LIFE-PLATFORM MEETING ON AIR , 26-27 September, Barcelona (Spain)

Monitoring and modeling NOx removal efficiency of photocatalytic materials: A strategy for urban air quality management

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What is *Photocatalysis*?

"Change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible or infrared radiation in the presence of a substance (photocatalyst) that absorbs light and is involved in the chemical transformation of the reaction partners."

PAC, 2007, *79*, 293 *Glossary of terms used in photochemistry, 3rd edition (**IUPAC** Recommendations 2006)*

The photocatalysis takes place on certain semiconductor materials when they are adequately illuminated (light energy > band gap), generating electron-hole pairs that can produce catalytic effects on the surface.

The basic principles of photocatalysis were discovered more than forty years ago with TiO_2 in water.

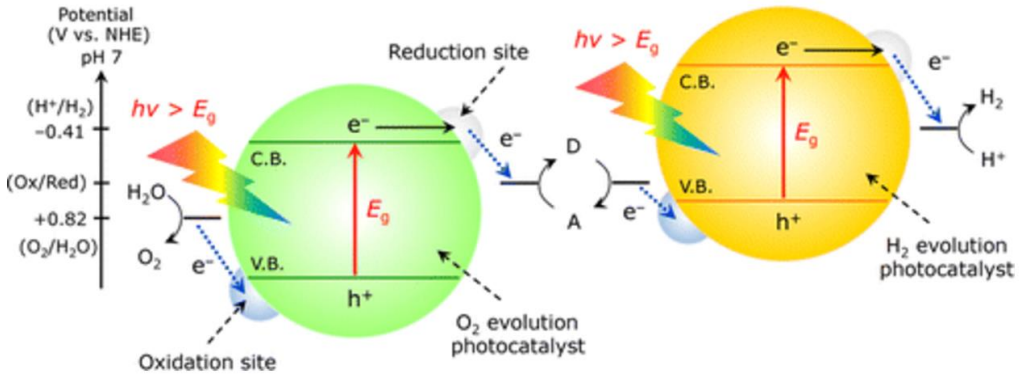
(A. Fujishima and K. Honda (1972), Nature 238, 37)

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb}$$

$\lambda < 384$ nm

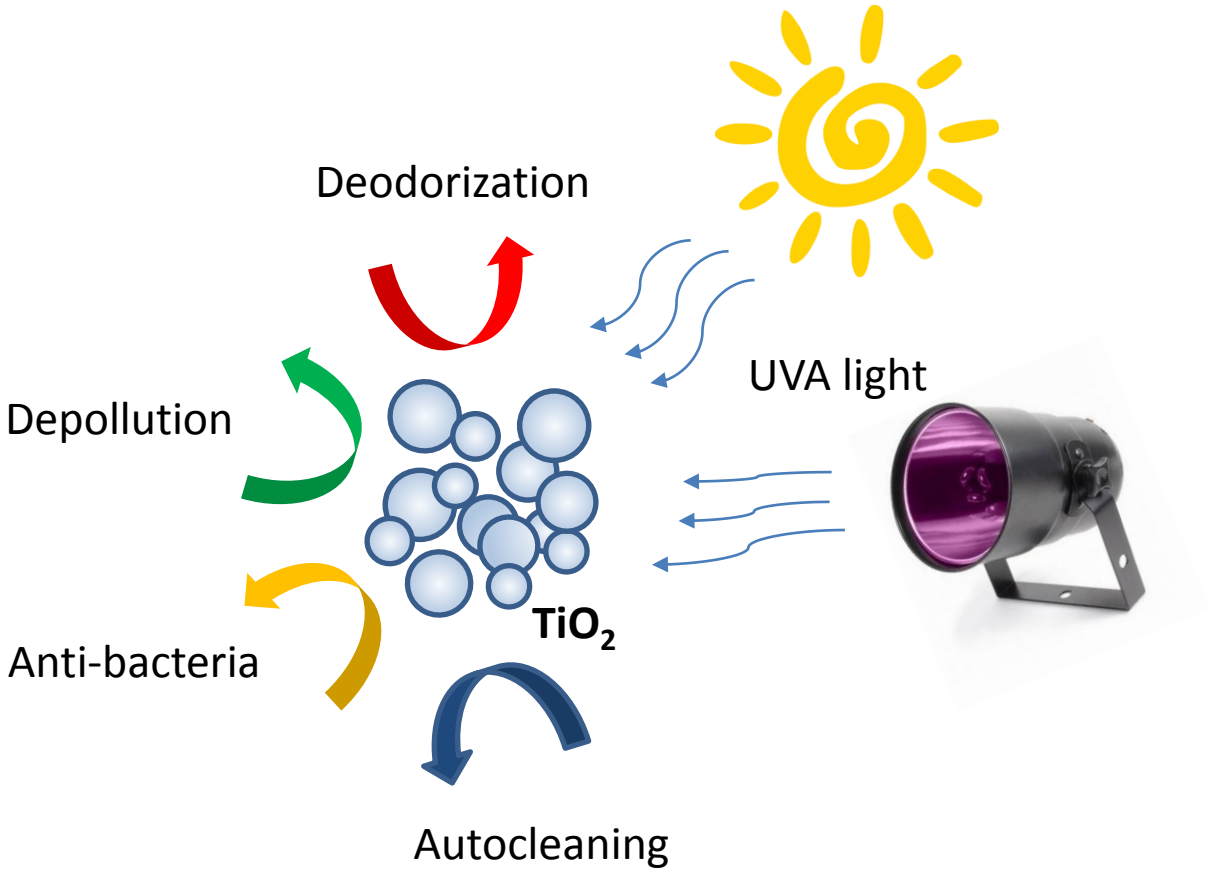
$$h^+_{vb} + OH^- \rightarrow {}^{\cdot}OH$$

$$e^-_{cb} + O_2 \rightarrow O_2^{-\cdot}$$



K. Maeda (2013), *ACS Catalysis*, 3, 1486-1503

Environmental (outdoor/indoor) applications of the photocatalysis



How can photocatalysis help us to clean urban air?

Air purification is possible by photocatalytic oxidation of inorganic gaseous pollutants (NO_x, SO_x, CO, H_2S, etc) and volatile organic compounds (VOCs).

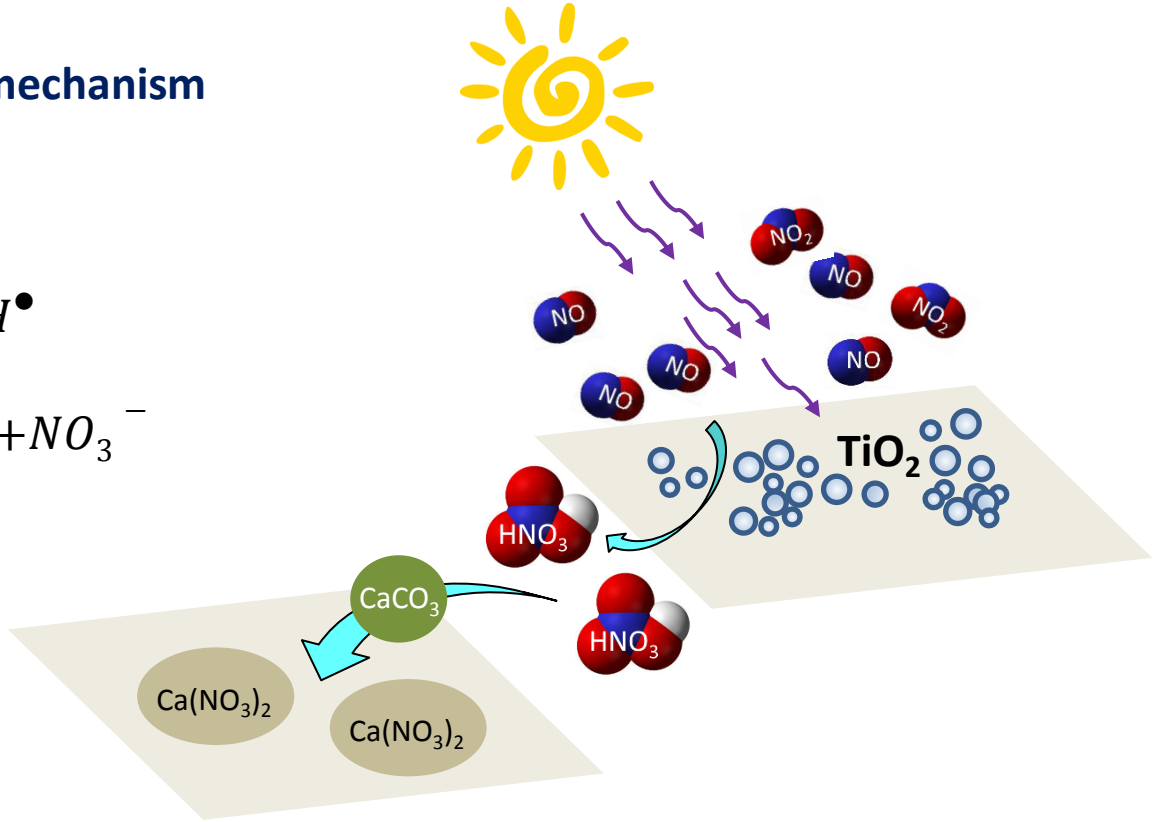
Example: NO photoxidation mechanism

$$O_2^- + H^+ \rightarrow HO_2^\bullet$$

$$NO + HO_2^\bullet \rightarrow NO_2 + OH^\bullet$$

$$NO_2 + OH^\bullet \rightarrow HNO_3 \rightarrow H^+ + NO_3^-$$

....



But … What is the real effect on outdoor air quality by the use of photocatalytic materials?

Important efforts have been dedicated (other LIFE projects, etc.) to answer this question but there is still a lot of open issues …

LIFE MINOx-STREET was concieved from a scientific approach to provide new information about the real potential and effectiveness of air pollution abatement measures based on the use of photocatalytic building materials in urban outdoor applications.

LIFE MINOx-STREET *(LIFE 12 ENV/ES/000280)*

Total Budget: 1.912.619 € (UE co-financing 46%)

Beneficiaries:
- INECO (Coordinator)
- CIEMAT
- CEDEX
- Ayuntamiento de Alcobendas

Duration: July 2013 - March 2018

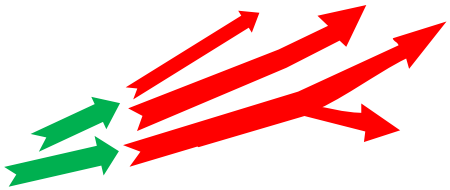
LIFE MINOx-STREET

Objectives:

- ✓ *Test and compare the potential efficiencies as NO_x sinks of a range of commercial photocatalytic materials and make a selection of the most promising products to be used on real urban surfaces.*
- ✓ *Document and evaluate in real ambient conditions the effects that the use of those photocatalytic materials could produce in urban air quality.*
- ✓ *Developing and setting up a prototype (microscale model) capable of simulating the effect of implementing specific photocatalytic materials in any particular urban scenario in order to estimate their potential effects on air quality .*
- ✓ *Offering local authorities a technical guide for applying in optimal conditions commercial photocatalytic materials designed for air purification.*

LIFE MINOx-STREET

Actions:



Preparatory actions:

- *Selection of commercial photocatalytic materials representative of the state of the art (air purification).*
- *Testing the mechanical and physical properties of building photocatalytic materials.*
- *Experimental assesment of NO_x removal capacity of those materials in laboratory and real ambient (characterization of NO_x dry deposition process).*
- *Final selection of three photocatalytic products for application on roads, sidewalks and facades.*

Implementation actions:

- *Characterizing NO_x dry deposition velocities in ambient conditions at a controlled site.*
- *Study of depolluting activity dependence on external conditions, product ageing, wear, etc.*
- *Study of NO_x depolluting effects in three urban scenarios (Alcobendas city): road, sidewalk and facade.*
- *Developing and setting up a prototype model (microscale CFD model, coupled to the urban atmospheric chemistry and NO_x deposition velocities).*
- *Mathematical simulation of the behaviour of photochemical products applied in the three urban scenarios of Alcobendas.*
- *Estimating the cost/benefit of actual complementary NO_x control strategies.*

Methodologies (1/8)

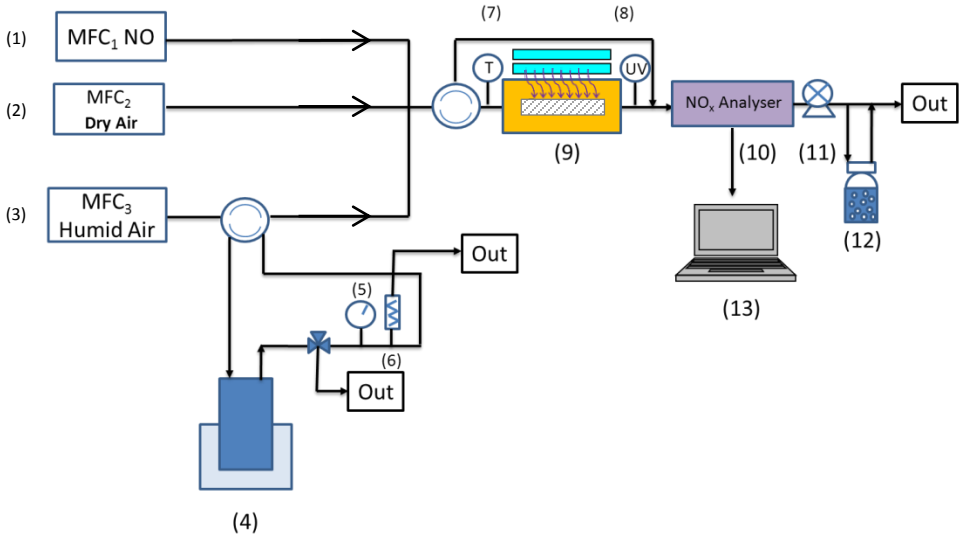
Selection of commercial photocatalytic materials to be studied in the project (INECO)

Method: Market study of commercial photocatalytic materials (declared efficiency, availability, cost, etc.)

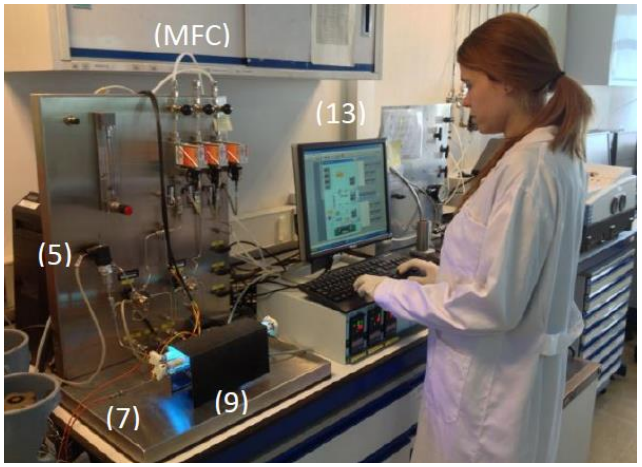
Methodologies (2/8)

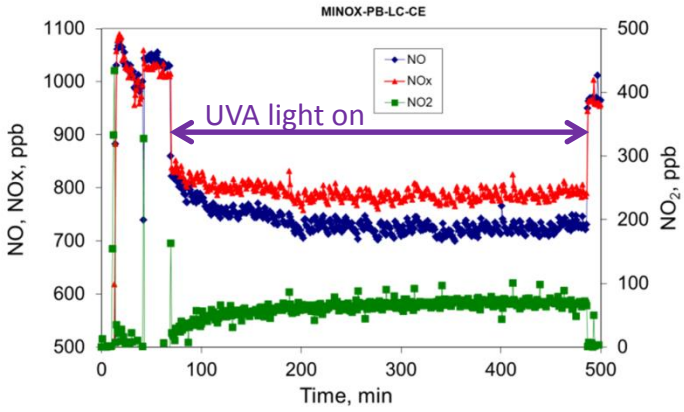
Laboratory Tests for studying NOx removal capacity of photocatalytic materials (CIEMAT)

Method: International standard ISO 22197-1:2007



1-3	*Input Mass-flow controllers*
4	*Humidifier*
5	*Pressure gauge*
6	*Valve*
7	*Temperature sensor*
8	*UV sensor*
9	*Reactor &UVA lamp & test piece*
10	*NO_x analyser*
11	*Pump*
12	*Bubbler NO_x - removal (output)*
13	*Sistema adquisición de datos*





Methodologies (3/8)

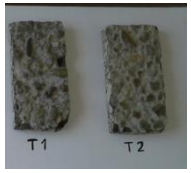
Study of mechanical/safety performance of surfaces (bituminous and sidewalk pavements) treated with photocatalyst (CEDEX – Min. Fomento y MAPAMA)

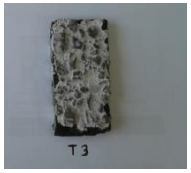
Methods: EN standards for testing pavements (Road Technology and Studies Area of CEDEX)

- **Concrete pavements**
- **Bituminous pavements**

Mechanical resistance assays :
- **ice formation**
- **water uptake**
- **bending and breaking load**
- **slippering and skid**

Accelerated wear of asphalts treated with photocatalytic materials

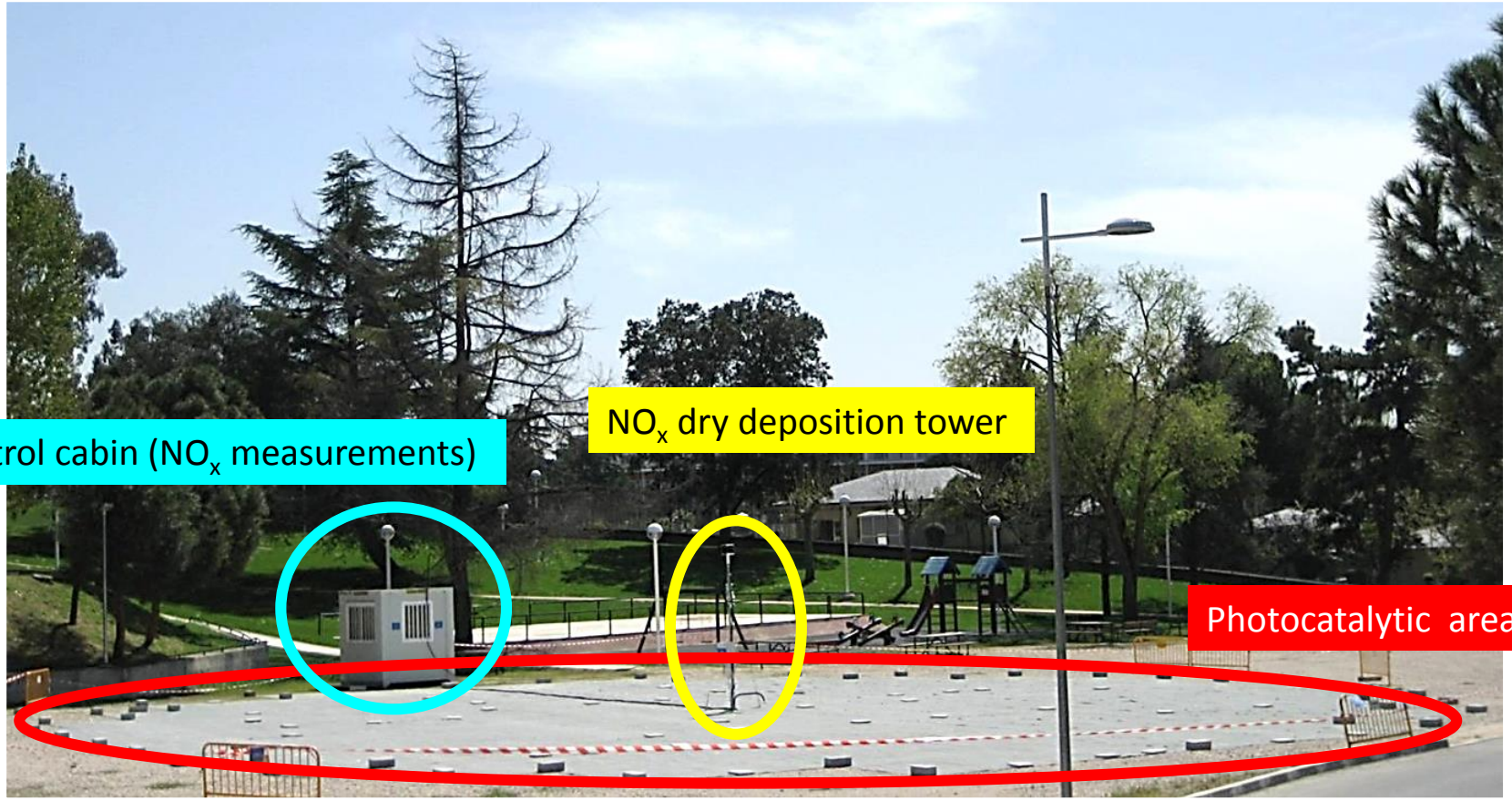




Methodologies (4/8)

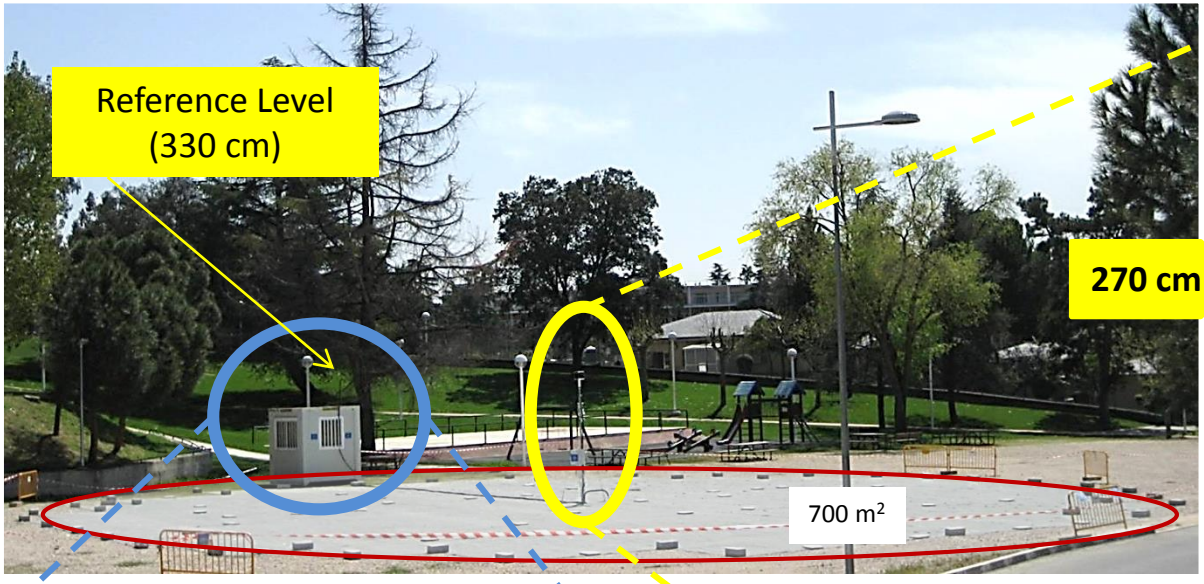
Measurement of NO_x dry deposition velocity on outdoor photocatalytic surfaces (CIEMAT)

Method: Instrumented Photocatalytic Platform (photoactive area = 700 m^2)



Methodologies (4/8)

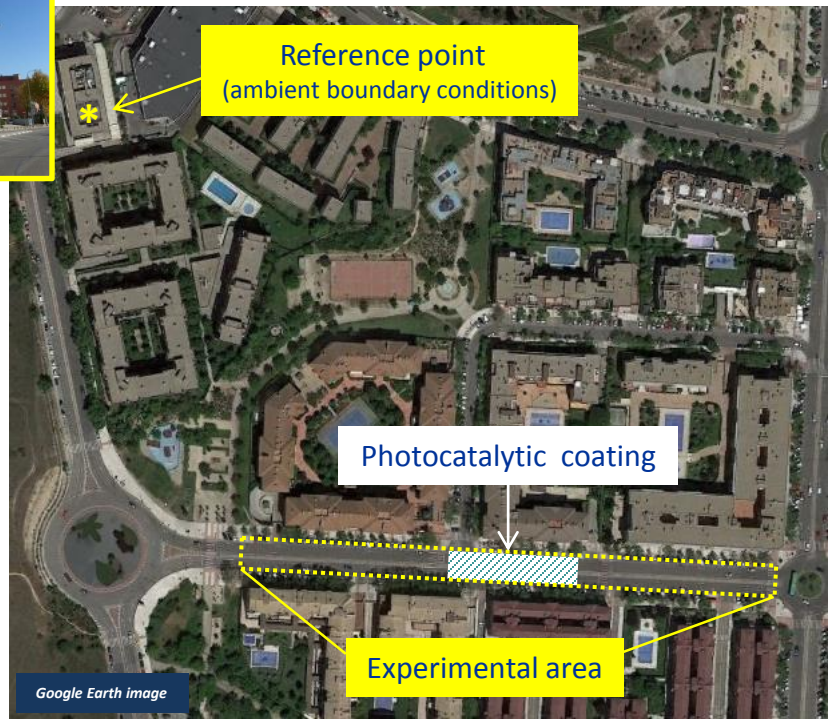
Measurement of NO_x dry deposition velocity on outdoor photocatalytic surfaces (CIEMAT)



Methodologies (5/8)

Experimental study of ambient effects of a photocatalytic urban road (CIEMAT & Ayto. Alcobendas)

Method: Experimental deployment of "bituminous pavement scenario" in *Paseo de la Chopera* (Alcobendas)



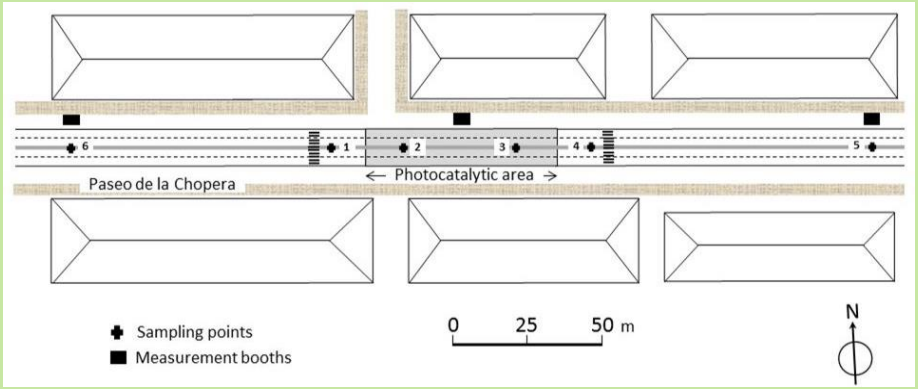
Paseo de la Chopera experimental area (Alcobendas)

Methodologies (5/8)

Experimental study of ambient effects of a photocatalytic urban road (CIEMAT & Ayto. Alcobendas)

On road continuous measurements

***Paseo de la Chopera* experimental area**



6 air sampling points & lines

NO, NO_2

Reference point measurements

Monitoring ambient boundary conditions

Continuous measurements at 15 m high

- ***NO_x and O_3***
- ***Wind speed and direction***
- ***Temperature and relative humidity***
- ***Solar irradiance***

Methodologies (5/8)

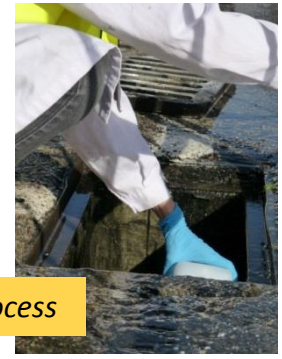
Experimental study of ambient effects of a photocatalytic urban road (CIEMAT & Ayto. Alcobendas)

Intensive campaigns

Ambient PM analysis: resuspended and deposited TiO_2

Traffic load monitoring

VOC measurements

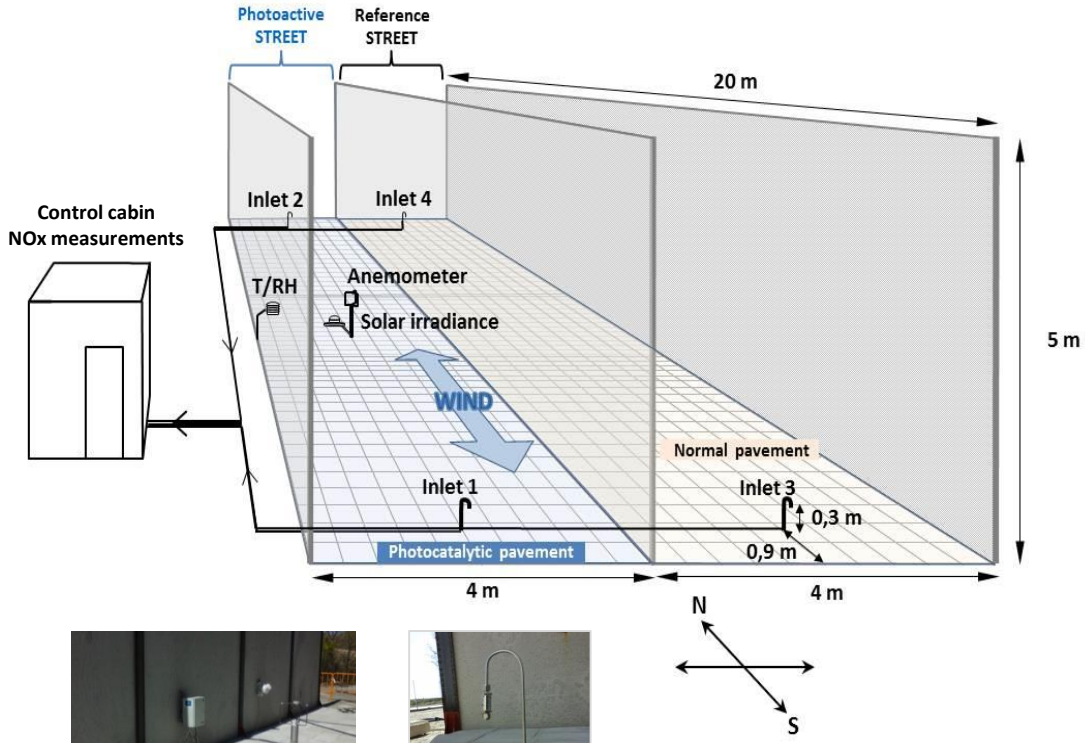


Cleaning and Lixiviation process

Methodologies (6/8)

Experimental study of ambient effects of a photocatalytic sidewalk (CIEMAT & Ayto. Alcobendas)

Method: Scale recreation of "sidewalk scenario" by a double street canyon (Alcobendas)



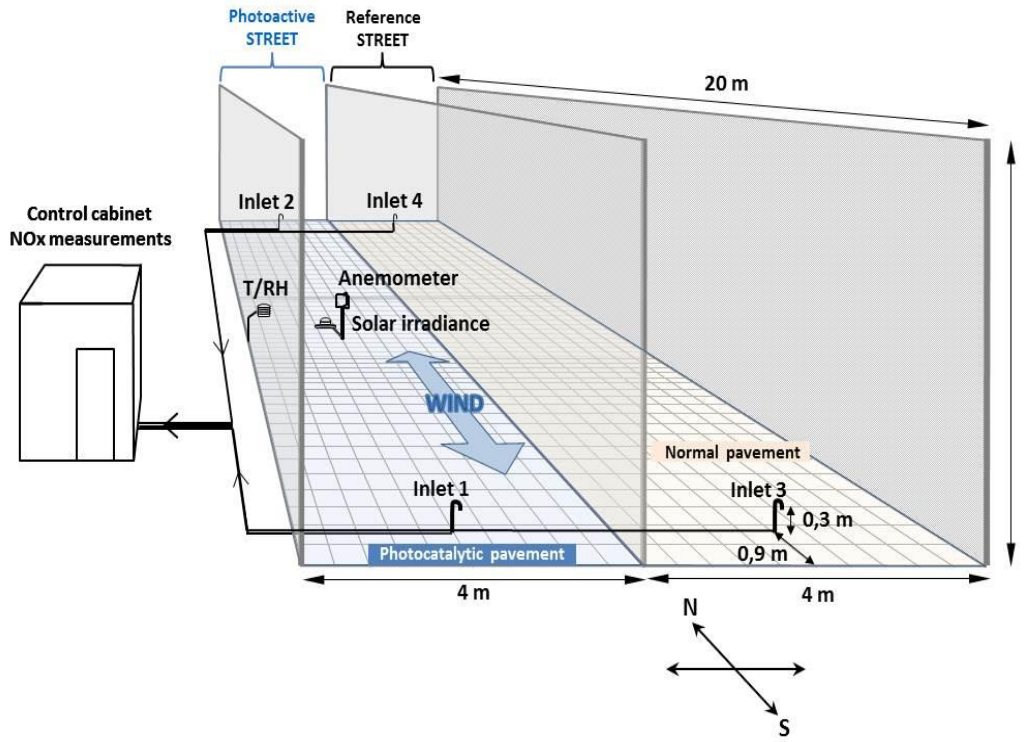
Meteo sensors

Air inlets

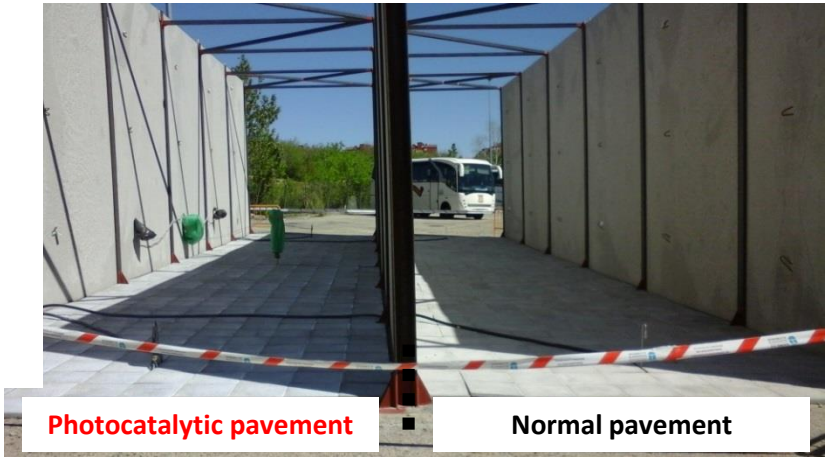
Construction of double street canyon

Methodologies (6/8)

Experimental study of ambient effects of a photocatalytic sidewalk (CIEMAT & Ayto. Alcobendas)



Application of photocatalytic coating

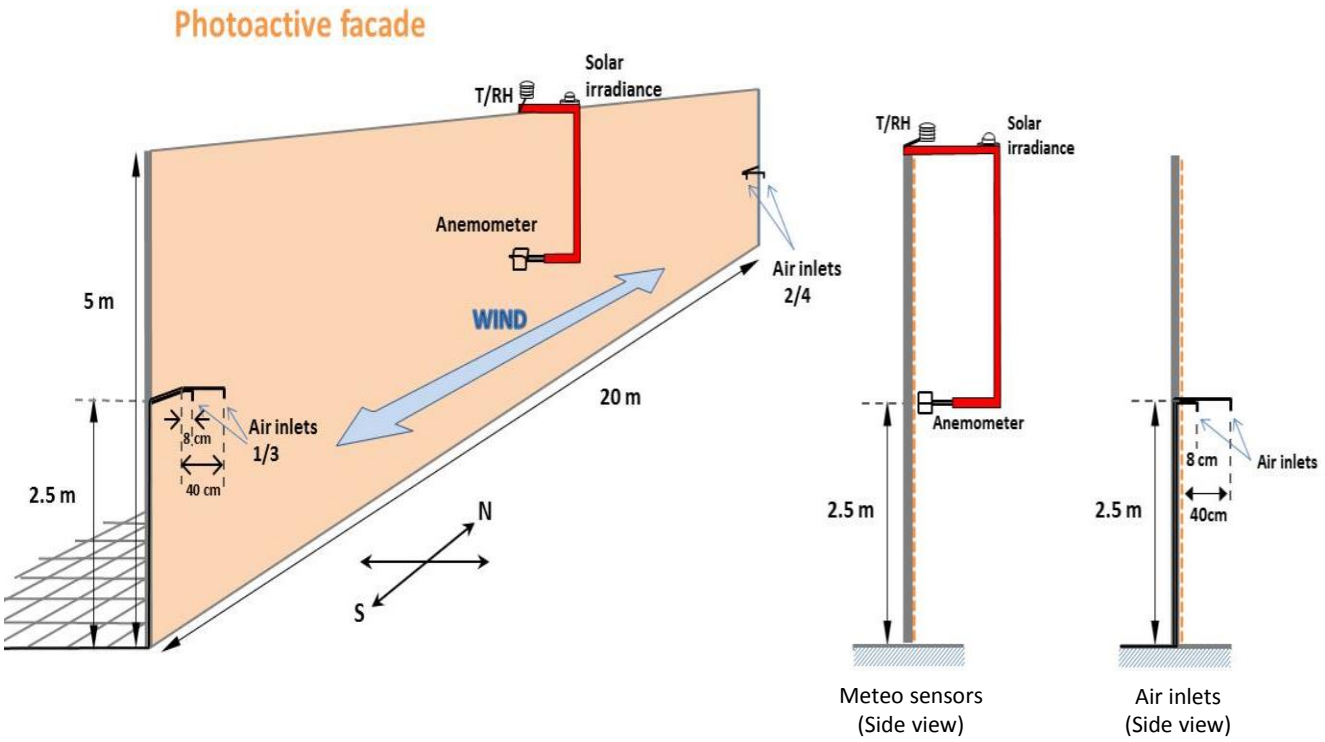


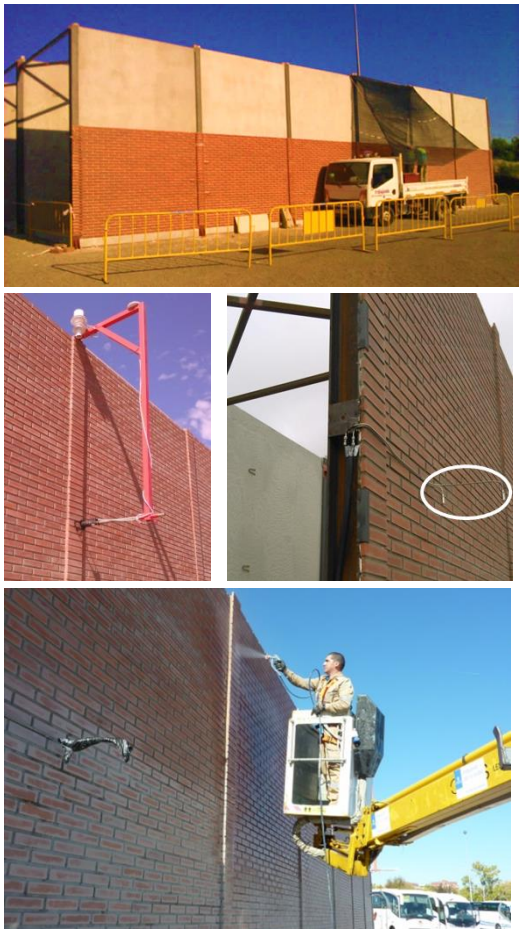
Photocatalytic pavement ■ **Normal pavement**

Methodologies (7/8)

Experimental study of ambient effects of a photocatalytic facade (CIEMAT & Ayto. Alcobendas)

Method: Scale recreation of "facade scenario" by a brick wall (Alcobendas)





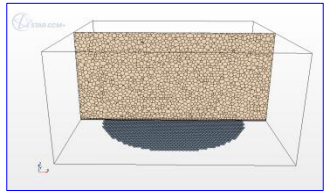
Methodologies (8/8)

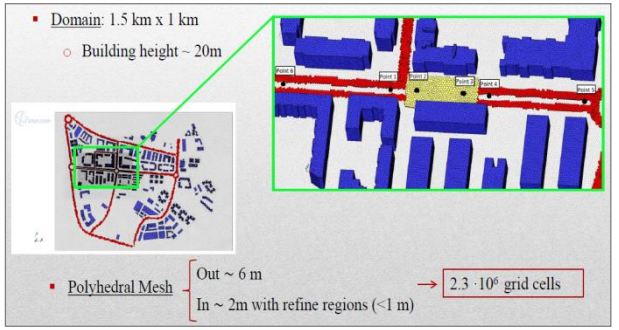
Mathematical simulation of depolluting effects of photocatalytic materials in urban scenarios (CIEMAT)

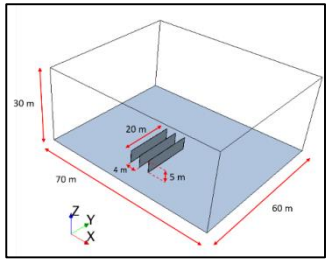
Method: Development of a prototype (*Microscale CFD Model + Chemical reactive module + NO_x deposition velocities module*) and validation (data from outdoor scenarios)

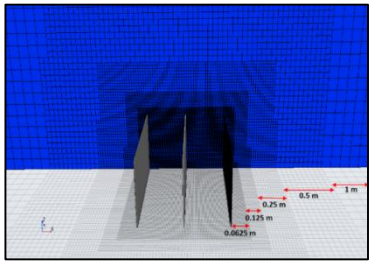
Numerical simulations based on :

- CFD-RANS model: Unsteady simulations
- Neutral atmospheric conditions
- NO_x-O_3 photostationary state
- Deposition Flux: $F_{dep} = - NO \cdot V_d$
- Inlet data from Reference point (boundary conditions)
- Experimental deposition velocities for each material









RESULTS (1/8) Selection of photocatalytic products (INECO)

Bituminous concrete pavements:

- open graded or close graded +
  - + photocatalytic mortar
  - + photocatalytic water emulsion

Sidewalk concrete pavements:

- photocatalytic paving block
- photocatalytic paving slab
- paving block or paving slab +
  - + photocatalytic sol-gel
  - + photocatalytic water emulsion
  - + photocatalytic coating

Facade:

- Concrete surface or face brick +
  - + concretal lasur
  - + photocatalytic paint
  - + photocatalytic coating

RESULTS (2/8) Resistance & Safety Tests (CEDEX)

Bituminous pavement + photocatalytic product

- *Mechanical resistance* : the results use to be in accordance within the norms.

- *Surface behaviour* : Photocatalytic products affect the sliding properties but, in general, the results can be considered within the norms.
Some products can affect sensibly the drainage properties.

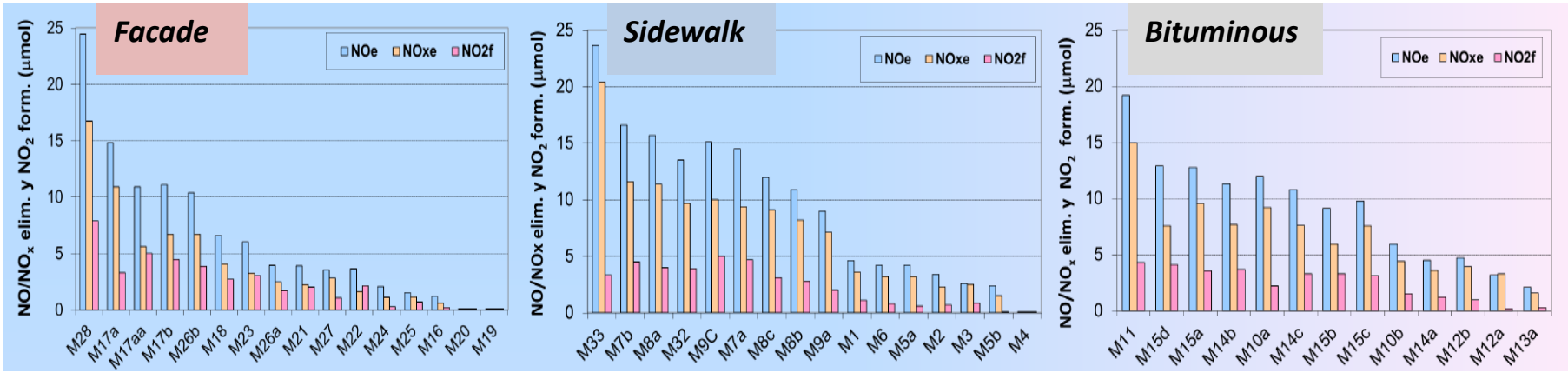
Sidewalk pavement + photocatalytic product

- *Mechanical resistance* : all the results are in accordance within the norms.

- *Surface behaviour* : some of the materials have worse performance in the following tests
  - water uptake
  - ice formation
  - sliding properties (reduction 5-40%)

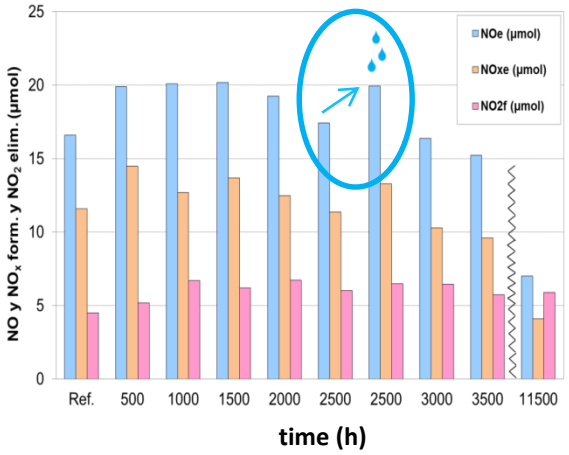
but, in general, the results can be considered within the norms.

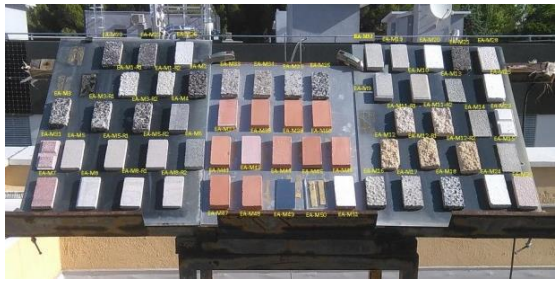
RESULTS (3/8) Air purification efficiency of commercial products Lab. Tests (ISO 22197) (CIEMAT)



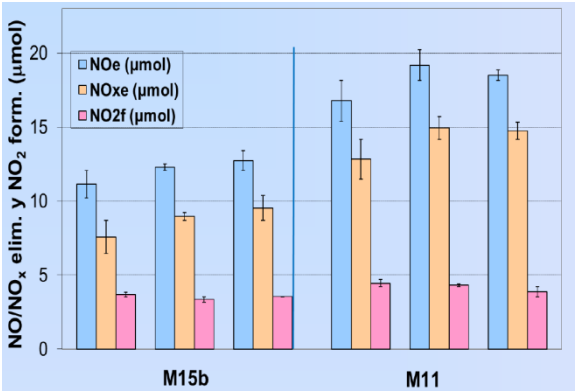
High variability of efficiencies depending on product and substrate

Outdoors exposition and Cleaning effect





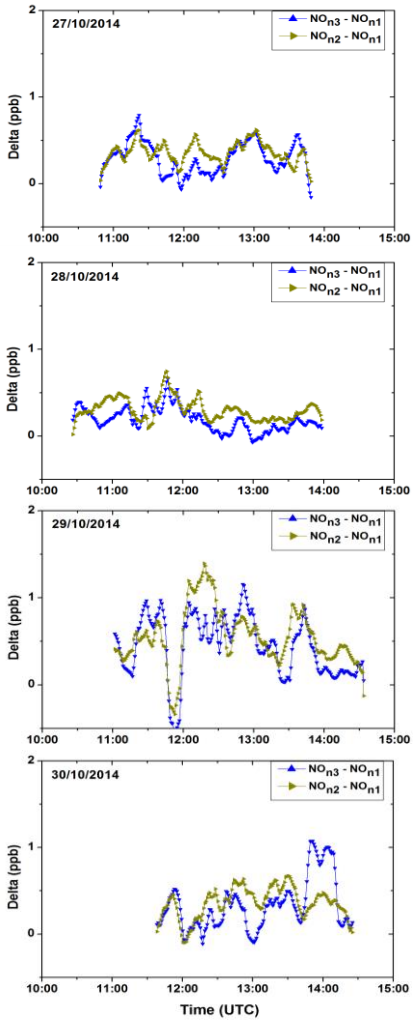
Substrate effect

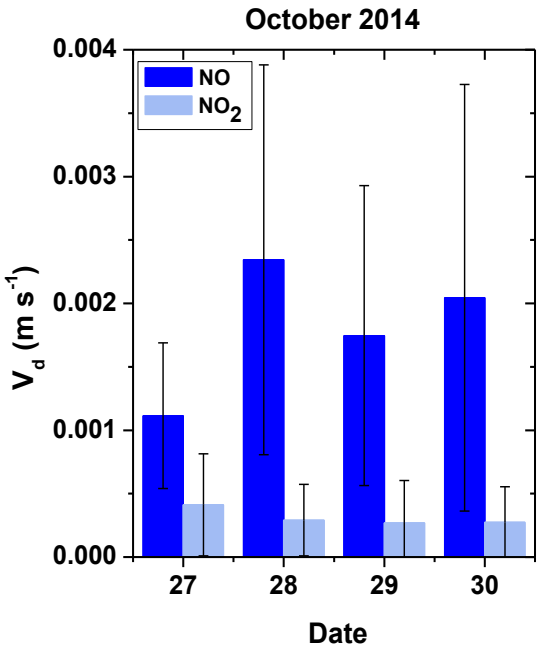


RESULTS (4/8)

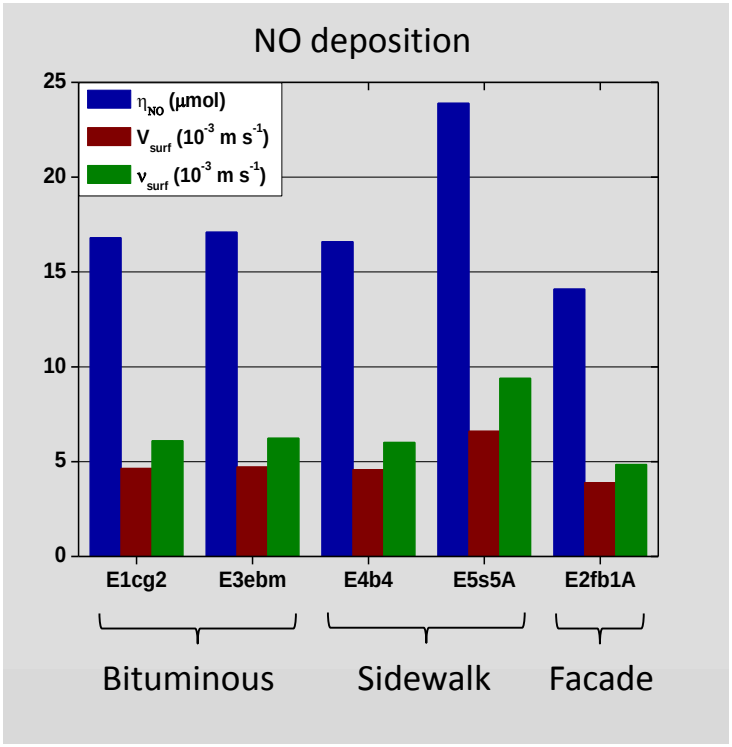
NO_x dry deposition velocity (CIEMAT)

From the photocatalytic platform measurements





From laboratory data estimations



RESULTS (5/8)

NO_x depolluting effects
(bituminous pavement scenario) (CIEMAT)

NO concentration at sampling points (1, 2, 3 and 4 lines)

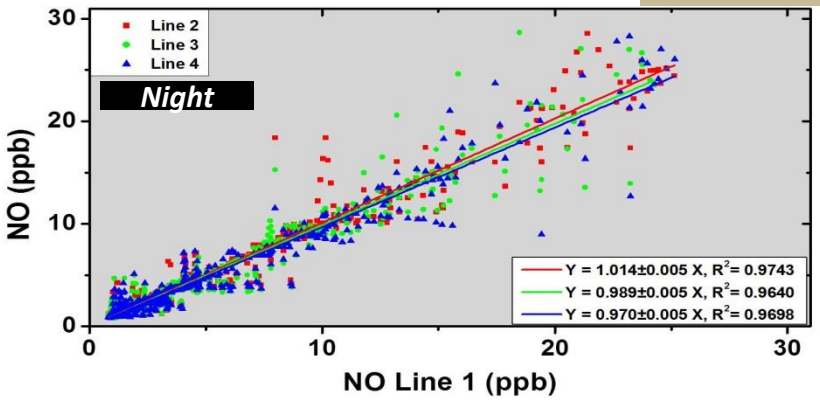
wind

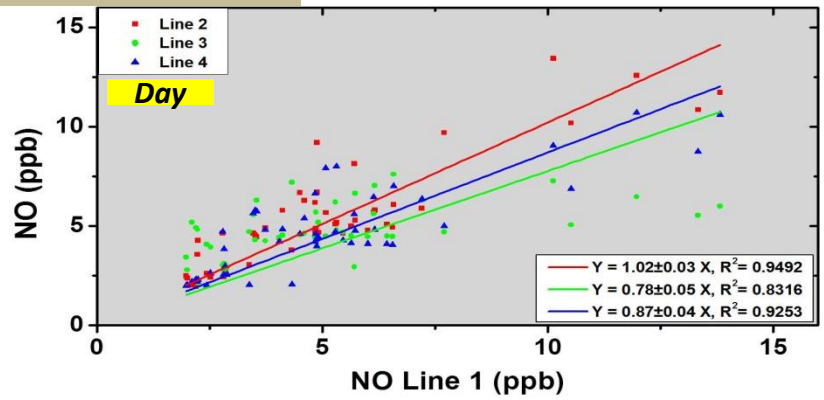
1 2 3 4

Nocturnal data (00:00 to 04:00 UTC) ; Diurnal data (Rad >400 Wm^{-2})

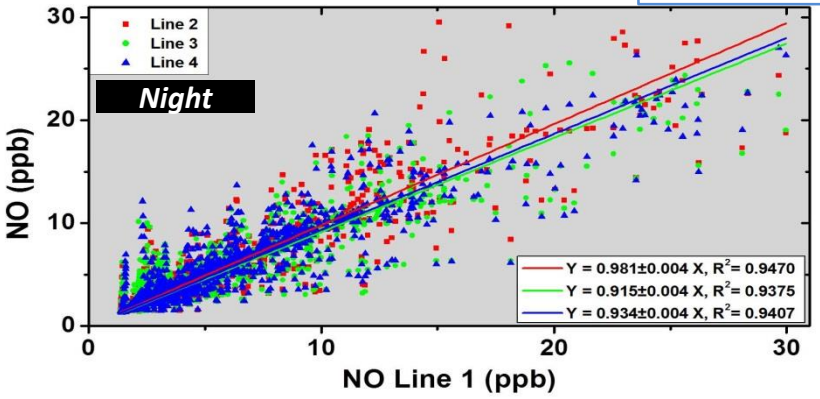
Applied filters: RH<65%, W speed <5 ms^{-1}, 45º< W Dir <135º, NO<20ppb (for diurnal periods due to traffic influence)

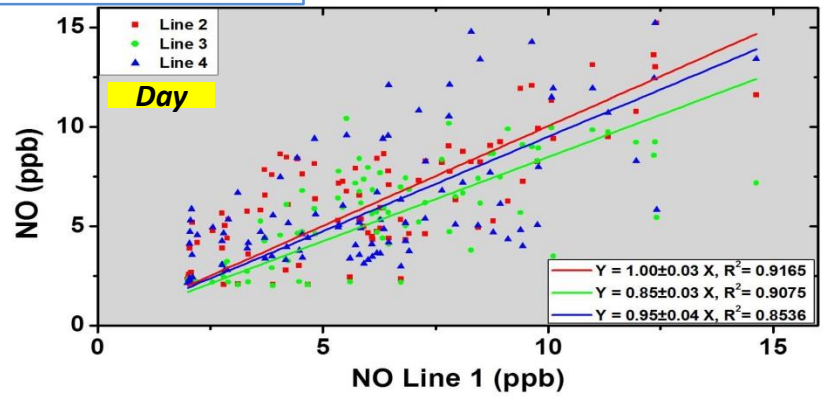
Before photocatalytic coating





After photocatalytic coating





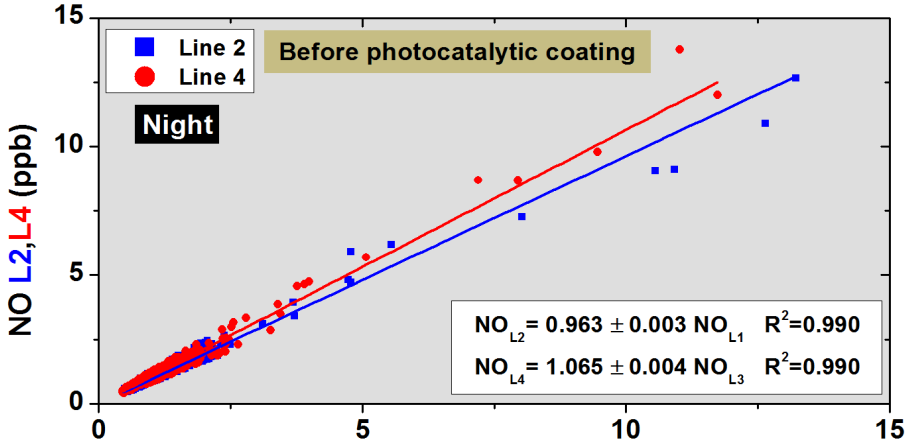
RESULTS (6/8)

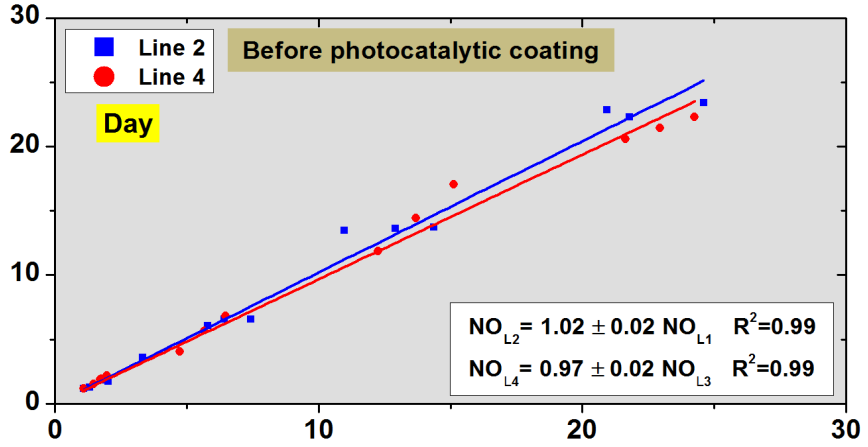
NO_x depolluting effects *(sidewalk scenario)* (CIEMAT)

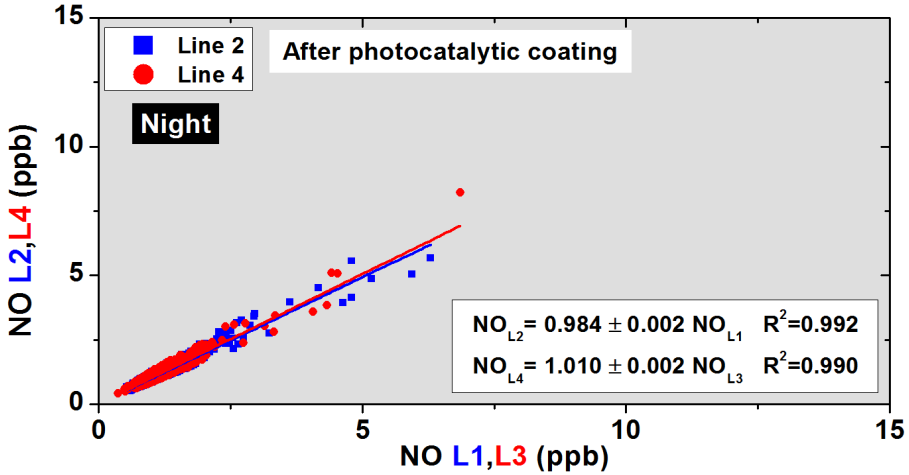
NO concentration at photoactive street (1-2 lines) vs reference street (3-4 lines)

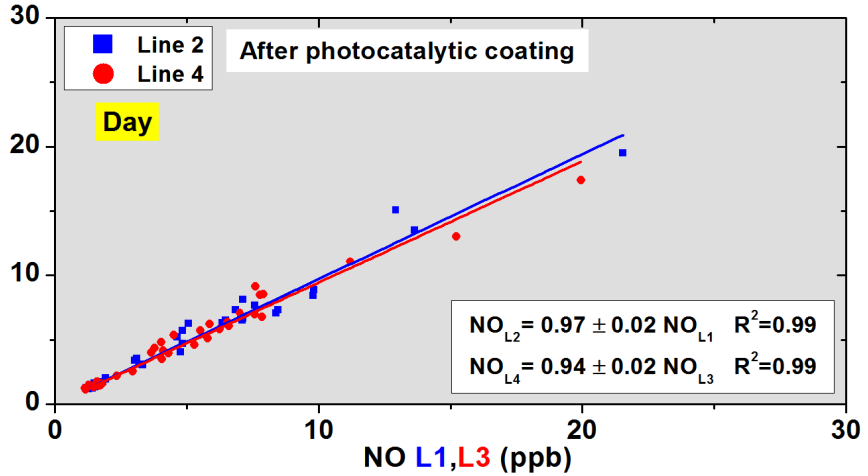
Nocturnal data (00:00 to 04:00 UTC) ; Diurnal data (inside the street Rad >400 Wm^{-2})

Applied filters: RH<65%, 0.5< W speed < 2.5 ms^{-1}, 160º< W Dir <200º, NO_{Line1}/NO_{Line2}, NO_{Line3}/NO_{Line4} *in the range of ±20 %*



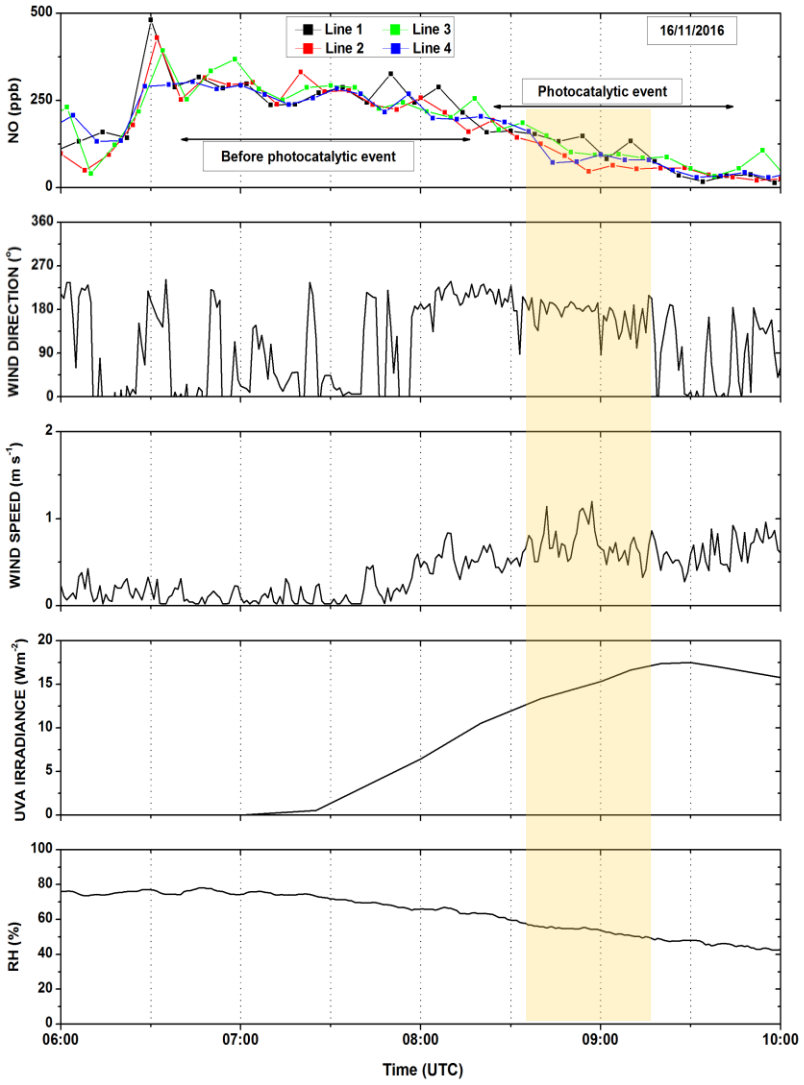






RESULTS (7/8)

NO_x depolluting effects *(facade scenario)* (CIEMAT)



Sampling lines	NO (ppb) Before photocatalytic event	NO (ppb) During photocatalytic event
1	266±22	108±46
2	260±37	86±44
3	271±35	110±42
4	255±30	94±44

Ratio NO	Before photocatalytic event	During photocatalytic event
Line 2 / Line 1	0.98	0.79
Line 4 / Line 3	0.94	0.85
Line 1 / Line 3	0.98	0.99
Line 2 / Line 4	1.02	0.91

***NO* concentration gradients produced by the photocatalytic facade**

RESULTS (8/8)

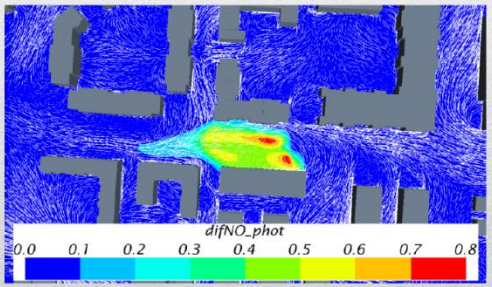
Modeling of NO_x depolluting effects

Paseo de la Chopera simulation

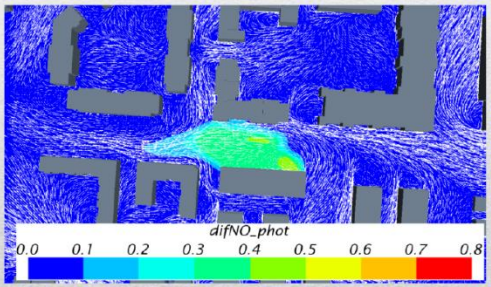
Deposition velocity applied = $5 \cdot 10^{-3}$ m s^{-1}

- Spatial distribution at t= 60 min → $difNO = NO - NO_{dep}$

h=1m



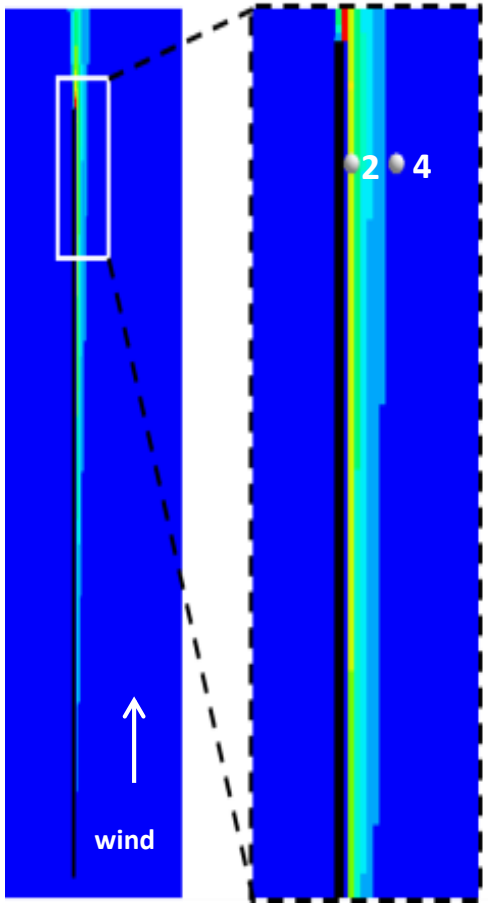
h=3m



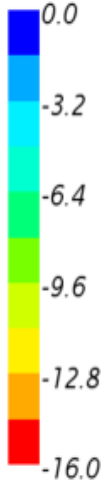
- The photocatalytic effect is negligible and it is only observed over the pavement.

Photocatalytic facade simulation

Deposition velocity applied = $3.5 \cdot 10^{-3}$ m s^{-1}

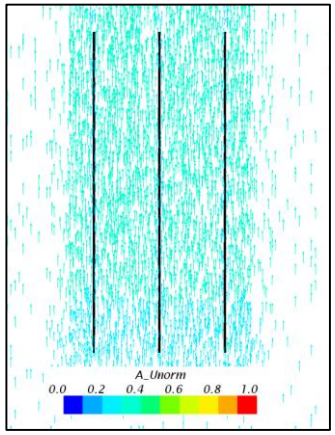


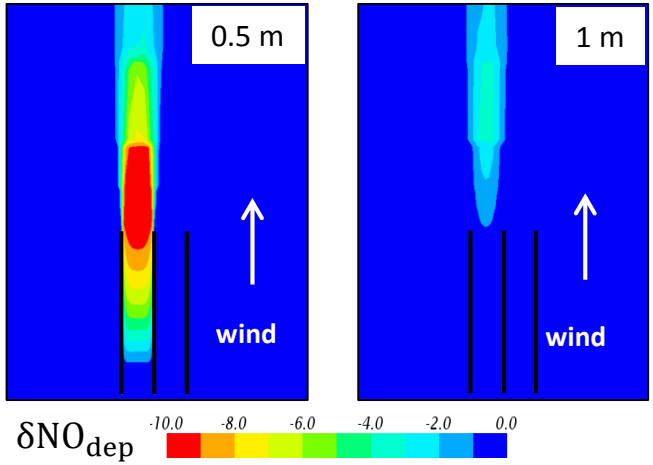
δNO_{dep}



Double street canyon simulation

Deposition velocity applied = $10.1 \cdot 10^{-3}$ m s^{-1}





CONCLUSIONS (1/2)

- *The photocatalytic products may modify some mechanical/surface properties of bituminous and sidewalk pavements (drainage and sliding resistance). Tests should be done to know the real situation in every case.*

- *Great variability among the air purification efficiencies (ISO 22197 tests) of the different commercial photocatalytic products based on TiO_2. Some of the products labeled as "photocatalytic" work badly (laboratory assays).*

- *The performance of a photocatalytic product on air purification depends on several factors: the photocatalytic product itself, the implementation procedure, the substrate, ambient conditions, wear, fouling, conservation, etc.). The durability is a pending issue.*

- *NO_x dry deposition rates (1-10 10^{-3} m/s) on photocatalytic surfaces have been obtained experimentally (outdoor photocatalytic platform) and estimated (ISO laboratory test) with good agreement. The low uptake coefficients obtained imply that the macroscopic effect (NO_x sink) produced by these photoactive surfaces is weak in open air (very high ratio Air volume/Photoactive surface).*

- *Great difficulty in urban scenarios to establish the possible cause-effect relationship between any observed ambient NO_x reduction and the presence of photocatalytic surfaces. In road bituminous pavement and sidewalk scenarios, the NO_x removal effect of photocatalytic materials has not been proven experimentally but in the case of facade scenario this effect has been documented very close the wall surface.*

CONCLUSIONS (2/2)

- *The modeling results of the three urban scenarios studied in Alcobendas are in good agreement with the registered measurements. This prototype has been validated and is ready to simulate any real urban scenario to estimate the maximum potential NO_x reduction derived from a hypothetical photocatalytic surface.*

- *Before implementing any photocatalytic material at real scale it should be assayed in laboratory on the real surface/substrate where it will be applied on to characterize its performance in that conditions.*

- *Physico-chemical characteristics of heterogeneous photocatalysis (low quantum yield in solar energy absorption by TiO_2, heterogeneus molecular process, high dependence on ambient conditions) explains the weak macroscopic effects observed in open urban air. As a consequence, a low NO_x concentration reduction is only produced very close to the photoactive surfaces with poor global incidence on ambient air.*

- *In order to get a real effectiveness of urban air pollution abatement measures based on the use of photochemical building materials, is strongly recommended to continue research to achieve a general improvement of their performance as well as to explore new engineering designs and applications.*

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Thank you for your attention!