18th International Conference on
Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes
9-12 October 2017, Bologna, Italy

REAL SCALE TESTS OF THE DEPOLLUTING CAPABILITIES OF A PHOTOCATALYTIC SIDEWALK PAVEMENT AND A FACADE IN AN URBAN SCENARIO

Manuel Pujadas[1], Magdalena Palacios[1], Lourdes Núñez[1], Mónica Germán[1], Jaime Fernández-Pampillón[2], Beatriz Sanchez[1], Jose-Luis Santiago[1], Benigno Sánchez[3], Rafael Muñoz[4], Félix Moral[4], Guzmán Arias[4]

[1]CIEMAT, Environmental Department, Avda. Complutense 40, 28040 Madrid, Spain
[2]National University of Distance Education (UNED), Madrid, Spain
[3]CIEMAT, Energy Department, Avda. Complutense 40, 28040 Madrid, Spain
[4]Alcobendas City Council, Madrid, Spain

Abstract: In the framework of the LIFE MINOx-STREET European project, several commercial photocatalytic products have been evaluated in laboratory in order to select the most suitable ones to be implemented on different material substrates in real urban areas of Alcobendas (Madrid region, Spain).
In this work we present the results corresponding to the experiments developed in two scenarios: a sidewalk pavement and a brick wall. Although the sidewalk photocatalytic material had showed a high activity in laboratory essays, no significant NO_x concentration reduction could be observed during these experiments. The ambient NO_x reduction effect due to the presence of the photocatalytic facade could be detected but only during a short time period and under very specific ambient and meteorological conditions.
All these experimental data have been used to simulate mathematically both scenarios with computational fluid dynamics (CFD) modelling.

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

INTRODUCTION

The use of photocatalytic building materials is considered a promising air pollution abatement strategy that is specially indicated for urban areas. These construction materials are treated with different TiO_2 enriched products and the photocatalytic characteristics of this semiconductor are the key of their depolluting capabilities. These performances are specifically tested and characterized in laboratory essays applying standard methodologies. Nevertheless, there is an important lack of experimental evidences demonstrating the effective removing pollution potential of these materials in real urban scenarios.

In the framework of the LIFE MINOx-STREET European project (co-financed by the EU), a strict protocol based on UNE-ISO 22197-1:2012 to test and compare the potential usefulness of a variety of commercial photocatalytic materials has been followed. As a result, two photoactive coatings were selected to be applied and tested at large scale under real outdoor conditions: one for using on sidewalks and another for facades. Both products have been implemented in a model of street canyon built in an urban area of Alcobendas (Madrid, Spain), and the assessment of its effect on the degradation of atmospheric nitrogen compounds is presented here.

METHODOLOGY

A scale model of a double pedestrian street canyon, consisting on two parallel twin streets constructed next to each other, was installed in an urban area of Alcobendas next to a public road with moderate traffic and air pollution levels (see Fig.1). These contiguous streets of 20 m in length and a width of 4 m, delimited by walls of 5 m in height, were paved with the tiles selected in the previous actions of the project. The photocatalytic material (coating) was only applied on the tiles of one of the streets, "photoactive street", while the other was used as "reference street". This material had shown a NO depolluting efficiency of 65% under the ISO international standard (Palacios et al, 2015a). The monitoring system deployed to detect any measurable reduction of NO_x ambient concentration in the photoactive street vs the reference street is presented in Fig.1. From a dynamic point of view, the air flows in both streets were essentially identic and for a correct interpretation of the results meteorological parameters were monitored in the photoactive streets. Two air sampling points were located inside each street on its central axis, 30 cm above the surface and 90 cm at the respective ends, as is shown in Fig.1. The four lines (1 to 4) were implemented for the measurement of the NO and NO_2 ambient concentrations near the surfaces in order to detect and characterize the possible sink effect produced by the photocatalytic sidewalk vs the normal situation in the reference street. The main interest was on those situations in which the air flow is produced along the axis of both streets in order to compute the NO_x concentration differences between the entrance vs the exit of the streets.

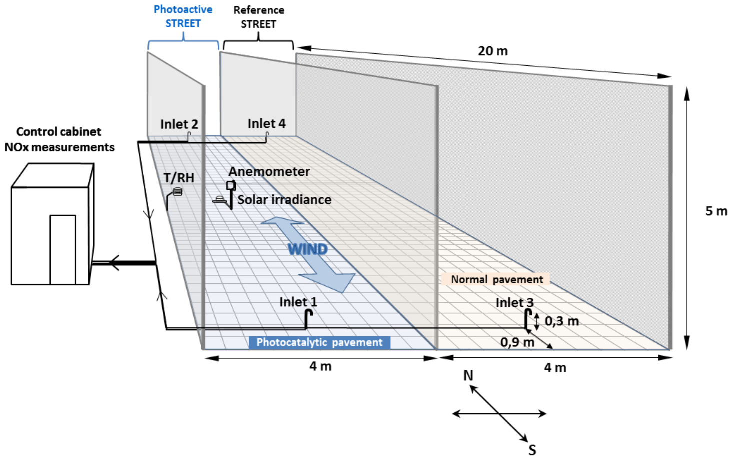

Figure 1. Schematic overview of the experimental set up of the sidewalk scenario in the street canyon

In order to study this process on facades, the external side of one the walls of the double street canyon was used for supporting a wall of bricks, that was built and treated with the photocatalytic product selected for use on facades. The photoactive coating had given a NO removal efficiency of 27% under the ISO international standard (Palacios et al, 2015a). The experimental set up consisting of two measurement zones on the wall located 90 cm from both ends and 2.5 m high. In both positions, two air sampling points located 8 cm and 40 cm from the facade surface were installed and the correspondent sampling lines carried the air flows up to the control cabinet for NO_x sequential analysis. For a correct interpretation of the results, the air movements on the facade were monitored by means of suitable meteorological instrumentation placed on the geometric centre of the wall (2D sonic anemometer), and the solar irradiance, air temperature and relative humidity were also registered. This measurement configuration had the objective of detecting and characterizing the appearance of possible NO_x concentration horizontal and/or vertical gradients on the facade as a consequence of the presence of the photocatalytic coating (see Fig.2).

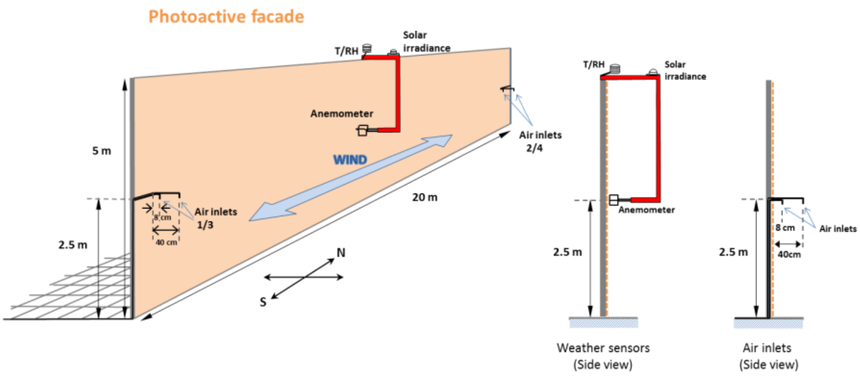

Figure 2. Schematic overview of the experimental set up of the facade scenario in the street canyon

A mobile monitoring station was installed near the street canyon for the continuous measurement of NO, NO_2 and O_3 concentrations and meteorological parameters (wind speed and direction, temperature, relative humidity, solar radiation) during both measurement campaigns in order to document the evolution of the physico-chemical characteristics of the air mass existing in the zone and obtain fundamental information for a correct interpretation of the results.

NO_x concentration measurements in both scenarios were done by applying the chemiluminescence technique (Thermo Scientific NO_x analyser Model 42i) was used for sampling lines 1 to 4 of the sidewalk and facade. In the mobile station, NO_x was monitored with a Model 42iTL and ozone concentrations were measured with a Teledyne API 400 A analyser. All the gas analysers were calibrated before and during the experimental campaign and the instruments were operated in temperature controlled 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 and 2) although an external pump maintained a constant sampling flow for all the lines and a system of four solenoid valves which were switched every two minutes allowed the NO_x analyser performs alternating measurements associated to each valve. Only the data associated to the second minute of each cycle were taken into account in order to assure that the sampling was not affected by the measurement with the previous line.

Part of the collected data have been used as inputs to evaluate a CFD model capable of simulating microscale by calculating the dispersion of air pollutants at urban scale (see poster Sánchez et al).

RESULTS

Sidewalk pavement

In order to obtain background information about the behaviour and dynamics of the double street canyon, the experimental campaign started on April, 6th 2016, one month before the photocatalytic coating was implemented over one of the streets, and continued till June, 30th 2016. An example of NO measurements along the two street canyons (sampling lines 1 to 4) together with the meteorological parameters registered in the photoactive street are shown in Fig.3.One minute average data allow detecting the presence of high NO and NO_2 concentration levels associated to almost every vehicle emissions in the near road located southern of the streets. This large amount of peaks is superimposed to a background profile that correlates with the traffic patterns with maximum values in the morning and in the late afternoon. The orientation of the street canyons allowed both streets to be mostly illuminated during the central hours of the day (11-13 UTC) with a prevalence of south-north flows in the area, that is, parallel to the axis of the streets, with average wind speeds around 2 ms^{-1}.

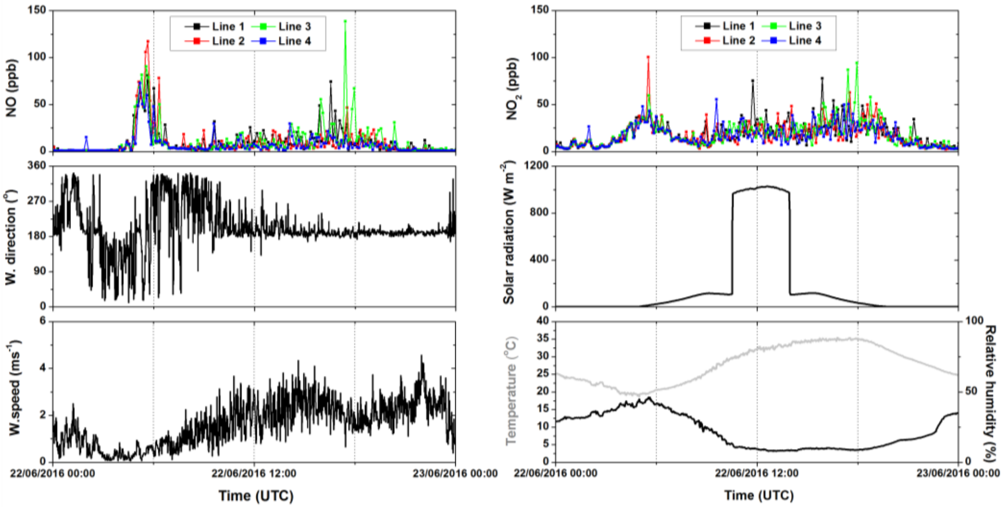

Figure 3. One minute averaged NO and NO_2 concentrations measured on June 22nd, 2016 along the two street canyons and meteorological variables registered at the photoactive street.

The similar dynamic behaviour of the air in both street canyons allowed a statistical treatment of data and the results of it that is illustrated in Table 1 in which the slopes of the correlation of nocturnal (00:00-04:00 UTC) NO concentration from sampling line 2 vs line 1 (photoactive street) and sampling line 4 vs line 3 (reference street) are presented. In order to avoid the influence of instantaneous NO direct emissions from traffic, data were filtered and only were used for statistics those pairs of values with ratios NO_{Line1}/NO_{Line2}, NO_{Line3}/NO_{Line4} in the range of ±20%. The slope values close to unity reflect that the NO content in the four air samples are indistinguishable.

Table 1. Slopes from the correlation for NO concentration of sampling line 2 against line 1 (photoactive street), line 4 against line 3 (reference street) before and after the implementation of the sidewalk photocatalytic coating (00:00 to 04:00 UTC, $0.8<NO_{Li}/NO_{Lj}<1.2$)

Sampling lines	Before application of photocatalytic coating	After application of photocatalytic coating
2 vs 1	0.963±0.003	0.984±0.002
4 vs 3	1.065±0.004	1.010±0.002

In order to evaluate the possible NO reduction effect by the photocatalytic sidewalk pavement, the NO concentration data were previously filtered, not only avoiding the data influenced by instantaneous traffic emissions but also selecting those periods with favourable meteorological conditions (Palacios et al, 2015b): solar irradiance (SI) higher than 400 Wm^{-2}, relative humidity (RH) lower than 65 %, wind speed (WS) between 0.5 and 2.5 m s^{-1}, wind direction (WD) from South sector which is the most suitable for observing the effect of the photocatalytic street because it is parallel to the street axis and air masses from this sector presents the highest pollutant concentration levels. The NO concentrations registered from the sampling lines 2 and 4 were correlated against the corresponding values from the line 1 and 3, respectively. It was expected that before implementing the photocatalytic coating the four sampling points were quite similar among them and that similarity would disappear from the time the photocatalytic coating was implemented. A summary of the experimental results are shown in Table 2.

Table 2. Slopes from the correlation for NO concentration of sampling line 2 against line 1(photoactive street), line 4 against line 3 (reference street) before and after the implementation of the sidewalk photocatalytic coating (SI>400 Wm^{-2}, RH<65%, 0.5<WS<2.5 ms^{-1}, $160^o<WD<200^o$, $0.8<NO_{Li}/NO_{Lj}<1.2$).

Sampling lines	Before application of photocatalytic coating	After application of photocatalytic coating
2 vs 1	1.02±0.02	0.97±0.02
4 vs 3	0.97±0.02	0.94±0.02

It can be observe that the slope values for nocturnal (Table 1) and diurnal periods (Table 2) before and after implementing the photocatalytic coating are actually very similar and without compatible features with any NO sink effect.

Facade

The experimental campaign started on November, 3rd 2016, one week before the photocatalytic paint was applied over the brick wall, and continued till December, 16th 2016. NO_x concentration measurements results showed a temporal pattern very similar to the one obtained in the previous spring campaign and the influence of near NO_x emissions from traffic was also observed. The eastern orientation of the facade allowed the ultraviolet radiation incident on the wall to be sufficient from early morning to noon (8:30-12 UTC) and the photocatalytic effect of the coating material could be observed during several hours.

Meteorological parameters showed that the air masses of the north/south component generate a well-defined flow along the facade, which allowed suitable comparisons between the NO_x concentrations measured at both ends of the wall (lines 1 and 3 in the southern sampling zone, lines 2 and 4 in the northern one) in order to characterise the appearance of NO_x concentration gradients in the parallel and/or perpendicular dimension to the facade as a consequence of the possible depolluting effect. Like in the case of the double street canyon, the statistical analysis of the nocturnal concentrations monitored for the four lines showed that the NO content in the four air samples was indistinguishable (see Table 3).

Table 3. Slopes from the correlation for NO concentration of sampling line 2 against line 1, line 4 against line 3 before and after the implementation of the facade photocatalytic paint (00:00 to 04:00 UTC, $0.8<NO_{Li}/NO_{Lj}<1.2$)

Sampling lines	Before application of photocatalytic paint	After application of photocatalytic paint
2 vs 1	1.013±0.003	0.987±0.002
4 vs 3	1.011±0.005	1.000±0.002

Beyond the statistical analysis itself, an exhaustive study of the situations along the measurement period shows that the meteorological conditions that took place on November 16th, 2016 (high solar radiation, low wind speeds of mainly southern component) provided a good chance for detecting the photocatalytic depolluting effect. During that day air pollutants were accumulated during several hours in the early morning as evidenced by the high levels of NO concentration measured at the four sampling points (Mean NO: 259±40 ppb) and after sunrise a slow ventilation process began (Mean NO: 97±48 ppb). A meticulous inspection of the NO_x concentration data during the daytime period 6:40 to 9:40 UTC has allowed isolating a possible NO reduction event due to the presence of the photocatalytic material in the facade. The mean values of the NO concentration obtained after the data process for the four sampling points before and during the photocatalytic event are shown in Table 4.

Table 4. NO mean concentration values measured at the sampling points 1 to 4 of the facade before and during the photocatalytic event on November 16th, 2016.

Sampling lines	Before photocatalytic event	During photocatalytic event
1	266±22	108±46
2	260±37	86±44
3	271±35	110±42
4	255±30	94±44

The concentration differences between sampling line 4 and 3 remains nearly invariable for the two distinct periods (16 ppb). However, the NO concentration difference obtained for the sampling lines closest to the wall (1 and 2) is greater during the photocatalytic event (23 ppb) than that obtained before sunrise (6 ppb). In this specific case, we consider that this horizontal gradient of NO concentration near the surface wall could be reasonably attributed to a sink effect generated by the presence of the photocatalytic material on the facade.

CONCLUSIONS

The results obtained after analysing the measurements made on the double street canyon have not allowed detecting any reduction of the NO ambient concentration attributable to the depolluting effect of the implemented photocatalytic material. In the case of the facade, during a short period of time and under specific ambient and meteorological conditions, a short NO abatement episode could be observed that has been associated to the presence of the photocatalytic coating. The main reasons that have prevented to unequivocally detect the development of the sink effect on the NO_x on both real scenarios are the small magnitude of the photocatalytic effect at macroscopic scale and the disturbances induced by recent emissions from traffic close to study areas. A complementary CFD study has been carried out (see poster H18-165) also showing the effect of photocatalytic materials on NO ambient concentration is small.

ACKNOWLEDGMENTS

With the contribution of the LIFE financial instrument of the European Union (LIFE12/ENV/ES/000280).

REFERENCES

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 Env.* **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.*