Experimental study of NO_x depolluting capabilities of a photocatalytic coating tested under suburban ambient conditions

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Abstract One emerging strategy to mitigate air pollution at urban areas is the extensive use of photocatalytic products which are implemented on a vast variety of urban infrastructures. Theoretically, these materials allow removing nitrogen oxides (NO_x) from the ambient air via heterogeneous photocatalysis. This option could be especially interesting for different European urban agglomerations exceeding the limit values for NO_2 (Directive 2008/50/EC), like the case of Madrid city and the close municipalities. Nevertheless, there are noticeable unknowns about the real potential of these materials as NO_x sink.

In the framework of the LIFE MINO$_x$-STREET European project, devoted to clarify some of the remaining technical doubts, a variety of commercial photocatalytic building and construction materials and coatings have been subjected to rigorous laboratory essays and, then, some of them selected in order to evaluate their impact at real scale. For this purpose, a set of new techniques and essays have been designed and implemented to study the depolluting capabilities of the selected materials on real environments.

Here, we present one of these methods based on an experimental outdoor platform designed as a circular photocatalytic island (700 m^2) and equipped for continuous measurement of meteorological parameters and relevant gases concentrations on its geometric centre. The system was implemented on a horizontal and homogeneous base, located in a suburban area of Madrid far away from the direct influence of pollutant emission sources. This deployment allows characterizing the vertical gradients of NO_x and temperature generated in the centre of this photocatalytic island, enabling the parameterization of the sink effect on NO_x levels induced by a photocatalytic surface under episodic atmospheric conditions. The results of applying this experimental method are presented. Additionally, the influence of some relevant variables on the depolluting capabilities of the selected photocatalytic coating at real conditions is also discussed.

Keywords: Atmospheric pollution, photocatalytic materials, NO_x removal, outdoor conditions, LIFE $MINO_x$-STREET

1 Introduction

Air pollution is nowadays one of the most pressing problems of our society, causing about 7 million premature deaths every year: 3.7 million in the case of ambient air pollution and 4.3 million from household air pollution (the whole is less than the sum of its parts because the effects are not fully independent of each other) [1]. In spite of legislation which establishes health based standards and objectives for a number of pollutants in air, including nitrogen oxides, as new Directive 2008/50/EC [2], legal NO_2 limit values are frequently exceeded in metropolitan areas in which road traffic is the main source of this pollutant. It is necessary to implement diverse measures to offset this serious concern in urban areas. One emerging strategy to mitigate air pollution, especially NO_x, is the use of photocatalytic materials, such as titanium dioxide (TiO_2), incorporated in the structure of building materials or applied over their surface.

TiO_2 photocatalytic properties have been known for decades [3] but it has been in recent years when its use has spread [4]. When TiO_2 is activated by sunlight, it can eliminate NO_x in the air via heterogeneous photocatalysis (Photocatalityc Oxidation, PCO [5, 6]), through its photochemical transformation to nitrates and nitrites, soluble compounds that can be washed away by rain or irrigation. So, these materials have self-cleaning properties and, potentially, air depolluting capabilities.

Assessing the role that the use of commercial photocatalytic materials designed to air purification could play in combination with other strategies for air quality management is necessary to provide evidences from rigorous essays and tests on their physical-chemical properties and expected efficiency, not only under controlled laboratory conditions but also in real atmosphere.

In this work, the air purifying ability of a selected commercial product is studied by using an experimental system designed for measuring NO_x deposition flows over photocatalytic surfaces in ambient air.

2 Photocatalytic Material Selected

In order to test and compare the potential usefulness of a variety of different commercially available photocatalytic materials to act as NO_x sink when are implemented on urban surfaces at real conditions, an accurate selection of the materials and use conditions have been done in the framework of LIFE MINO$_x$-STREET project.

For this purpose rigorous laboratory essays have been conducted to test their mechanical and physical properties, operation-induced changes and durability, and also their photoactivation and air-purifying capacity, chemical and structural properties and changes induced by ageing and regeneration processes. Finally, a TiO_2 based water emulsion applied over a bituminous substrate was selected to be implemented at the large scale platform at CIEMAT enclosure under real ambient conditions.

3 Experimental design

An experimental system has been designed, installed and put into operation based on a method that consists in measuring, in ambient air, vertical gradients of temperature and concentration of the gases directly related to the flow of dry deposit of said gases. This system allows estimating the removal of NO and NO_2 from the air to the photocatalytic surfaces, without precipitation, due to the interaction of these gases with the active centres of TiO_2 present in such surfaces.

The measurement site must meet a set of stringent requirements in their boundary conditions, physical and chemical aspects, related to the behaviour of the atmosphere in the area where it is located, which determine the choice of the experimental site.

These requirements imply that the measurement site must be a space located far from the direct influence of traffic emission sources, and open enough so that obstacles do not disturb the flow. For this purpose, the selected site was set at CIEMAT enclosure, placed in a suburban area of Madrid.

The experimental platform is a quasi-circular surface of approximately 700 m^2 with the selected photocatalytic material, making up a real "Photocatalytic Island" (Fig. 1).

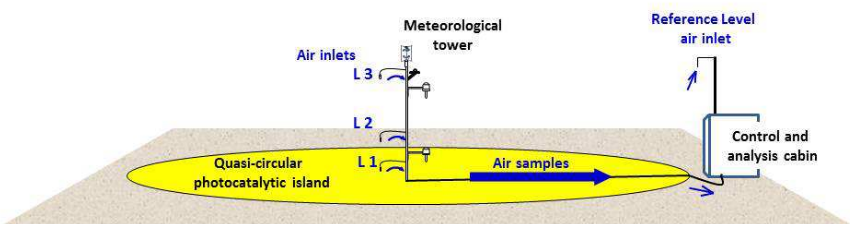

Fig. 1. Experimental platform at CIEMAT.

The experimental assembly is located in the geometrical centre of this platform and consists of a mast that supports a set of meteorological sensors and probes installed at different heights (16, 85 and 270 cm) on the same vertical for continuous sampling of environment air by means of thermally-insulated Teflon tubes (Fig. 2). With this measurement system, it can determine, above surface level, the vertical gradient of temperature (27 and 220 cm), air humidity (27 cm), global solar radiation at the surface (270 cm) and speed and wind direction (342 cm).

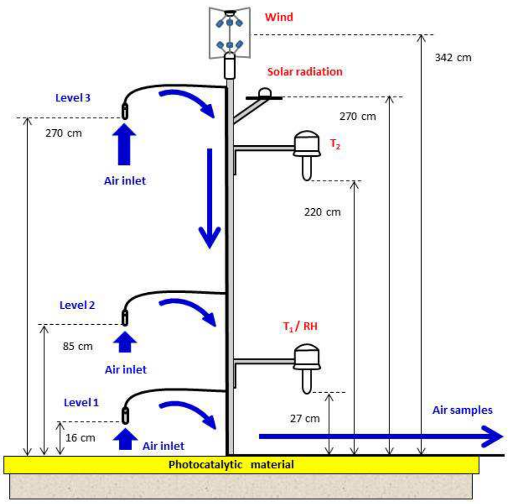

Fig. 2 Scheme of the mast with meteorological sensors and probes for measuring ambient air**.**

Additionally, an air sampling tube was placed at a reference point, at 330 cm height and outside the photocatalytic surface far from its influence. The four lines have the same length, and the sampling air is transported to the control booth.

Inside the control booth, there is a chemiluminescence NO-NO_2-NO_x analyser (Thermo Scientific Model 42i), a system for a sequential analysis of the sampling air from the four lines, and a computer program that implements the control functions of the whole experiment and data acquisition. All components of the test system are checked periodically to ensure a proper operation and measurement quality.The described system implemented is very versatile and allows changing its geometry.

Moreover, CIEMAT has also a meteorological tower that provides meteorological data for the following variables: ambient temperature at two levels (10 m and 70 m) and relative humidity, wind speed and the wind direction, irradiance, precipitation, and atmospheric pressure. This tower complements the meteorological data given by the sensors located at the experimental platform and allows characterizing the air flows during the measurement period.

4 Results and Discussion

The experimental system has been continuously operating from September, 25th 2014 to January, 31st 2015. During this time, anticyclonic stagnant conditions have occurred in three distinct periods (from October, 20th to 31th 2014, from November, 8th 2014 to December 11st 2014, and from December 30th 2014 to January 10th 2015). Under this kind of meteorological conditions, the development of a consistent urban plume is very fast (in 1-2 days) and the limit values for NO_2 ambient concentrations are usually exceeded after few days of stability when the ventilation conditions of the air basin is poorer than normally.

Nevertheless, not in all conditions macroscopic vertical gradients of NO_x could be observed. The air depolluting capability of a photocatalytic material in ambient air depends not only on the product itself and its photocatalytic properties [7], but also on the meteorological variables. In this work, the dry deposit of NO and NO_2 from the air to the photocatalytic surface has been highly dependent on the relative humidity, the solar radiation, the pollutant concentration and the wind speed.

After a thorough analysis of the data obtained during the measurement time and the proper filtering of data in relation to the variables that influence more decisively in the photocatalytic properties, a NO_x sink effect could only be observed from 27th to 30th of October 2014. As can be seen in Fig. 3, from October, 27th to 30th 2014, wind speed decreases, favouring the stagnation of the air mass in the measurement zone. As described above, stagnant conditions make harder the dispersion of pollutants, favouring the emergence of pollution episodes.

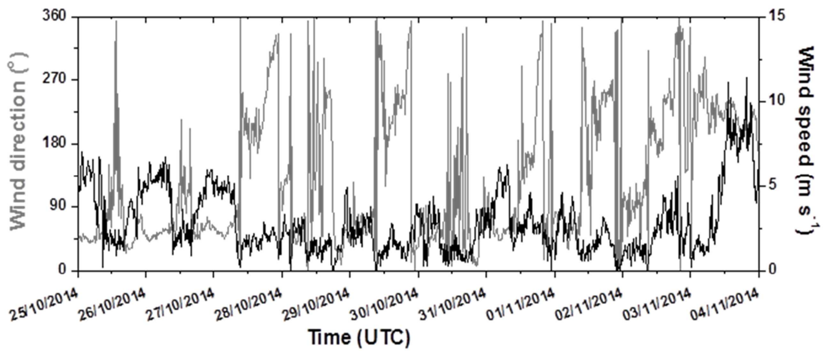

Fig. 3. Wind speed and wind direction recorded by the meteorological tower in CIEMAT during the first episode.

November, 1st and 2nd 2014 showed the same episodic weather conditions but, in this case, low traffic road emissions, typical of the weekends, induced lower NO_x values.

NO and NO_2 concentration registered during the mentioned period are shown in Fig. 4. NO concentration is higher than non-episodic average values (lower than 50 ppb) and NO_2 is accumulated over time, and does not decrease as expected in a normal day-night cycle, reaching values up to near 150 ppb.

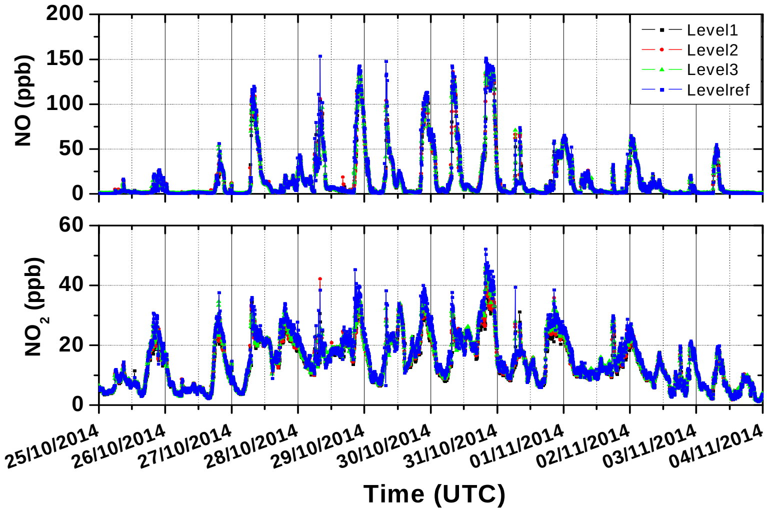

Fig. 4. Temporal evolution of NO and NO_2 during the selected episode.

The average NO vertical gradients registered during this period were 0.39 ± 0.23 ppb, between level 2 and level 1, and 0.32 ± 0.28 ppb, between level 3 and level 1. Another way to express NO removal photocatalytic efficiency from the experimental data is the conversion χ,

$$\chi = ((NO_{level2} - NO_{level1})/(NO_{level2}))100 \quad (1)$$

which is a dimensionless measure of the NO abatement and is a function of the NO concentration at different levels. The average value obtained for χ was nearly 4 %.

The average NO_2 vertical gradients observed were not significant with values one order of magnitude lower that the ones obtained for NO. Positive NO_2 gradients were only observed for two days of the mentioned period.

NO positive vertical gradients between the mentioned levels for October, 27th 2014, are shown in Fig. 5. Positive gradients sustained over time were observed only under specific weather condition during the episode (wind speed less than 1.5 m s^{-1}, solar radiation greater than 400 W m^{-2}, and relative humidity lower than 63%).

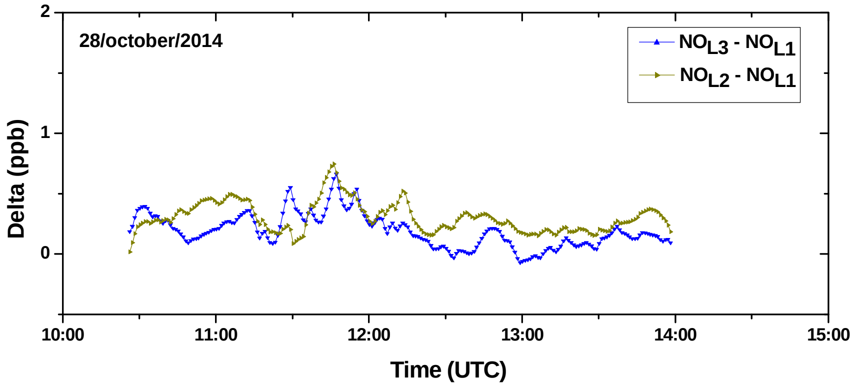

Fig. 5. Vertical NO concentration gradients between different levels.

5 Conclusions

A method to evaluate depolluting effect of photocatalytic materials at real scale has been designed, installed, put into operation and validated. This system allows quantifying NO and NO_2 vertical gradients, as a result of interaction of these gases with the active centres of TiO_2 present in photocatalytic surfaces.
A sink effect on NO_x concentration induced by a photocatalytic surface has been observed in an ambient scenario for specific episodic atmospheric conditions.

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