LAYMAN REPORT

LIFE MINOx-STREET PROJECT

LIFE12 ENV/ES/00280

LAYMAN REPORT
LIFE MINOx-STREET PROJECT

MONITORING AND MODELLING OF NITROGEN OXIDE REMOVAL EFFICIENCY OF PHOTOCATALYTIC MATERIALS: A STRATEGY FOR URBAN AIR QUALITY MANAGEMENT

www.lifeminoxstreet.com

Project co-financed by the EU's financial instrument supporting environmental and nature conservation.

ÍNDICE

WHAT IS THE MAIN OBJECTIVE OF THE LIFE MINOx-STREET PROJECT? BACKGROUND

Urban air pollution from road traffic is one of the major problems of some European cities.

The negative impact on human health has been demonstrated: WHO (World Health Organisation) estimates that 11.6% of deaths worldwide is related to air pollution and the European Environment Agency states that around 90% of the EU's urban population is exposed to high levels of air pollution.

It is therefore an urgent priority to establish measures to improve urban air quality. In this respect, the aim of European policies is to reduce exposure to air pollution by reducing emissions and establishing air quality limits and values to be complied with by member states.

Average period	*Maximum value*
1 hour	200 µg/m³, which may not be exceeded more than 18 times per calendar year
Calendar year	40 µg/m³

Maximum values of NO_2 for protecting human health
Directive 2008/50/EC (annex XI)

In this context, the LIFE MINOx-STREET project aims to evaluate **support for eventual strategies to reduce urban air pollution by nitrogen oxides**, particularly caused by road traffic, **by studying the feasibility of using photocatalytic materials on roads, pavements and/or façades**.

WHAT ARE PHOTOCATALYTIC MATERIALS?

They are materials that incorporate photocatalytic compounds like titanium dioxide (TiO_2) which, when activated with UV light, removes compounds like nitrogen oxides (henceforth NO_x), one of the major road traffic pollutants, from the air.

Despite the numerous lines of research open to the development and study of the characteristics and potential of photocatalytic materials, there are important unknown aspects regarding their behaviour in real conditions.

WHAT ARE THE BENEFITS OF THE LIFE MINOx-STREET PROJECT? OBJECTIVES

The main objective of the project consists of performing an in-depth analysis of the application and efficiency of photocatalytic materials in the reduction of NO_x in specific urban environments.

This integrated approach requires sound knowledge of the commercial materials on the market, through an analysis under controlled conditions and the synergy between real-world experiments and numerical models.

Consequently, the LIFE MINOx-STREET project:

» It provides rigorous evidence on the real capacity of commercial photocatalytic materials to reduce the concentrations of urban NOx.
» It develops a numerical model that allows us to predict the capacities of these materials to reduce the concentration of NOx in different urban environments before their implementation, facilitating the development and improvement of air quality management strategies.

The results of the study are shown in a **Guide for the use of photocatalytic materials to reduce urban pollution with nitrogen oxides (NO_x)** that is available to competent air quality management bodies, and to the general public on the project website: http://www.lifeminoxstreet.com.

DEVELOPING THE PROJECT
MAIN ACTIONS

To fulfil the objectives described above, the LIFE MINOx-STREET project has performed the following main actions:

- » Market study and selection of commercial photocatalytic materials to be tested.
- » Characterisation of the mechanical properties and decontaminating capacity of NO_X in different commercial photocatalytic materials, in accordance with Standard ISO 22197-1.
- » Study of the influence of ageing, wear and tear and regeneration processes on their physical/chemical and photocatalytic properties.
- » Parameterisation of the sink effect of NO_X (deposition rate) in the presence of photocatalytic materials in the air.
- » Characterization of the decontaminating effect of the selected photocatalytic materials in urban scenarios
- » Implementation of an atmospheric chemistry module in a CFD ("Computational Fluid Dynamics") model adapted to urban scale. Simulation of the photocatalytic NOx removal process through the introduction of the NO deposition rate parameter on photoactive surfaces, as well as reactive chemistry. Evaluation of the decontaminating effect of photocatalytic materials in urban scenarios (at street and district level) and analysis of their environmental effects.
- » Elaboration of a reference guide for the use of photocatalytic materials in the framework of urban air quality control policies.

DEVELOPING THE PROJECT
PREPARATORY ACTIONS

Characterisation of photocatalytic materials

The photocatalytic materials analysed in the project were initially selected from a study of the materials available on the market for use on roads, pavements and façades. The main selection criteria used were:

» Optimal behaviour in relation to the reduction of NO_X (according to information supplied by the supplier/manufacturer)
» Easy implementation and setup
» Technical and economic feasibility

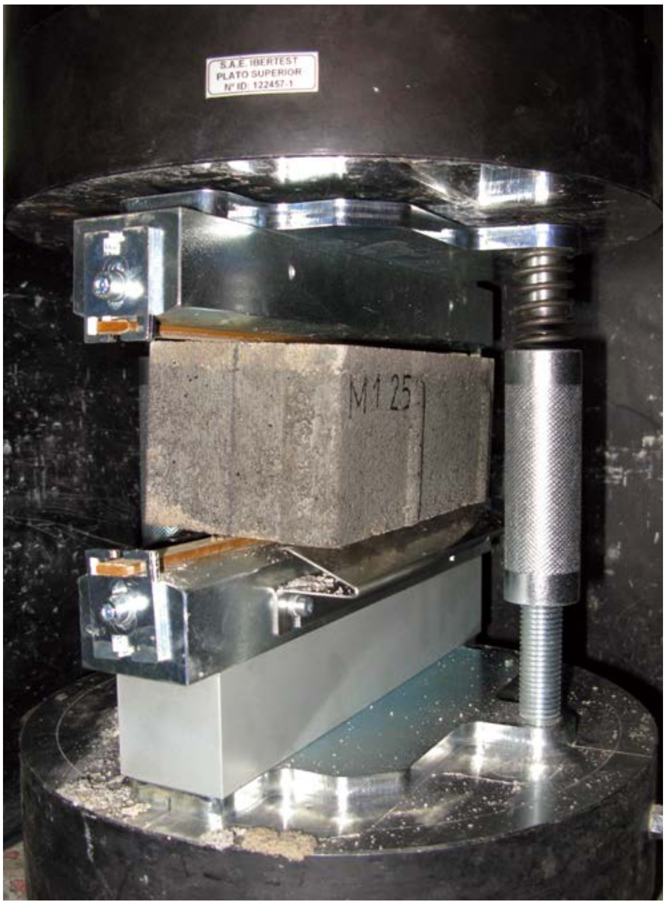
The actions in this phase (indicted below) mainly consisted in standardised tests developed in laboratories and on test tracks to determine the physical/mechanical characteristics and the photocatalytic activity of different commercial materials to be used, as well as their durability and behaviour over time.

Mechanical and durability tests on bituminous and concrete mixtures

Physical, mechanical and durability tests were carried out on different concrete products treated with photocatalytic materials for pavements, as well as different bituminous pavements also treated with photocatalytic materials specifically used for roads, in the Central Laboratory for Structures and Materials and on a Test Track at the CEDEX Transport Study Centre.

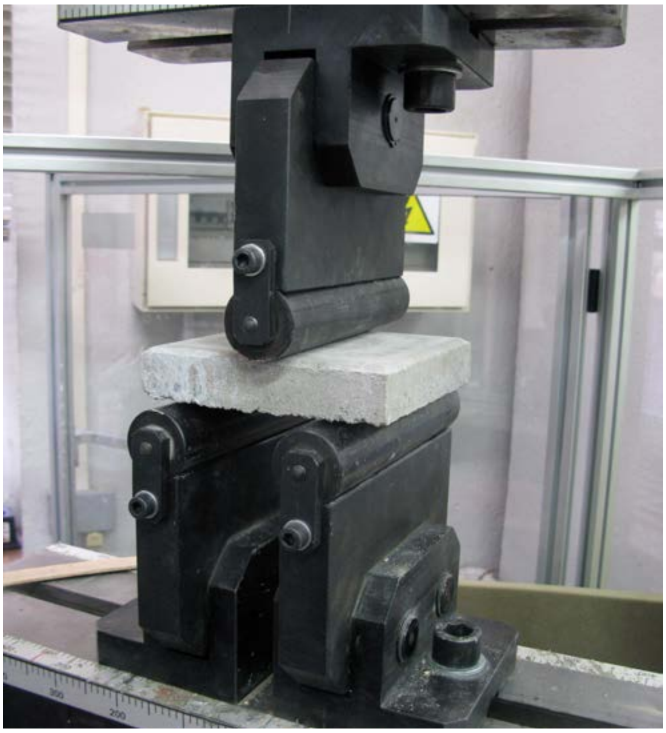
The objective was to analyse the effects of the use of photocatalytic products on the physical/mechanical characteristics (shape and dimensions, resistance and breaking load, wear, slip and weather resistance) to be complied with by the materials in accordance with the corresponding UNE-EN Standards.

Sample dimensions measurement



Mechanical strenght test

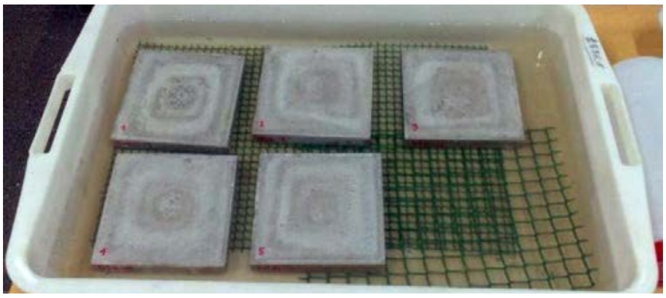
Abrasion resistance test



Mechanical strenght test

Slipping resistance test

Frost resistance test



Capillary absorption test

Implementation of photocatalytic products on a test track

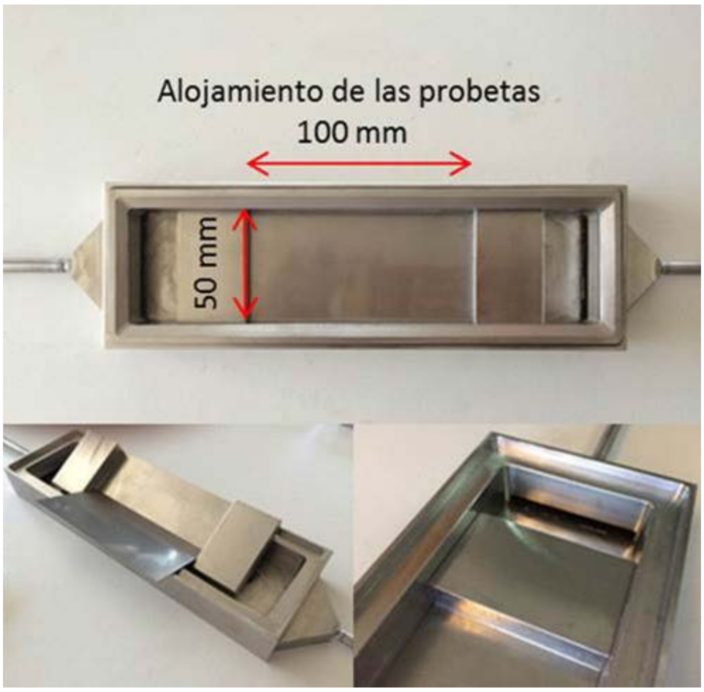
Transverse evenness measurement on a test track

Photocatalytic activity tests and aging on bituminous, concrete and paint mixtures

The FOTOAIR Unit of CIEMAT's Energy Department carried out over 400 photocatalytic activity tests in the laboratory (in accordance with Standard ISO 22197-1).

That Department evaluated the durability of the photocatalytic properties of the selected materials through aging studies (in weather conditions and in accelerated ageing chamber) and, in the case of bituminous pavements, the effects of rolling wear (for which, different products were implemented on various types of bituminous mixture on the CEDEX test track, evaluating their efficiency after different rolling cycles).

Photocatalytic activity test



Different views of the reactor, in accordance with Standard ISO 22197-1

Test specimens submitted to ageing from weathering (durability tests)

Representative photocatalytic products found on the market

Test specimens ready for testing (in ISO dimensions)

Pavement test specimens (dimensions ISO 22197-1)

The results obtained in these tests allowed the best materials to be selected for use in different urban scenarios (road, pavement and façade) in the successive actions, and led to the following **conclusions**:

- Huge variations have been detected in NO_x reduction efficiency of the different commercialized photocatalytic materials (8% of them have none or very little photocatalytic activity). Those selected for the project show NO_x laboratory conversion values between 25 and 55%, depending on the product and substrate used.
- The surface characteristics of pavement and roadway materials may be adversely affected by the use of photocatalytic products, especially texture and slip resistance (the latter is more affected in relation to the age of the pavement)
- The stability of the coating against adverse weather conditions is important: some photocatalytic materials maintain their efficiency after long periods of exposure, whilst others undergo a gradual decrease in their NO_x removal capacity
- All bituminous products show low durability in the accelerated wear teat using traffic simulators, although dense-graded mixtures perform better than open ones
- The characteristics of the substrate and the way the photocatalytic product is applied, significantly influence the results obtained in the reduction of NO_x

Development of an experimental system to measure the deposition rate of NOx on photocatalytic surfaces in an outdoor environment

As part of the project's preparatory actions, an experimental device (and the corresponding software for data collection and processing) was designed and developed to detect the establishment of a NO_X concentration gradient between the levels closest to and farthest from the photoactive surface.

The objective was to estimate the speed at which the pollutants are removed by the photocatalytic surface in order to characterise the sink effect induced by the photoactive surface and to supply data for the numerical model used to simulate the potential decontamination capacity of NO_X when implementing these materials in urban scenarios.

Experimental platform (left) and mast with weather sensors and samples (right)

This device enabled estimates to be taken of NO_X deposition rates for the material implemented on the experimental platform and their comparison with those obtained from laboratory data (ISO 22197-1: 2007), which proved to be similar.

The range of estimated deposition rates for the different materials tested was between 0.5 and $10*10^{-3}$ ms^{-1}.

DEVELOPING THE PROJECT
IMPLEMENTATION ACTIONS

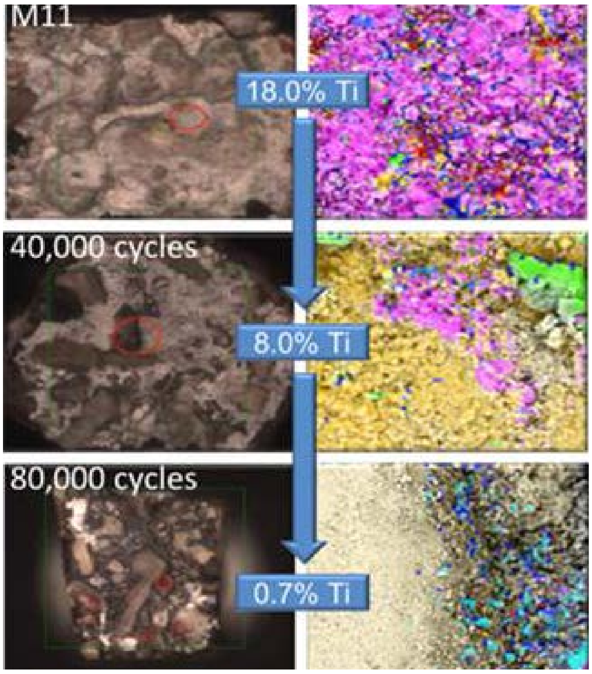
Tests that allow to understand the influence of the variables that are vital to photocatalytic activity under controlled conditions and regeneration tests

Real-scale accelerated test of road surfaces

The study of the influence of traffic loads on photocatalytic products used in bituminous mixtures was carried out on the test track at the CEDEX Transport Study Centre, where rolling and non-rolling sections are analysed in order to identify the effect climate changes have on traffic flows.

A study of the stability of the different additives against rolling wear and irrigation (roadway cleaning) was also carried out by means of a photographic analysis.

Extraction of samples in sections of the CEDEX test track



SEM-EDX analysis of one of the samples after ageing through rolling

Test on photocatalytic activity and its self-regeneration test after washing

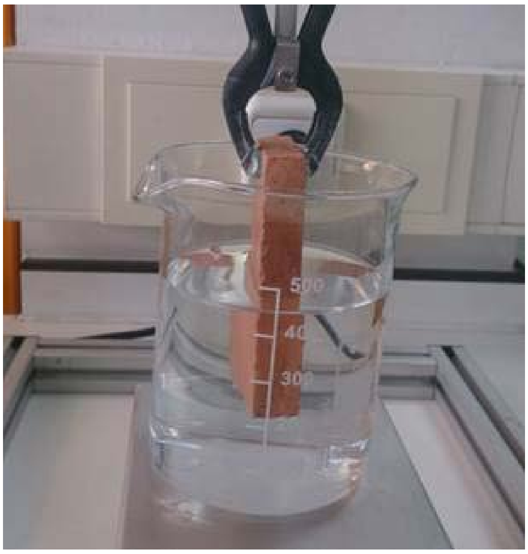
The FOTOAIR Unit of CIEMAT's Energy Dept. conducted the multi-variable correlation parametric study, analysing the effect of the flow, NO_X concentration, irradiance and relative humidity on the photocatalytic activity of the selected materials.

The effect of the porosity of the sample (open or dense-graded) on bituminous pavements and the ageing of the asphalt in the final properties of the material was studied, analysing the rolling wear caused by the passage of a heavy electric vehicle on the CEDEX track.

Photocatalytic regeneration tests were also performed after real-time exposure to outdoor weather conditions in order to recover photocatalytic activity affected by the presence of adsorbed nitrates (as a consequence of the photocatalysis process itself) and organic matter (particles, oils, etc.) deposited on the material.

These tests included washing with water and diluted solutions of commercial or hydrogen peroxide surfactants. The effect the stirring rate, washing time, pH and temperature had on photocatalytic activity was analysed.

Bituminous mixture test specimens from the Paseo de la Chopera after different exposure times to traffic



Regeneration study: washing of materials with water-based solutions

Tests performed in this phase showed **the following results:**

- The type of asphalt mixture (open or closed porosity) and the ageing of same considerably influences the behaviour of the samples. The materials lose their high photocatalytic activity with the number of loads, which increases when used in open-grade asphalt mixtures and on non-aged substrates
- Implementation of the materials in real urban settings implies a change in the photocatalytic activity measured in the laboratory: the surface to be covered must be as clean as possible before applying the photocatalytic product
- Multi-variable correlation studies indicate a similar behaviour for all materials studied: there are optimal flow, irradiance and relative humidity conditions for which a higher yield of the photocatalyst is obtained
- The photocatalytic materials implemented show a 10% conversion rate of NO_x in the laboratory even after long periods of exposure under real conditions of use
- Nitrates adsorbed on the surface of photocatalytic materials, which detract from the efficiency of the material, can be removed by a simple washing process that resembles washing with rainwater
- Other elements that detract from photocatalytic efficiency (such as organic matter accumulated on the material) can be removed by washing with diluted solutions of oxidizing agents or commercial degreasers usually used by city councils in street cleaning

Characterisation of the decontaminating effect of the photocatalytic materials in the real environment

Air Pollution Characterisation Units, COPs and Pollutant Emission Units belonging to the Atmospheric Pollution Division of CIEMAT's Department of the Environment, in collaboration with the FOTOAIR Unit and the Alcobendas City Council, characterised the decontaminating effect of selected photocatalytic materials during the course of preparatory actions to be carried out on the roads, pavements and façades of Alcobendas.

Characterisation on roads

A straight two-way road with moderate traffic, the Paseo de la Chopera in Alcobendas, was selected. The photocatalytic material was implemented on approximately 1,000 m^2 a 60 meter stretch of road.

Before applying the photocatalytic material, the environmental and atmospheric characteristics of the selected scenario were studied, as well as its behaviour as a linear source of atmospheric pollutants.

Following the application of the photocatalytic material, its NO_X decontamination capacity was analysed by continuously measuring the concentrations of pollutants and meteorological variables in terms of surface and height for two months. The NO_X concentration was measured at six different points along the street, 40 cm above the mean surface, in order to verify whether said concentration decreased in the area treated with the photocatalytic material.

Application of the photocatalytic product on the surface of the Paseo de la Chopera road in Alcobendas

View of the road with the photocatalytic product applied

Besides, intensive studies of the following measures were also performed:

» Particullate matter in air and deposited on the road, to study the possible generation of potentially harmful health products (by resuspension of TiO_2 as a consequence of rolling wear)
» Volatile Organic Compounds (VOCs)
» Road Traffic
» UV-A radiation and temperatures in horizontal and vertical facings of the street
» Extraction of road surface samples to evaluate the decline in photocatalytic activity and loss of surface titanium due to the wear as a result of road traffic
» Flushing to characterise the possible presence of nitrates and titanium in collected leachates

Flushing for collection and analysis of leachates

The study showed that **no improvement was detected in concentrations of NOx for the presence of photocatalytic material** despite the fact that the material with the best photocatalytic activity and durability was used, that NO_x concentration measurements were performed at low levels above the treated surface and that just the data associated with optimal weather conditions were used. Low deposition rates and disruptions caused by road traffic prevented any sink effect from being observed.

On the other hand, **it is important to note that no negative impact was detected with regard to the generation of by-products derived from the application of the photocatalytic material.**

Characterisation on pavements

The scenario chosen was a double "street canyon", a scale model consisting of two parallel and contiguous linear streets, 20 m long and 4 m wide, with 5 m high walls on both sides and paved with tiles previously selected in preparatory actions, located in an urban area of Alcobendas near the public highway, with moderate levels of pollution, but without direct traffic.

Construction of the double "street canyon" for pavements and façades

Layout of the double "street canyon" in the municipality of Alcobendas

Before applying the photocatalytic product on a pavement, the dynamic and chemical behaviour of air masses in the double street canyon was described and measurements were taken of environmental concentrations of pollutants and different weather parameters outside same.

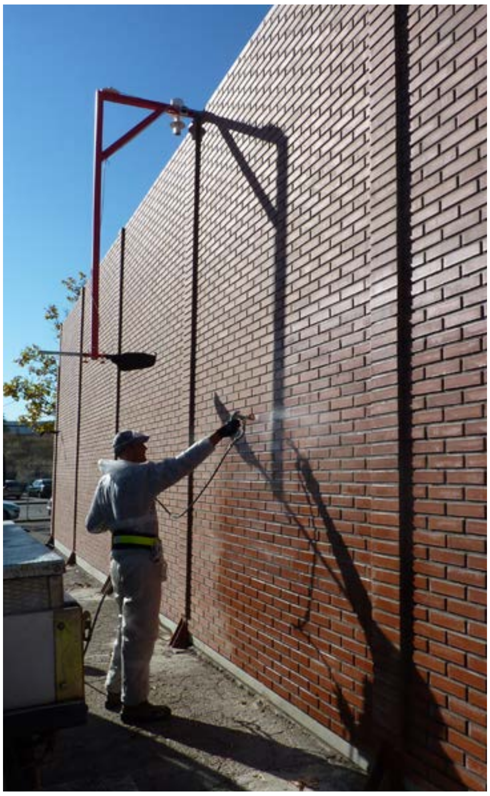
The photocatalytic material was applied in a photoactive canyon street and the other was used as reference street (since it remained untreated). Once the product was applied, continuous measurements of the NO_X concentration were taken in both streets, for two months, resulting in the same conclusion as that reached for roads: **no reduction in the NOx concentration attributable to the decontaminating effect of the photocatalytic material could be detected.**

Application of a photocatalytic product on a pavement in one of the canyon streets

Façade scenario

The outer wall of the "street canyon" facing the east was used due to better insulation and brick coating on which the photocatalytic material was applied.

As in the previous case, the dynamics of the air mass close to the surface were described above and, following the application of the photocatalytic product, continuous measurements of the NO_X concentration as well as the weather parameters were taken for a month and a half, to determine possible NO_X concentration gradients parallel or perpendicular to the façade.



Application of a photocatalytic product on the brick façade in the street canyon

Street canyon brick wall used to measure NO_X and continuous weather parameters

The results obtained show that, for a short period of time and under specific environmental and weather conditions, **a significant reduction in NO_X concentration was registered, which could be unmistakably attributed to the presence of the photocatalytic coating**.

The following **conclusions were drawn from campaigns developed in the three urban scenarios** described above:

- There was no evidence of the effect the removal of NO_X from photocatalytic materials had on roads or pavements
- A positive impact was registered for façades (NO_X sink effect of around 15 to 20%), very close to the photocatalytic surface and in very specific environmental conditions, with a low overall incidence in the surrounding air
- It is very difficult to establish the possible cause-effect relationship between any observed NO_X reduction and the presence of photocatalytic surfaces in urban settings
- Low deposition rates and the high volume of air on the photoactive surface make the photocatalytic macroscopic effect induced very weak
- There is no evidence of local effects on the surrounding air or on leachates due to the use of photocatalytic materials

Modelling of the evolution of concentration levels and NOx gradients in the presence of photocatalytic materials implemented in urban and district-scale scenarios

The Atmospheric Pollution and Ecotoxicity Modelling Unit of the CIEMAT's Department of the Environment developed a prototype to simulate concentration levels and NO_X gradients in different scenarios in the municipality of Alcobendas.

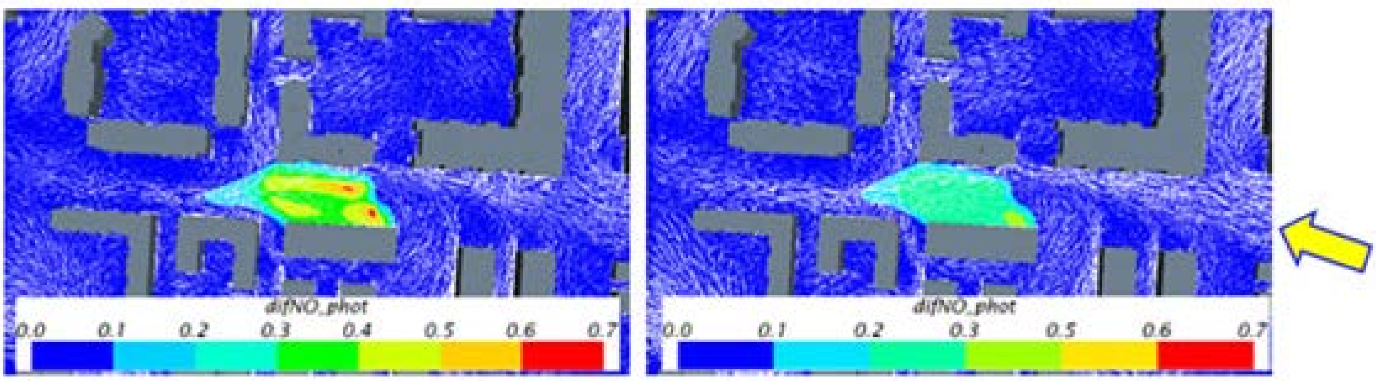
The following tasks were performed:

» Development, validation and adjustment of a Computational Fluid Dynamics (CFD) model adapted to simulate the dispersion of reactive air pollutants (NO and NO_2).
» Modelling of the photocatalytic effect, dispersion and the effect of NO_X deposition on the photocatalytic surface based on the NO deposition rate obtained in previous actions.
» Comparison of model results with measurements under environmental conditions.
» Simulation of reactive flows and pollutants in the urban setting of Alcobendas to select the ideal locations for the experimental (road) campaigns.

After that, the following tasks were carried out based on data obtained in on-site experimental campaigns:

» Modelling of the NO_X deposition effect due to the photocatalytic material implemented on roads (Paseo de la Chopera), with a NO deposition rate of 0,005 ms^{-1}.
» Modelling of the NO_X deposition effect due to the photocatalytic material implemented on pavements and façades (street canyon), with NO deposition rates of 0,01 ms^{-1} and0,004 ms^{-1}, respectively.

For that purpose, it was therefore necessary to include in the model, the geometry of the streets and buildings of the municipality, NO, NO_2 and O_3 input concentration values and pollutant emission calculations (from traffic gauging), besides the NO deposition velocity.



Differences of NO concentration with and without photocatalytic asphalt at a height of 1 m (left) and 3 m (right), with wind direction indicated by the yellow arrow

Once the model has been developed and validated, a methodology has been developed to use it for prior evaluation (without the need to implement them) of the eventual impact of different scenarios in which photocatalytic materials are used. In order to quantify the impact of these materials on the suspended NO_X, two simulations are carried out under the same weather conditions, one of which includes NO deposition on the photoactive surface and the other not. The impact is therefore evaluated by the difference of NO_X concentration in both simulations (δNO_{xdep}).

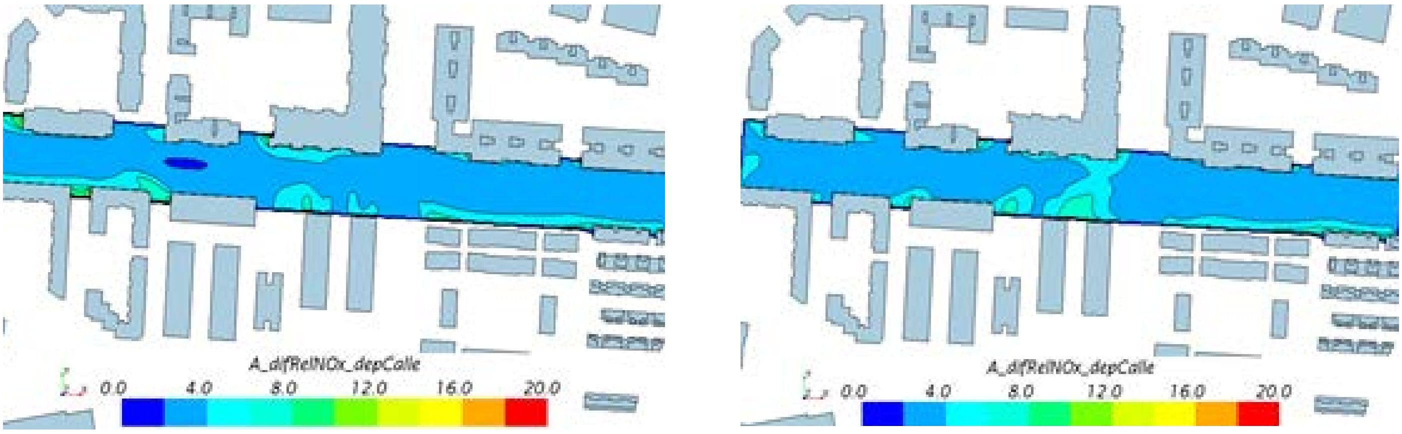
This was applied to a neighbourhood of Alcobendas where all surfaces in an area of 1 km^2 are supposedly photocatalytic and also sunlit, in order to calculate the maximum reduction of NO_X that could be obtained in the study area considered (although it is not real as the whole area cannot be sunlit equally).

This study area is marked in the black box as it contains the highest concentration of pollutants (since it has heavier traffic) and therefore, pedestrians are more exposed.

The area treated with photocatalytic material classified according to each surface is marked in orange: façades, pavements and roads. The study area marked in black

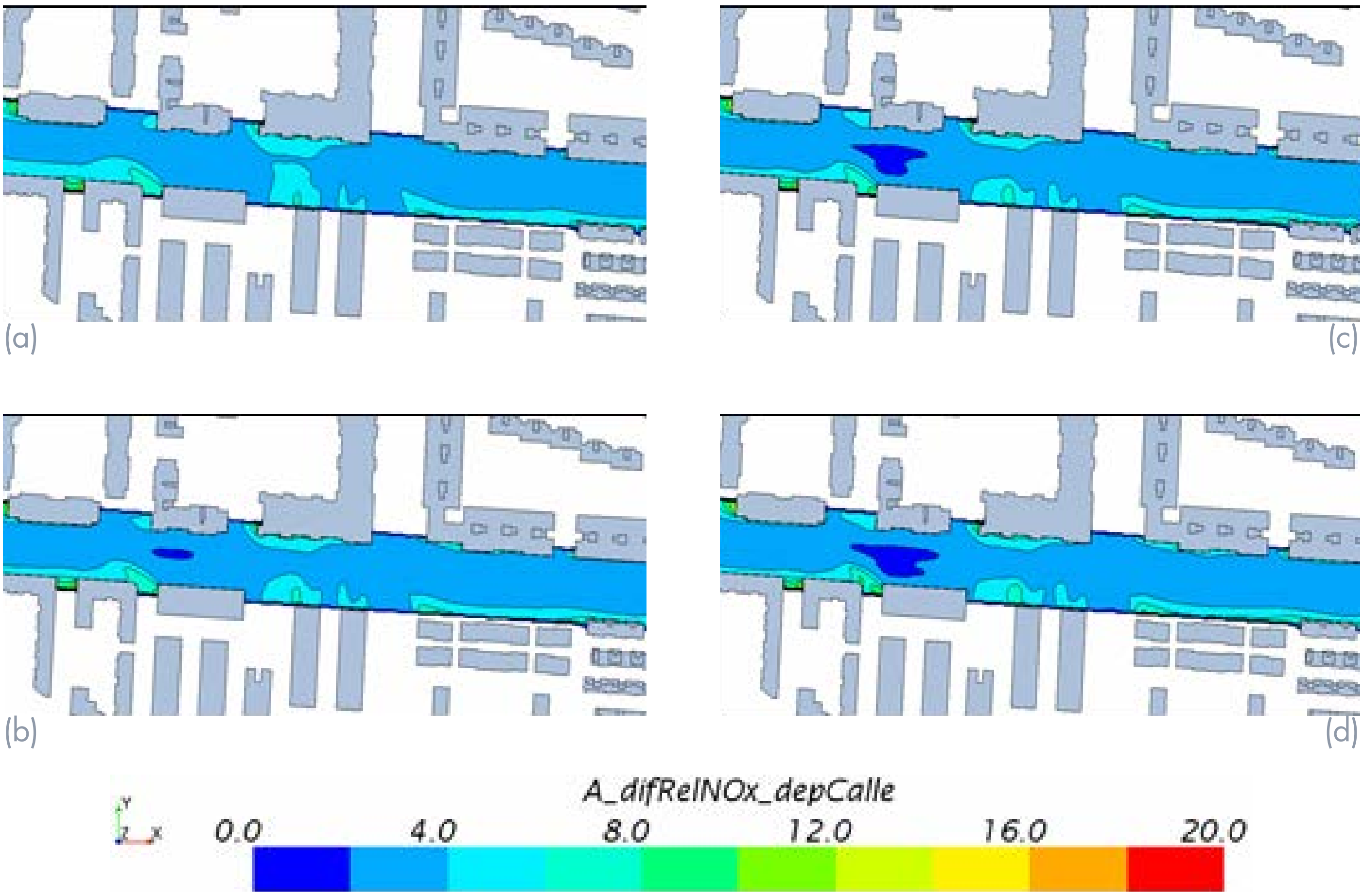
The simulation was performed under prevailing atmospheric conditions in the area, based on data obtained during on-site campaigns, and the following cases were analysed:

» Study of the influence of wind direction on the effectiveness of the photocatalytic material: the predominant directions, SE and SW, were studied, with no evidence of any significant differences between them.



Average NOx reduction for wind directions in the studied street (SE on the left, SW on the right)

» Study of the impact of traffic emissions on the effectiveness of photocatalytic material, with a prevailing wind speed of 2 ms^{-1} (from 900 to 10,800 veh/h, approximately)



Plans at pedestrian height of δNO_{xdep} for each traffic emission scenario: (a) base (900 veh/h); (b) Em1(3600 veh/h); (c) Em2 (7200 veh/h) and (d) Em3 (10800 veh/h)

The following **conclusions** were reached:

- Atmospheric characteristics (irregular flow and turbulence) prevent clear evidence of the NO_X impact, due to the photocatalytic effect of the materials, on air at pedestrian height
- The possible reduction of NO_X depends on several factors such as air concentration, traffic emissions, wind speed and direction, treated area, distance to the photoactive surface or its illumination by sunlight
- The irregular layout of buildings in a city and the heterogeneity of traffic emissions results in a complex distribution of the flow that prevents the effect of the NO_X deposition from being homogenous or equal along the whole length of a street
- In all simulated cases, NO_X reduction was significant when measured close to treated surfaces, decreasing when further away
- In global modelling, considering a treated area of 1 km^2 and in the unrealistic case that this whole area were illuminated at the same time, an average maximum reduction of 3% of NO_X was obtained in the street at pedestrian height, in the prevailing atmospheric conditions
- Wind speed has a decisive influence on the efficiency of the material. The lower the former, the higher the latter, since contact time between contaminants and the photocatalytic surface increases
- With similar weather conditions and concentration of background pollutants, the effect of photocatalytic material is virtually the same regardless of the existing traffic density (and therefore direct NO_X emissions)

Development of a guide for the use of photocatalytic materials

As a result of the project, a guide has been drawn up for the use of photocatalytic materials by competent Bodies in the management of urban air quality, as a way of reducing NO_X air pollution in cities.

This guide provides useful information for air quality managers to decide whether or not to implement this type of materials in certain areas of cities based on the results obtained in the LIFE MINOx-STREET project. It provides information on:

» Main project results
» Cost-benefit analysis of the implementation of photocatalytic materials in real urban scenarios.
» Criteria for selecting the photocatalytic materials to be applied
» Conditions for the use and maintenance of these materials: application, cleaning, etc.

The guide is available on the project's web page: http://www.lifeminoxstreet.com

AND FROM HERE ONWARDS?
IMPACT OF THE PROJECT

Current air quality plans, both at local and national levels (Plan Aire II 2017-2019) do not include - for the most part of them - the use of this type of materials, beyond the commitment of some administrations with research projects in the matter.

On the other hand, the 2017-2020 Transport and Infrastructure Innovation Plan considers the application of photocatalytic technologies for transport infrastructures. The fact that this Plan has incorporated a strategic line of action, to be developed in 2020 with a budget of approximately 600,000 Euros, leaves open the door for investigating the eventual use of these materials in stations, airport terminals, transport hubs, Public Works Ministry buildings, etc.

The LIFE MINOx-STREET project **only contains document regarding a NO_x sink effect induced by the presence of photocatalytic materials under very specific environmental conditions and close to the photoactive surfaces.** It is therefore considered **necessary to further improve the properties of these materials**, both in terms of their photocatalytic performance and their durability and eventual regeneration.

It is also recommended that **research be carried out on new engineering designs and applications** that can take advantage of the decontaminating capabilities of these materials to achieve a positive and significant macroscopic impact on the air quality of environments in which these systems are installed, **taking into account the following two parameters: surface photoactive ratio/volume of air to be decontaminated and permanence time** (time the air remains in contact with the photoactive surface).

On the other hand, given the heterogeneity of the results of the different materials tested in the laboratory, it is necessary to regulate the market of these products so that the information provided by manufacturers/distributors is reliable and comparable with each other.

The large number of variables that intervene in the photocatalytic efficiency of the materials also makes it necessary to continue investigating them; in terms of weather conditions and eventual reactions with the substrate on which they are fixed (e.g. interaction of the photocatalytic material with paint components - as some sources cite - or, if applied to bricks, mortar components - as identified in the LIFE MINOx-STREET project).

Finally, the eventual adverse effect of these materials should be investigated for large-scale applications and the generation of possible by-products analysed.

Project data

LIFE MINOx-STREET
Monitoring and modelling NOx removal efficiency of photocatalytic materials: A STRategy for urban air quality managEmEnT
LIFE+ Environment Policy and Governance. Theme: Air and Noise: Air quality monitoring

Project duration: July 2013 - June 2018
Total budget: 1.982.619 euros
Eligible budget: 1.833.829 euros
EU contribution: 916.913 euros (50% of the eligible budget)

Beneficiaries

Coordinator:
INECO Transport engineering and consulting company
Partners:
CIEMAT Energy, environmental and technological research centre
CEDEX Centre of Studies and Experimentation of Public Works
Alcobendas Town Council

Contact data

Project coordinator:
Gemma Caballero Íñigo
gemma.caballero@ineco.com

lifeminoxstreet@ineco.com