AN OVERVIEW OF THE EUROPEAN PROJECT PICADA ON FACADE COATINGS (CEMENTITIOUS MATERIALS AND PAINTS) CONTAINING PHOTOCATALYTIC TiO_2

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European program on photocatalytic paints and cement-based materials (3.4 M€; 2002-2005)

Photocatalytic Innovative Coverings Applications for Depollution Assessment

picada-project.com

Developing and optimizing de-soiling and air-depolluting building coatings

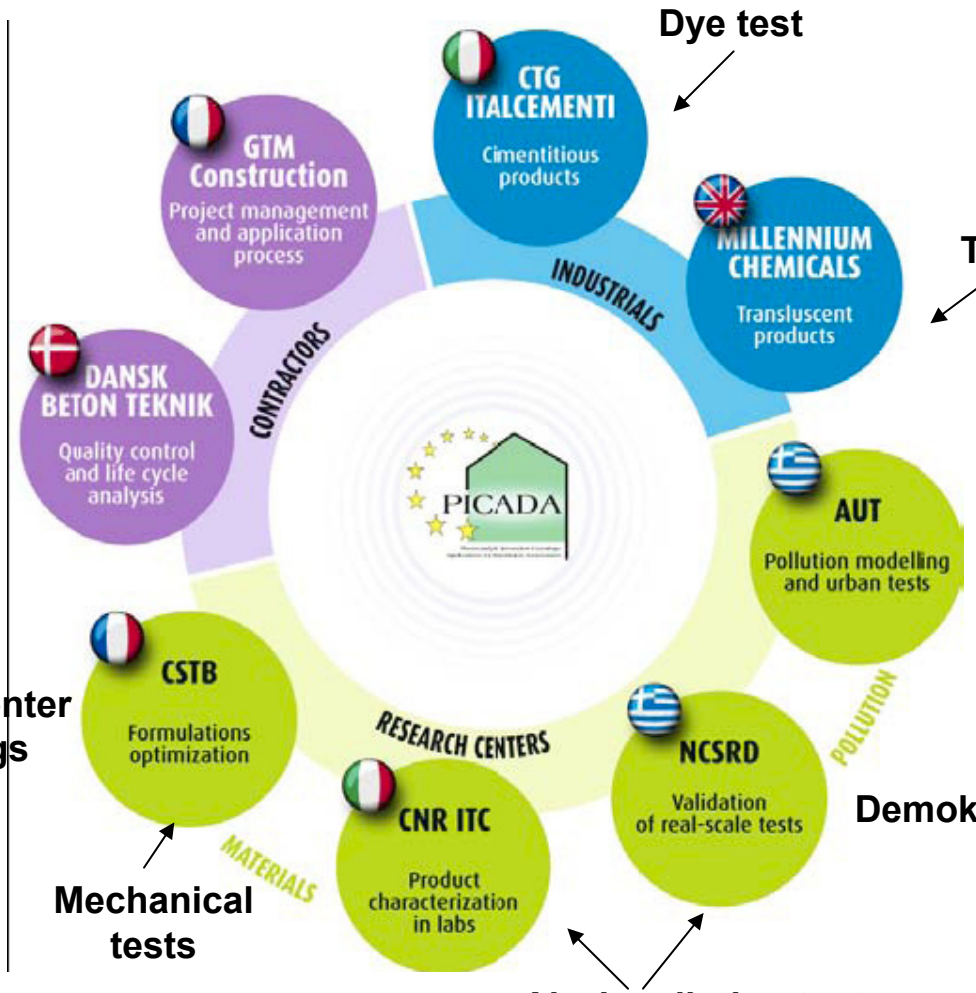
For scientific expertise, the Consortium has appealed to :

N. Allen (Manchester Metropolitan University, UK) for polymeric materials

P. Pichat (CNRS/ECL, France) for photocatalysis

A well-balanced partnership between industrial and public research centers

5 partners dealing with <u>building</u> materials



Dye test

TiO_2 production

University of Thessanoliki, modeling

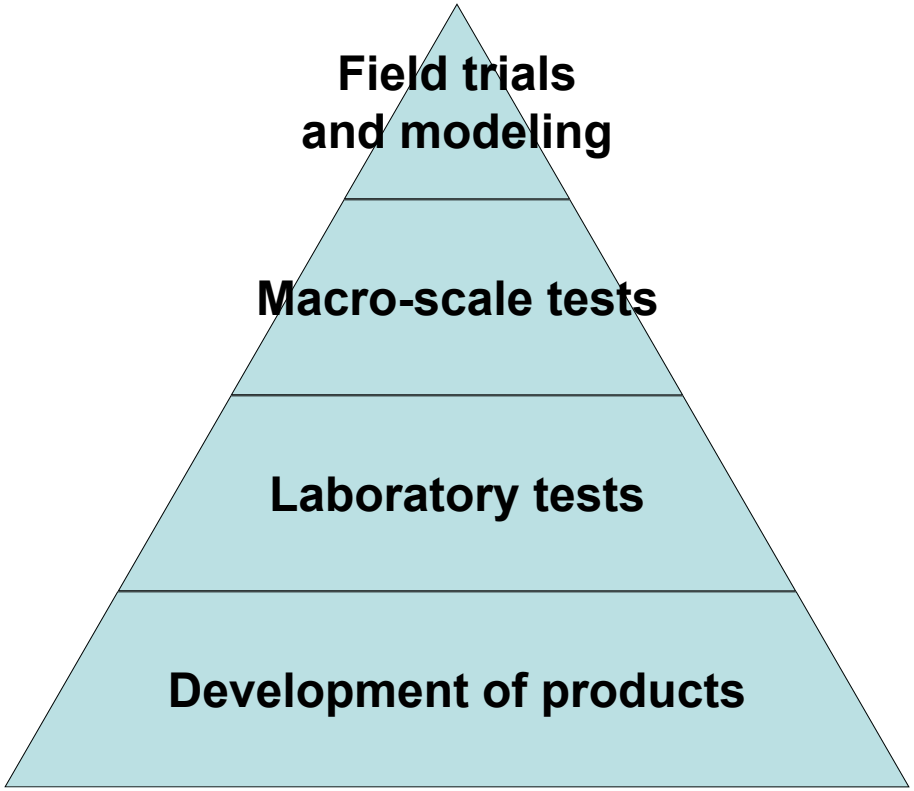
Research Center on buidings

Demokritos

Mechanical tests

Air-depollution tests

Diagram of the tasks



Types of cementitious materials

TiO_2 is added into:

- **Mortar (gray cement + sand)**
- **10 mm-coating (white cement, lime, mineral fillings, additives)**
- **0.1-1 mm-mineral paint (white cement, fillings, additives)**

Now commercialized

Colored by mineral pigments

Application (trowel or roller/brush/sprayer) after water addition on site

⇩

Customer guide

PICADA self-cleaning, translucent paints

Millennium Chemicals

Incorporation of TiO_2 nanoparticles in fluorinated or siliconized, water-based paints (e.g. Wacker siloxane polymer latex system)

Surface area, elementary crystallite size and porosity of Millennium TiO_2 samples

Brand name	Surface area ($m^2\ g^{-1}$)	Crystallite size (nm)	Average pore size (nm)
Millennium PC 10	10	65-75	24.1
Millennium PC 50	54	20-30	20.1
Millennium PC 105	85-95	15-25	15.3
Millennium PC 500	317	5-10	6.1

PC 500 prepared by thermohydrolysis of $TiOSO_4$
Other PC x obtained from PC 500 by calcination

Effect of the type of Millennium TiO_2 (3 wt%) upon the photocatalytic activity

Decolorization of deposited rhodamine B:
PC105 (90 $m^2 g^{-1}$) > PC50 (54 $m^2 g^{-1}$) > PC500 (317 $m^2 g^{-1}$) ≥ PC10 (10 $m^2 g^{-1}$)

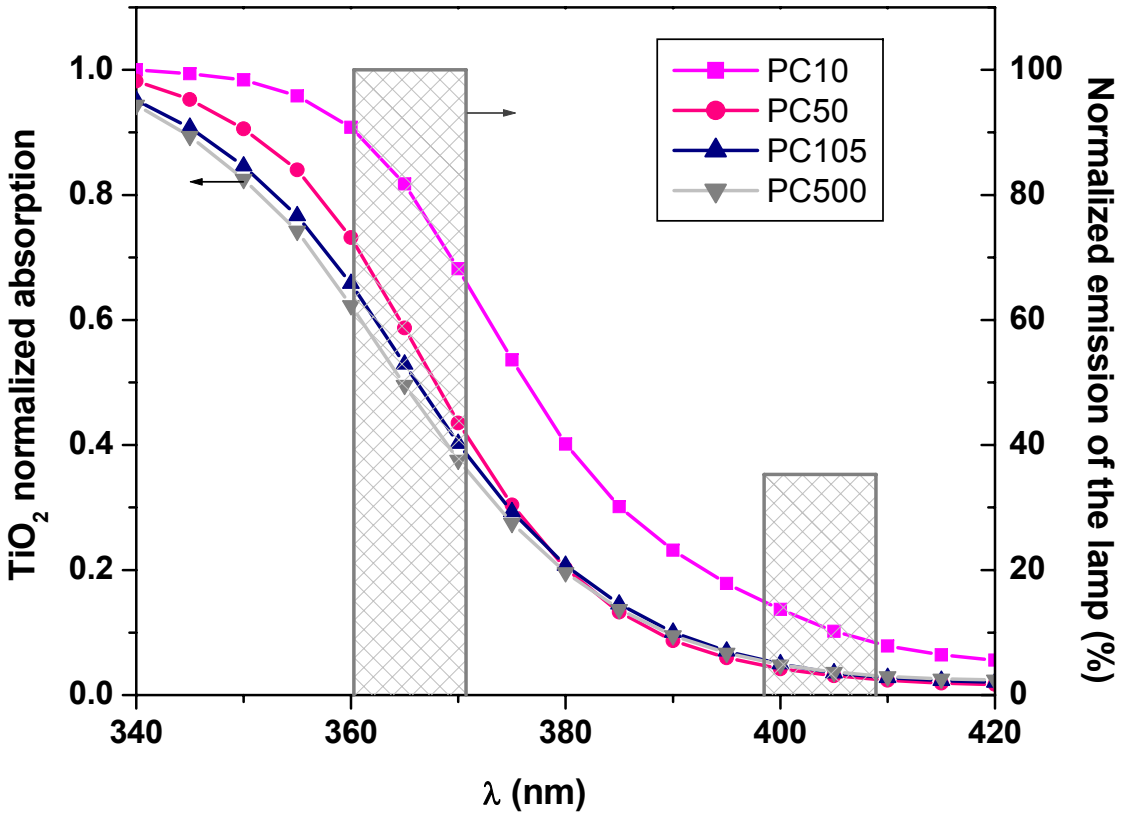
Formation of nitrate from NO_x:
PC500 (317 $m^2 g^{-1}$) > PC50 (54 $m^2 g^{-1}$) > PC105 (90 $m^2 g^{-1}$) > PC10 (10 $m^2 g^{-1}$)

Ranking does not follow the order of surface areas and is reactant-dependent

Other factors that can be involved:

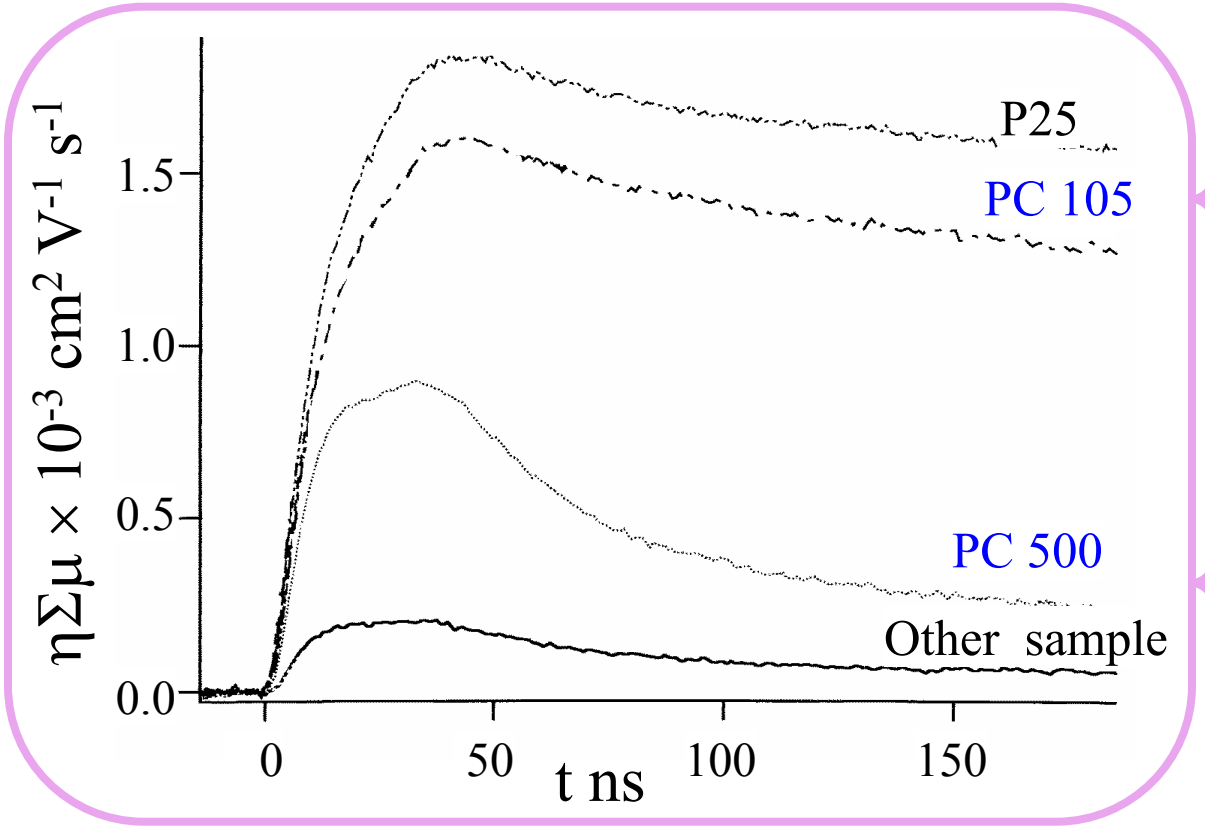
Absorption of light (spectrometry)
Recombination of photoproduced charges (microwave conductivity)
Lability of surface O (isotopic exchange)
Embedding in the cementitious matrix (n.d.)

Distinct absorption by the four TiO_2 samples cannot be the cause of the activity order observed



The absorption was significantly higher only for PC10, the less active sample!

The higher the sintering T, the lower the recombination rate of photoproduced charges as shown by TRMC



higher calc. T

slower decay

higher conductivity

lower calc. T

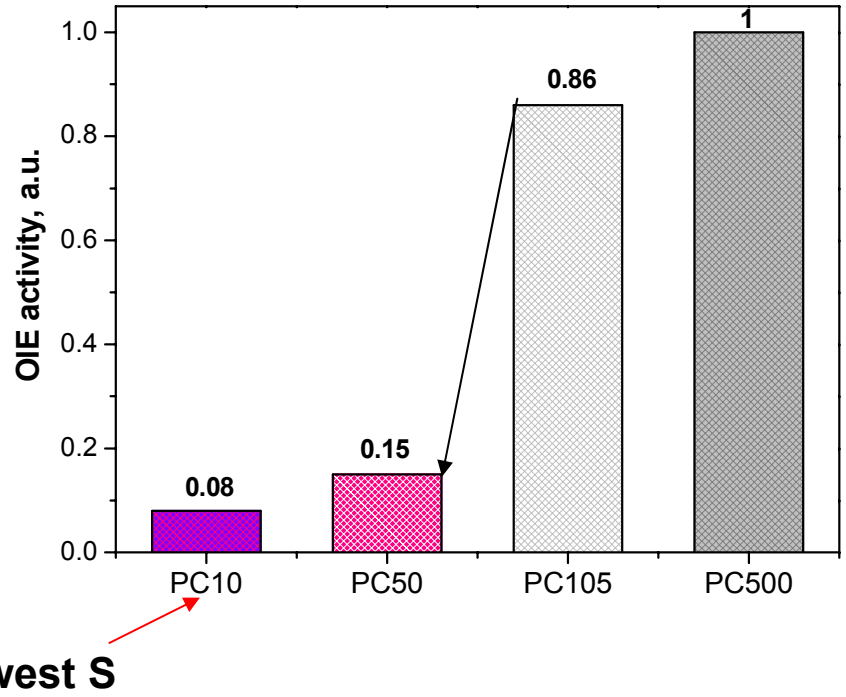
faster decay

lower conductivity

As expected, increased sintering temperature improves crystallinity and thus decreases the density of defects

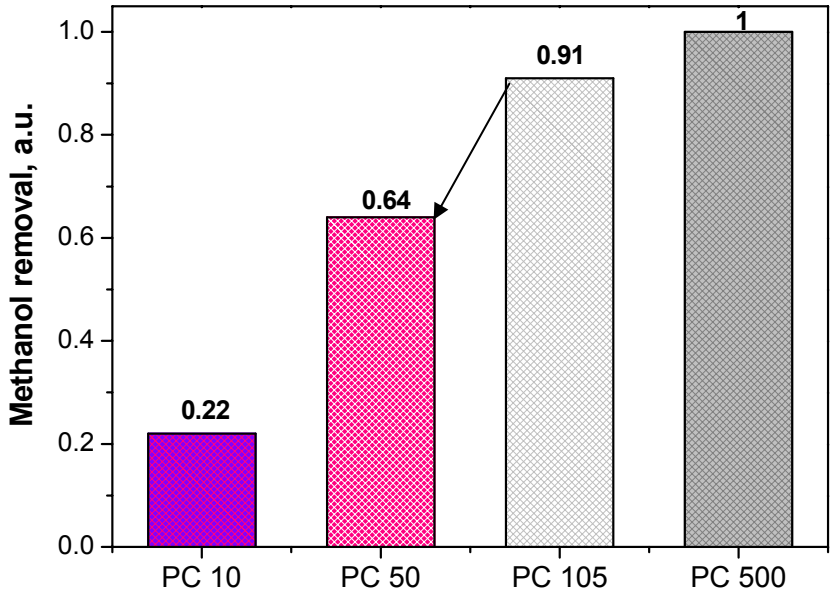
Comparison of oxygen isotope exchange and CH_3OH removal for a series of TiO_2 samples (Millennium Chemicals)

Oxygen isotopic exchange



lowest S

Methanol removal



Different patterns are observed for the two reactions

Increasing the calcination temperature decreases the surface oxygen lability

Mechanistic differences due to the pollutants chemical structures makes the photocatalytic efficacy pollutant-dependent

- **Benzene derivatives** can react by ring hydroxylation and the reaction rates indeed follow the ring electron density
- **Pyridine** can also react by hole-induced formation of a radical cation which can subsequently react with superoxide
- **Organic acids** can be decarboxylated

In practice

- **One test pollutant does not suffice to quantitatively compare photocatalytic activities**

- **There is not a universal TiO_2 (and furthermore a TiO_2-based material) that exhibits the best properties under all conditions**

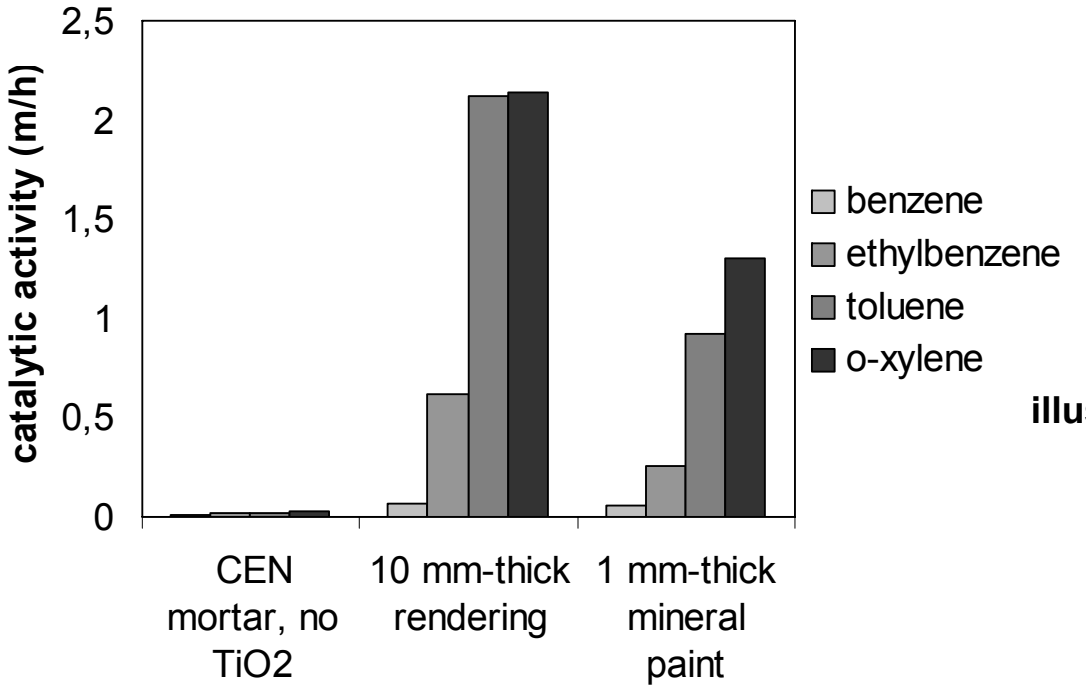
Effect of the wt% of TiO_2 Millennium PC105

- **Removal of benzene hydrocarbons (0.5 wt% < [TiO_2] < 5.5 wt%):**
  rate increase less pronounced in passing from 3 to 5.5 wt%

- **Formation of nitrate from NO_2 and decolorization of deposited rhodamine B ([TiO_2] = 3 or 10 wt%):**
  rate increase by 20-23 % for the higher content

Given the high cost of TiO_2 relative to that of the cement-based matrix, a content of 3% was selected as a compromise

Effect of the cement-containing matrix (3 wt% of TiO_2 PC105)



As expected, the relative activities illustrate a preferential attack on the side chain

Marked effect of the matrix on the removal rate of benzene derivatives
However, no significant difference for NO removal

Can photocatalytic building/paving materials help purify outdoor air ?

- **Photocatalytic transformations are limited to adsorbed pollutants at a given time, i.e. an extremely small fraction in open spaces**

- **Consequently, the photocatalytic effect is likely to be significant only in partially confined spaces such as canyon streets**

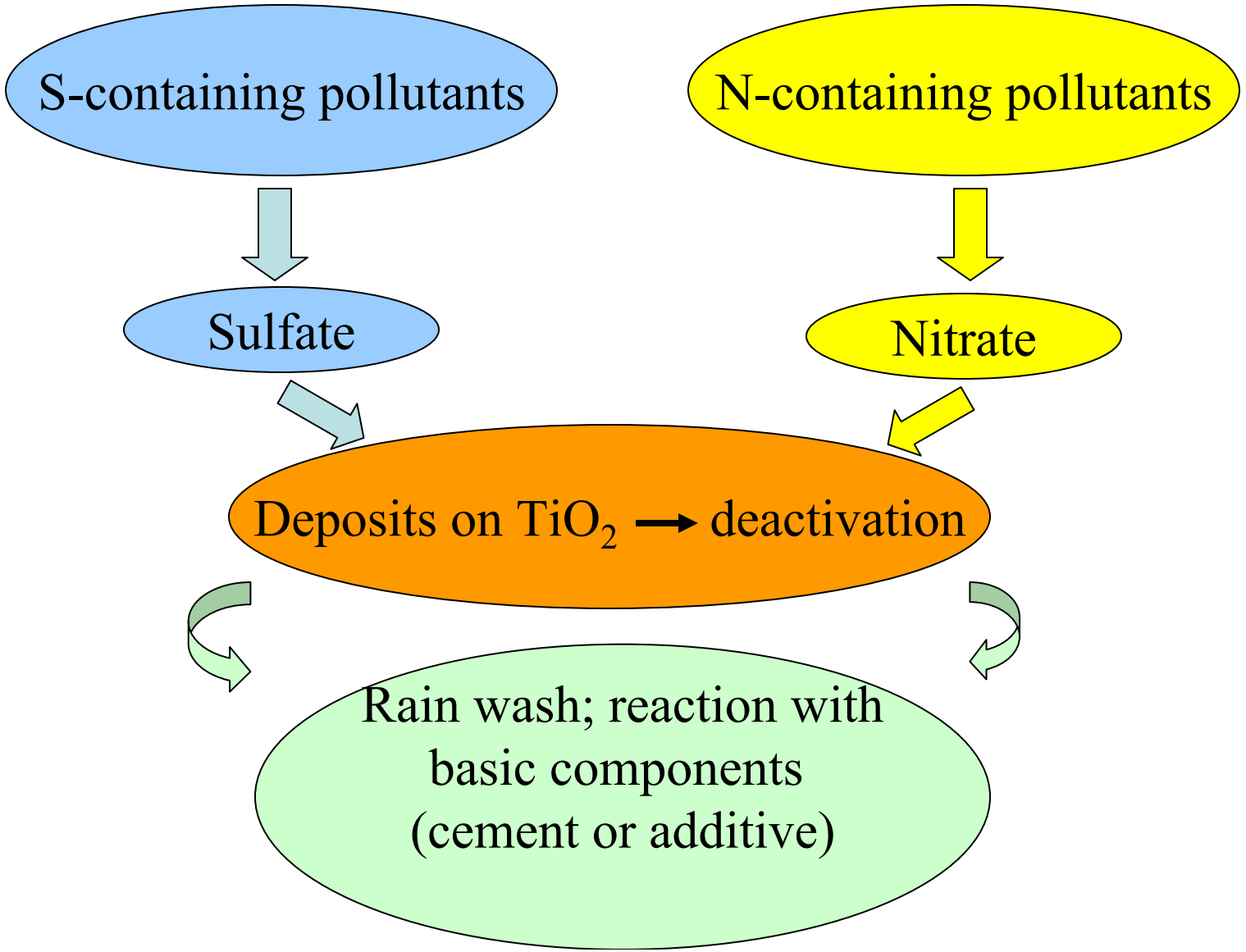
- **Pollutants adsorption can be favored by highly porous coatings, which is detrimental to self-cleaning efficacy and coating adhesion, and affects the visual aspect**

Photocatalytic transformations of atmospheric pollutants

- **CO is oxidized to CO_2**
- **NO is oxidized to NO_2 and then to NO_3^- ions (effect on [O3]?)**
- **SO_2 is oxidized to SO_3 and then to SO_4^{2-} ions**
- **Consequence: acidity produced by NO_x and SO_x**
- **Organics are gradually oxidized/eventually mineralized**
- **Consequence of organics oxidation: concentrations of low-molar mass carbonyls can be increased**

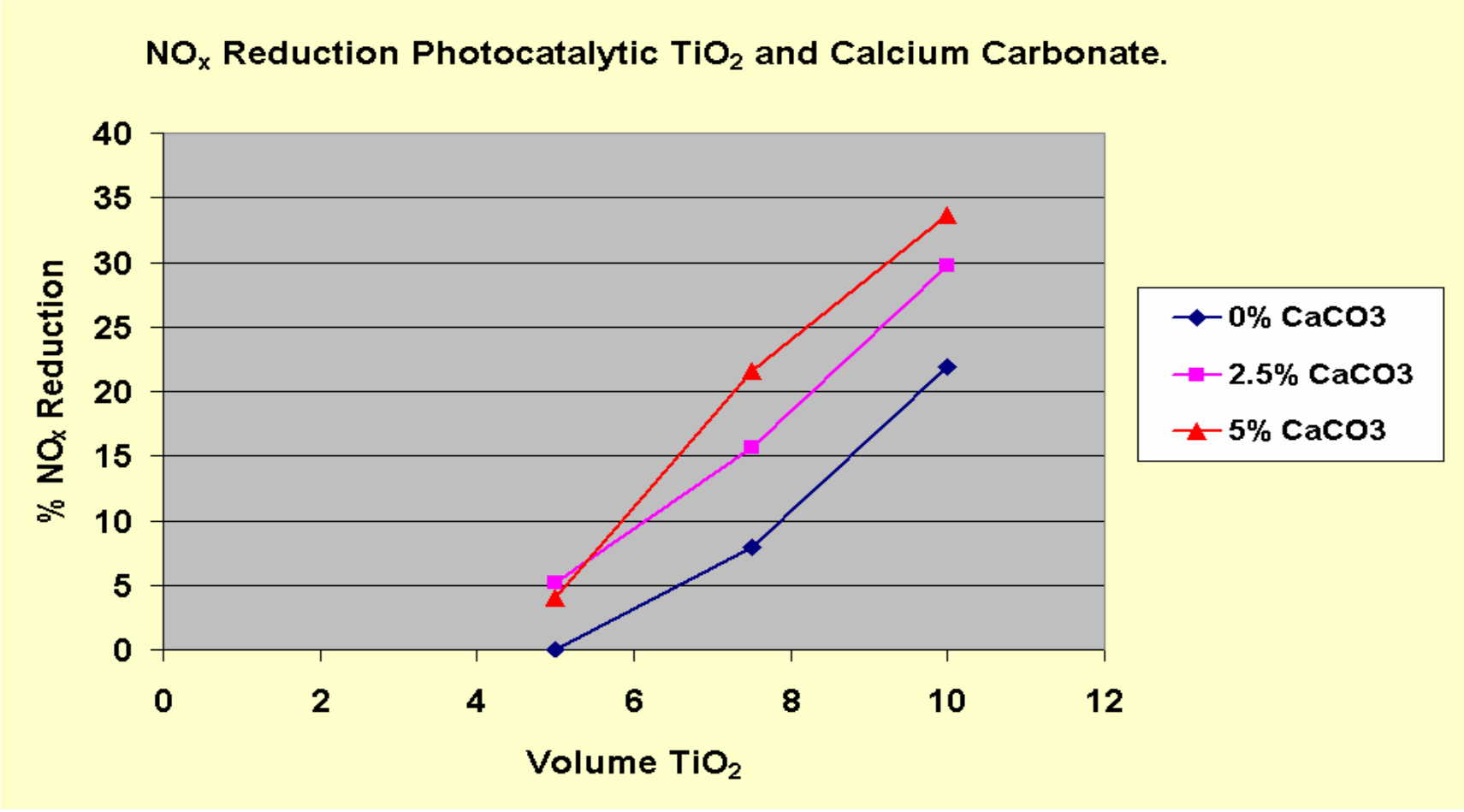
Problem of gaseous pollutants containing S and N atoms

For ambient air : SO_x and NO_x principally



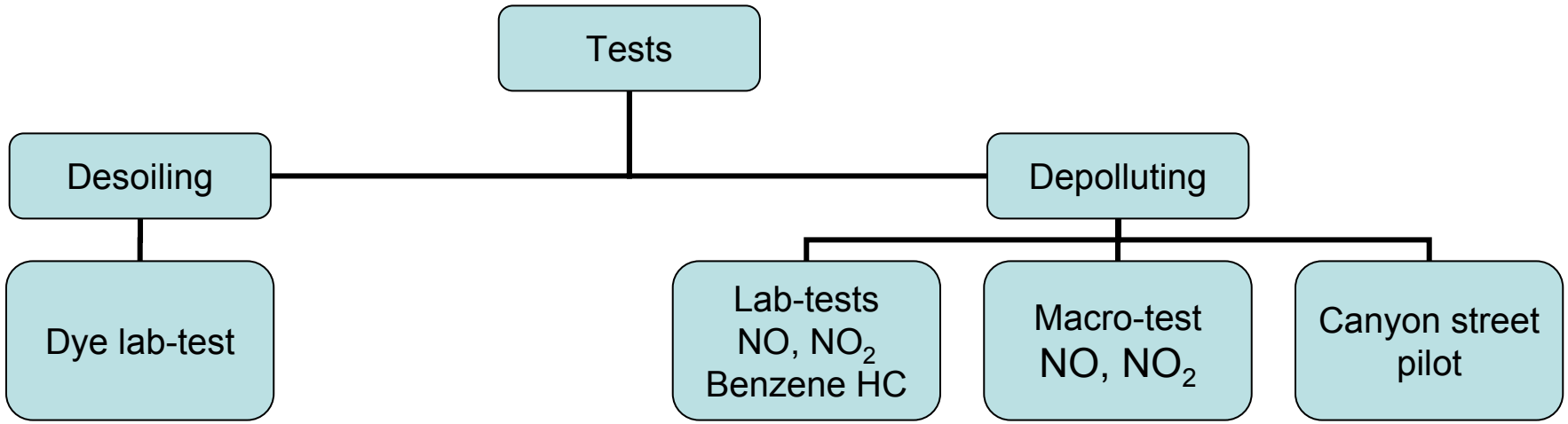
Addition of $CaCO_3$ increases the removal of NO because of porosity change

PICADA translucent paint (Millennium Chemicals)



However, $CaCO_3$ can have a detrimental effect on the translucency

Testing is an important and difficult task!

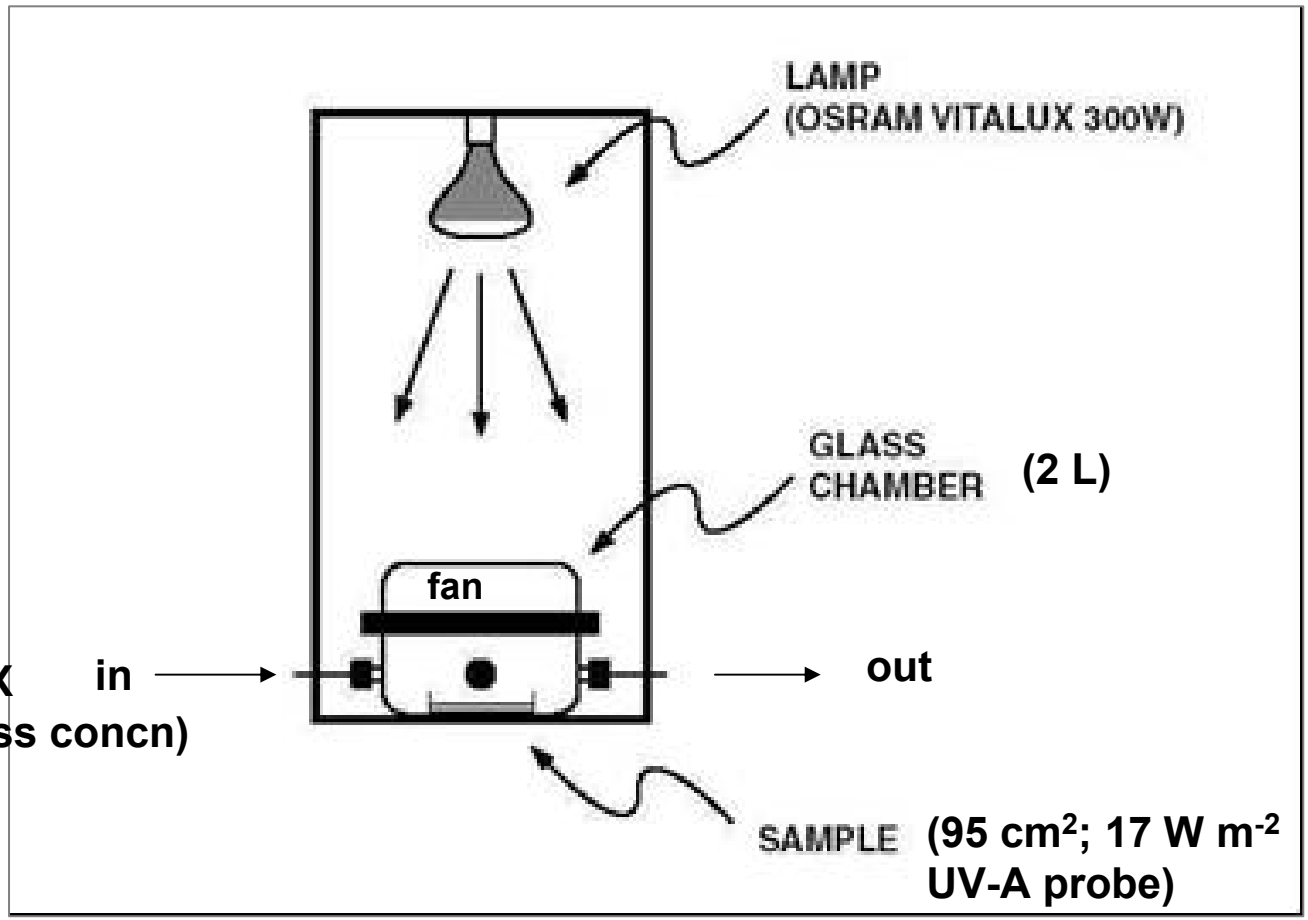


Photocatalytic reactors must meet severe conditions

- Made of poorly adsorbing materials
- Airtight: must operate in the concn. range < 300 ppbv
- Homogeneous irradiance on the photocatalytic material
- High air volume may be preferable at some stage

Photocatalytic reactor used for the removal of benzene, toluene, ethylbenzene and *o*-xylene

Institute of Construction Technology ***Alberto.Strini@itc.cnr.it***



50-500 ng/L BTEX
(nearly equal mass concn)
in O_2/N_2 50% RH
100 mL/min

Removal rates from 0.15 (benzene) to 1.3 (*o*-xylene) µmol m^{-2} h^{-1} for samples containing 1 wt% TiO_2

Comments about the BTEX test

- **Interests:**

Representative conditions, viz.
ppbv concentrations;
irradiance

Continuous flow reactor

Accuracy: *ca. 5%* except for C_6H_6

- **Drawbacks:**

1 week-long experiments

O_2-N_2 mixture: absence of competing CO (ppmv conc.) and more powerful oxidants than O_2, viz. interrelated O_3 and NO_2

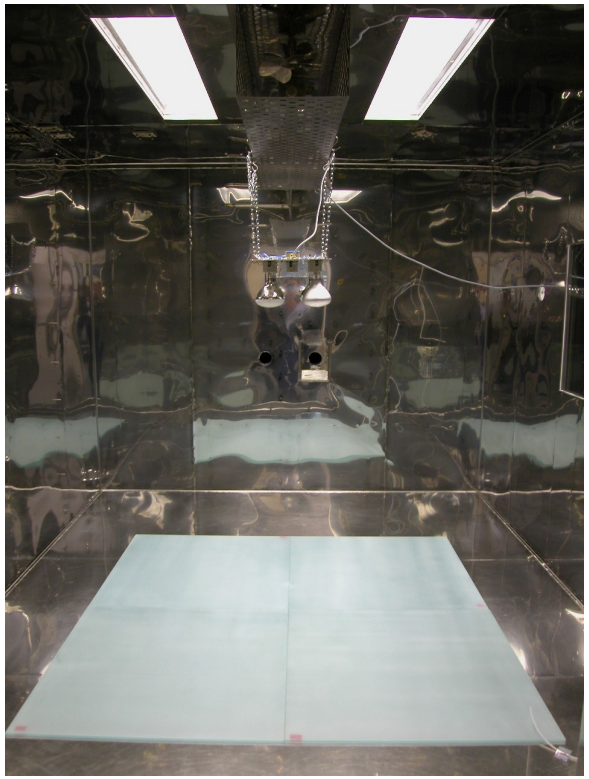
% of each BTEX not representative

Small volume (2 L)

0.45 and 30 m^3-chambers for NO or NO_2 removal

National Scientific Research Centre "Demokritos" bartzis@ipta.demokritos.gr

Glass walls



Stainless steel walls

0.45 m^3; 0.058 m^2, ie 0.13 m^2 of mater./m^3 of air
UV-A: 6.8 W m^{-2}

30 m^3; 4 m^2, ie 0.13 m^2 of mater./m^3 of air
UV-A: 4.8 (center)-2.1 (corners) W m^{-2}

250 ppbv of NO or NO_2; RH: 50%; mixing by fans (*ca.* 0.2 m/s airflow on material)

Comparing NO or NO_2 removal rates in both chambers

Photocatalytic rates obtained by substracting rates corresponding to non-photocatalytic conditions (controls)

	NO	NO_2
0.45 m^3-chamber	0.29 µg m^{-2} s^{-1} or 9.35 nmol m^{-2} s^{-1}	0.17 µg m^{-2} s^{-1} or 3.62 nmol m^{-2} s^{-1}
30 m^3-chamber	0.21 µg m^{-2} s^{-1} or 6.77 nmol m^{-2} s^{-1}	0.13 µg m^{-2} s^{-1} or 2.77 nmol m^{-2} s^{-1}

1 mm-thick cement-based paint

Removal rates higher for NO than for NO_2
Rate difference due to the chamber roughly accounted for by irradiance difference

⇓

No need of a "large" chamber for evaluating removal rates in natural conditions

Comments on the chambers used for NO or NO_2 removal

- **Interests:**

Representative conditions, viz. ppbv concentrations; irradiance

High volumes

- **Drawbacks:**

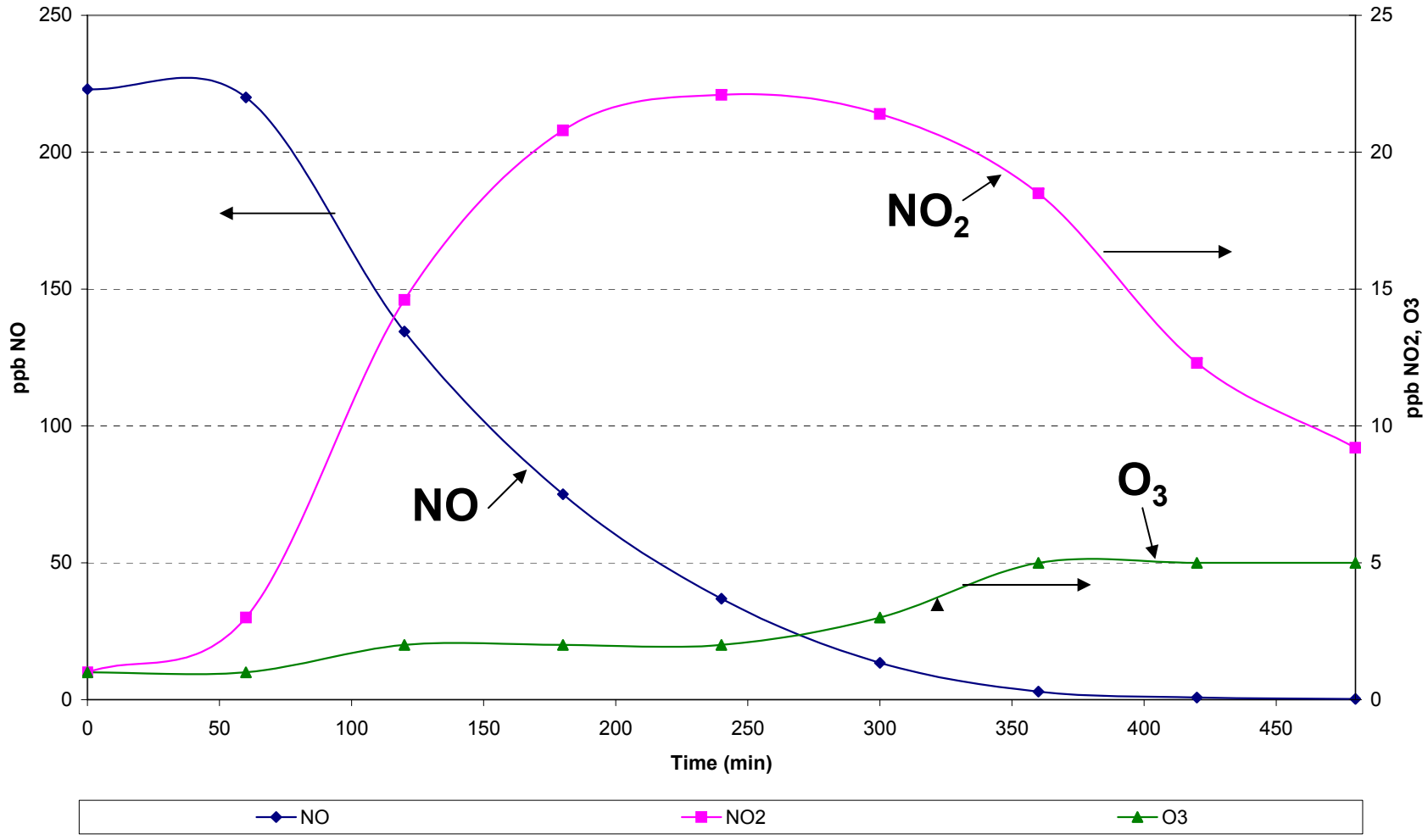
Long experiments (control experiments unavoidable)

O_2-N_2 mixture: absence of competing CO (ppmv conc.)

Non-homogeneous irradiation of the photocatalytic material in the 30 m^3-chamber

Static reactor

Variations in [NO_2] and [O_3] during NO removal



Formation of O_3 from NO_2

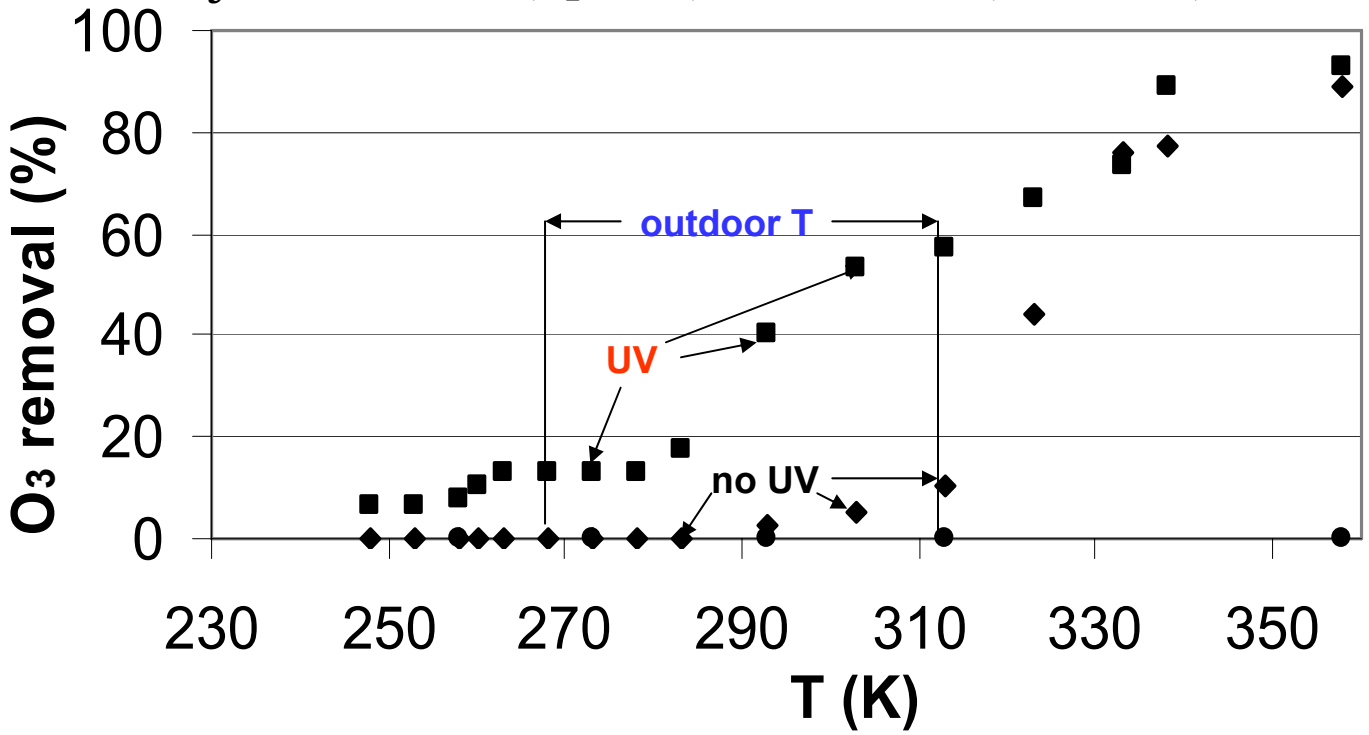
Relationship between NO, NO_2 and O_3:

$$NO_2 + h\nu \rightarrow O + NO \quad \lambda < 435 \text{ nm}$$
$$O + O_2 \rightarrow O_3$$
$$NO + O_3 \rightarrow NO_2 + O_2$$

$$[O_3] = k\,[NO_2]/[NO]$$

Potential effect of photocatalytic materials on [O_3]

Comparison of O_3 removal with (squares) and without (diamonds) UV irradiation



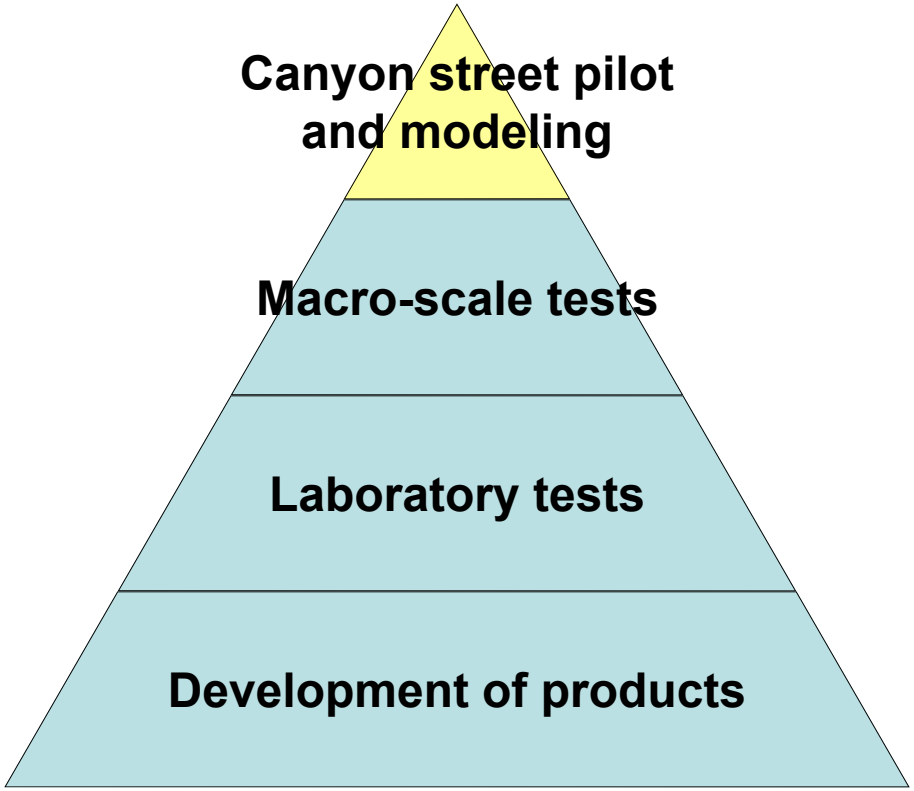
Catal. Today, 63 (2000) 363; TiO_2-coated fiberglass mesh

Photocatalysis markedly increases O_3 removal at ambient temperature
Modeling required to estimate the effect of photocatalytic materials on [O_3]

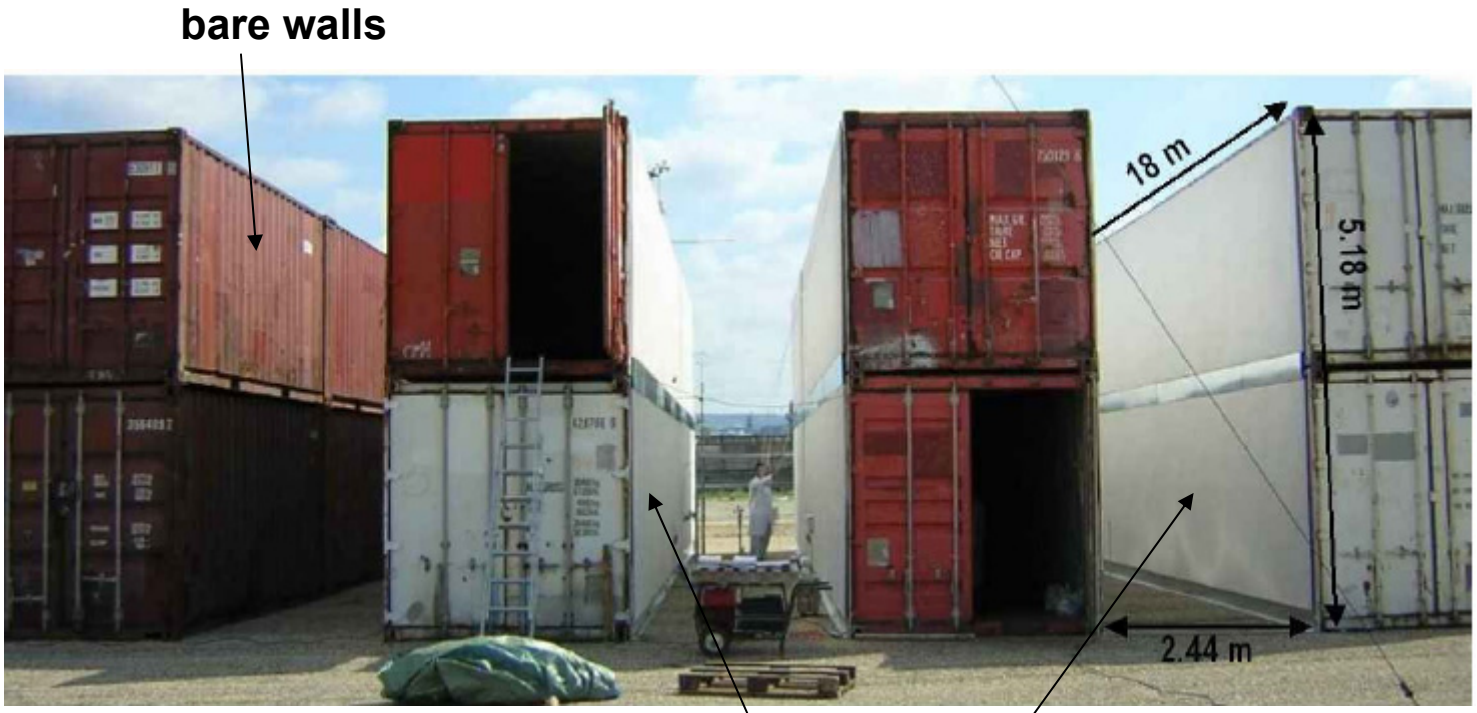
Additional test to distinguish photocatalysis from photochemistry of NO_2

- **Same type of reactor as for benzene hydrocarbons (however, static conditions)**
- **Measurements of nitrate recovered by dissolution in water after an irradiation time corresponding to 100% removal of NO_2 (400 ppbv) for the most active sample**
- **Complete conversion into nitrate can be achieved with TiO_2-containing materials**

Final task for assessing the air-depolluting potentialities of the photocatalytic cement-based coatings



Canyon street pilot *CTG aplassais@ctg.fr*

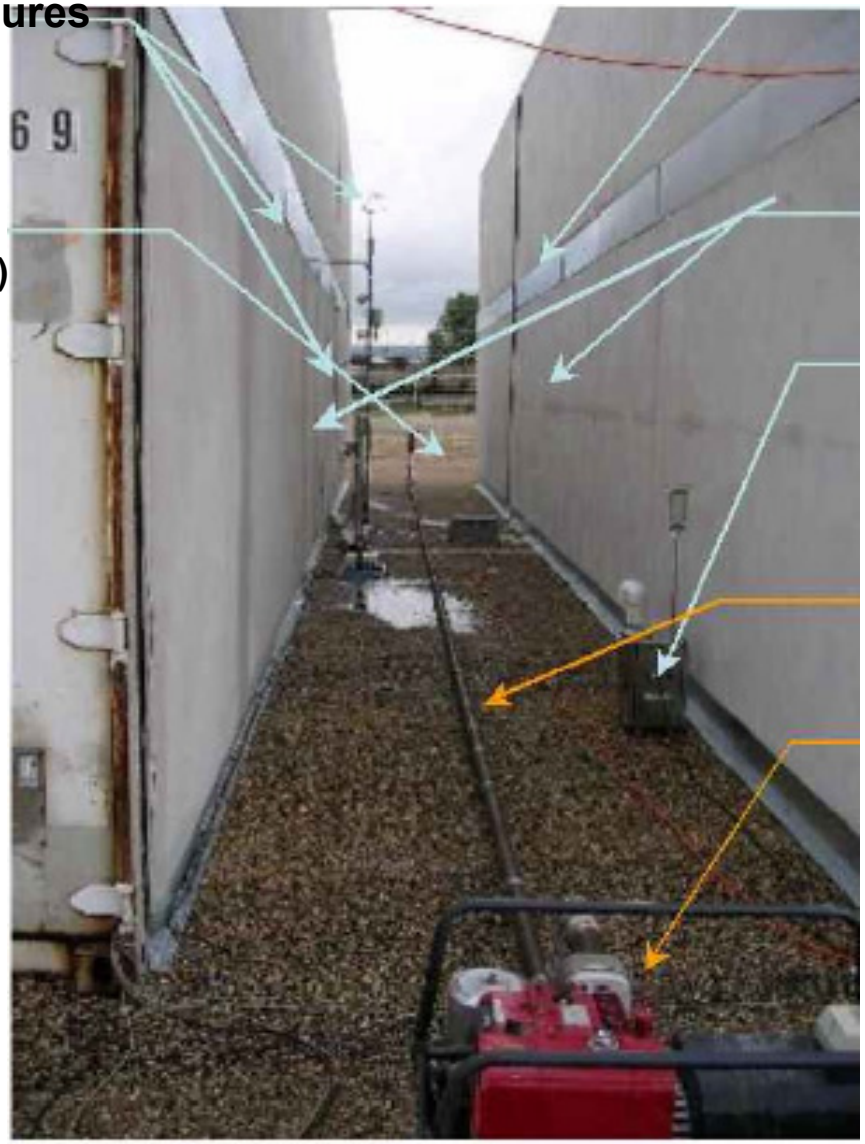


200 m^2-walls . Coating with or without TiO_2

Canyon street pilot. Pollution and measurements

Meteorological measures

Gas collectors
(in the street middle)



Gas collectors
(near the walls)

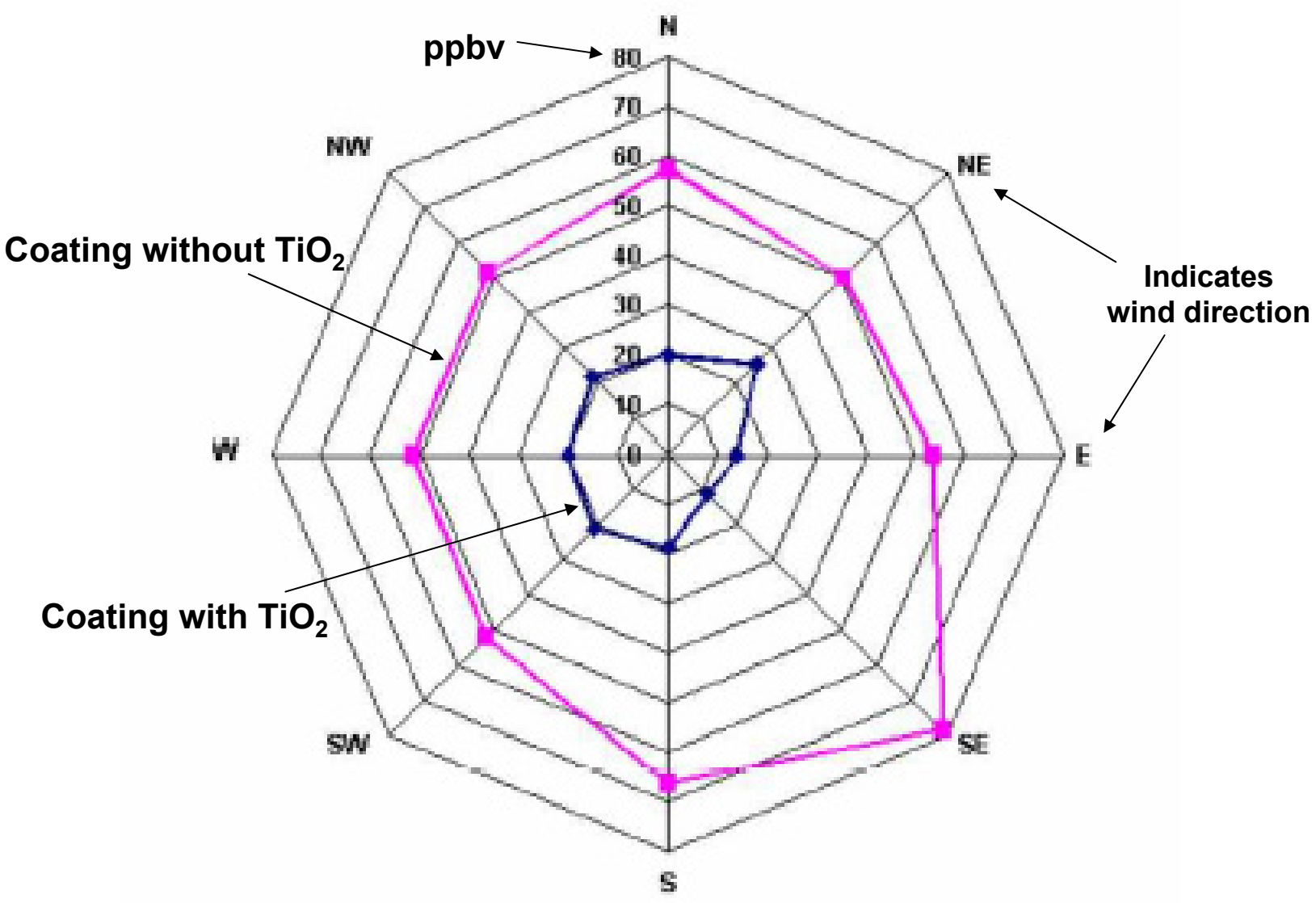
Perforated pipe

Engine exhaust

[NOx] background
was substracted

Canyon street pilot. [NO_x] vs wind direction (example)

Marked effect of the TiO_2-containing coating: 37 to 82% decrease in [NO_x]



Comments about the canyon street pilot measurements

- **Interests:**

Atmospheric air + appropriately simulated pollution

Dimensions reduced by a factor of only about 5 relative to a typical canyon street

Meteorological measurements

- **Present lacks:**

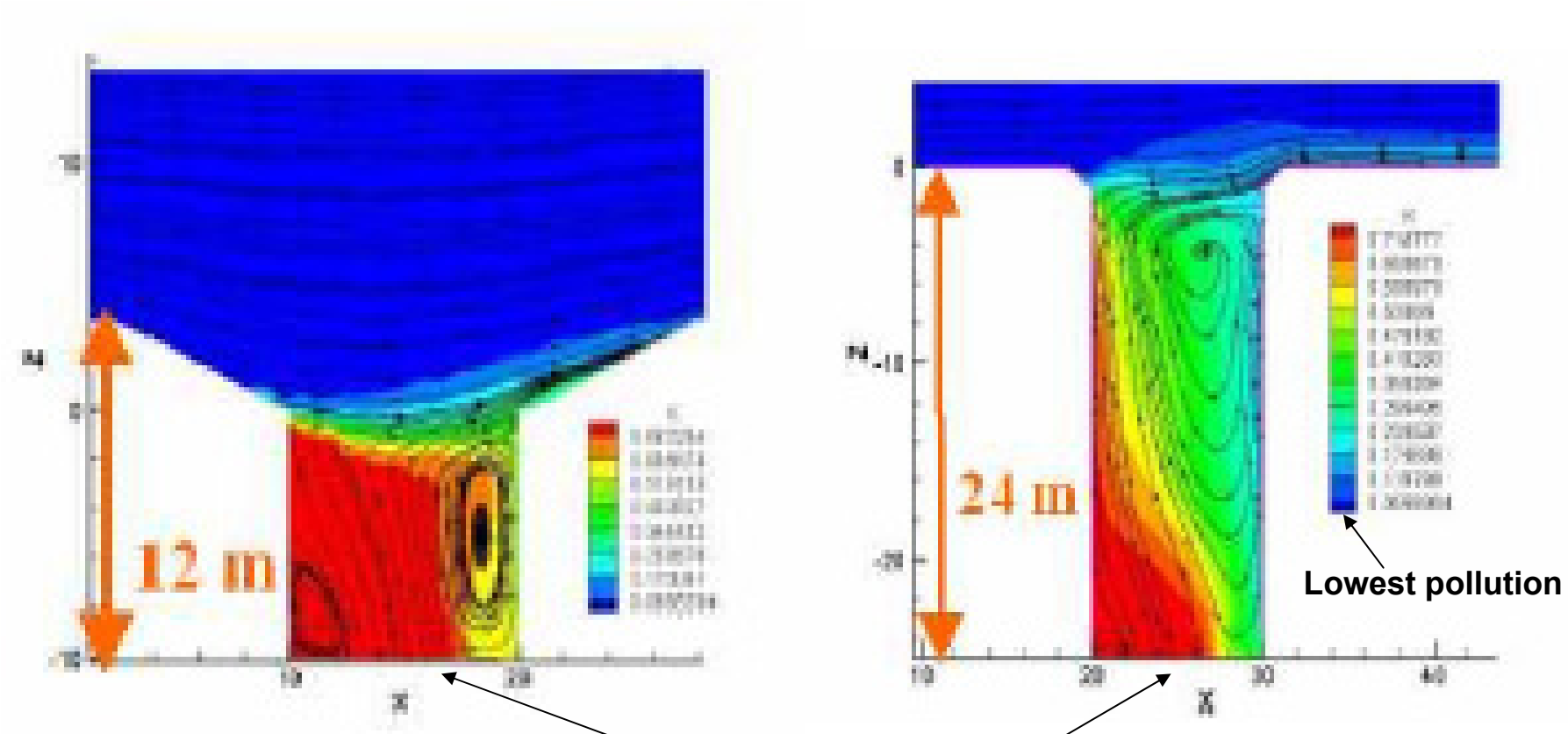
No measurements of concentrations of hydrocarbons and low molar-mass carbonyls

Parameters included in the modeling of air flow and pollutant concentration in a canyon street

Aristotle University of Thessaloniki *moussio@eng.auth.gr*

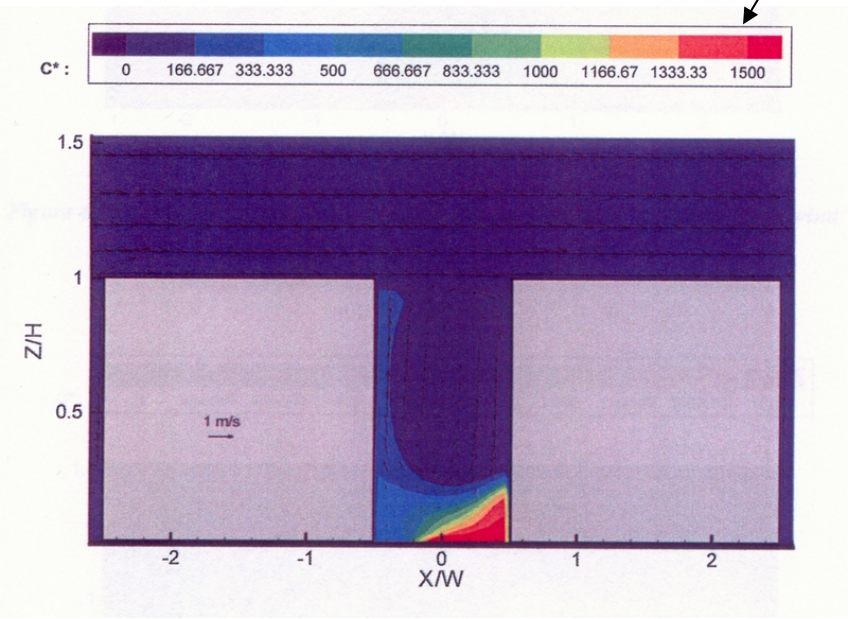
- **Canyon street geometry**
- **Wind speed**
- **Wind direction**
- **Turbulence due to traffic**
- **Heating of street sides and ground by solar irradiation**
- **NO/NO_2 ratio depending on photolysis of NO_2**
- **Photocatalytic removal of NO and NO_2**

Pollutants distribution using a microscale software (MIMO). Effect of building height and shape

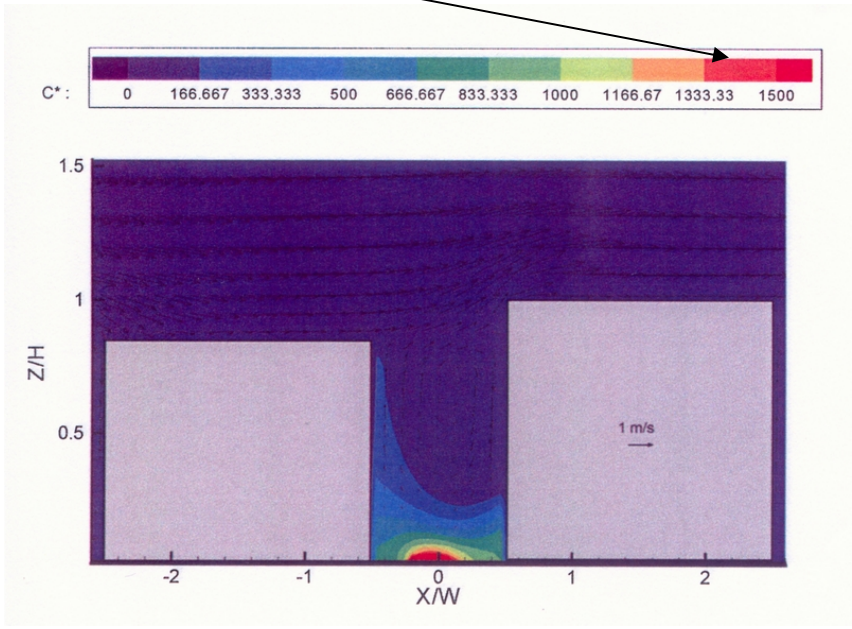


Pollutants distribution using a microscale software (MIMO). Effect of unequal building heights

Highest pollution



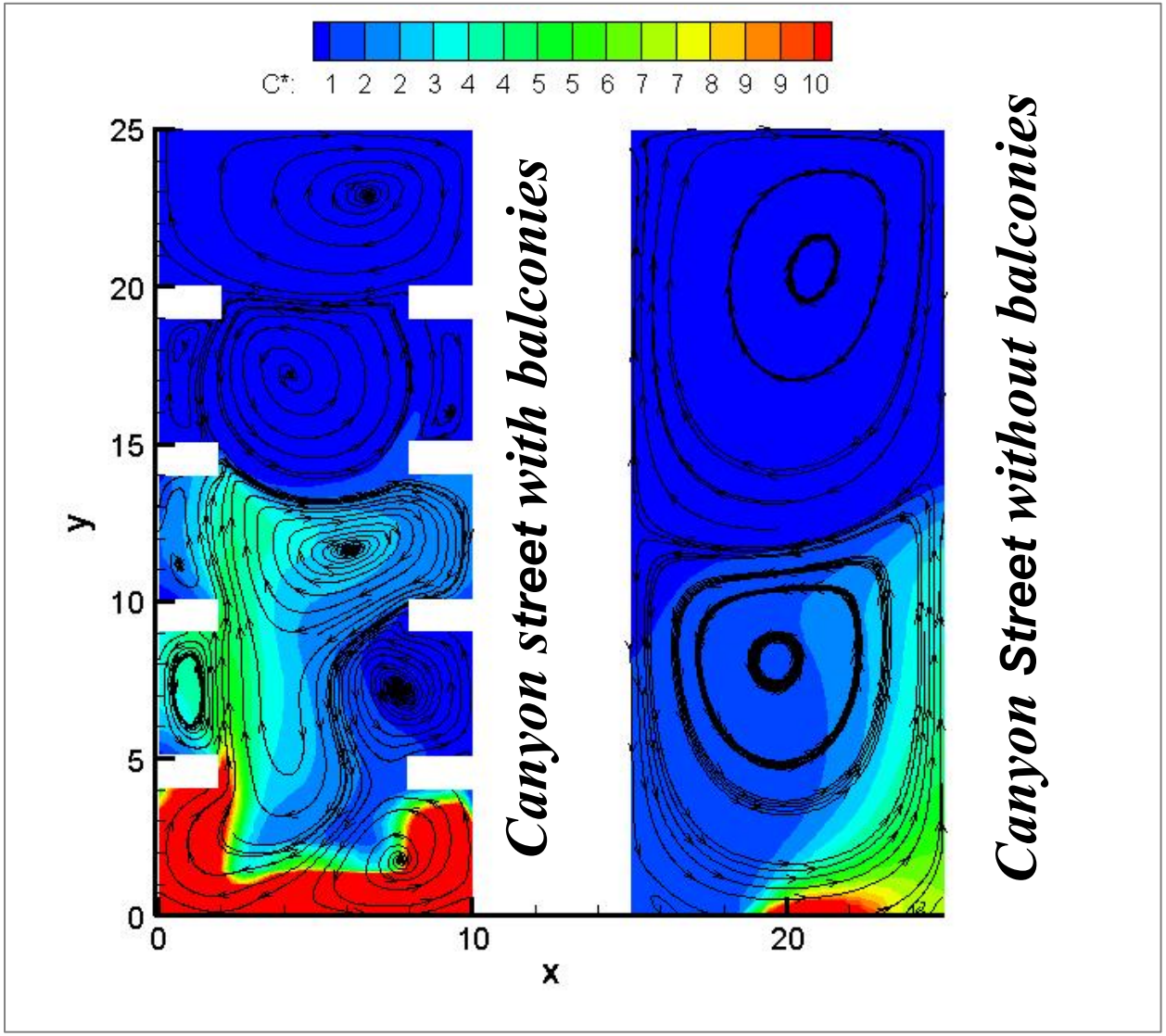
Equal building height



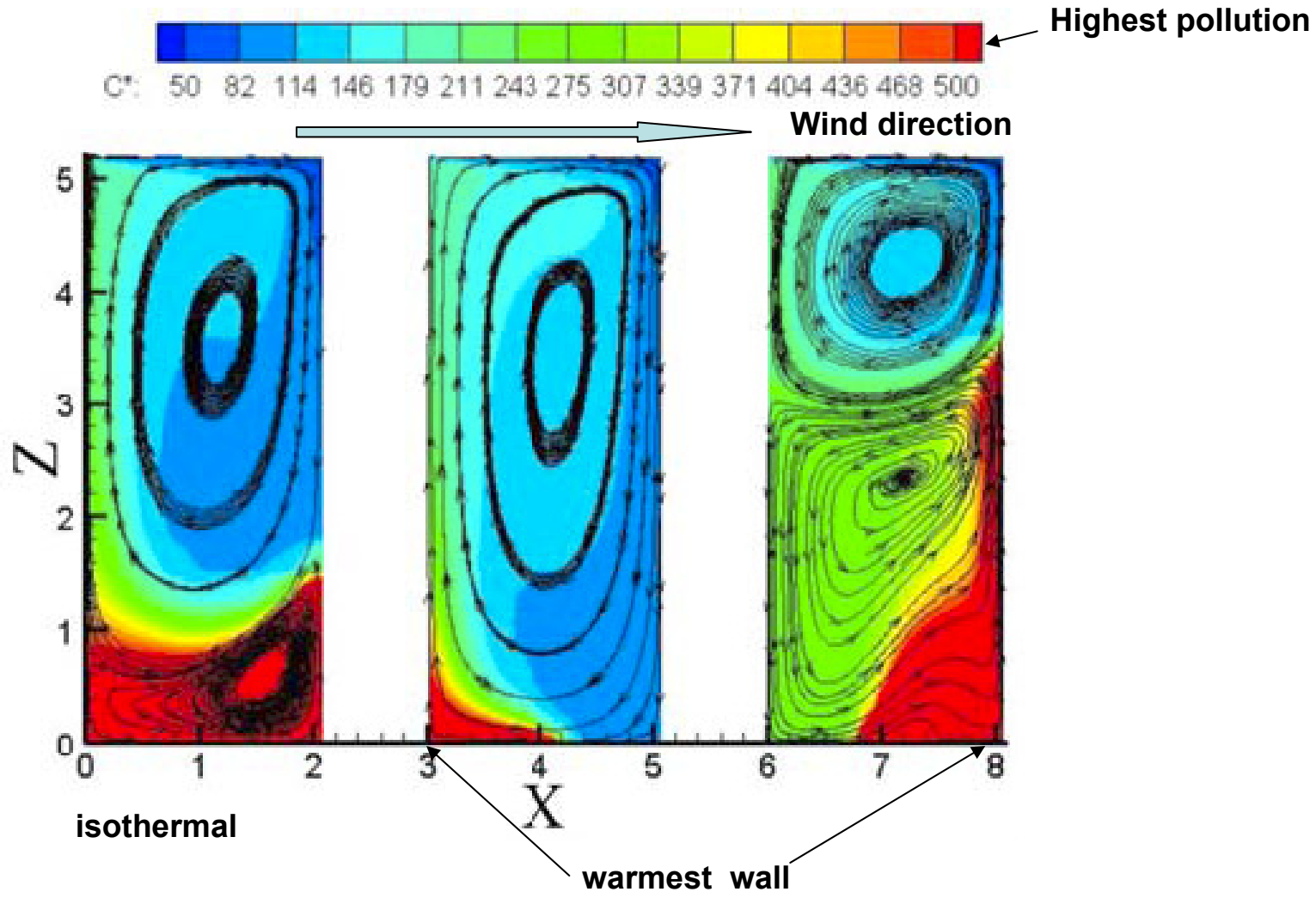
Unequal building height

Wind direction

Pollutants distribution using a microscale software (MIMO). Effect of balconies

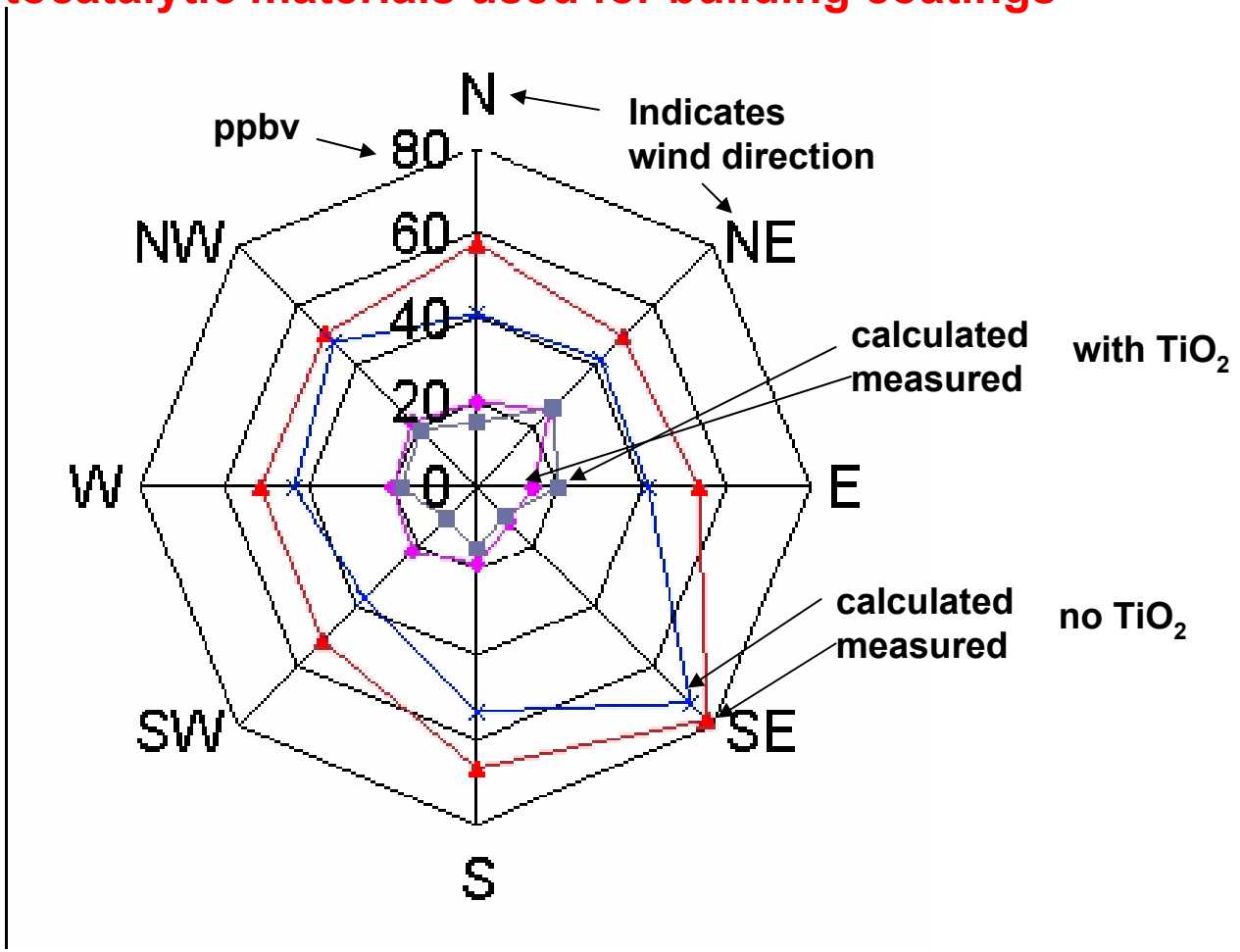


Pollutants distribution using a microscale software (MIMO). Effect of solar heating of the street sides



Canyon street pilot : excellent agreement between MIMO-calculated and measured [NOx]

Clearly shows that the software can predict the depolluting effect of photocatalytic materials used for building coatings

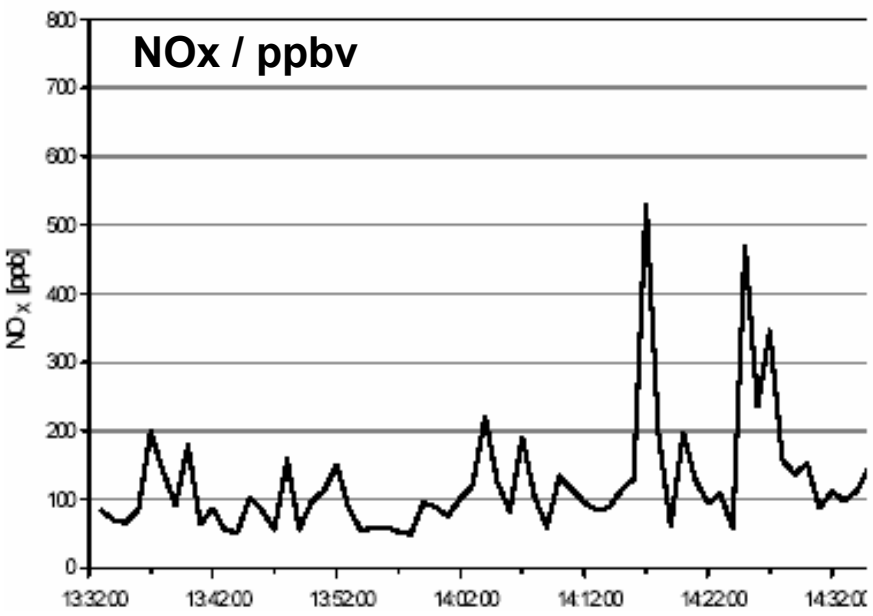


PICADA indoor car park test

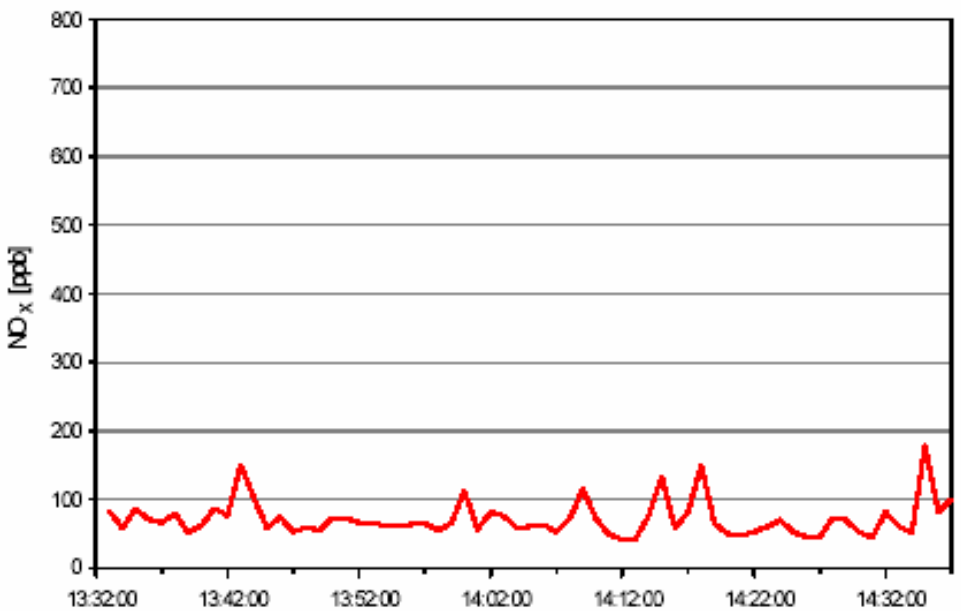
- 917 m^3. Photocatalytic Millennium paint on ceiling (322 m^2). 2 ventilators to achieve transfer of pollutants to ceiling. 20 lamps at 20 cm from ceiling: 1 W/m^2 UV
- Pollution source: car exhaust
- NO and NO_2 measured continuously
- Average % of removal over 3 days: 14 for NO; 21 for NO_2

Field experiment: street paving
Paving additional cost: 10-20%
Demand from municipalities (costly; representative?)

Standard paving



Italcementi TiO_2- containing paving



Paved area: 600 m^2 ; *ca.* 1200 vehicles/h

As expected, photocatalytic effect higher at 30 cm than at 180 cm above street level

Another field experiment: countryside road

- **4000 m^2 covered with ECORIVESTIMENTO FOTOFLUID ® for heavy traffic, a premix poured in the form of a fluid mortar onto bitumen**

- **Fotofluid developed by Global Engineering and Record using**

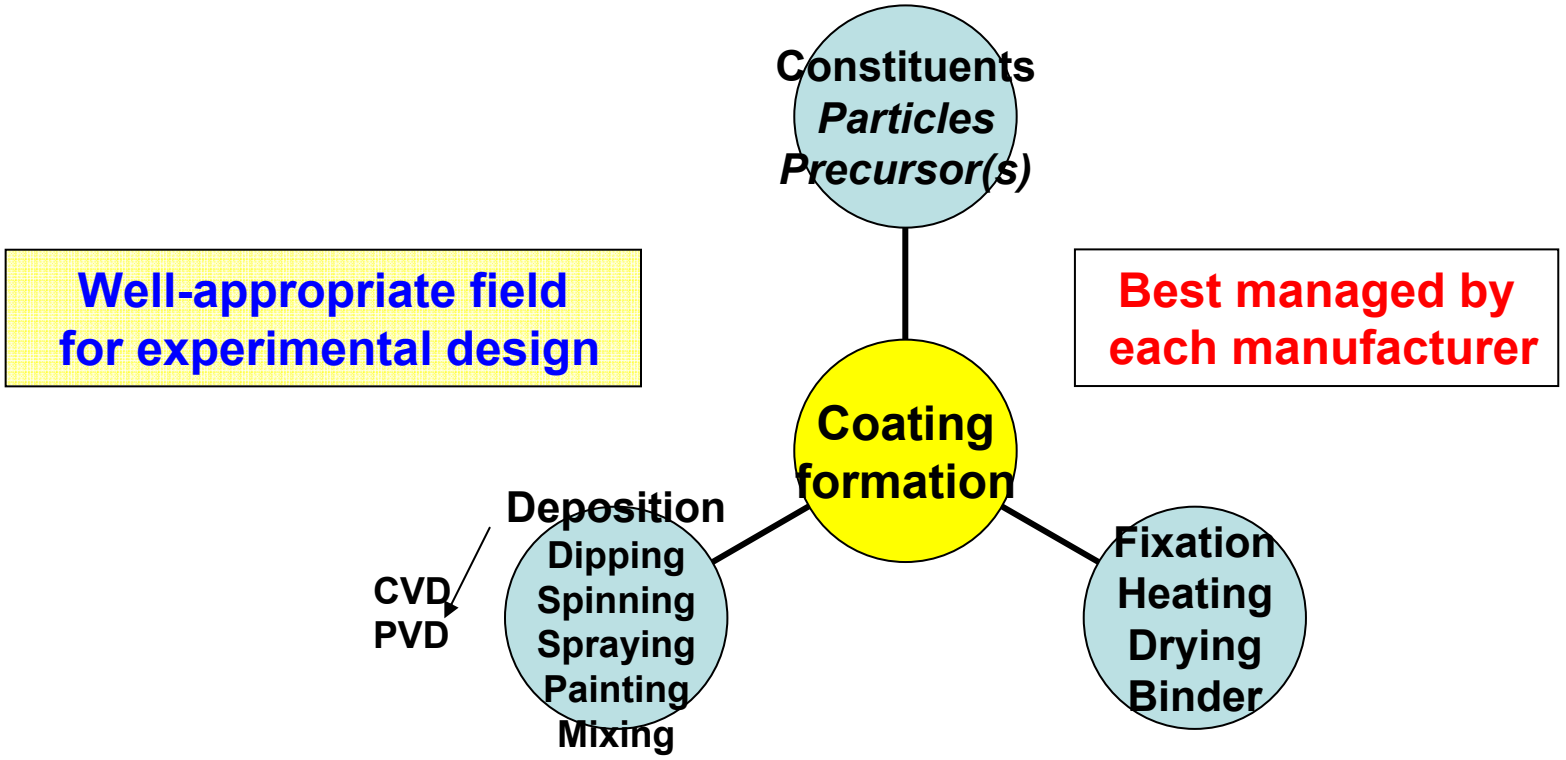
  Millennium TiO_2 powders

- **NO and NO_2 reduced from 85 to 3 and 24 to 5 ppbv, respectively. Sunny August in Italy. Measurements level above road?**

More efficient materials/coatings

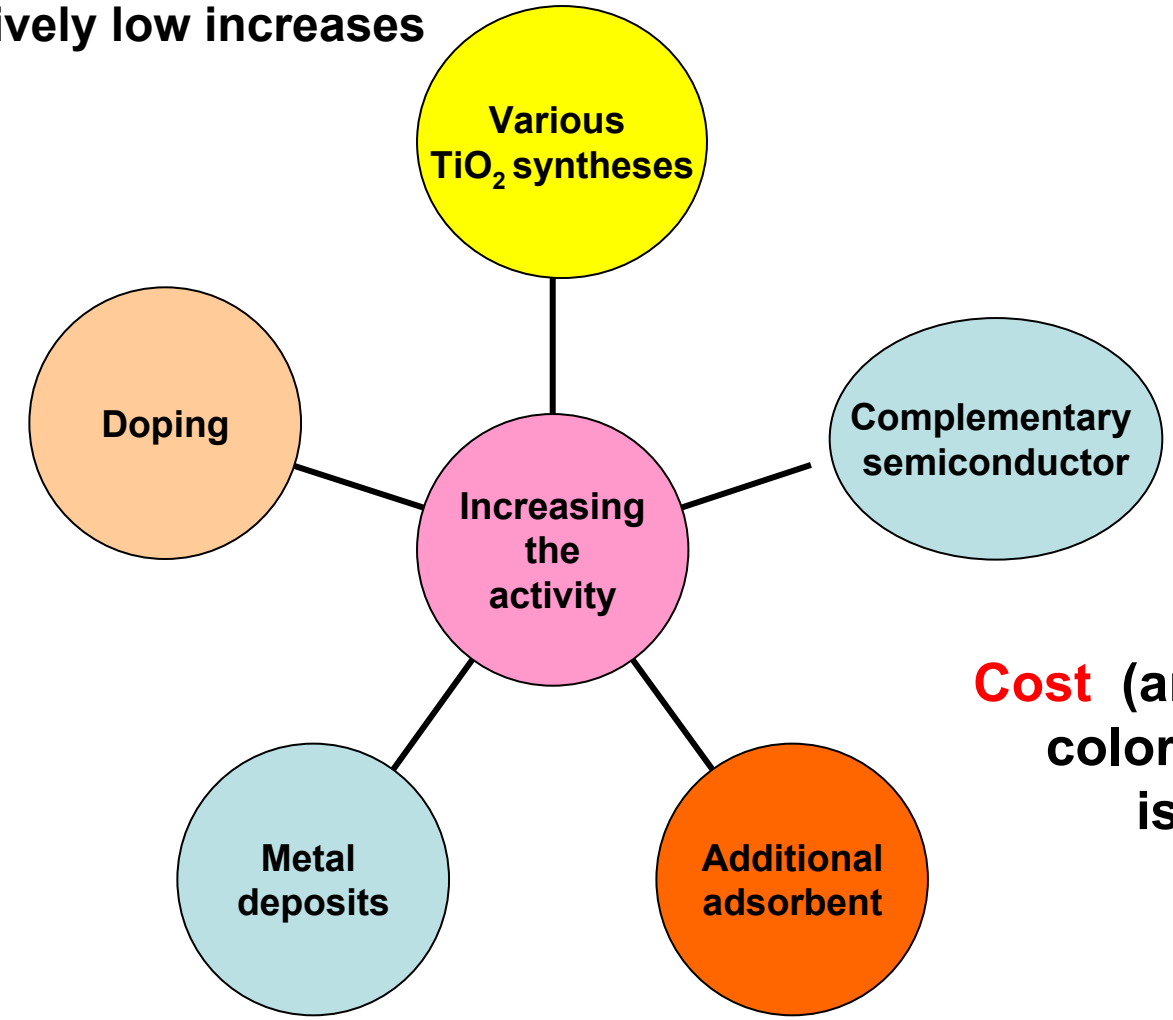
Deposition-fixation/incorporation of TiO_2

Compromise between efficacy (TiO_2 accessibility and activity) **and durability**
Dependency on the material (nature; form) and on the use
Possible necessity of an intermediate layer (for glass,steel, plastics)



Attempts to enhance photocatalytic activity

Until now, relatively low increases



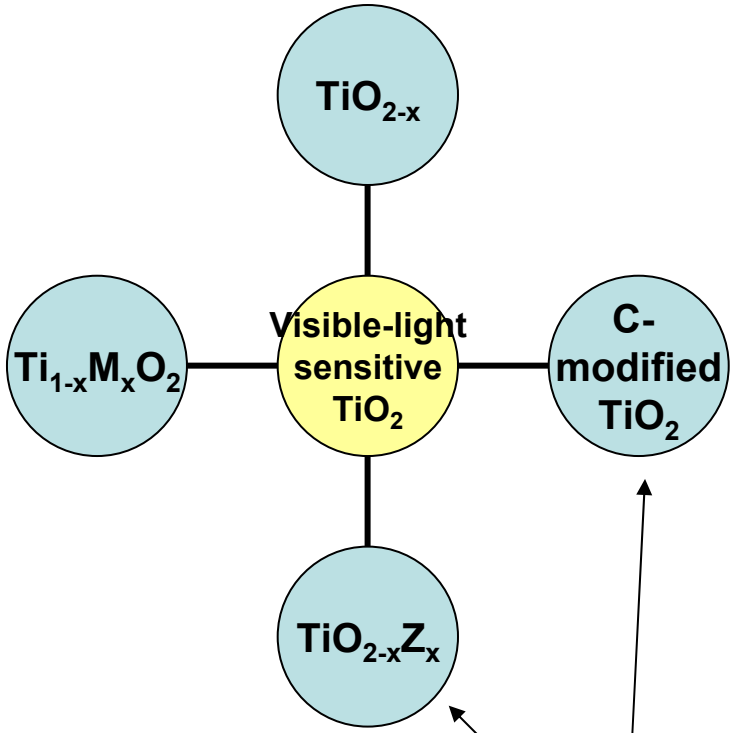
Cost (and possibly color) are key issues

Attempts to better adapt TiO_2 to the solar spectrum

Goal: energy levels within the band gap and/or adequate shifts of the bands

Drawbacks: charge recombination at the created defects (the activity in the UV region is sometimes reduced); colored materials

Are the changes cost-effective?

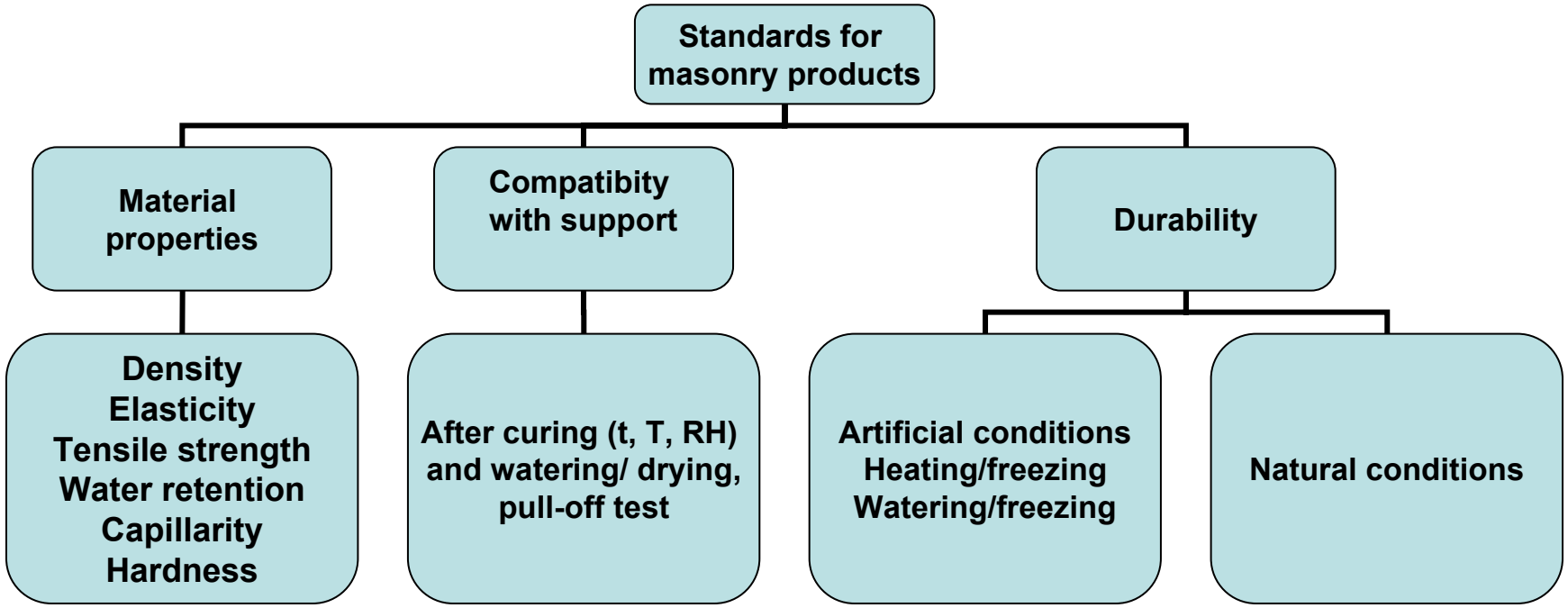


Very active research area presently

The coatings must not have only self-cleaning and air-depolluting properties!

They must first possess appropriate properties (mechanical, optical, etc.)

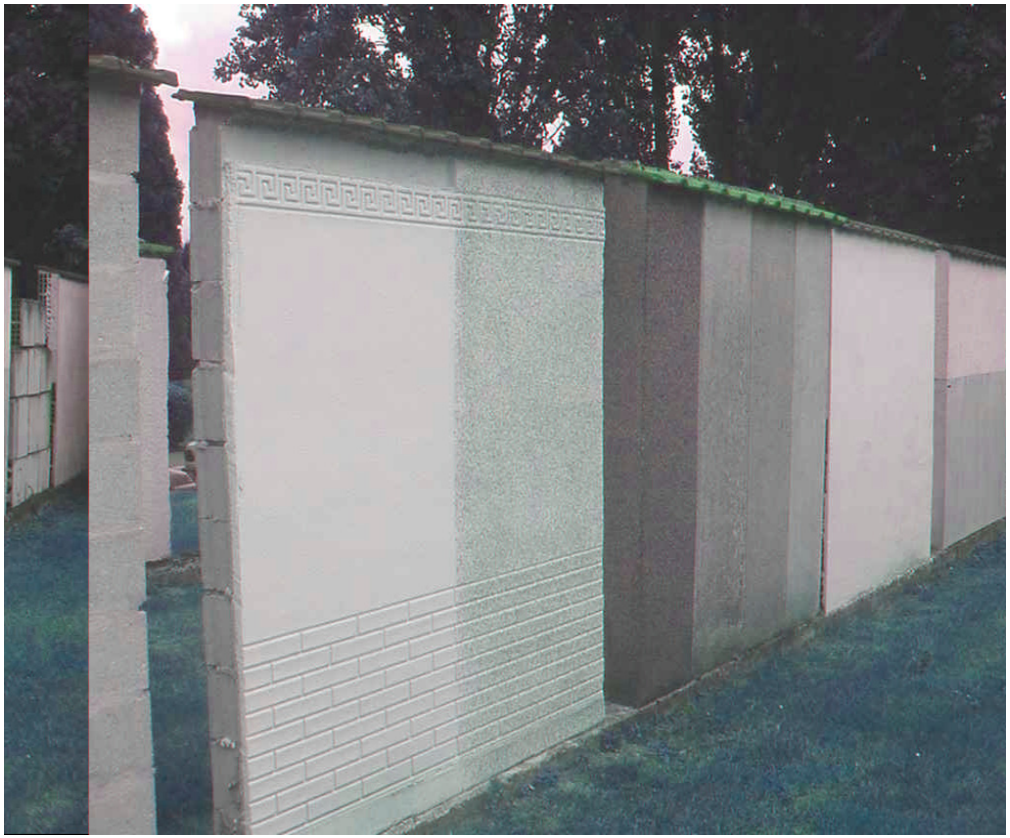
For instance: Standard for glass: transparency. Standard for paints: gloss



Results of mechanical tests (*CSTB b.ruot@cstb.fr)*

Satisfactory behavior in:
Lab tests
Artificial conditions
Natural conditions →

Expected as only 3 wt% of TiO_2 replaced an equal amount of cement

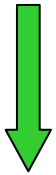


3-m^2 walls for testing cementitious materials

Conclusions

- **Much attention paid to test reliability, including material preconditioning. However, problem of standards**
- **Ranking of self-cleaning and air de-polluting properties depends on the reactant**
- **Photocatalytic coatings are commercialized as a result of PICADA**
- **Life Cycle Analysis showed no significant environmental effect of TiO_2 addition regarding manufacturing and transportation**
- **Significant removal of air pollutants in narrow streets has been demonstrated (canyon street pilot) and modeled for NO_x**
- **The use of photocatalytic coatings is affordable, specially if the impact on human health is taken into account**
- **Potentiality? Depends on city policy, building owners and various local characteristics**

Warm thanks to the PICADA partners



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