instructions to use Radiello, the radial symmetry passive sampler. Fondazione Salvatore Maugeri-Environmental Research Centre, INFO-UK-0599.
- [3] Échantillonneurs passifs pour le dioxyde d'azote. Passive Samplers for nitrogen dioxide. ADEME Éditions, Paris, 2002. Réf. : 4414.
- [4] Fondazione Salvatore Maugeri-Environmental Research Centre. Instructions for NO<sub>2</sub>-SO<sub>2</sub> sampling by Radiello. Last update, March 20<sup>th</sup> 2007.  
[http://www.Radiello.it/english/no2\\_en.htm](http://www.Radiello.it/english/no2_en.htm)
- [5] W. Swaans, E. Goelen, R. de Fré, E. Damen, P. van Avermaet, E. Roekens, V. Keppens. Laboratory and field validation of a combined NO<sub>2</sub>-SO<sub>2</sub> Radiello passive sampler.
- [6] D. Buzica, M. Gerboles, L. Amantini. Laboratory and field inter-comparisons of NO<sub>2</sub> diffusive samplers. EUR report 20860, 2003.
- [7] M. Gerboles, F. Detimmermann, L. Amantini, E. De Saeger. Validation of Radiello Diffusive sampler for monitoring NO<sub>2</sub> in ambient air. JRC-IES. Report EUR 19593 EN, 2000.
- [8] LIFE 99 ENV/IT/000081 RESOLUTION Project, Final report, part B (in Italian) Fondazione Salvatore Maugeri, Padova, 2002.
- [9] Dña. Juana Maria Delgado Saborit. Validación e implementación de técnicas de captación pasiva para el estudio de los niveles y efectos de ozono troposférico y dióxido de nitrógeno en un área costera mediterránea. Tesis Doctoral (in Spanish). Universitat Jaume-Departamento de química inorgánica y orgánica Castellón de la Plana, 20 de Diciembre de 2004.
- [10] 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.
- [11] Gerboles, M., Detimerman, F., Amantini, L, and de Saeger, E. ,Validation of Radiello diffusive sampler for monitoring NO<sub>2</sub> in ambient air, EUR 19593 EN, 2000.

## 7 Other samplers : the Analyst

### 7.1 Sampler design

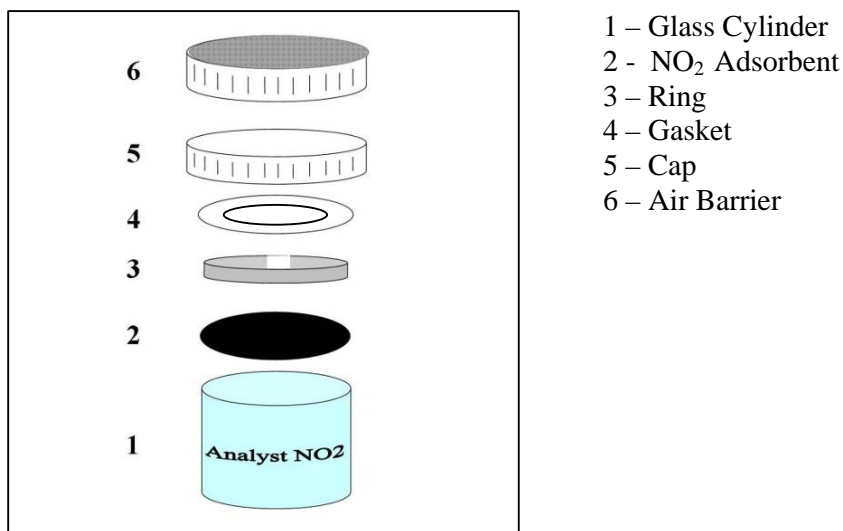


Figure 7.1: Analyst sampler design

The body of the sampler (see figure 7.1, part 1) is a cylindrical glass vial (inner =2,04 cm, length=2,54 cm) with a threaded cap at one end (parts 4 and 5). NO<sub>2</sub> is collected on a disc of impregnated carbon paper filter (part 2) placed at the bottom of the vial and held in position by a stainless steel ring (part 3). To avoid turbulent diffusion inside the vessel, the open end is protected during sampling using a fine stainless steel and plastic screen (part 6). Before and after sampling, the screen is replaced with a polyethylene cap (part 5), which houses a silicone gasket (part 4).

#### *Application range and conditions*

The following information was compiled for the application range and conditions of the sampler [1].

*Detection limit:* 1 ppb (corresponding to 3 standard deviations of 12 blanks for a one-week exposure).

*Exposure time:* From 1 week to 2 months. Shorter exposure times for high concentrations

*Shelter:* The experience gained in many monitoring study showed that a rain and wind shield (see figure 7.2 a) was sufficient for an effective protection of the Analyst sampler. When a strong influence of wind is expected it is recommended to use the shelter shown in figure b.

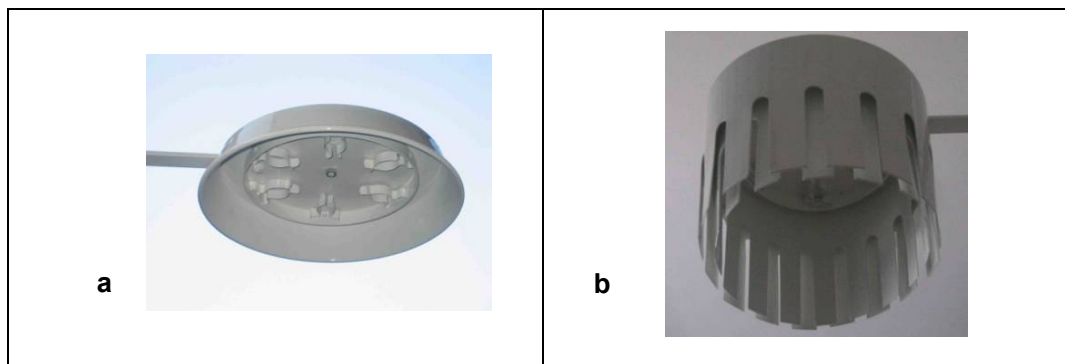


Figure 7.2: Shelters for the Analyst sampler

## 7.2 Sampler storage

*Before use:* 6 months.

*After exposure:* 2 months in a cold and dry place.

The stability of the nitrite collected decreases if the samplers are withdrawn from the field, when they have been recently exposed to very high relative humidity (e.g. rain). If the samplers cannot be analysed immediately (within two or three days after exposure), the manufacturer advises to collect the samplers when the weather is fine and stable for one or two days before ending the sampling. If this is not possible, the samplers must be dried over silica gel or allowed to equilibrate indoors before closing them and storing them in a fresh and dry place.

## 7.3 Extraction and analysis

Nitrogen dioxide, adsorbed as nitrite, can be determined by ion chromatography. A method using the standard Griess-Saltzman reaction for nitrite followed by colorimetric analysis can also be used.

After exposure, the filters are extracted with eluent (2,7 mM Na<sub>2</sub>CO<sub>3</sub> and 0,3 mM NaHCO<sub>3</sub>). The extraction of nitrite is carried out in the same sampler by adding 5 ml of the extraction solution (eluent). The nitrite ion concentration is determined using ion chromatography (Dionex equipped with a column IONPAC AS12A). The concentration of nitrite is calculated from calibration graphs with sodium nitrite standards.

Stock standard solutions of 1000 µg.ml<sup>-1</sup> may be purchased as certified solutions from different manufacturers, or can be prepared by dissolving 0,7499 g of oven-dried sodium nitrite in 0,5 l of de-ionised water. The working standard solutions for the preparation of the calibration curve are made as follows:

- 10 ml of the stock solution are added to a 200 ml flask that is filled to the mark with the Dionex eluent;
- Subsequent dilutions are carried out using a 10 ml pipette and the appropriate volumetric flasks;
- A set of standards in the range 0 to 3,0 of µg.ml<sup>-1</sup> nitrite anion are prepared to calibrate the ion chromatograph.

For low-level applications, more diluted standards may be necessary.

## 7.4 Calculation of ambient air concentration

Equation 7.1 is used to calculate the NO<sub>2</sub> concentration in air (expressed in µg.m<sup>-3</sup>) in which  $v$  is 11.7 cm<sup>3</sup>.min<sup>-1</sup> at 20 °C (see 7.5).

$$C_{\text{NO}_2} = \frac{(m_s - m_b)}{v \times t \times 10^{-6}} \quad (\text{eq 7.1})$$

where

$C_{\text{NO}_2}$  = NO<sub>2</sub> concentration in µg m<sup>-3</sup> at 20 °C;

$m_s$  = mass of nitrite measured in the exposed sampler in µg;

$m_b$  = mass of nitrite measured in a blank sampler in µg;

$v$  = uptake rate in cm<sup>3</sup>.min<sup>-1</sup> at 20 °C;

$t$  = sampling time in min.

This formula assumes that the average temperature during sampling is 20 °C. If the temperature  $T$  is significantly different, a correction to  $C_{\text{NO}_2}$  can be applied multiplying by coefficient calculated using equation 7.2.

$$v_{T,P} = v_{ref} \left( \frac{273,2 + T}{273,2 + T_{ref}} \right)^{1,8} \quad (\text{eq. 7.2})$$

where

- $u_T$  = uptake rate in  $\text{cm}^3 \cdot \text{min}^{-1}$  at temperature T during sampling;
- $u_{\text{ref}}$  = uptake rate in  $\text{cm}^3 \cdot \text{min}^{-1}$  at the reference temperature of 20 °C,  $11.7 \text{ cm}^3 \cdot \text{min}^{-1}$ ;
- $T$  = actual temperature during sampling in °C;
- $T_{\text{ref}}$  = reference temperature in °C at which  $u_{\text{ref}}$  rate is given (20 °C).

## 7.5 Uptake rate and environmental effects

The  $\text{NO}_2$  uptake rate may be calculated directly from the theoretical diffusion coefficient of  $\text{NO}_2$  and the geometry of the sampler. The rate at which  $\text{NO}_2$  is transferred through the vial depends on the average concentration in the ambient air according to Fick's law which is integrated along the diffusion path length to give equation 7.3.

$$m = \frac{(C - C_0)DA t}{L} \quad (\text{eq. 7.3})$$

where

- $m$  = mass uptake in  $\mu\text{g}$ ;
- $C$  = concentration of  $\text{NO}_2$  in  $\mu\text{g} \cdot \text{m}^{-3}$ ;
- $C_0$  = concentration of  $\text{NO}_2$  at the surface of the sorbent in  $\mu\text{g} \cdot \text{m}^{-3}$  (close to zero);
- $D$  = diffusion coefficient of  $\text{NO}_2$  in air in  $\text{m}^2 \cdot \text{min}^{-1}$ ;
- $A$  = cross-sectional area of the diffusion path in  $\text{m}^2$  ( $3,27 \cdot 10^{-4} \text{ m}^2$ );
- $t$  = exposure time in min;
- $L$  = length of the diffusion path in cm (0,0254 cm).

By substitution and using the diffusion coefficient at 25 °C, the  $\text{NO}_2$  uptake rate was calculated using equation 7.3 and found to be  $12,3 \pm 0,5 \text{ cm}^3 \cdot \text{min}^{-1}$ .

The uptake rate was also determined by comparing measurements of the chemiluminescence reference method and of the Analyst samplers for concentrations between 100 and  $1300 \mu\text{g} \cdot \text{m}^{-3}$  at 20 °C and 50 % of relative humidity. When calculating the slope of the regression line of the two methods of measurements, the uptake rate of the Analyst sampler was  $11,7 \pm 0,6 \text{ cm}^3 \cdot \text{min}^{-1}$  [1].

The fairly good agreement between the estimation of the uptake rate using the theory of diffusion and by indirect measurements demonstrates both that  $\text{NO}_2$  absorption on the carbon coated surface is very rapid and that the  $C_0$  term in equation 7.3 must be close to zero.

A series of laboratory tests were undertaken to demonstrate the effect of fluctuating concentrations of  $\text{NO}_2$  on the sampler response. In these experiments, dilution of  $\text{NO}_2$  from a permeation tube was varied over the exposure time by using a pump.  $\text{NO}_2$  changed between 50 (i.e. when the pump was on) and  $500 \mu\text{g} \cdot \text{m}^{-3}$  (i.e. when the pump was off) every hour. This concentration change was repeated overnight. The results of these experiments showed that the uptake rate of variable  $\text{NO}_2$  concentrations was within 5 % of those obtained at constant concentration [1].

To study the influence of relative humidity on the collection efficiency of the sampler, the amount of nitrite collected per unit time and concentration was determined over a range of 20 % to 80 % relative humidity at  $500 \mu\text{g} \cdot \text{m}^{-3}$  of  $\text{NO}_2$  for 10 h at 25 °C. The uptake rates were unaffected by relative humidity and averaged around  $11,9 \pm 0,8 \text{ cm}^3 \cdot \text{min}^{-1}$ .

The interference of ozone was studied by exposing samplers previously loaded with  $\text{NO}_2$  to an ozone mixture in an exposure chamber (3 samplers were exposed to  $400 \mu\text{g} \cdot \text{m}^{-3}$   $\text{O}_3$  for 5 h). Ozone was measured using UV absorption analyzer. Ozone had no measurable interference effect.

## 7.6 Validation of sampler performance

In 2001-2002 CEN/TC264 WG11 “Diffusive samplers” performed a small-scale pilot study at two locations in which 6 samplers were exposed for two weeks, accompanied by parallel measurements with a reference monitor. The results for the exposed Analyst samplers are reported in table 7.1.

**Table 7.1: Results of CEN pilot study for the Analyst sampler**

<b>Willebroek</b>	<b>NO<sub>2</sub> (µg.m<sup>-3</sup>)</b>	<b>Ratio Analyst/reference</b>
Reference	40,8	
Analyst	112	2,74
<b>Teddington</b>	<b>NO<sub>2</sub> (µg.m<sup>-3</sup>)</b>	<b>Ratio Analyst/reference</b>
Reference	13,8	
Analyst	18,0	1,30

Analyst samplers were found to overestimate NO<sub>2</sub> concentrations. The overestimation for the experiment at Willebroek could be explained by the fact that the sampler was exposed without a shelter in very windy conditions in an open field, contrary to manufacturer recommendations.

A validation study carried out at an urban background site (Villa Ada, Rome, Italy), side-by-side with a chemiluminescence analyser, showed that the Analyst sampler for NO<sub>2</sub> is characterised by an expanded uncertainty lower than 21 %, well within the limit required by EU Directive 2008/50/EC for indicative measurements [1].

This field validation consisted of two elements:

- A study into the integrated response of samplers over different sampling periods;
- A comparison with a reference analyzer according to ISO 13752.

The study entailed the comparison of 35 pairs of results from the chemiluminescence analyser and the Analyst sampler over a full range of average wind-speed conditions ranging from 1,4 m.s<sup>-1</sup> to 2,0 m.s<sup>-1</sup> over fortnight sampling periods. Average daily wind velocity values ranged from 0,7 m.s<sup>-1</sup> to 4,2 m.s<sup>-1</sup>.

Buzica et al. [2] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days except in the laboratory trial “high” (see table 7.2).

**Table 7.2: Laboratory conditions (intercomparison of Buzica et al.)**

<b>Parameter</b>	<b>High</b>	<b>Low</b>
Exposure time (d)	7	14
Concentration (µg.m <sup>-3</sup> )	80	40
Air velocity (m.s <sup>-1</sup> )	2,5	1,0
Temperature (°C)	25	5
Relative humidity (%)	75	30

The results obtained for the Analyst sampler operated by Lab B are presented in table 7.3.

**Table 7.3: Results of the Analyst sampler operated by Lab B (intercomparison of Buzica et al.)**

<b>Location</b>	<b>CLS (µg.m<sup>-3</sup>)</b>	<b>Analyst (µg.m<sup>-3</sup>)</b>	<b>Ratio</b>
Laboratory, high	76,8	111 ± 5	1,44
Laboratory, low	43,5	43,3 ± 1,0	1,00
Genevilliers	41,6	55,9 ± 1,4	1,34
Fontainebleau	14,1	15,0 ± 0,5	1,06

These results show a somewhat “mixed” performance, although the laboratory “high” trial yielded large variations in results for all participants, with mean results ranging from 54 to 188  $\mu\text{g}\cdot\text{m}^{-3}$ . The precision of the results was good, usually within 10 %.

### 7.7 Measurement uncertainty

The accuracy of the samplers in comparison to the chemiluminescence technique, expressed as percent relative error was found to be better than  $\pm 20$  % at 20 ppb of  $\text{NO}_2$ . The relative standard deviation on 12 samplers is 7 % [1].

No further information is available, e.g. assessments based on application of the Guide to the Expression of Uncertainty in Measurement.

### 7.8 Application in EU monitoring networks

Applications appear to be mostly in indoor air monitoring, e.g., for studies into protection of cultural heritage. No references to applications in ambient air monitoring have been found.

### 7.9 Conclusions

The Analyst badge-type diffusive sampler may be used for long-term monitoring of  $\text{NO}_2$  in ambient air. Exposure periods of 1 to 2 weeks are feasible. The lower detection limit for a one-week exposure period was reported to be 1,9  $\mu\text{g}\cdot\text{m}^{-3}$ .

The precision of replicate samples was generally within 10 %. However, the number of studies reported is limited.

The comparability of sampler results with those obtained with continuous reference monitors (chemiluminescence) was acceptable, with ratios ranging from 1,0 to 1,4. However, it must be emphasized that the number of studies on which this conclusion was based is limited.

No information was available on the availability of sampler results upon long-term exposure. However, from the laboratory experiments it could be concluded that an exposure period of at least 4 months is feasible for sites characterized by concentrations up to 200  $\mu\text{g}\cdot\text{m}^{-3}$ .

When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of  $\text{NO}_2$ , the accuracy was reported to be  $\pm 20$  %.

No information was found about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

### 7.10 References

- [1] F. De Santis, T. Dogeroglu, A. Fino, S. Menichelli, C. Vazzana, I. Allegrini. Laboratory development and field evaluation of a new diffusive sampler to collect nitrogen oxides in the ambient air. *Anal. Bioanal. Chem.* 373 (2002) 901-907.
- [2] D. Buzica, M. Gerboles, L. Amantini. Laboratory and field inter-comparisons of  $\text{NO}_2$  diffusive samplers. EUR report 20860, 2003.
- [3] F. De Santis, M. Montagnoli, D. Pasella, I. Allegrini. The measurement and model predictions of photochemical pollutants in the Uffizi Gallery, Florence. *Annali di Chimica*, 89 (1999) 679-688.

- [4] F. De Santis, A. Fino, S. Tiwari, C. Vazzana, I. Allegrini. A performance evaluation of the open tube diffusion sampler (Palmer sampler) for monitoring nitrogen dioxide. *Air Pollution VIII*, J.W.S. Longhurst, C.A. Brebbia, H. Power, Eds, WIT Press, Southampton, pp 421-429.
- [5] F. De Santis, A. Fino, C. Vazzana, I. Allegrini. Monitoring of nitrogen dioxide by passive sampling. *Euroanalysis XI*, 3-9 Sept. 2000, Lisbon, Portugal, OC-62.
- [6] F. De Santis, M. Montagnoli, D. Pasella, I. Allegrini. A study on indoor air quality and photochemical pollution in the Uffizi Gallery, Florence, Italy. *Air Pollution VII*, C.A. Brebbia, N.Jacobson, H. Power, Eds, Stanford 26-29 July 1999, 497-505.
- [7] F. De Santis, A. Fino, C. Vazzana, I. Allegrini. Monitoring of Nitrogen Oxides by Passive Sampling. *Atti del Congresso Euroanalysis XI – European Conference on Analytical Chemistry*, Lisbona, Portogallo, 3-9 Settembre 2000, p.OC-62.
- [8] F. De Santis, A. Fino, C. Vazzana. Valutazione dell'Impatto dell'Inquinamento Atmosferico tramite Campionamento Passivo nella Zona Monumentale di Ortigia (Siracusa). *Atti del Congresso "La Chimica dei Beni Culturali – L'Ambiente, la Diagnostica, la Conservazione"*, Urbino (PS), 4-5 Ottobre 2000, p.13.
- [9] F. De Santis, A. Fino, C. Vazzana, I. Allegrini. Applicazione del Monitoraggio tramite Campionamento Passivo per la Valutazione dell'Impatto dell'Inquinamento Atmosferico sul Degrado dei Monumenti. *Atti del Congresso "Aria di Città – La Qualità dell'Aria in Ambiente Urbano"*, Bologna, 28-30 Novembre 2000, pp.163-167.
- [10] F. De Santis, I. Allegrini, S. Menichelli, C. Vazzana. Diffusive Monitoring of Air Quality around a Petroleum Refinery. *Atti della 12<sup>a</sup> Conferenza Internazionale "Euroanalysis"*, Dortmund (Germania), 8-13 Settembre 2002, p.P2-191.
- [11] F. De Santis, C. Vazzana, S. Menichelli, I. Allegrini. The measurement of atmospheric pollutants by passive sampling at the Uffizi Gallery, Florence. *Annali di Chimica*, 93 (2003) 45-53.
- [12] F. De Santis, I. Allegrini, T. Dogerouglu, S. Menichelli, C. Vazzana. Diffusive samplers for monitoring atmospheric pollution at the Uffizi Gallery, Florence. *Proceedings of the 3rd International Congress on Science and technology for the Safeguard of Cultural Heritage in the Mediterranean Basin*, Alcalá de Henares (Spain) 9-14 July 2001, 1213-1218.
- [13] F. De Santis, I. Allegrini, R. Bellagotti, F. Vichi. Validation of the diffusive sampler Analyst. *Abstract Book of the International Conference "QA/QC in the field of emission and air quality measurements, harmonisation, standardisation and accreditation"*. Praha, Czech Republic, 21-23 May 2003.

## 8 Summary of findings, conclusions and recommendations

### 8.1 Summary of findings

A number of diffusive samplers that are used for long-term monitoring of nitrogen dioxide (NO<sub>2</sub>) were subjected to a review of their use and performance characteristics. The samplers were selected on the basis of their general availability in the European Union:

- The Palmes tube sampler;
- The Passam tube sampler;
- The Ogawa badge sampler;
- The Radiello radial sampler;
- The Analyst badge sampler.

The IVL sampler, although a sampler in frequent use throughout the European Union, was not included in the review, since most information about this sampler is considered a proprietary secret by the manufacturer.

The information collected was used to:

- Draft conclusions about the feasibility of using the samplers for the long-term monitoring of NO<sub>2</sub>, with the particular aim of assessing compliance with the European Union annual limit value of 40 µg.m<sup>-3</sup> (at 20 °C and 101,2 kPa);
- Draft a proposal method for monitoring NO<sub>2</sub> using diffusive samplers, for future use by CEN Technical Committee 264 “Air Quality” Working Group 11 “Diffusive Samplers” as a CEN standard devoted to the measurement of NO<sub>2</sub> in ambient air.

Main criteria for the assessment of sampler feasibility for both purposes were:

- The validation level of the samplers, based either on application of EN 13528 part 2 or the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods, including information about the uncertainty of results obtained using the samplers;
- From this: the potential to meet European Air Quality Directive data quality objectives for indicative and/or fixed measurements;
- The extent or lack of information available to underpin the validity of results obtained using the different samplers;
- The number of different sources providing the above information;
- Differences in performance depending on site type (tube type): traffic, urban, rural;
- The possibility for users to analyse the samplers, e.g., based on procedures specified by manufacturers;
- Their current use throughout the European Union for measuring ambient air quality related to concentrations of NO<sub>2</sub>.

The conclusions for each individual sampler are reported below.

#### 8.1.1 The Palmes tube sampler

Palmes tube samplers are extensively used e.g. in Denmark, France, the Netherlands, Spain and the United Kingdom for supplementary measurements to the fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

A number of methods exist for the preparation of the TEA-based sampling substrate. Only 3 of these have been proven to give reliable results in practice.

Palmer tube samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Palmer tube-type diffusive sampler is suitable for long-term monitoring of NO<sub>2</sub> in ambient air. Exposure periods of 1 to 8 weeks are feasible. The most commonly used exposure period is 2 or 4 weeks. The lower detection limit for a 2-week sampling period will vary with the meticulousness of the sampler preparation procedure, and will generally be between 0,7 and 1 µg.m<sup>-3</sup>. The upper limit for a 2-week exposure period is at least 375 µg.m<sup>-3</sup>.

Unused and exposed samplers may be stored for several months under specific conditions (dark; air tight; reduced temperatures).

A large body of literature evidence from various sources was available about the application of Palmer tube samplers for the monitoring of NO<sub>2</sub> in ambient air. A considerable number of studies reported the performance in side-by-side comparisons with reference monitors (chemiluminescence).

Generally, these comparisons gave varying results; however, the results are generally consistent within the uncertainties of the methods. At urban sites, where unprotected open tubes were used, a tendency was observed towards overestimation of NO<sub>2</sub> concentrations.

When using membrane-capped tubes in combination with model equations describing the uptake rate as a function of temperature, humidity, wind speed etc., the comparability improved.

When the uncertainty associated with the measurement results was evaluated according to the Guide to the Expression of Uncertainty in Measurement, the relative expanded uncertainty of individual results was estimated to be 32 % for worst-case conditions (when using a single value for the uptake rate independent of environmental conditions).

Assessments of measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO<sub>2</sub>, generally gave relative expanded uncertainties below 25 %. These findings suggest that the Palmer tube is at least suitable for performing long-term measurements of NO<sub>2</sub> for indicative purposes, and possibly even for fixed measurements.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

### **8.1.2 The Passam tube sampler**

Passam tube samplers are used e.g. in Cyprus, France, Germany, Italy, Lithuania and Romania for supplementary measurements to the fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

The preparation of the TEA-based sampling substrate is performed by the manufacturer.

Passam tube samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Passam diffusive sampler is suitable for long-term monitoring of NO<sub>2</sub> in ambient air. Exposure periods of 1 to 6 weeks are feasible. The lower detection limit for a 2-week sampling period is reported to be 0,4 µg.m<sup>-3</sup>. The most commonly used exposure period is 2 or 4 weeks.

Unused and exposed samplers may be stored for several months under specific conditions (dark; air tight; reduced temperatures).

A large body of literature evidence from various sources was available about the application of Passam tube samplers for the monitoring of NO<sub>2</sub> in ambient air. A considerable number of studies reported the performance in side-by-side comparisons with reference monitors (chemiluminescence).

The comparability of sampler results with those obtained with reference monitors varied somewhat, with ratios of average results generally ranging from 0,9 to 1,3. This variability may be reduced, when:

- Sampling rates are converted to actual conditions of temperature and pressure;
- Membranes are introduced into the sampler inlet particularly for traffic-related sites.

When the uncertainty associated with the measurement results was evaluated according to the Guide to the Expression of Uncertainty in Measurement, relative expanded uncertainties of individual results from 20 to 25 % resulted. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO<sub>2</sub>, similar and even better results were obtained. When combining results from a number of studies in France, a relative expanded uncertainty of 13 % was calculated, qualifying the sampler for the fixed measurement regime of EU Directive 2008/50/EC.

These findings suggest that the Passam tube is at least suitable for performing long-term measurements of NO<sub>2</sub> for indicative purposes and possibly even for fixed measurements. When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

### **8.1.3 The Ogawa badge sampler**

The Ogawa sampler has been used in Spain. To date, there is no reference found of the sampler being used for ambient air monitoring purposes in the EU. Applications are mainly in the field of indoor air and exposure monitoring. The preparation of the TEA-based sampling substrate is performed by the manufacturer.

Ogawa samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Ogawa badge-type diffusive sampler is suitable for long-term monitoring of NO<sub>2</sub> in ambient air. Exposure periods of 2 to 4 weeks are feasible. Lower detection limits reported vary somewhat, but are below 1 µg.m<sup>-3</sup> for a 2-week exposure period.

Unused and exposed samplers may be stored for several months under specific conditions (dark; air tight; reduced temperatures).

A number of studies from various sources were available about the application of Ogawa samplers for the monitoring of NO<sub>2</sub> in ambient air mainly in the United States of America. A limited number of studies reported the performance in side-by-side comparisons with reference monitors (chemiluminescence).

When exposed for 14 days or more in the field, the comparability of sampler results to those obtained with continuous reference monitors (chemiluminescence), was good, with ratios of average results ranging from 0,90 to 1,07. The availability of sampler results upon long-term exposure was better than 90 %. Absence of data in comparisons was due to malfunctioning of reference monitors rather than malfunctioning of the sampler.

No information is available about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

When using the methodology of the EU Guide to the Demonstration of Equivalence to the results of the US-EPA El Paso study, the sampler was found to pass the uncertainty requirement for indicative measurements. The random uncertainty found for the relation between sampler results and reference

method indicated that by correcting the uptake rate the sampler may pass the criterion for fixed measurements. However, the study was performed under conditions that are atypical of the EU.

#### **8.1.4 The Radiello radial sampler**

The Radiello sampler is used in the EU e.g. in Belgium, France, Italy, Slovakia and Spain for surveys aimed at, e.g. identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

The preparation of the TEA-based sampling substrate is performed by the manufacturer.

Radiello radial samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Radiello radial-type diffusive sampler may be used for long-term monitoring of NO<sub>2</sub> in ambient air. Exposure periods of 1 day to 2 weeks are feasible. The lower detection limit for a 2-week sampling period was reported to be 0,9 µg.m<sup>-3</sup>. Results of a laboratory study in which the sampling period was restricted to one day showed an underestimation of NO<sub>2</sub> concentrations of a factor of 2 when applying the uptake rate specified by the manufacturer. The reason for this may be a transient period of sorption at the beginning of the sampling period.

The comparability of sampler results with those obtained with continuous reference monitors (chemiluminescence) varied, with ratios of average results ranging from 0,6 to 1,4. In general, Radiello showed a trend to underestimate concentrations measured by reference monitors. However, the number of field data available was too limited to be conclusive.

When the uncertainty associated with the measurement results for a one-day exposure was evaluated according to the Guide to the Expression of Uncertainty in Measurement, a relative expanded uncertainty of individual results of 31 % was found. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO<sub>2</sub>, similar results were obtained.

These findings suggest that the Radiello does not satisfy the uncertainty data quality objective for indicative measurements of NO<sub>2</sub>, for which the uncertainty shall not exceed 25.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 25 % due to the reduction of random effects on uncertainty.

The information collected about the uncertainty of individual measurement results does not correspond with information supplied by the manufacturer stating an expanded measurement uncertainty of 12 %. However, information about the assessment approach used by the manufacturer is (currently) unavailable.

The possible effect of concentration level, high humidity and exposure time for NO<sub>2</sub> needs further research.

#### **8.1.5 The Analyst badge sampler**

Applications of the Analyst sampler appear to be mostly in indoor air monitoring, e.g., for studies into protection of cultural heritage. No references to applications in ambient air monitoring were found apart from the ones of the manufacturer.

To date, the preparation of the sampling substrate is performed by the manufacturer.

Analyst samplers are generally analysed by ion chromatographic determination of the nitrite formed after sorption on the sampling substrate.

The Analyst diffusive sampler is suitable for long-term monitoring of NO<sub>2</sub> in ambient air. Exposure periods of 1 to 2 weeks are feasible. The lower detection limit for a one-week exposure period is 1,9 µg.m<sup>-3</sup>.

The comparison of sampler results with those obtained with continuous reference monitors (chemiluminescence) showed ratios ranging from 1,0 to 1,4. On one occasion a ratio of 2,7 has been found in an early study. However, the number of studies was very limited.

No information was available on the availability of sampler results upon long-term exposure, e.g. for a period of one year.

When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO<sub>2</sub>, a single study reported the accuracy to be ± 20 %.

No further information was found about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

## 8.2 Conclusions and recommendations

Based on the findings summarised above, the following conclusions were drawn.

- The Palmes tube, Passam tube and Radiello radial sampler are in general use in the European Union for monitoring NO<sub>2</sub> in ambient air. Of these, the two tube-type samplers are used in ongoing air quality monitoring for supplementary measurements to the fixed measurements at the level of an indicative method.
- The Ogawa badge and Analyst badge are not in general use in the European Union for ambient air monitoring of NO<sub>2</sub>.
- The extent to which results of validation studies are available differs considerably between samplers. For the tube-type samplers, a substantial number of sources were identified. For the Ogawa badge and Radiello radial sampler information was more restricted. For the Analyst badge information was even scarcer.
- The available information suggests that, in general, the tube-type samplers may at least meet the EU uncertainty data quality objectives for indicative measurements. Application of membranes or shelters generally improves their performance. In some cases uncertainties were found that would qualify the samplers for fixed measurements.
- For the Ogawa badge sampler, the current limited information available suggests a potential to meet the EU uncertainty requirement for indicative measurements. However, the conditions of the study on under which this finding is based were not really representative for average European Union conditions. More information would be needed to draw firmer conclusions about the validity of the results produced by the sampler for monitoring NO<sub>2</sub> in ambient air.
- For the Radiello radial sampler, the current limited information available suggests that the sampler is not able to meet the EU uncertainty requirement for indicative measurements. The sampler generally appears to systematically underestimate NO<sub>2</sub> concentrations. More information would be needed to draw firmer conclusions about the validity of the results produced by the sampler for monitoring NO<sub>2</sub> in ambient air. It is recommended to further investigate the possible effects of concentration level, high humidity and exposure time for NO<sub>2</sub>.
- For the Analyst badge insufficient information is currently available to draw a quantitative conclusion about its potential to meet EU data quality objectives for the monitoring of NO<sub>2</sub> in ambient air. The limited information available gives mixed findings. More information would be

needed to draw firmer conclusions about the validity of the results produced by the sampler for monitoring nitrogen dioxide in ambient air.

On the basis of the above conclusions it is recommended that experts draft, a proposal method, based on the tube-type sampler, for monitoring nitrogen dioxide using diffusive samplers to be later used by CEN/TC 264 Working Group 11 "Diffusive Samplers" to prepare a new standard. Should further information become available in time on the performance of the Radiello radial sampler, which provides supporting evidence of its validity and its potential to meet EU data quality objectives, this sampler may still be considered and be included in the standard.

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**Abstract**

A number of diffusive samplers that are used for longer-term monitoring of nitrogen dioxide in the European Union were subjected to a review of their use and performance characteristics. The information collected was used to evaluate the capacity of diffusive samplers for monitoring the European Union annual limit value of 40  $\mu\text{g}\cdot\text{m}^{-3}$ .

A bibliographic review was carried out to determine the availability of validation data for these samplers, their capacity to meet the data quality objectives for indicative and/or fixed measurements of the European Directive, the possibility for users to analyse the samplers and their current use throughout the European Union for measuring ambient air quality.

Two tubes-type samplers and a radial sampler were found to be used throughout the European Union. Based on the findings of the review, only for tube-type samplers based on the application of triethanolamine as the sorbent, sufficient information was available to underpin the potential of these samplers for meeting the European Union data quality objectives for nitrogen dioxide monitoring.

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