17th International Conference on
Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes
9-12 May 2016, Budapest, Hungary

REAL SCALE DEMONSTRATION OF THE DEPOLLUTING CAPABILITIES OF A PHOTOCATALYTIC PAVEMENT IN A REAL URBAN AREA

M. Pujadas[1], M. Palacios[1], L. Núñez[1], M. Germán[1], J. Fernández-Pampillón[2], J. D. Iglesias[3], J. L. Santiago[1]

[1]Department of Environment, Research Center for Energy, Environment and Technology (CIEMAT), Madrid, Spain
[2]National University of Distance Education (UNED), Madrid, Spain
[3]Alcobendas City Council, Madrid, Spain

Abstract: In the framework of the LIFE MINO$_x$-STREET European project (co-financed by the EU), once a variety of commercial photocatalytic products have been subjected to rigorous laboratory essays, one of them has been selected and implemented in a main road of the Municipality of Alcobendas (Madrid, Spain) in order to evaluate its depolluting effect. After a first phase of monitoring meteorological parameters and air quality conducted in the selected street, the photocatalytic coating has been applied on the road, covering an area of approximately one thousand square meters both ways. The designed and installed experimental system has allowed the continuous measurement of the ambient concentration of NO$_x$ at several different points located along the longitudinal axis of the road, both inside and outside the treated area with photocatalytic material, allowing experimentally evaluate the ability of this decontaminating photocatalytic coating under different climatic and weather conditions. All the collected data have given valuable information for the development and evaluation of a mathematical model capable of simulating microscale by calculating the dispersion of air pollutants at urban scale.

Key words: *Photocatalytic pavement, TiO_2, air pollution abatement.*

INTRODUCTION

The lessening of pollutants as nitrogen oxides (NO_x) constitutes one of worrying challenges in densely populated areas, where atmospheric pollution problems are mainly caused by road traffic emissions. As a consequence, the development of emerging abatement techniques, as those based on photocatalytic oxidation, is nowadays being fostered. Applying titanium dioxide (TiO_2)-modified coatings or cementitious materials onto the external covering of buildings or roads might be a supplement to conventional technologies, such as catalytic converters fitted on the vehicles, for mitigating air pollution. Nevertheless, although some photocatalytic materials have been deeply studied in laboratory, their efficiency as sink of NO_x at real scale is still matter of debate.

In the framework of LIFE MINOx-STREET European project, a variety of commercial TiO_2 based photocatalytic building materials have been subjected to rigorous laboratory essays in order to study, on one hand, their mechanical and physical properties, operation-induced changes and durability, and, on the other, their photoactivation and air-purifying capacity, chemical and structural properties, and the changes induced by ageing and regeneration processes (Palacios et al, 2015a). Then, the most promising materials have been selected and essayed by means of both outdoor experiments and controlled essays under ambient conditions (German et al, 2015, Palacios et al, 2015b). The selected photocatalytic coating designed for use on bituminous mixtures has been implemented in a real urban scenario in Alcobendas, Madrid, and the assessment of its effect on the degradation of atmospheric nitrogen compounds is presented here.

EXPERIMENTAL

The photocatalytic coating was implemented in the road of Paseo de la Chopera, a main street of the Municipality of Alcobendas (Madrid), consisted of two lanes in each traffic direction and a median strip. The street has an east-west orientation that assured enough solar irradiation of the bituminous pavement from 7 to 16 UTC. An area of about one thousand square meters (sixty meters along the road) was covered by means a distributor truck with a spray bar with nozzles fitted on the back. The application was done after the roadway was cleared of any debris. Traffic was reopened on September, 25th 2015, two days after the product application.

The air quality monitoring started on September, 11th 2015, two weeks before the implementation of the photocatalytic coating to obtained background information and continued till October, 25th 2015. Ambient concentrations of NO_x (NO and NO_2) were measured continuously at six different points located along the longitudinal axis of the road, two inside and four outside the treated area with the photocatalytic material (Figure 1). The air sampling lines consisted in perfluoroalkoxy (PFA) tubing with 0.4 cm inner diameter and 53 m (lines 1 to 4) and 12 m (lines 5 and 6) long (Figure 1). They were properly protected and buried under the asphalt surface to prevent damage from road traffic. Sampling points were located at 40 cm high in the middle of the road and protected with a meshed cages anchored to the pavement. Particulate filters (cut-off diameter of 15 μm) were placed at the beginning of the sample lines. The sampling height has been selected taking into account the results obtained from previous measurements of NO_x concentration vertical gradients over a similar photocatalytic coating in a suburban area (German et al, 2015).

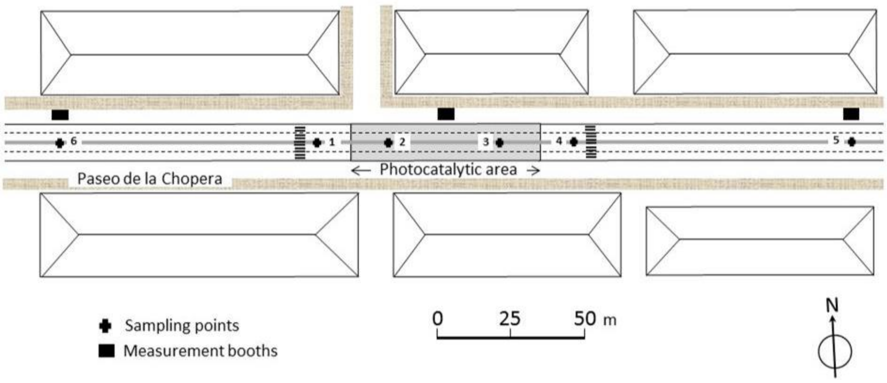

Figure 1. Schematic overview of the experimental set up in Paseo de la Chopera.

Apart from measurements at ground level, ambient NO_x, ozone (O_3) and meteorological parameters (air temperature, solar radiation, relative humidity, wind speed and direction) were measured continuously at a height of 15 m from September, 15th 2015 to October, 25th 2015. Meteorological sensors and gas analyzers were deployed at the roof of a building located near the Paseo de la Chopera in order to characterize the general air dynamics of this area.

NO_x concentration measurements were done by applying the chemiluminescence technique. Thermo Scientific NO_x analyzers were used in five lines, Model 42i for sampling lines 1 to 4 and Model 42iTL for line 5, and two Teledyne API 200 A for both line 6 and at roof level. Ozone concentrations were measured with a UV absorption ozone analyzer (Teledyne API 400 A). The gas analyzers were calibrated before the beginning of the experimental campaign. All the instruments were located in temperature controlled rooms or booths.

An automatic switching system was developed for consecutive 1-minute averaged NO_x measurements from sampling points corresponding to lines 1 to 4 (see figure 1). An external pump maintained a constant flow for all the lines, and a system of four solenoid valves which were switched every two minutes allowed the NO_x analyzer performs alternating measurements associated to each valve. Only the data associated to the second minute of the cycle were taken into account in order to assure that the sampling was not affected by the measurement with the previous line.

Additionally, intensive measurement campaigns were performed during four days in which stagnant meteorological conditions occurred that favored the accumulation of air pollutants. In those occasions volatile organic compounds, particulate matter and road traffic were characterized during the diurnal periods. Moreover, UVA radiation across the street and temperature of facades, sidewalks and bituminous photocatalytic pavement were also registered.

Part of the collected data have been used as inputs to evaluate a mathematical model capable of simulating microscale by calculating the dispersion of air pollutants at urban scale.

RESULTS

The overall NO_x concentration results obtained from the measurements along the road (sampling lines 1 to 4) are presented in Figure 2. Maximum values were registered during traffic rush hours in the morning and in the late afternoon. The evolution of NO_x concentrations profiles correlated quite well with the traffic patterns observed during selected days. The cadence of one minute averaged measurements allowed to detect the influence of almost every vehicle emissions in this road as it is shown in Figure 2. It is noticeable the presence of a large amount of peaks superimposed to a NO and NO_2 background level. This fact has hampered the assessment of the NO_x depolluting ability of the photocatalytic road pavement.

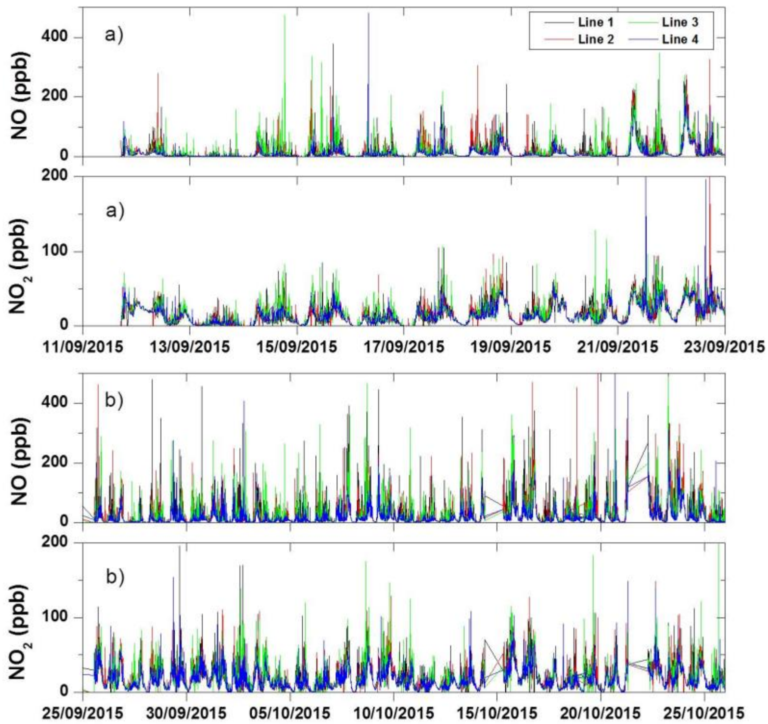

Figure 2. One minute averaged NO and NO_2 concentrations measured during the periods without (a) and with (b) the photocatalytic coating over the bituminous pavement.

Meteorological variables registered during the campaign are show in Figure 3. During this time, anticyclonic stagnant conditions have occurred in three distinct periods (from September, 18^{th} to 22^{nd} 2015, from October, 8^{th} to 9^{th} 2015, and from October 15^{th} to 16^{th} 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.

The air depolluting capability of a photocatalytic material, obtained from laboratory essays, depends not only on the active product itself and its photocatalytic properties, but also on several parameters of the own test (Sikkema et al, 2015). The photocatalytic activity of the photocatalytic coating over a similar bituminous pavement of Paseo de la Chopera was essayed under the ISO international standard (ISO, 2007) giving a NO depolluting efficiency of 45%. After varying the test conditions (NO inlet concentration, irradiance intensity, relative humidity and flow rate), the amount of NO removed from the gas phase by photocatalytic oxidation was strongly affected by changes of the light intensity as well as of the relative humidity (Palacios et al, 2015b). This dependence has also been observed in measurements of NO_x concentration gradients made in a suburban area (German et al, 2015).

Taking into account these results, the effect of the presence of the photocatalytic pavement on the NO concentration has been studied for specific meteorological conditions: solar radiation (SR) higher than 400 Wm^{-2}, relative humidity (RH) lower than 65 %, and wind speed (WS) lower than 5 m s^{-1}. A comparison of the wind speed registered at roof level with the wind speed monitored in a near meteorological station of the Alcobendas municipality at ground level indicates that the selected value of 5 m s^{-1} corresponds to approximately 2 m s^{-1} in the street. Moreover, in order to avoid the influence of instantaneous NO emissions from traffic, only NO concentration values lower than 20 ppb has been considered. The wind direction was also included in the analysis to distinguish between east and west sectors. These wind directions were the most favorable for observing the effect of the photocatalytic pavement in reducing the concentration of NO because they were parallel to the street axis and thus to the sampling points on the road median strip.

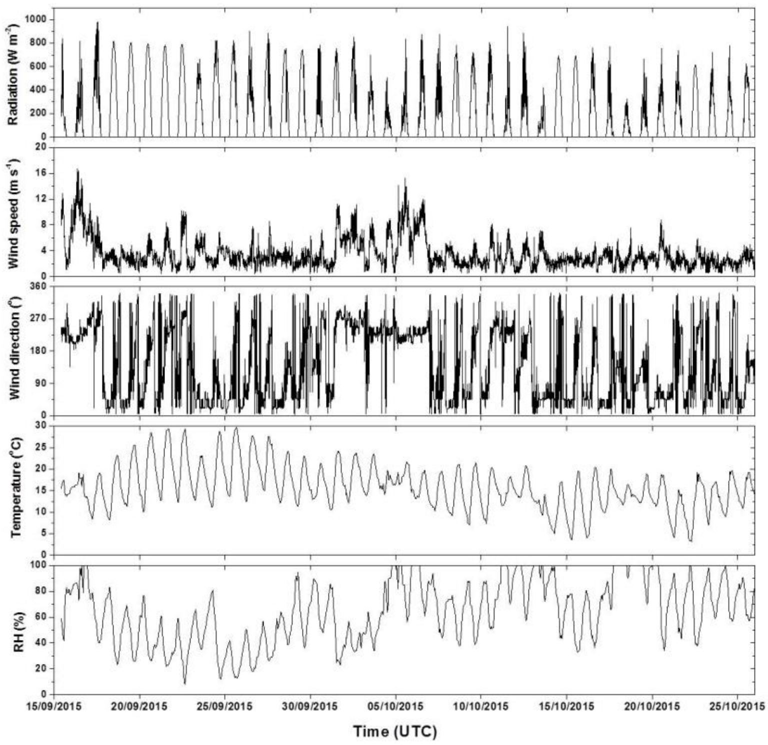

Figure 3. Meteorological variables registered at roof level during the measurement campaign in Paseo de la Chopera

The NO concentrations registered from the sampling lines 2, 3 and 4 were correlated against the corresponding values from the line 1. It was expected that before implementing the photocatalytic coating on the bituminous pavement the concentration of NO measured in the four sampling points were quite similar among them. In the NO selected data set that similarity would disappear from the time the photocatalytic coating was implemented. A summary of the obtained results are shown in Table 1.

Table 1. Slopes from the correlation of sampling lines 2 to 4 against line 1 for NO concentration before and after the implementation of the photocatalytic coating (SR>400 Wm^{-2}, RH<65%, WS<5ms^{-1})

Sampling lines	Before application of photocatalytic coating (E direction)	After application of photocatalytic coating (E direction)	Before application of photocatalytic coating (W direction)	After application of photocatalytic coating (W direction)
2	0.77±0.03	0.73±0.03	1.05±0.08	1.07±0.08
3	0.73±0.05	0.74±0.03	1.41±0.17	1.03±0.06
4	0.64±0.03	0.70±0.03	0.89±0.06	0.90±0.07

The remediation of NO cannot be distinguished from zero as the slopes values for the two distinct periods are almost very similar. Moreover, although there is a tendency of a lower slope value for the line 4 it happens not only when the road was photoactive but also when there were no photocatalytic coating.

In order to ascertain if there were a bias due to an instrumental systematic problem of the sampling line 4, the nocturnal NO concentration values (from 00:00 to 04:00 UTC) were analysed. During that period there were almost no traffic emissions, preventing the point effect of individual vehicles, and the absence of solar light avoids the potential photocatalytic activity of the treated pavement. Under these conditions only an instrumental problem could produce different NO concentration measurements among the four lines. The values obtained for nocturnal conditions (Table 2) reflect that the correlation between the sampling lines is approximately the unity, thus there is not a bias due to any systematic instrumental error, so the deviation of the individual slopes from unity presented in Table 1 may result from general differences in the pollution levels between both ends of the street and along it.

Table 2. Slopes from the correlation of sampling lines 2 to 4 against line 1 for NO concentration before and after the implementation of the photocatalytic coating (00:00 to 04:00 UTC)

Sampling lines	**Before application of photocatalytic coating**	**After application of photocatalytic coating**
2	1.014±0.005	0.983±0.004
3	0.977±0.005	0.915±0.004
4	0.985±0.005	0.946±0.025

Therefore, the results obtained during the selected optimal measurement periods indicate that NO photocatalytic remediation has not been observed.

CONCLUSIONS

The depolluting capability of a selected TiO_2-based photocatalytic material applied over a bituminous pavement has been evaluated in an urban scenario with real traffic. Despite a) having used a product with good performance according to the results of laboratory ISO tests, b) NO measurements were performed low over the treated surface and c) the data evaluated were selected according to the optimal weather conditions under which potentially the sink effect of the photocatalytic material on the NO should have produced measurable horizontal concentration gradients, the application of the photocatalytic product to an important section of the road did not allow to detect any improvement effect on NO concentrations detected in the median strip directly attributable to the presence of such material.

REFERENCES

Germán M., M. Palacios, M. Pujadas, L. Núñez and J. Fernández-Pampillón, 2015: Experimental study of NOx depolluting capabilities of a photocatalytic coating tested under suburban ambient conditions. *12th Urban Environmental Symposium–Urban Futures for a Sustainable World. Oslo, (Norway), 01 - 03 June 2015. Book of Abstracts*, 37-44.

International standard ISO 22197-1:2007, 2007, ISO, Geneva.

Palacios M., L. Núñez, M. Pujadas, J. Fernández-Pampillón, M. Germán, B. S. Sánchez, J. L. Santiago, A. Martilli, S. Suárez and B. S. Cabrero, 2015a: Estimation of NO_x deposition velocities for selected commercial photocatalytic products. *WIT Transactions on The Built Environment*, **168**,12 pp.

Palacios M., S. Suárez, L. Núñez, B. Sánchez, M. Pujadas and J. Fernández-Pampillón, 2015b: Influence of parameters on the photocatalytic oxidation of nitric oxide at the surface of titanium dioxide-modified concrete materials. *International Conference on Chemical and Biochemical Engineering, Paris, France, July 20-22. ISBN: 978-84-944311-1.*

Sikkema J.K., S.K. Ong and J.E. Alleman, 2015: Photocatalytic concrete pavements: Laboratory investigation of NO oxidation rate under varied environmental conditions. *Construction and Building Materials*, **100**, 305-314.