PHOTOPAQ

Demonstration of PHOTOcatalytic remediation Processes on Air Quality

photopaq.ircelyon.univ-lyon1.fr

Can photocatalysis help to improve urban air quality?

Results from the LIFE+ Project PhotoPAQ

The PhotoPAQ team,

Jörg Kleffmann (kleffman@uni-wuppertal.de)

Bergische Universität Wuppertal, Germany

Introduction

- Photocatalysis known since ~100 years (*Carl Renz, 1921*)
- In the presence of UV light, pollutants are removed on photocatalytic surfaces
- Examples:
  - VOCs → CO_2
  - NO_x → HNO_3/Nitrat

  $NO_x + VOC + h\nu \rightarrow O_3$, “summer smog“
- Especially the reduction of NO_x ($NO+NO_2$) would be of high importance for urban air quality

Introduction

- NO_2 and reaction products (HONO, HNO_3, PAN,…) are directly harmful

➔ **NO_2:** from 2010 EU limit value of 40 μg/m^3 (~20 ppb)

- Typically exceeded under urban conditions
- NO_x-reduction from combustion processes not sucessful for NO_2 (NO_x↓ NO_2➔)

➔ „Urban NO_2-problem“

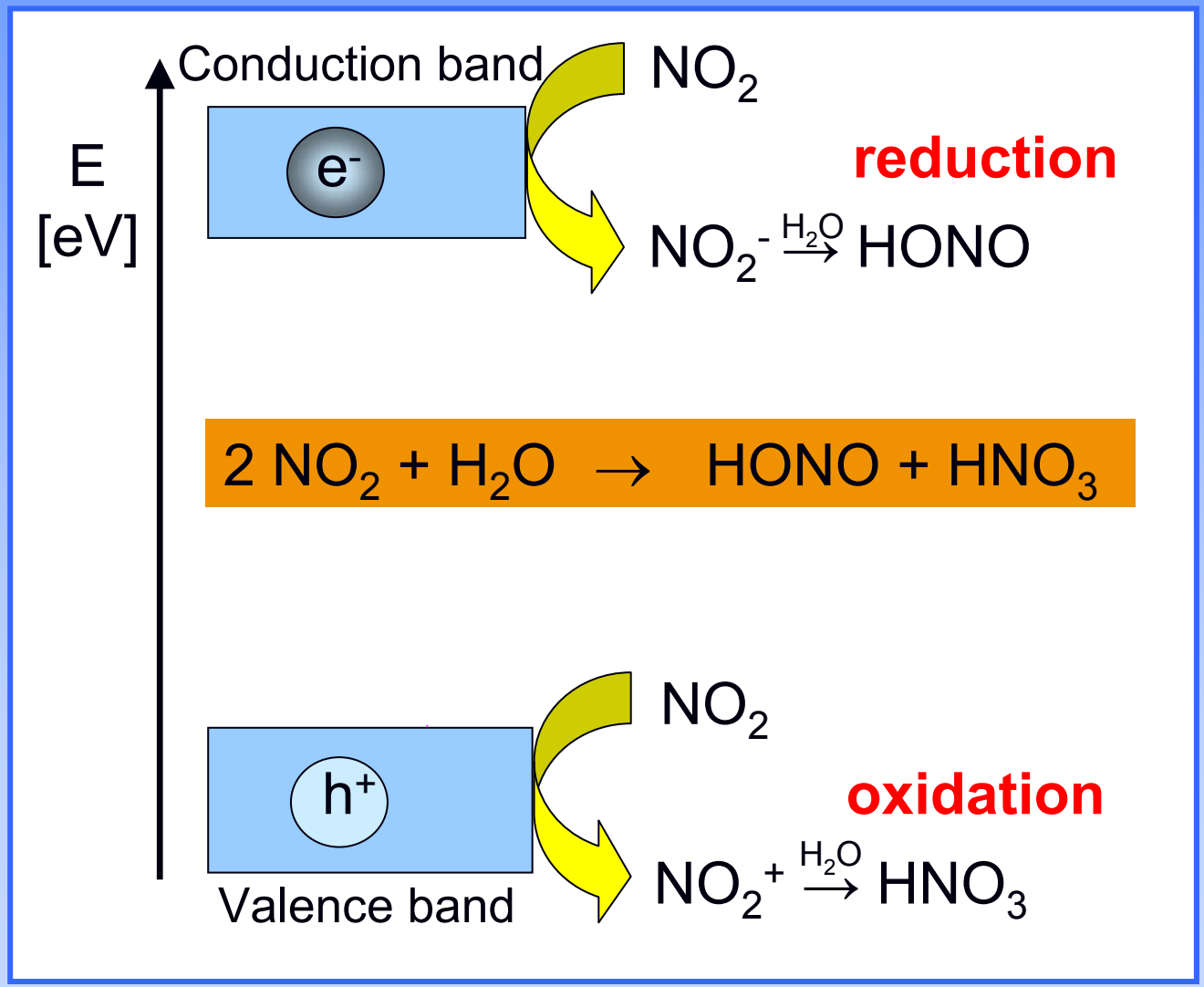
- To solve the problem:
  - Reduction $O_{3\ (background)}$: complex + global problem…
  - Strong reduction of NO_x to ≤$O_{3\ (background)}$

Introduction

➔ **Photocatalytic surfaces as a NO_x-sink?**

- **TiO_2** is a well-known photo-catalyst for NO_x (<390 nm)
- As products HONO and $HNO_{3(ads.)}$ documented

Photocatalysis on TiO_2



Introduction

➔ **Photocatalytic surfaces as a NO_x-sink?**

- **TiO_2** is a well-known photocatalyst for NO_x(<390 nm)
- As products HONO and $HNO_{3(ads.)}$ documented
- Commercial materials:
  concrete, roof tiles, window glass, paints, etc.
- Very optimistic results in some photocatalytic field studies

Introduction

- ***PICADA***-study:

Introduction

- ***PICADA***-study: NO_x-reduction = 40-80 %!

- Unrealistic experimental conditions: $S_{active}/V = 1\ m^{-1}$;
  S_{active} = photocatalytic surface; V = Volume Canyon

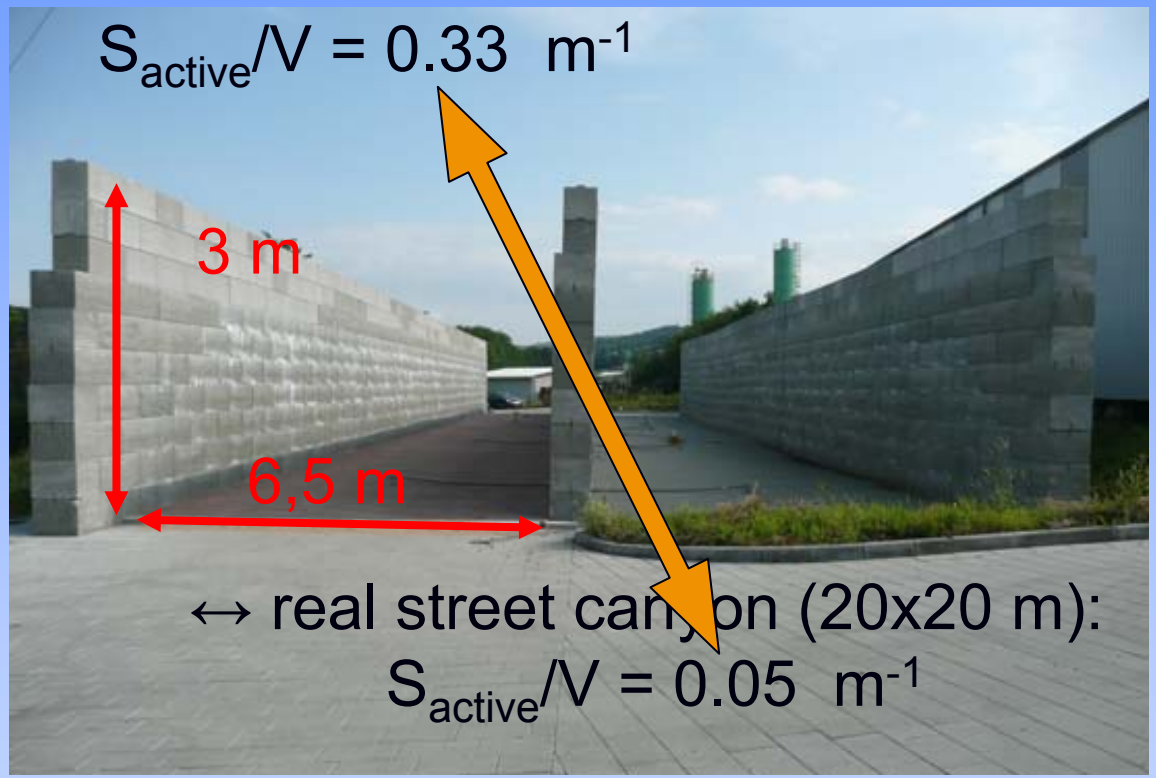
- Typical street canyon (20×20 m): $S_{active}/V = 0.1\ m^{-1}$

- For a heterogeneous reaction – even when transport limited: Conversion effciency ∝ $\mathbf{S_{active}/V}$

➔ ***Expected NO_x-reduction*** ***ca. 6 % (4-8 %)***
(only rough estimation…)

Introduction

- Other example: ***FCN/Fraunhofer study (DBU)***



- Observed NO_2 reduction: **18 %**
- Expected real reduction: **3 %**
  (only rough estimation…)

Introduction

Expected Reduction Canyon 20x20 m

- Extrapolated from PICADA: **ca. -6 %** (S/V: **0.1 m^{-1}**)
- Extrapolated from FCN: **ca. -3 %** (S/V: **0.05 m^{-1}**)

➔ ***Both field studies fit perfectly!***

- But, still upper limits…
  - Numbers refer only to daytime reduction
  - NO_x measured close to the surfaces (not in 3 m…)

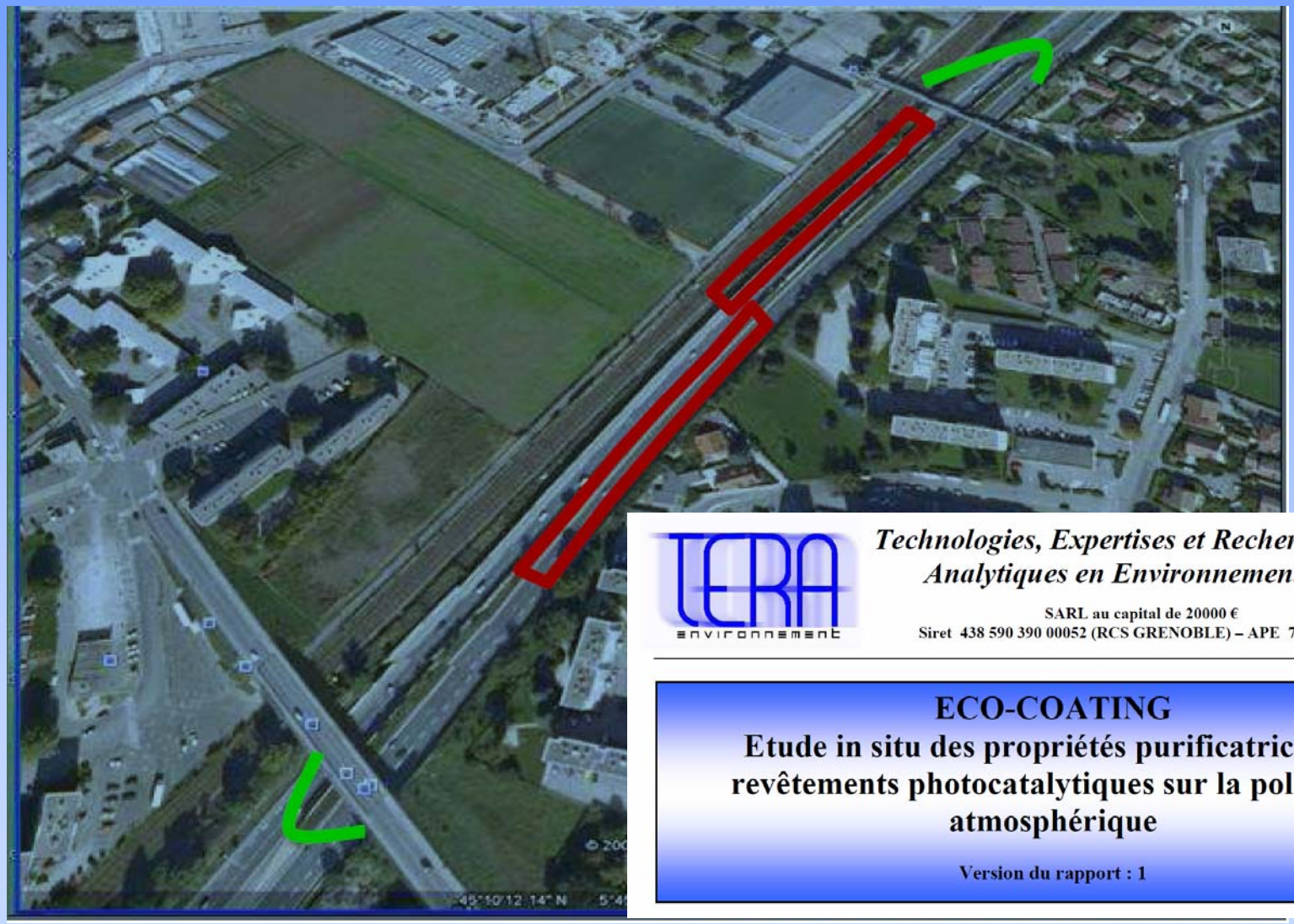
➔ ***Realistic average NO_x reduction: few %…***

Introduction

➔ Negative example: ***Putten/Netherlands***

Dutch Air Quality Innovation Programme concluded (2010): **Improved Air Quality with Coating of Titanium Dioxide not (…) Demonstrated**

➔ Another negative example: ***Grenoble/France***



TERA environnement

Technologies, Expertises et Recherches Analytiques en Environnement

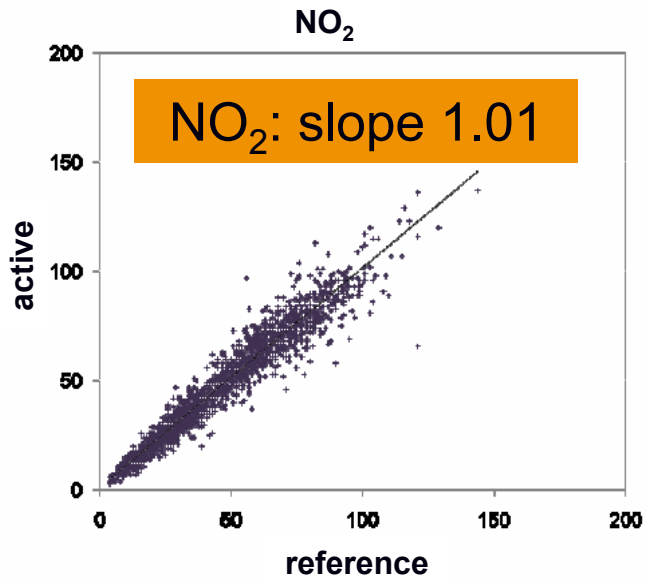
SARL au capital de 20000 €
Siret 438 590 390 00052 (RCS GRENOBLE) – APE 7490 B

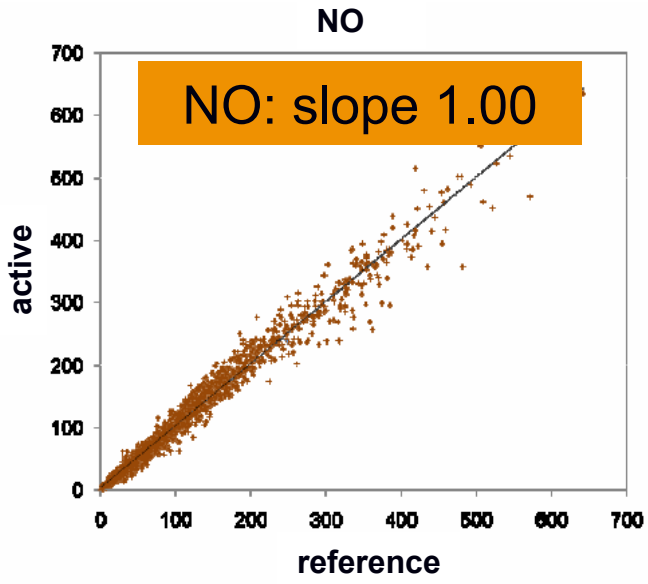
ECO-COATING
Etude in situ des propriétés purificatrices de revêtements photocatalytiques sur la pollution atmosphérique

Version du rapport : 1

Introduction

➔ Another negative example: ***Grenoble/France***



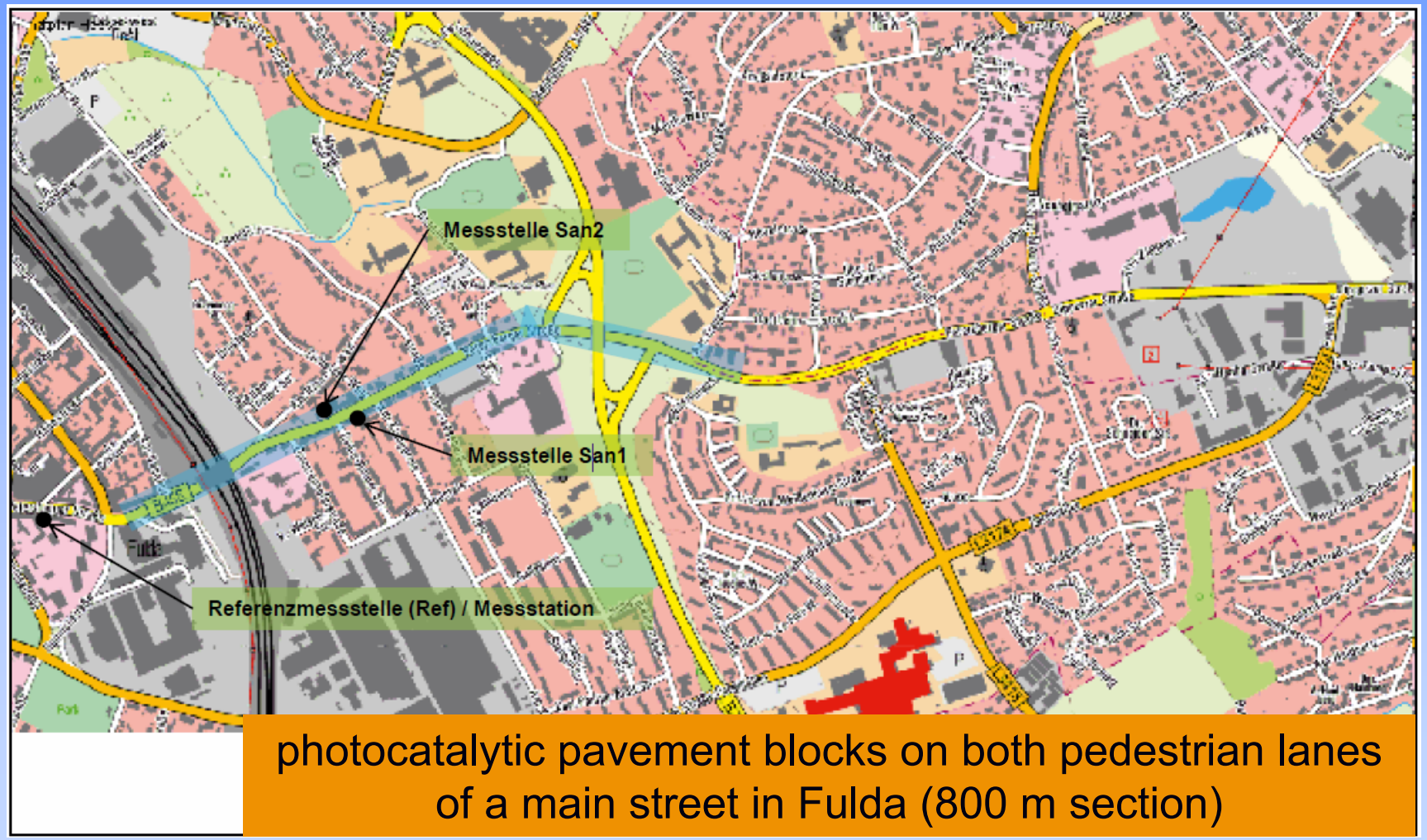


17 : Corrélation entre la concentration quart-horaire enregistrée au niveau de la section Témoin et de la section Traitée au cours des 2,5 mois de mesure pour le NO et le NO_2.

No measurable reduction…

Introduction

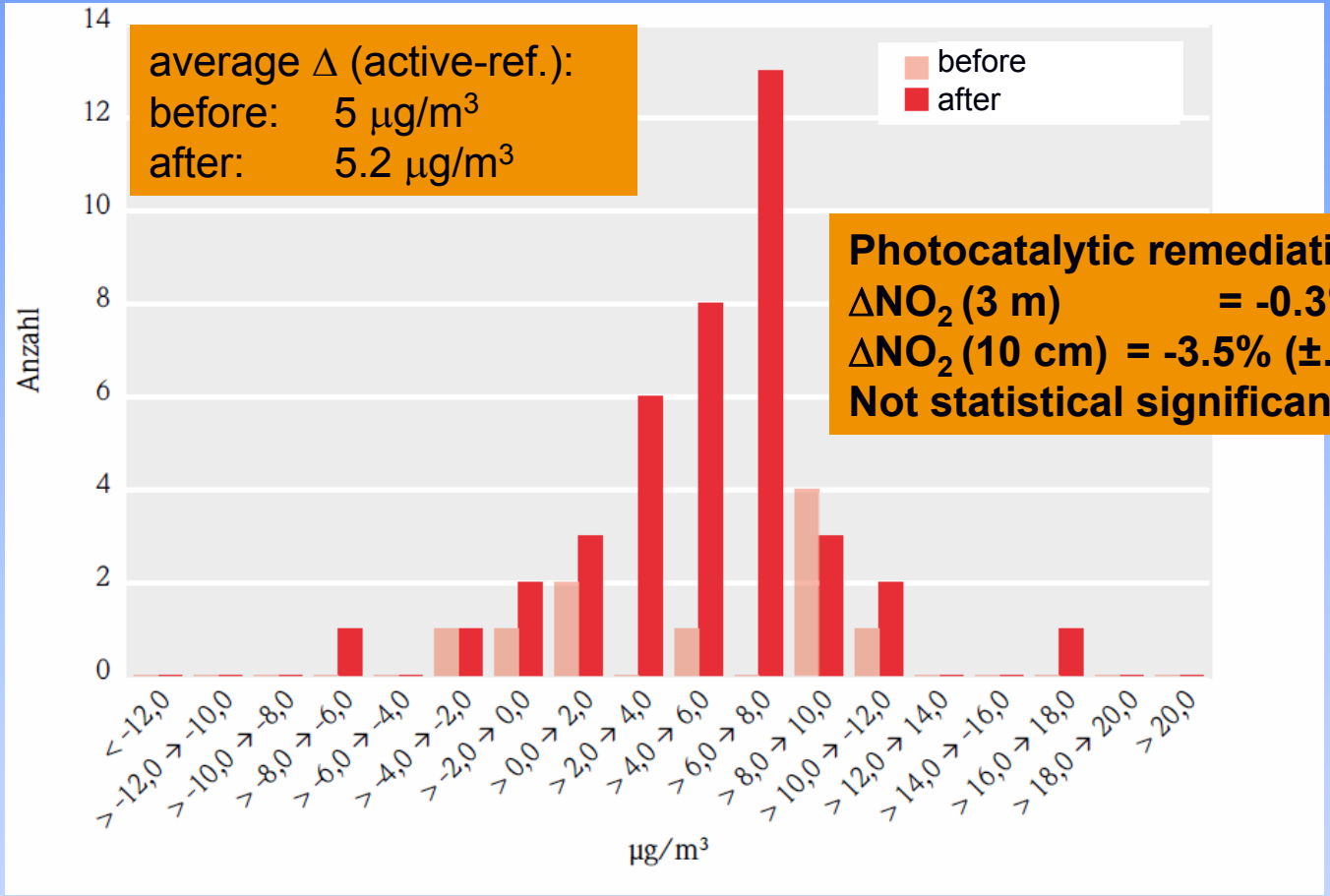
➔ Another negative example: ***Fulda/Germany***



photocatalytic pavement blocks on both pedestrian lanes of a main street in Fulda (800 m section)

Introduction

➔ Another negative example: ***Fulda/Germany***



Aim of the study

➔ International demonstration project to study the impact of photocatalysis on urban air quality

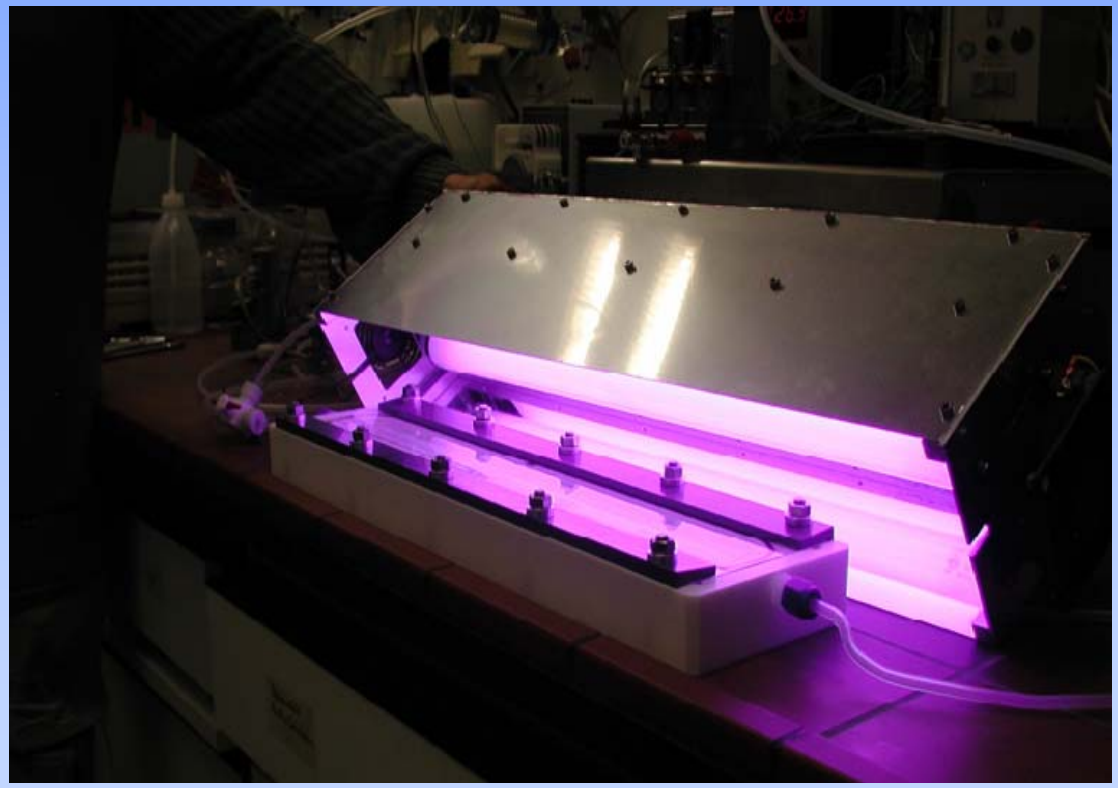
- What is the reduction potential for pollutants under realistic conditions?
- Formation of harmful reaction products?
- Can photocatalysis be recommended?

- EU-project as part of the LIFE+-program
- Co-ordinator: CNRS (Lyon)
- Partners:
  - CRNS (Orléans)
  - TROPOS (Leipzig)
  - BUW (University Wuppertal)
  - CTG Italcementi Group
  - LHTEE (University Thessaloniki)
  - Belgian Road Research Centre (Brussels)
  - LISA (University Paris)

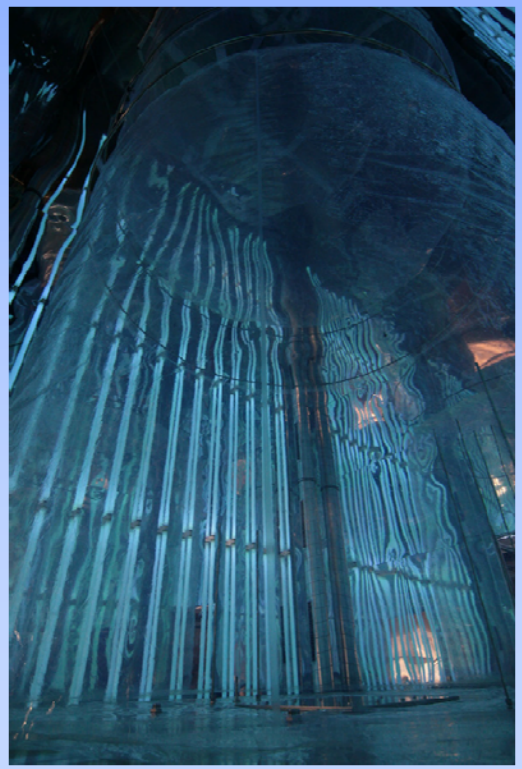
- Photocatalytic decomposition of pollutants should be demonstrated
  - Laboratory studies (NO_x, NO_y, O_3, VOC)
  - Smogchamber studies (NO_x, NO_y, O_3, VOC, particles)
  - Field studies (NO_x, NO_y , O_3, VOC, particles)
    - Leopold II tunnel in Brussels
    - Street canyon in Bergamo
  - Modell calculations

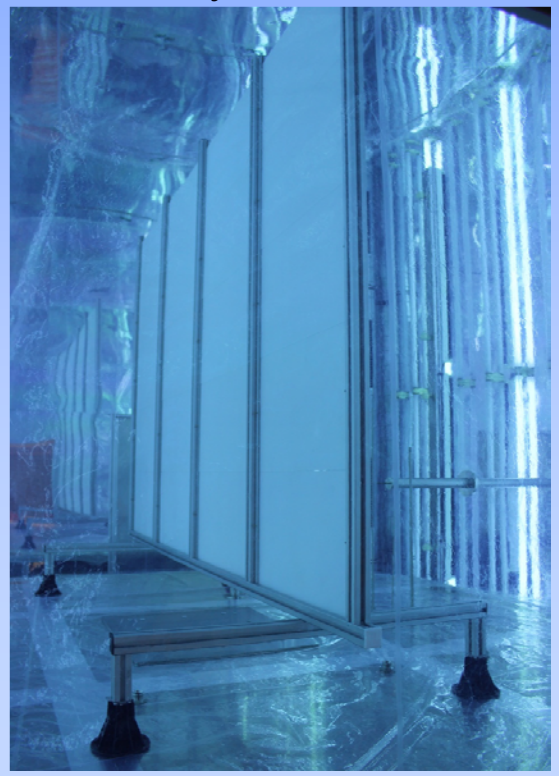
- Photocatalytic decomposition of pollutants should be demonstrated

  - Laboratory studies (NO_x, NO_y, O_3, VOC)



- Photocatalytic decomposition of pollutants should be demonstrated
  - Laboratory studies (NO_x, NO_y, O_3, VOC)
  - Smogchamber studies (NO_x, NO_y, O_3, VOC, particles)





- Photocatalytic decomposition of pollutants should be demonstrated
  - Laboratory studies (NO_x, NO_y, O_3, VOC)
  - Smogchamber studies (NO_x, NO_y, O_3, VOC, particles)
  - Field studies (NO_x, NO_y , O_3, VOC, particles)
    - Leopold II tunnel in Brussels (June/September 2011, January 2013

BAST Kolloquium, Luftqualität
5. März 2015

Experimental Tunnel

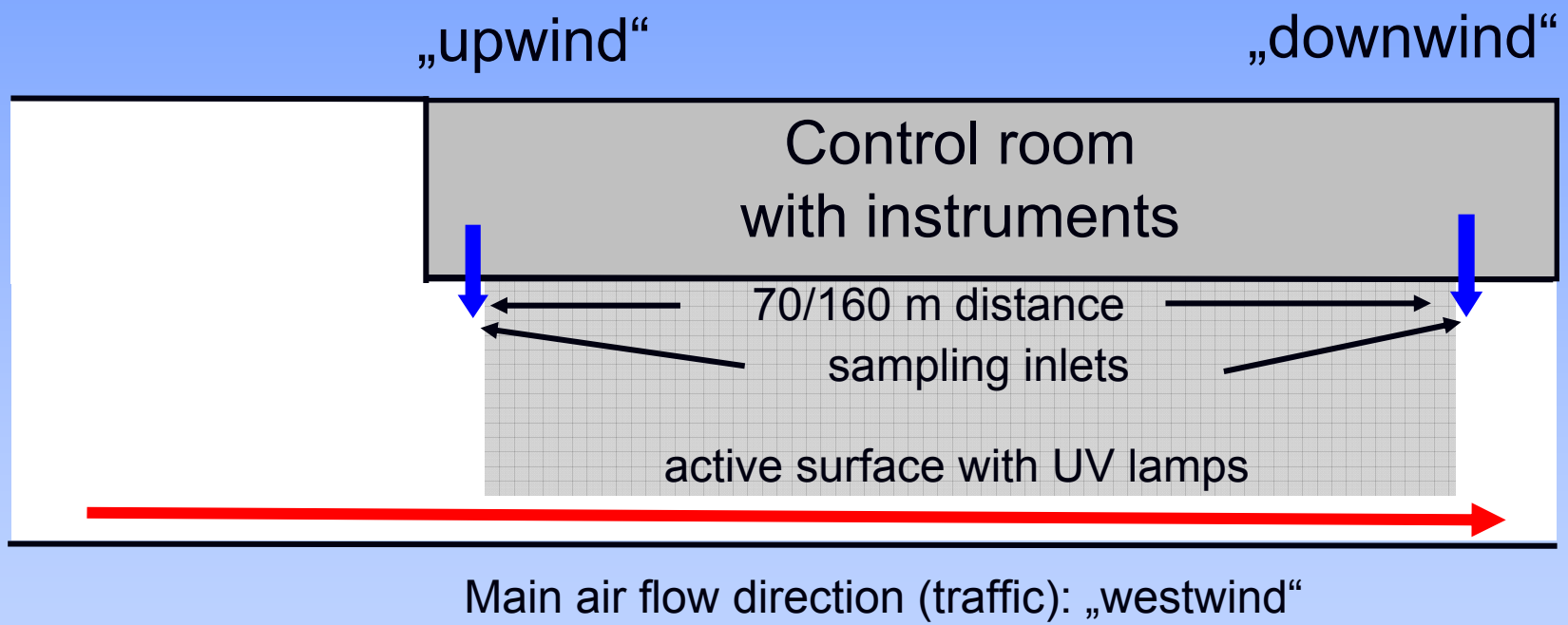
Experimental Tunnel

Tunnel Details:

- 2.3 km long (2x for both directions), ca. 2x20.000 vehicles/day, 7-9:00 h: 2300 vehicles/h
- Active section: 70 m / 160 m
- Photocat. material: TX Active®/ ”TX Boosted”
- UV-lamps: 0.6 W/m^2 / 1.6 W/m^2 (UVA)

Experimental Tunnel

Tunnel set-up:



Main air flow direction (traffic): „westwind“

Experimental Tunnel

Experimental Tunnel

Experimental Tunnel

Experimental Tunnel

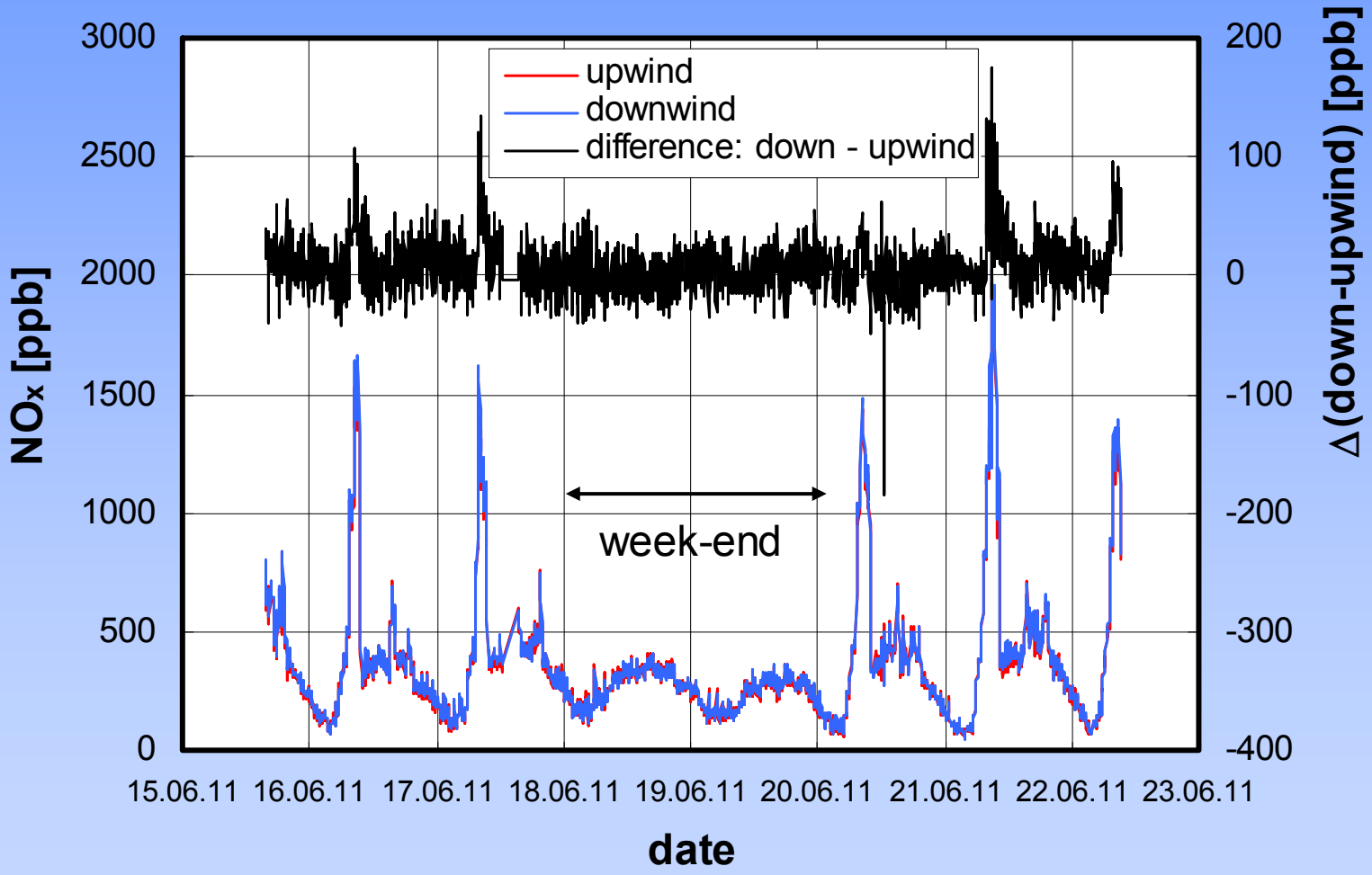
Experimental Tunnel

Experimental Tunnel

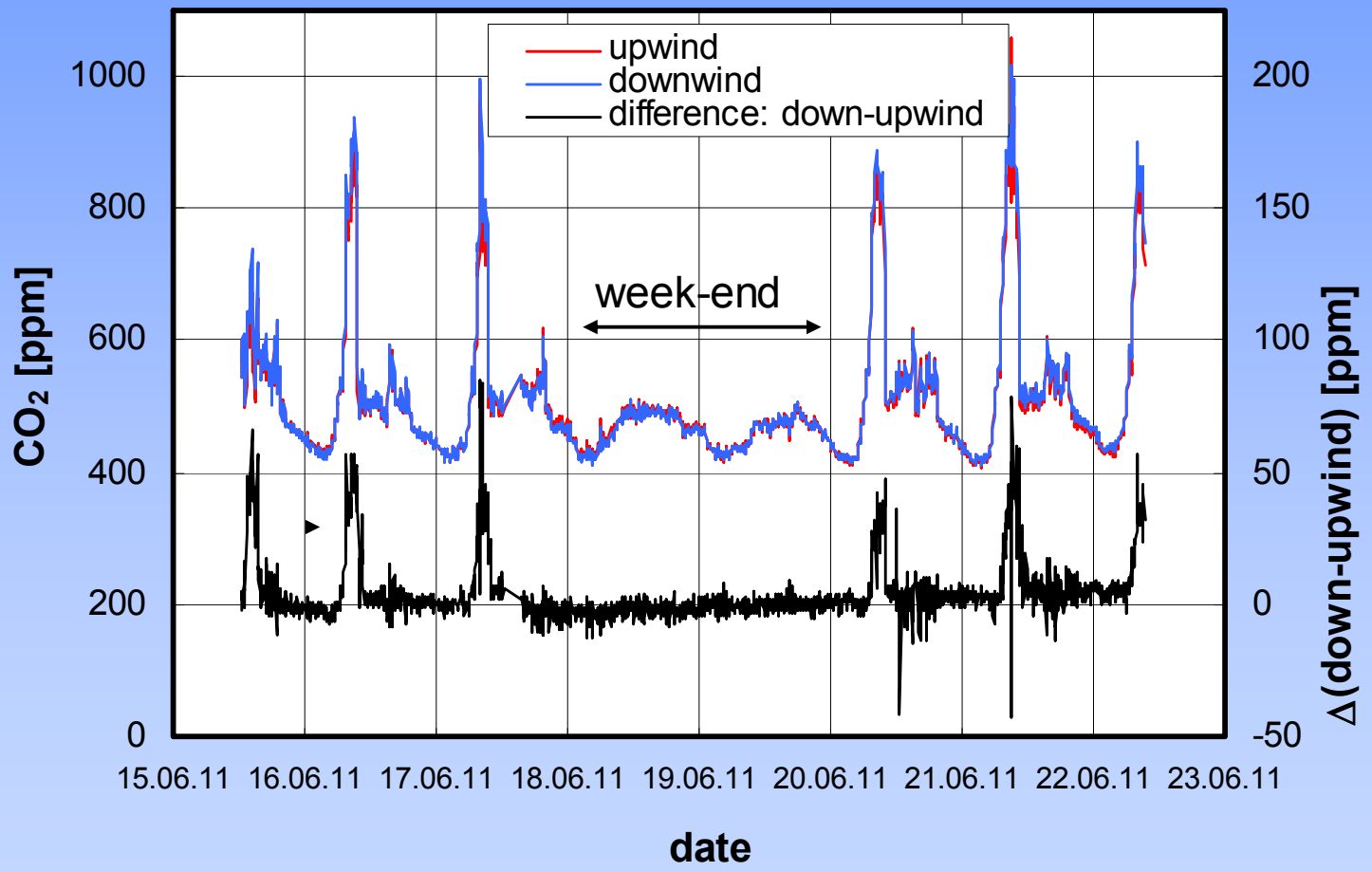
Measured pollutants (2x up-/downwind):

- **NO_x** ($NO+NO_2$)
- HONO
- **CO_2**, CO
- O_3
- HCHO (formaldehyde)
- aldehydes, ketones
- VOCs (C3-C12)
- particle mass
- particle size distribution
- particle composition
- meteorology

Experimental data: NO_x



Experimental data: CO_2



Results Tunnel

Experimental data:

- Very typical diurnal profiles
- Except Rush-hour periods (congestion) very similar concentrations at both sites

➔ Almost no emissions in the section (down slope -3°)

➔ Tunnel can be compared with a flow tube

- In contrast, during rush-hour periods (congestion) significant emissions (stop and go)

➔ Rush-hour data not used to determine the photocatalytic remediation

Photocatalytic NO_x Remediation

- Based on the laboratory data + simple model estimations, and based on the only available tunnel study significant remediation was expected

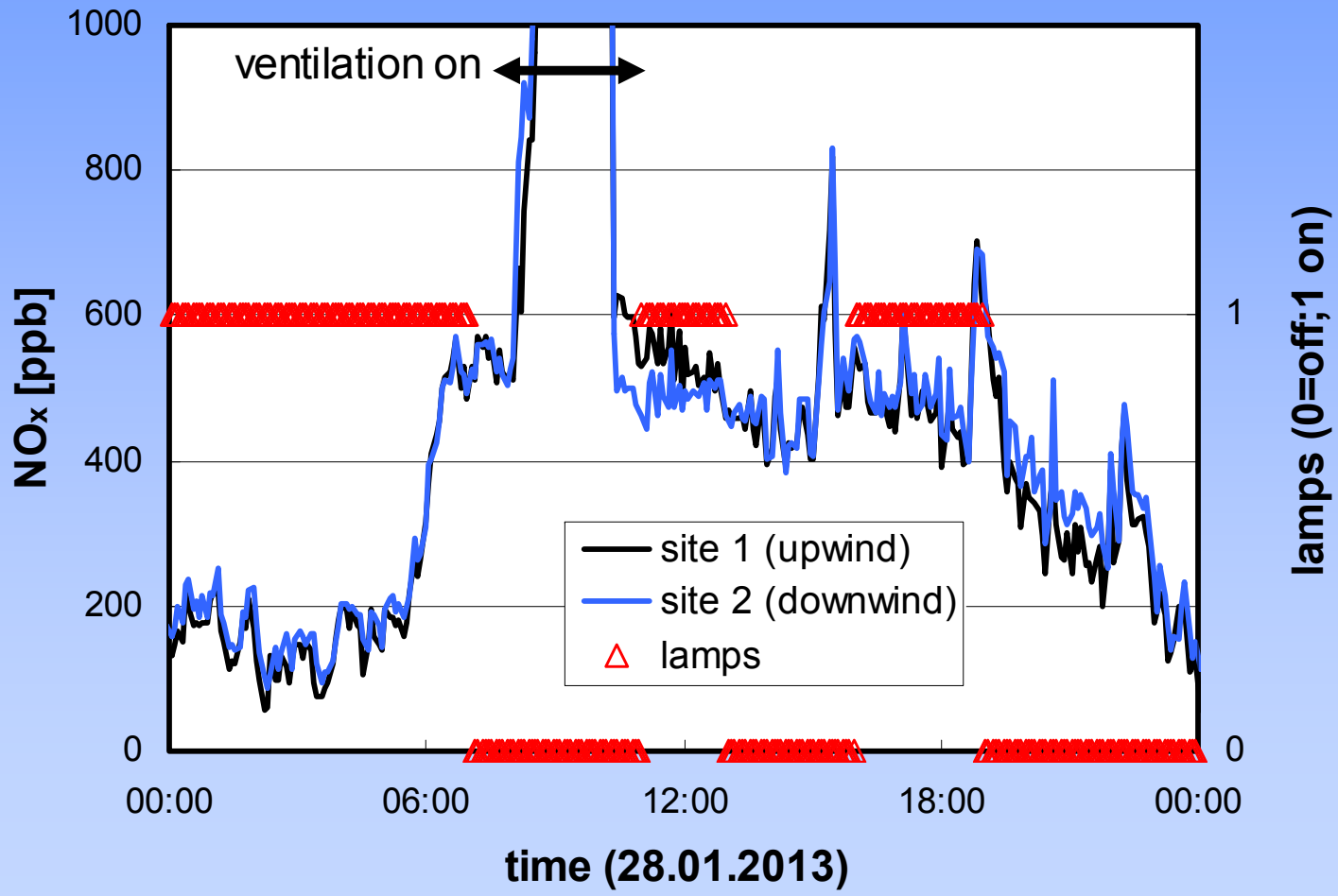
NO_x-reduction: -20 %!

Rome/Italy
Guerrini, 2012

Photocatalytic NO_x Remediation

- Based on the laboratory data + simple model estimations, and based on the only available tunnel study significant remediation was expected
- To verify, lamps were periodically switched on/off

Photocatalytic NO_x Remediation



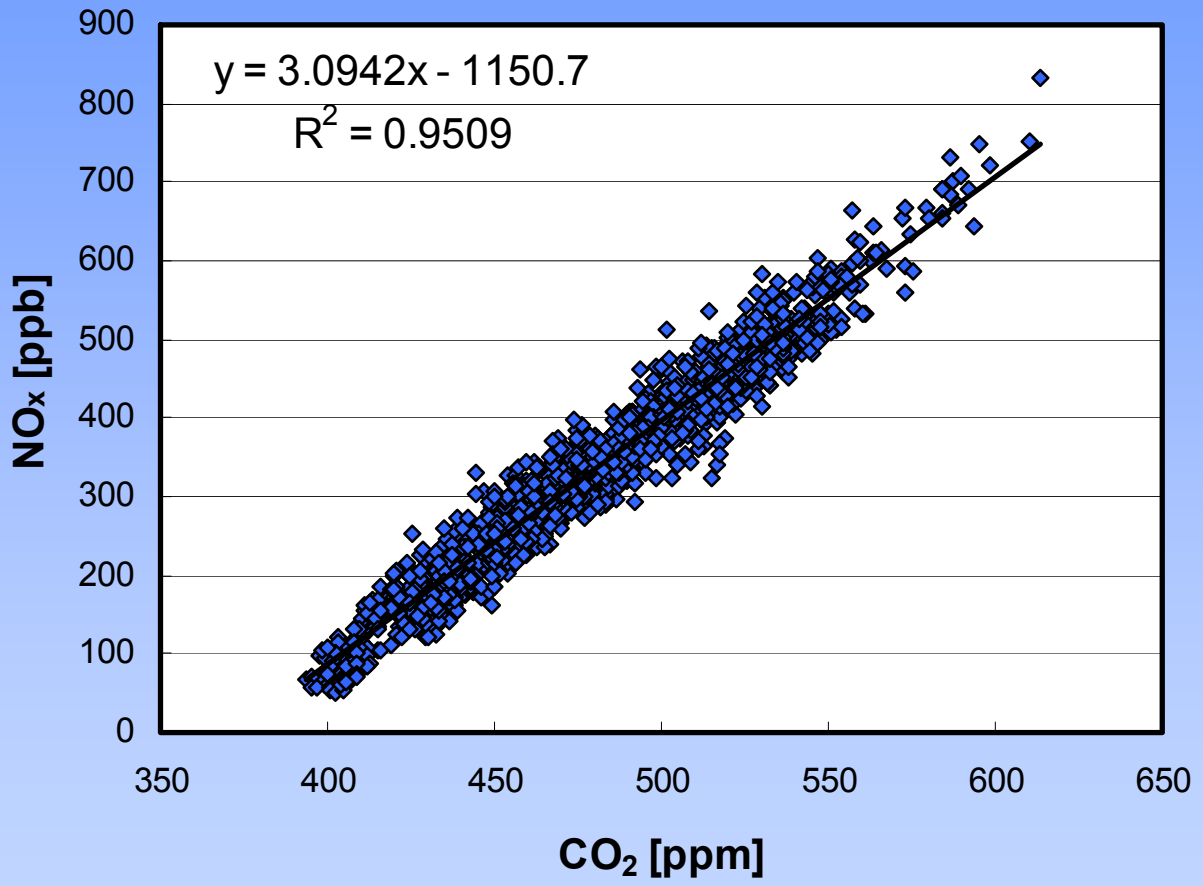
Photocatalytic NO_x Remediation

- Visually, no photocatalytic remediation observed
- Variability of the pollutants very high
- ➔ Quantification of the photocatalysis from the evaluation of all data (= mean campaign results…)

Photocatalytic NO_x Remediation

- Tracer approach (CO_2 tracer for traffic emissions)
- Photocatalysis influences only pollutants like NO_x, but not the tracer CO_2
- ➔ Quantification of the photocatalysis by the NO_x/CO_2-ratio
  - Independent of the variability of the emissions
  - Higher precision of the results

Photocatalytic NO_x Remediation



- Precision error of the slopes typically 2 %

Photocatalytic NO_x Remediation

Measurement concept 1: before/after

- NO_x/CO_2 [ppb/ppm], downwind, lamps on
  - June 2011 (before): **3.08±0.06**
  - September 2011(after, 70 m): **3.14±0.06**
  - January 2013 (after, 160 m): **3.10±0.05**

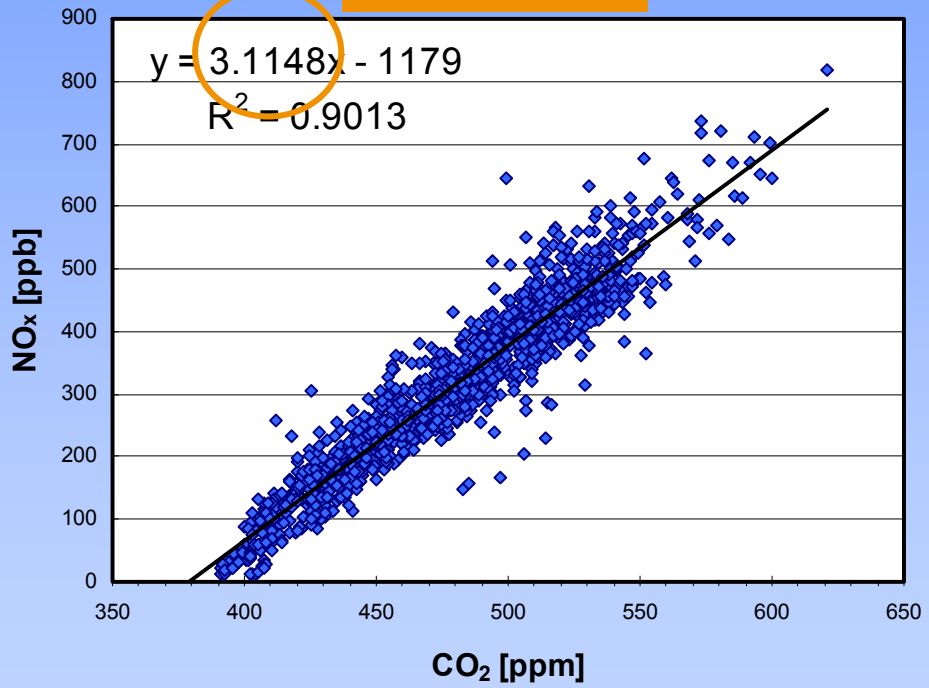
➔ No measurable effect…

- Average fleet emission factors may have been changed (unlikely…)

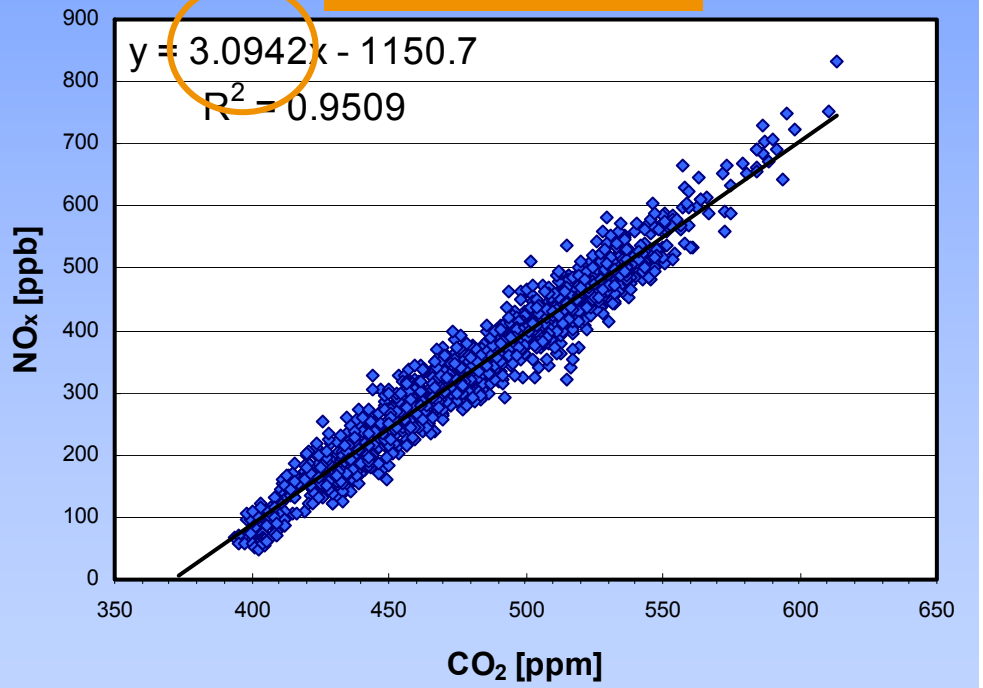
Measurement concept 2: up- / downwind

- Same measurement periods/same fleet emissions

"upwind"



"downwind"

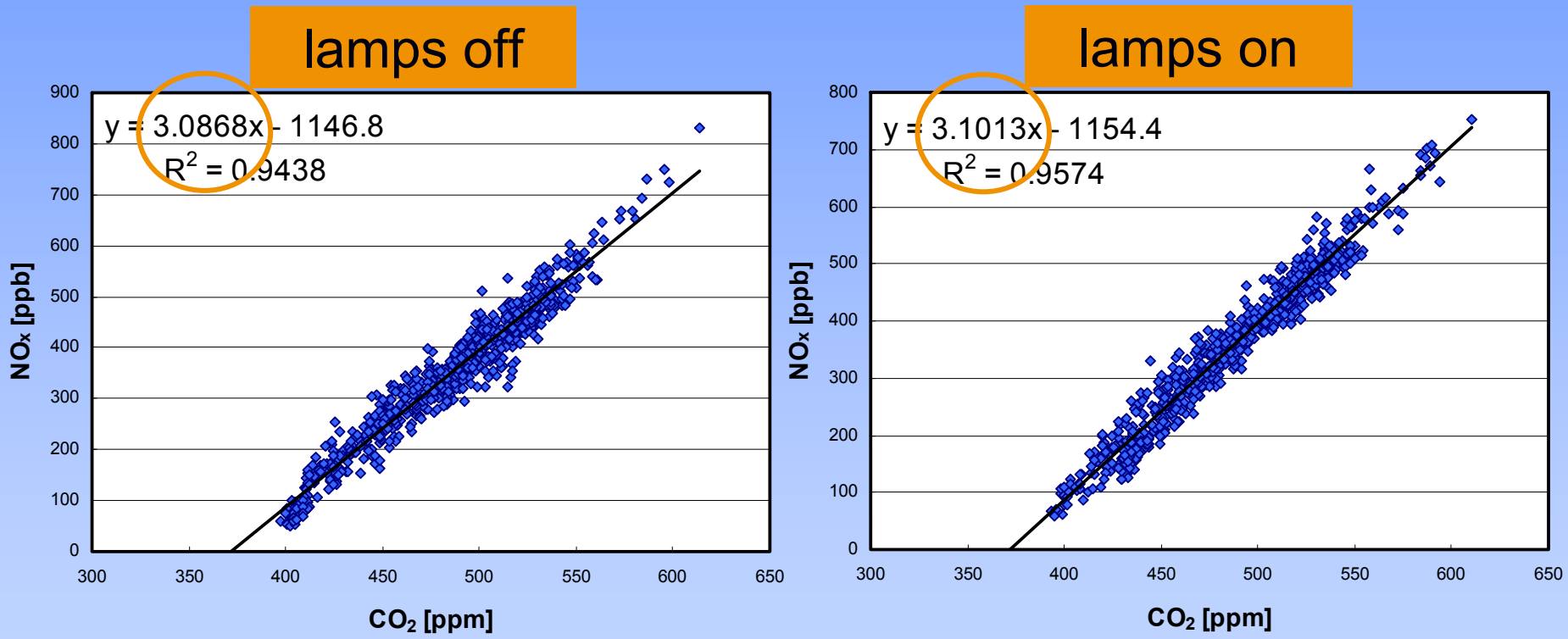


January 2013 (160 m, 1.6 W m^{-2}, TX-Boosted), data: only "westwind"

➔ No measurable effect (but precision errors of 2 instrum.)

Measurement concept 3: lamps on/off

- Only one instrument used



January 2013 (160 m, 1.6 W m^{-2}, TX-Boosted), data: only downwind

➔ No measurable effect

Results Tunnel: Photocatalytic NO_x Remediation

- None of the measurement concepts indicate a NO_x-decomposition.
- Upper limit (precision errors…): **≤2%**
- First theoretical estimations gave up to 10 %...?
- Main reason:
  Deactivation of the surfaces under the high pollution level, ***reactivity <1/10 of untreated samples (ISO)***

Results laboratory

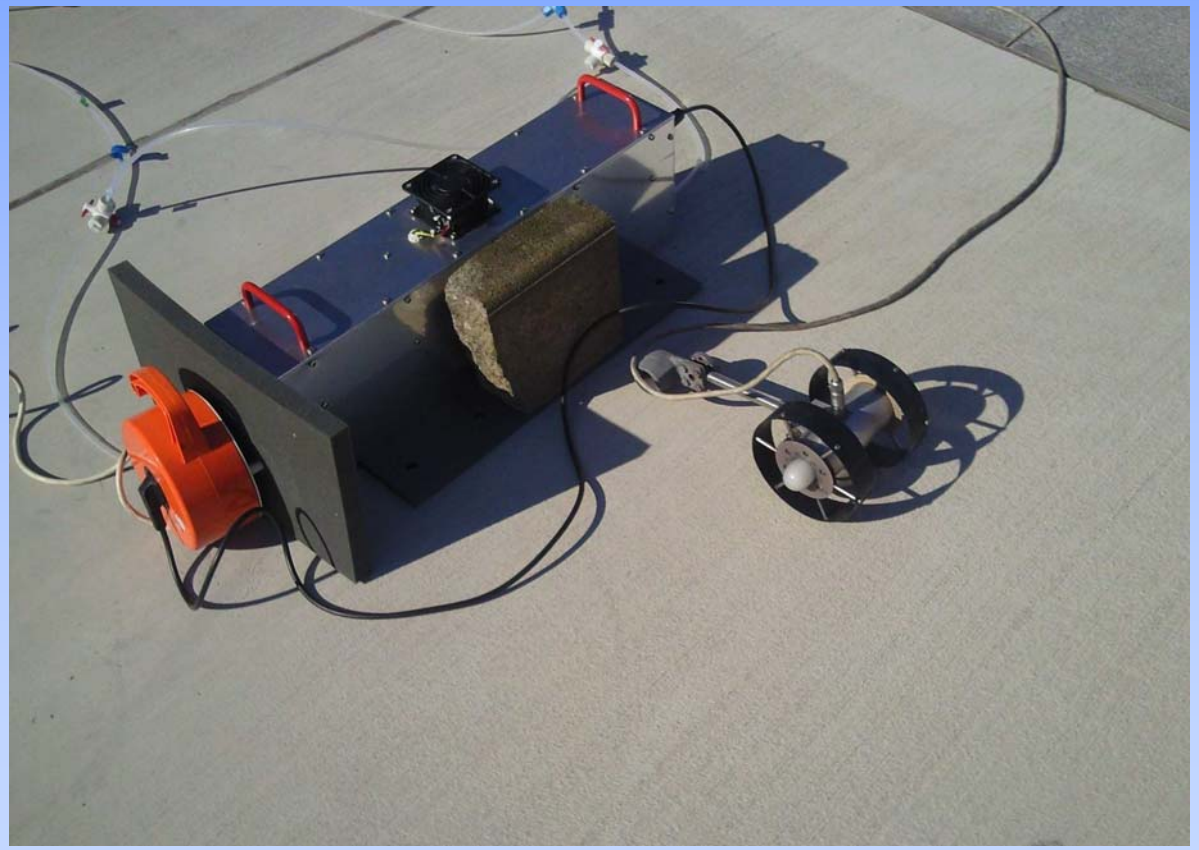
Lesson learnt:

➔ Before expensive applications, please test for deactivation in the real atmosphere…

Results laboratory

Lesson learnt:

➔ Before expensive applications, please test for deactivation in the real atmosphere…



Results laboratory

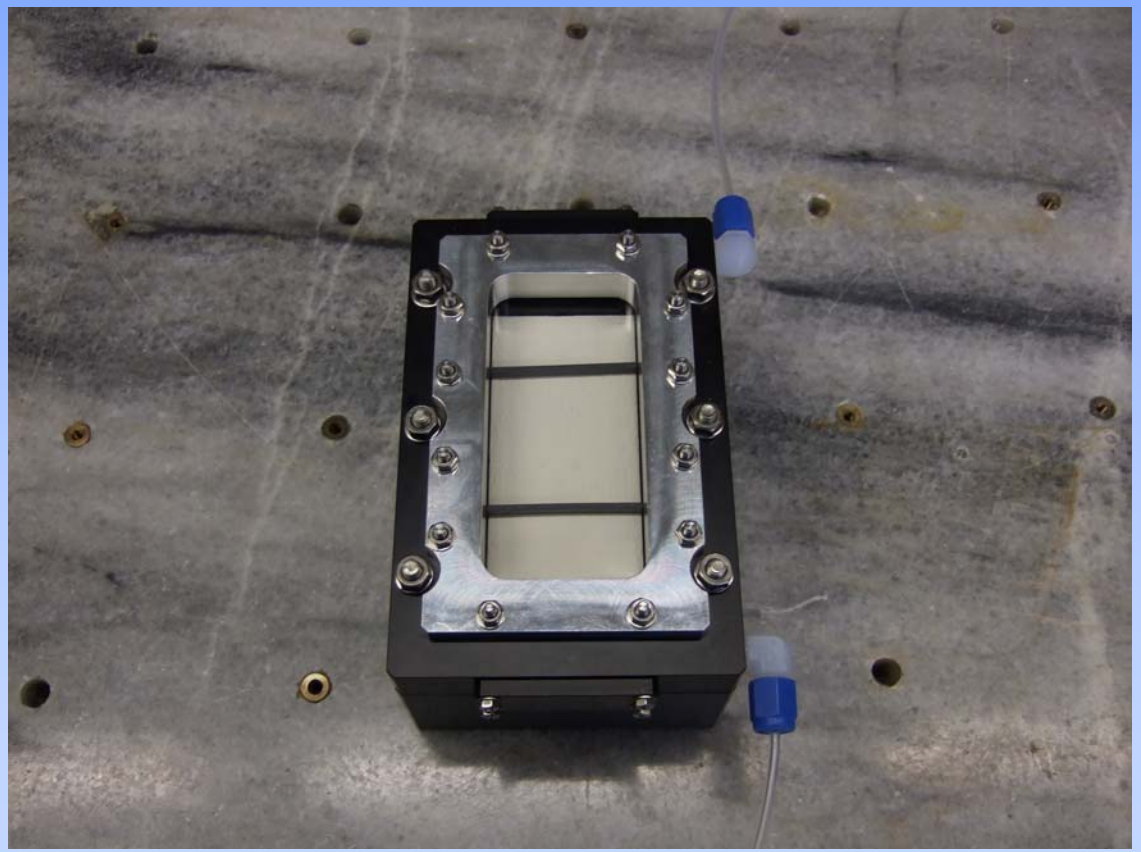
Lesson learnt:

➔ Before expensive applications, please test for deactivation in the real atmosphere…

Results laboratory

Lesson learnt:

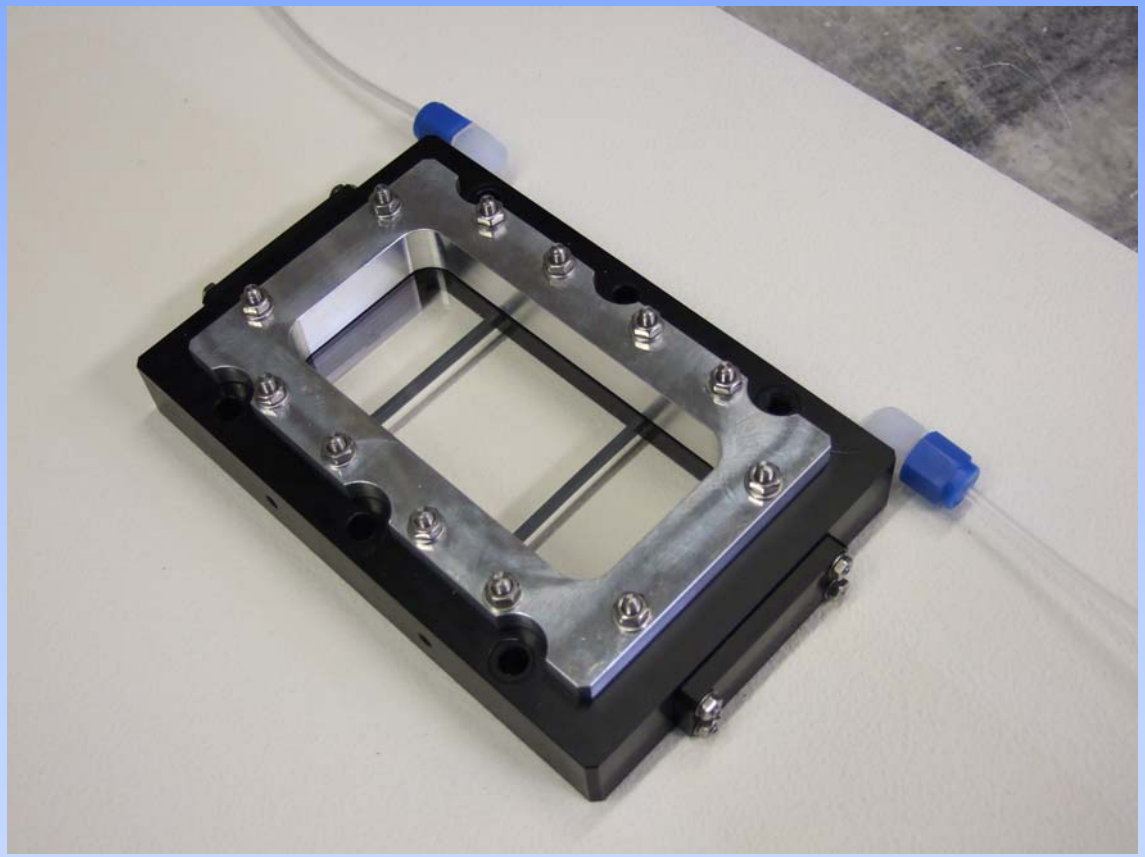
➔ Before expensive applications, please test for deactivation in the real atmosphere…



Results laboratory

Lesson learnt:

➔ Before expensive applications, please test for deactivation in the real atmosphere…



Results Tunnel

Theoretical remediation on the deactivated material:

- ➔ **$\Delta NO = -0.4$ %**
- ➔ NO_2 even less: $\gamma(NO_2)_{photo} < \gamma(NO)_{photo}$

❍ In excellent agreement with the experimental results:
NO_x reduction ≤2%

Simple "Model" Tool: *(kleffman@uni-wuppertal.de)*

❍ Input:

- lab data: k/γ/ν (e.g. ISO)
- tunnel parameters: geometry, UVA, WS, r.h.

➔ Upper limit remediation can be calculated for any tunnel…

Conclusion Tunnel

- No reduction of NO_x measurable (≤2%)

➔ **My personal view: photocatalysis makes no sense in a tunnel.**

Reasons:

- Deactivation of the surfaces under the high pollution and low UV irradiance
- High energy consumption (here ~0.5 kW/m tunnel to get 1.6 W/m^2 UVA)

➔ 0.5 MW for 1 km tunnel…

For details to the tunnel results:
Gallus et al., *Build. Environ.*, 2015, **84**, 125-133

- Photocatalytic decomposition of pollutants should be demonstrated
  - Laboratory studies (NO_x, NO_y, O_3, VOC)
  - Smogchamber studies (NO_x, NO_y, O_3, VOC, particles)
  - Field studies (NO_x, NO_y , O_3, VOC, particles)
    - Leopold II tunnel in Brussels
    - Street canyon Bergamo/Italy

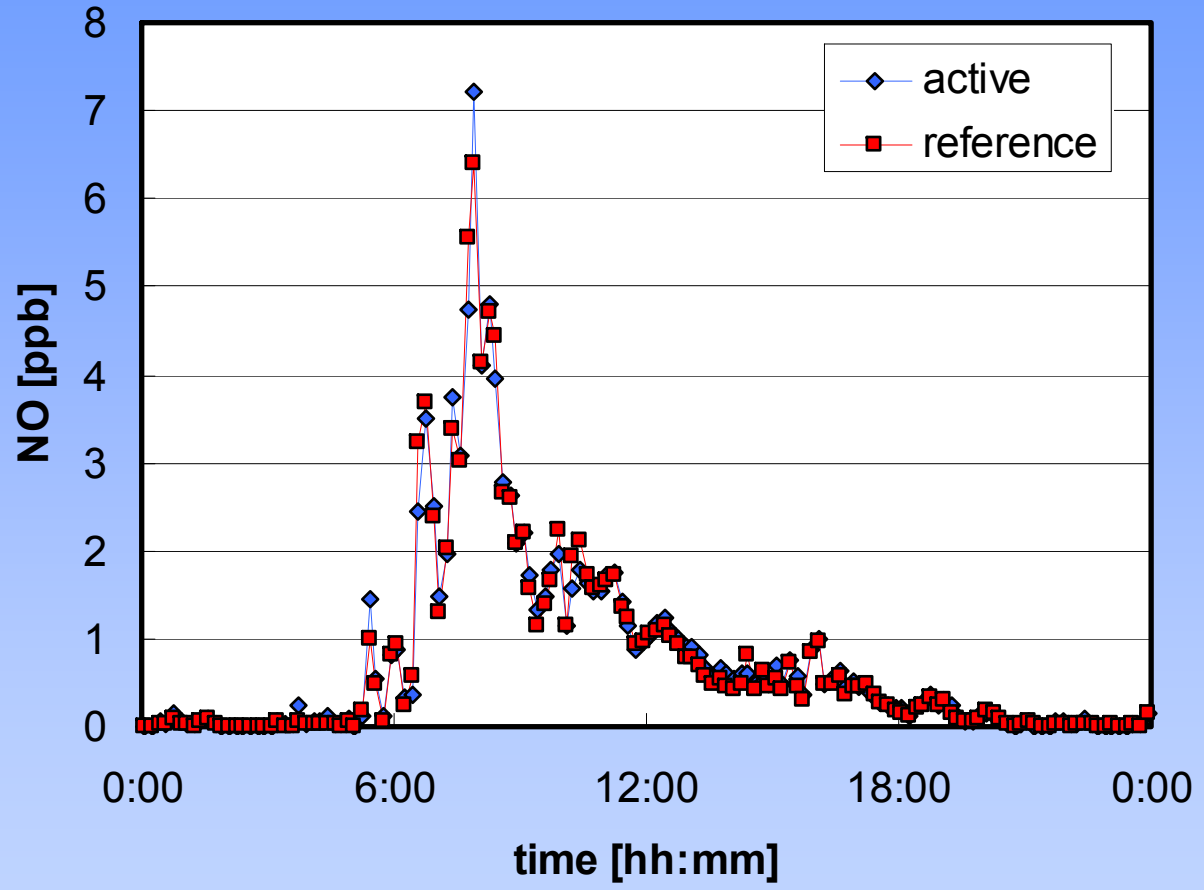
Experimental Canyon

Experimental Canyon

- Two canyons each 5x5x53 m (active/not-active)

Results Canyon

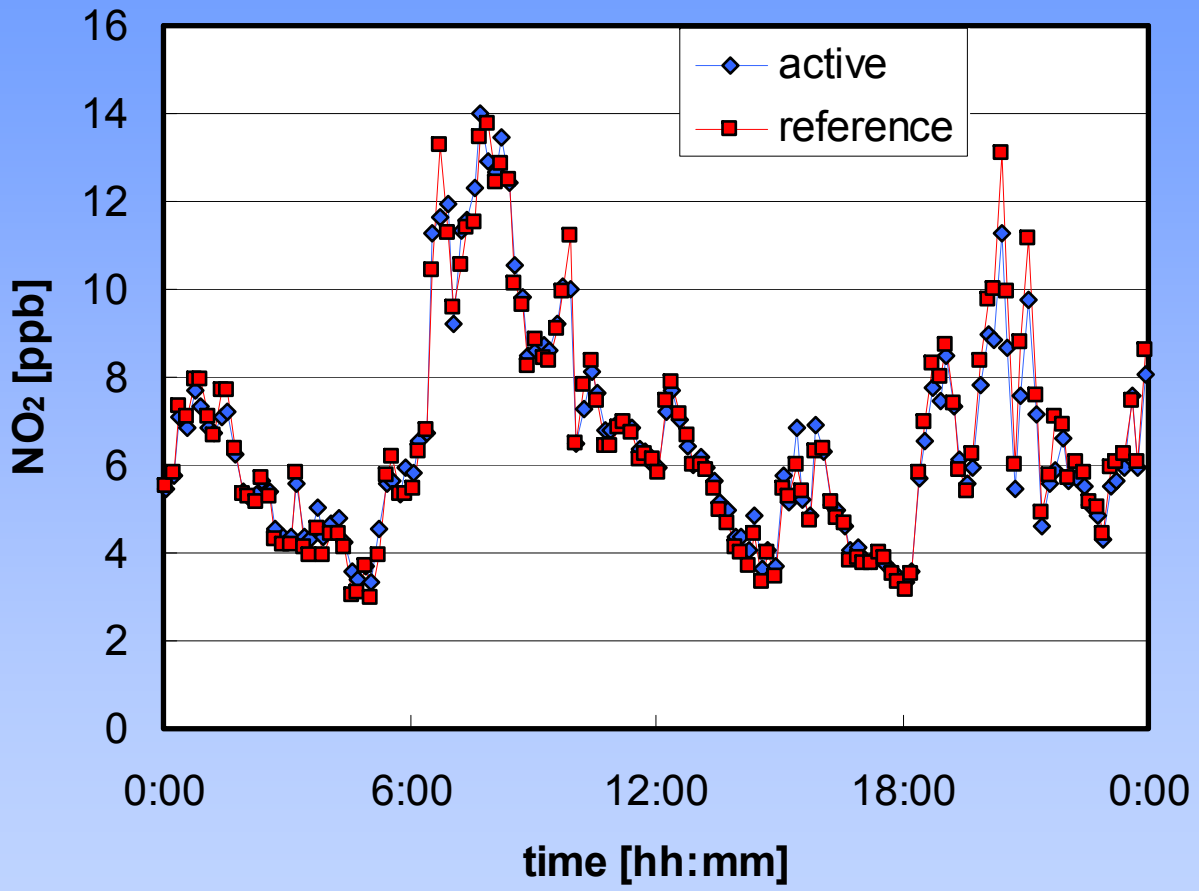
Average day all data: ***NO***



NO: *Active/Reference*:
0.77 / 0.76 ppb ➔ +1.6%; (only daytime: +0.6%)

Results Canyon

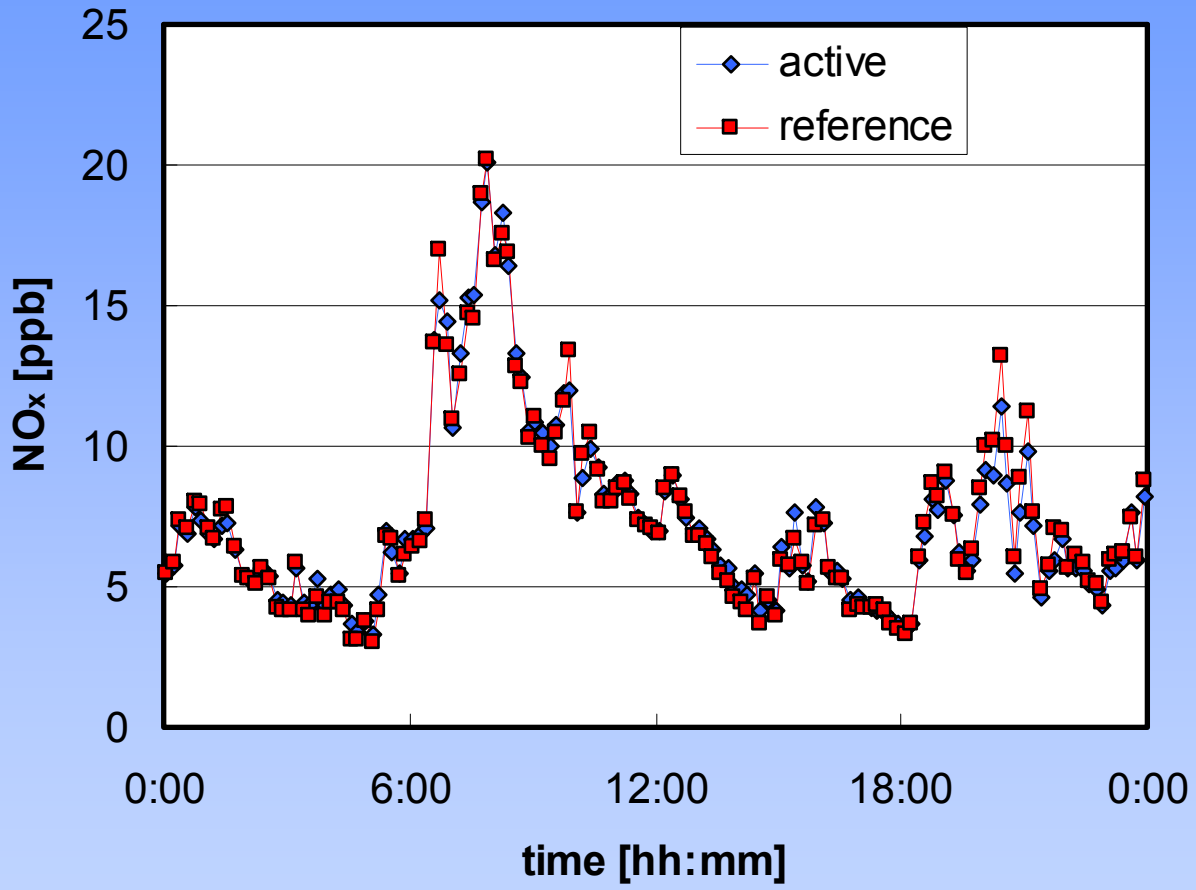
Average day all data: NO_2



NO_2: *Active/Reference*:
6.55 / 6.59 ppb ➔ *-0.7%*; (only daytime: +0.2%)

Results Canyon

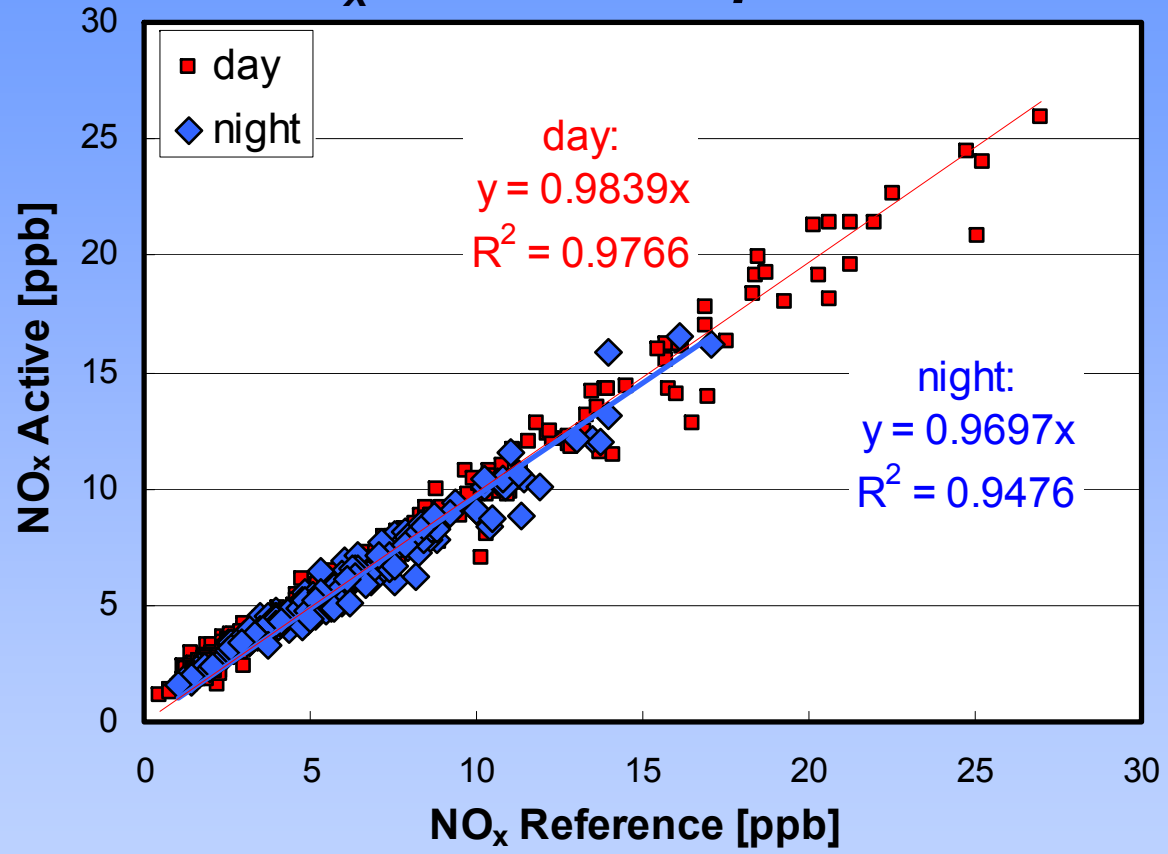
Average day all data: NO_x



NO_x: *Active/Reference*:
7.32 / 7.35 ppb ➔ *-0.4%*; (only daytime: +0.3%)

Results Canyon

All data: *NO_x correlation plot*



➔ Slope “Day” = slope “Night”

➔ No photocatalysis

➔ Precision errors ≤2 %

Conclusion Canyon

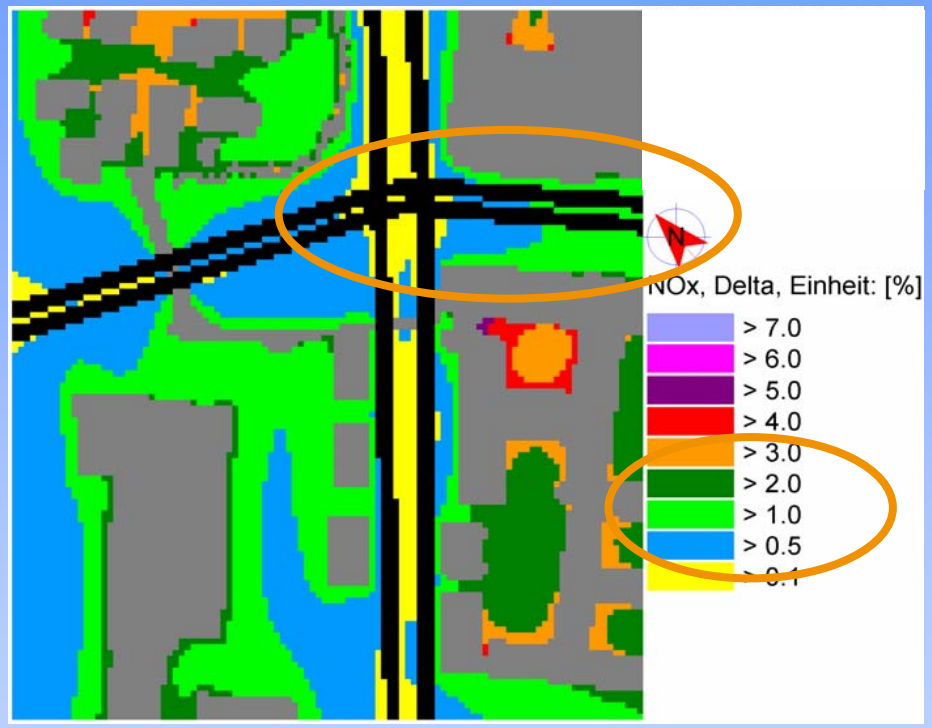
- Photocatalytic NO_x reduction **≤2%** (from correlation plots Active/Reference; day and night)
- ➔ Photocatalytic NO_x remediation not (…) confirmed
- Upper limit in agreement with almost all known studies, when results are extrapolated to realistic conditions (see introduction…)
- ➔ Based on available studies a realistic NO_x reduction in a typical main street canyon of ~2 % is estimated

For details to the canyon results:
Gallus et al., *Build. Environ.*, 2015, submitted.

- Photocatalytic decomposition of pollutants should be demonstrated
  - Laboratory studies (NO_x, NO_y, O_3, VOC)
  - Smogchamber studies (NO_x, NO_y, O_3, VOC, particles)
  - Field studies (NO_x, NO_y , O_3, VOC, particles)
    - Leopold II tunnel in Brussels
    - Street canyon Bergamo
  - 3D Modell calculations
    - Tunnel: good agreement with the exp. results
    - Street canyon: under evaluation…

Model results

- Model results from another study (Flassak et al.) on the expected reduction in a city center



- Annual average NO_x-reduction in canyons: **1-3 %**…
- Fits well with estimations from available canyon studies

Conclusion

- Generally, photocatalysis can be recommened for the improvement of the urban air quality

➔ Harmful pollutants are oxidized + less formation of secondary species (PAN, O_3,...)

- However, some commercial materials also emit harmful products, e.g. HONO, HCHO, O_3

➔ Reaction products should be include in ISO/CEN/etc. standards (Ifang et al., *Atmos. Environ.*, 2014, **91**, 154-161)

- Deactivation under polluted conditions possible

➔ Tests should be performed in the real atmosphere, e.g. ISO test in a tunnel before application (+definition of threshold activities in the standards!)…

Conclusion cont.

- Degradation rates on active surfaces in the real atmosphere are typically limited by the transport

➔ Expected average NO_x-reduction in a typical main street canyon **~2 %**

- Disappointing?
- Should be compared with other measures, like for example: “Euro standards”, “low emission zones“, etc. on a cost-benefit analysis basis

➔ For the “urban NO_2 problem” photocatalysis may be still a competitive approach (+self-cleaning, +”heat island”)

➔ **But:** will not solve the urban NO_2 problem alone…

Acknowledgement

- All the PhotoPAQ team
- European Commission through the Life+ grant LIFE 08 ENV/F/000487 PHOTOPAQ
- Ministry of the Brussels-Capital Region – Brussels Mobility

BRUXELLES MOBILITÉ
SERVICE PUBLIC RÉGIONAL DE BRUXELLES

UNIVERSITY OF WUPPERTAL

BERGISCHE UNIVERSITÄT WUPPERTAL

Thanks for your attention