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Photocatalytic abatement results from a model street canyon

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Abstract During the European Life+ project PhotoPAQ (Demonstration of Photocatalytic remediation Processes on Air Quality), photocatalytic remediation of nitrogen oxides (NO_x), ozone (O₃), volatile organic compounds (VOCs), and airborne particles on photocatalytic cementitious coating materials was studied in an artificial street canyon setup by comparing with a colocated nonactive reference canyon of the same dimension (5×5×53 m). Although the photocatalytic material showed reasonably high activity in laboratory studies, no significant reduction of NO_x, O₃, and VOCs and no impact on particle mass, size distribution, and chemical composition were observed in the field campaign. When comparing nighttime and daytime correlation plots of the two canyons, an average upper limit NO_x remediation of ≤2 % was derived. This result is consistent only with three recent field studies on photocatalytic NO_x remediation in the urban atmosphere, whereas much higher reductions were obtained in most other field investigations. Reasons for the controversial

results are discussed, and a more consistent picture of the quantitative remediation is obtained after extrapolation of the results from the various field campaigns to realistic main urban street canyon conditions.

Keywords Air pollution · Photocatalysis · TiO₂ · Outdoor application · Street canyon

Introduction

Urban air quality is of high importance for human health since the majority of the world's population lives inside metropolitan areas. Different methods to improve urban air quality have been implemented in the past, for example, improved combustion and exhaust after-treatment technologies and implementation of low emission zones, which typically have a positive impact on the environment. However, while

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concentrations of nitrogen oxides (NO_x) have been significantly reduced during the last three decades in European cities, annual averaged levels of nitrogen dioxide (NO_2) are stagnating. In addition, urban NO_2 levels are still commonly higher than the actual annual threshold limit value of $40 \mu\text{g m}^{-3}$ (~ 20 ppb) set by the European Commission (Carslaw et al. 2007; Kurtenbach et al. 2012). Besides NO_x , threshold limits for particles and ozone (O_3) are also often exceeded in Europe (EEA 3/2014; 5/2014) as a result, at least in part, of the high levels of precursors like volatile organic compounds (VOCs) (Finlayson-Pitts and Pitts 2000; Beekmann and Vautard 2010).

In view of the adverse effects of air pollution on human health, further improvement of the urban air quality is necessary. To this end, titanium dioxide (TiO_2)-based photocatalytic surfaces have been developed and tested over the two last decades, both, at a laboratory scale and in the open atmosphere as an alternative technical means for the remediation of NO_x (Maggos et al. 2008; Chen and Poon 2009; Ohama and Van Gemert 2011; Chen et al. 2012; Schneider et al. 2014), VOCs (Pichat et al. 2000; Strini et al. 2005, De Richter and Caillol 2011; Schneider et al. 2014), O_3 (De Richter and Caillol 2011), and particles (De Richter and Caillol 2011; Costa et al. 2012; Chang et al. 2013).

While typically an efficient reduction of pollutants, for example, NO_x , is observed in laboratory experiments on commercial photocatalytic surfaces, controversial results exist concerning the extent of NO_x reduction on treated surfaces in the real urban atmosphere. Two field trials in artificial model street canyons showed high NO_x remediation of 25–30 % (Fraunhofer 2010) and 40–80 % (PICADA 2006; Maggos et al. 2008), respectively. These studies are in general agreement with two experiments in real urban street canyons for which NO_x reductions of 19 % (Ballari and Brouwers 2013) and 26–66 % (Guerrini and Peccati 2007) were observed. In contrast, the measured NO_x reduction was below the measurement precision errors in recent field projects using photocatalytic noise protection barriers at Putten, Netherlands (IPL 2010) and Grenoble, France (Tera 2009), in agreement with a recent study using active pavement blocks on the sidewalks of an urban street in Fulda, Germany (Jacobi 2012). Reasons for these contradictory results are still under discussion, and further field studies are necessary in order to better accurately assess the impact of this technology on air quality.

Besides the reduction of primary pollutants by photocatalytic surfaces, the potential formation of harmful by-products is another controversial issue. While it is generally assumed that for example NO_x is quantitatively converted into nitrate (Laufs et al. 2010), some recent studies on pure photocatalysts and on self-cleaning window glass also observed the formation of the intermediate nitrous acid (HONO) (Gustafsson et al. 2006; Ndour et al. 2008; Beaumont et al. 2009; Monge et al. 2010a), which is even more harmful than the primary

reactants NO and NO_2 (Pitts 1983). In addition, renoxification and ozone formation originating from photocatalytic decomposition of adsorbed nitrate was recently observed in laboratory experiments (Monge et al. 2010a, b). Also, harmful oxygenated reaction products, for example aldehydes (Salthammer and Fuhrmann 2007; Auvinen and Wirtanen 2008; Geiss et al. 2012) were detected during the photocatalytic degradation of VOCs besides the expected end-product CO_2 .

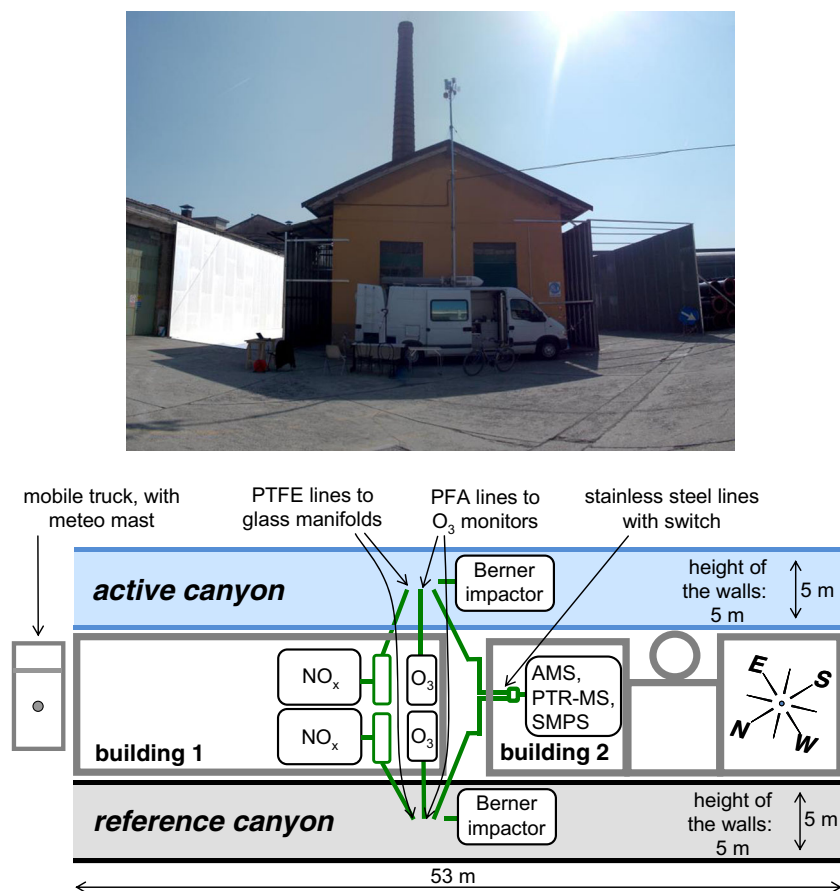
The European Life+ project PhotoPAQ (*Demonstration of Photocatalytic remediation Processes on Air Quality*) (PhotoPAQ 2014) was aimed at demonstrating the possible usefulness of photocatalytic construction materials for air purification purposes in the urban environment. Besides a tunnel campaign, which is presented elsewhere (Gallus et al. 2015; Boonen et al. 2015), a two-step field campaign was organized in an artificial model street canyon in Petosino, Italy, from April to May 2013. Photocatalytic cementitious coating materials were applied on the side walls and on the ground surface of the test section. The effect of the active coating on a large set of air pollutants was assessed, from which results for NO_x , VOCs, O_3 , and particles are presented here.

Experimental

Field site

Originally, the PhotoPAQ consortium intended to study photocatalytic air remediation in a real street canyon situation. However, during the course of the project, it turned out to be difficult to find a field site for which (a) both, the street surfaces and the walls of the buildings could be covered with the active materials to obtain high active surface to volume ratios (S_{active}/V) and a quantifiable pollutant reduction, and (b) a collocated nonactive reference site of similar geometry and pollution level was available to allow for correction of the meteorological variability in pre- and after-application measurement campaigns. Thus finally, the consortium decided to set-up two artificial street canyons of the dimensions $5 \times 5 \times 53$ m (width \times height \times length) at an industrial site belonging to the industry partner Italcementi in Petosino – Sorisole, a few kilometers north of Bergamo, Italy. To create conditions as similar as possible in both canyons, the walls were constructed of fiber cement boards mounted on metal scaffolding placed in front of the original buildings (see Fig. 1). During the *control campaign* (11th–17th April 2013), the surfaces of both untreated canyons were photocatalytically inactive and consisted of the fiber cement walls and the original concrete street surfaces. During the *main campaign* (30th April–7th May 2013), the walls and ground surfaces of one of the canyons (hereafter referred to as *active canyon*) were coated with a photocatalytically active mortar (Italcementi, TX-Active

Fig. 1 Model street canyon site in Petosino



Skim Coat Boosted, hereafter: *TX-Boosted*) specially designed for application in the PhotoPAQ project. The other canyon (hereafter referred to as *reference canyon*) was not modified.

The two street canyons were separated by two buildings (Fig. 1) which housed the analytical instruments. NO_x and some other gas phase pollutants were sampled through 7 m long 0.95 cm inner diameter (i.d.) polytetrafluoroethylene (PTFE) inlet lines to insure chemical inertia. These lines were connected to glass manifolds in *building 1* (Fig. 1) from which two sets of instruments sampled via shorter 0.4 cm i.d. perfluoroalkoxy alkane (PFA) tubes. In addition, a pump was connected to each manifold in order to achieve sufficient air flow, thus minimizing the residence time in the sampling inlet. The overall flow was $>1 \text{ m}^3 \text{ h}^{-1}$ resulting in a residence time in the sampling inlet of $<10 \text{ s}$. During most of the measurements, the inlets of the main sampling lines were positioned in the middle of the street canyons 2.5 m away from both walls at a height of 3 m and were protected against rain by down-facing plastic funnels. Toward the end of the main campaign (04th May 2013, 23:20 h), both inlets were moved to only 25 cm away from the east walls while maintaining a height of 3 m. Because of a leak in one of the main sampling lines during the control campaign, only NO_x data from the main campaign with active surfaces (30th April–7th May 2013) are presented here. For the other pollutants, for

which separate sampling lines were used, results from both campaigns could be evaluated and presented.

O_3 was sampled through two PFA sampling lines of 10 m length (0.4 cm i.d.), with each inlet situated in the middle of the street canyons 2.5 m away from both walls at a height of 3 m.

As a result of the limited availability of some instruments used in the campaigns, online measurements of particles and VOCs could only be performed by single instruments (see below). Hence, a specific stainless steel sampling line equipped with an automatic switching system was developed, which allowed alternative measurements (10 min switch period) in the two canyons (see Fig. 1) with inlets near to the other sampling lines. Although the data gathered from the two canyons via the aforementioned instrumentation were not simultaneous, for the needs of quantification of the photocatalytic remediation, this setup removed instrumental uncertainties.

For the Berner impactors, which were installed directly inside the canyons (see below), no additional inlet lines were used.

Monitored parameters

Nitrogen oxides (NO_x)

NO_x were measured by the chemiluminescence technique which is directly selective only to NO. For the additional

detection of NO_2 , photolytic converters were used in the NO_x channel of the instruments. For the present urban background study, negative interferences due to the presence of photolabile hydrocarbons (Villena et al. 2012) can be neglected leading to the selective detection also of NO_2 .

Two different chemiluminescence instruments, ECO PHYSICS CLD 770 AL ppt (ECO-1) and ECO PHYSICS CLD 88p (ECO-2) were used in this study at the two sites. For the ECO-1, a custom-made blue-light converter was used (converter efficiency, $31 \pm 1\%$), while for the ECO-2, a commercial metal halide lamp converter was applied (ECO PHYSICS PLC 860, converter efficiency, $78 \pm 2\%$). The instruments showed typical detection limits of 50 ppt (ECO-1) and 35 ppt (ECO-2), precisions of $\sim 2\%$ (both), accuracies of $\sim 7\%$ for NO (both) and $\sim 10\%$ (ECO-1) and 9% (ECO-2) for NO_2 . The NO channels of the instruments were calibrated with a certified NO calibration gas mixture (Messer, 50 ppm) diluted by a gas phase titration unit (Ansyc K-GPT). The NO-mixing ratio of the GPT unit was validated by measurement against an undiluted certified NO calibration gas mixture (Messer, 800 ppb) using the ECO-2. NO_2 was calibrated with a certified NO calibration gas mixture (Messer, 50 ppm) and titration with ozone ($\text{NO} + \text{O}_3$) using the gas phase titration unit.

Volatile organic compounds (VOCs)

Measurements were carried out using a commercial SRI-PTR-TOF-MS 8000 (Selective Reagent Ionization Proton Transfer Reaction Time of Flight Mass Spectrometer) instrument from Ionicon Analytik GmbH (Innsbruck, Austria). The PTR-TOF-MS sampled continuously with a flow rate of $200 \text{ cm}^3 \text{ min}^{-1}$ (0°C , 1 atm) through a 1.5 m long polyether ether ketone (PEEK) inlet of 0.16 cm i.d. from the end of the switchable inlet line. No particle filter was used at the PEEK inlet to avoid artifacts from possible adsorption of organics. Internal calibration of the TOF data and peak extraction were performed according to the procedure described in detail elsewhere (Lindinger et al. 1998). PTR-TOF-MS spectra were collected with a time resolution of 2 min, and the measurements were performed using the H_3O^+ ionization mode. VOC mixing ratios were calculated according to prior calibrations using a gas calibration standard containing 57 VOCs (Restek). Typical detection limits, precisions, and accuracies for the selected VOCs were 10 ppt, 3 %, and 6 %, respectively. Ten-minute average concentration measurements were used for the analysis presented in this manuscript. The following VOCs were selected as typical organic pollutants and summed to quantify the photocatalytic degradation of VOCs: butene, pentene, benzene, toluene, xylene, trimethylbenzene, diethylbenzene, acetone, and propanol.

Ozone (O_3)

Ozone concentrations in both canyons were measured continuously with two UV absorption ozone analyzers (O341M, Environnement S. A., France) with an internal integration time of 1 min. The detection limit and accuracy were 0.5 ppbV and 5 %, respectively. The two ozone monitors were provided with their own Teflon inlet lines to avoid sampling flow perturbation from the powerful pump of the common inlet manifold.

Particles

Two approaches were utilized to measure size distribution, mass, and chemical composition of airborne particles.

Offline measurements The offline measurements were performed using 5-stage Berner impactors in each canyon (see Fig. 1). Sampling was performed at a height of 1.5 m, next to the sampling inlets of the gas phase compounds with 12 h integrated measurements only during daytime (7 a.m.–7 p.m.). The sampled volume was 108 m^3 per run. The sampled size segregated particles were stored in a freezer and further analyzed in the laboratory after the campaign. The 5-stage Berner impactor and the different analytical procedures to derive the chemical composition are described in detail elsewhere (Scheinhardt et al. 2013).

Online measurements Because impactor measurements can only provide averaged values of the aerosol size distribution and composition, a scanning mobility particle sizer (SMPS) and a high-resolution time-of-flight aerosol mass spectrometer (AMS) were also deployed. Technical details on the SMPS and AMS instruments can be found elsewhere (Birmili et al. 1999; Canagaratna et al. 2007). The accuracy of the particle number and volume concentrations were $\pm 10\%$, and detection limits of the AMS were as follows: organics, 90 ng m^{-3} ; nitrate, 25 ng m^{-3} ; sulfate, 24 ng m^{-3} ; and ammonium, 127 ng m^{-3} .

Physical parameters

Meteorological measurements for temperature (T), humidity (r.h.), pressure (p), wind speed (WS), and wind direction (WD) were performed using three meteorological stations located at the top of a 9 m high mast installed on a mobile truck at the north-east end of the field site (Young) and inside both canyons (Davis Instruments, Vantage Pro2TM). Specified precisions and accuracies were as follows: WS: 0.1 m s^{-1} ; WD: 1° ; T: 0.1°C ; r.h.: 1 %; and WS: 1 m s^{-1} ; WD: 3° ; T: $0.5\text{--}1^\circ \text{C}$; r.h.: 3–4 %, respectively.

Light intensity was measured by different instruments inside the active canyon and also on the top of the mast. Inside

the canyon, the photolysis frequency of NO_2 , $J(\text{NO}_2)$, was measured with a filter radiometer (Meteoconsult). In addition, a filter radiometer (LSI SpA, model C502UVA) was used to measure the UVA irradiance level with an accuracy $\pm 12\%$ and a precision of $\pm 1 \text{ W m}^{-2}$. Both detectors were installed near to the sampling inlets of the active canyon. In addition, $J(\text{NO}_2)$ and the spectral actinic flux were measured on the mast by a filter radiometer and a spectroradiometer with an electronically cooled Charge Coupled Device (CCD) detector (both Meteoconsult), respectively.

Quality assurance (QA)

During each campaign, the NO_x instruments were calibrated by certified calibration gas mixtures and in addition also intercalibrated using ambient air from one common inlet before and after the campaigns. While the calibration of the NO_x instruments at high NO_x levels of 50–500 ppb exhibited the expected linear response, the intercalibration of NO in ambient air resulted in a nonlinear correlation between both instruments below ~ 1 ppb. Since the reason for this nonlinearity could not be clarified, the NO channel from the reference canyon (ECO-2) was harmonized according to the intercalibration exercise to obtain a similar response for both instruments during the main measurement campaign. Thus, accuracy errors of the instruments at very low NO_x concentrations may be higher than the stated 7 % for NO and 10 %/9 % (ECO-1/ECO-2) for NO_2 , respectively.

As it took a significant time to identify an inlet pressure problem of the O_3 instruments when using the main sampling manifold, the common intercomparison measurements were not considered long enough to allow a precise harmonization of the two ozone monitors' responses. To overcome this uncertainty, they were intercalibrated by placing their inlets side by side for more than 1 week during the period between the control and the main campaign. Based on the linear regression analysis of this intercalibration, the data of the ozone monitor from the active canyon was harmonized to the response of the one from the reference canyon.

For particles and VOCs, single instruments were used for both canyons. Thus, here, no intercomparisons were performed, and the errors for the photocatalytic remediation are limited only by the precision errors of each instrument.

Experimental results

Field measurement data

Nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$)

Figure 2 shows all 10 min averaged NO_x and UVA data from the main measurement campaign with the

photocatalytically active surfaces during May 2013 in Petosino. NO_x levels varied from 1 to 30 ppb, and thus, the field site represented only a moderately polluted urban background situation. During the first part of the campaign (1st–4th May 2013), the weather was typically good with only partial cloud coverage and high UVA irradiance of up to 40 W m^{-2} inside the canyon. From the morning of the 5th May to the end of the campaign, the weather became less favorable for photocatalysis with higher cloud coverage and lower UVA levels. The wind speed (WS) measured inside the active canyon was typically very low ($< 1 \text{ m s}^{-1}$), while the WS measured at 9 m height on the meteorological mast showed typical diurnal variation in the range of $0\text{--}2.5 \text{ m s}^{-1}$ with highest WS in the afternoon and with a daytime average WS of $\sim 1.5 \text{ m s}^{-1}$. Hence, for at least the first 4 days of the campaign, the low WS and high UVA favored photocatalytic remediation inside the canyon. However, from the difference of the 10 min averaged NO_x data between both canyons, on average, no significant remediation is visible (see Fig. 2). This general observation also did not change when the sampling inlets for NO_x were moved close to the side walls at 23:20 h on the 04th May 2013.

From all the NO , NO_2 and NO_x data campaign averaged diurnal profiles were derived which are shown in Fig. 3. Except for the morning rush-hour peak, NO levels were very low (< 2 ppb) and much lower compared to NO_2 . When comparing the diurnal NO , NO_2 and NO_x profiles of the two canyons, again visually no significant differences are observed even during daytime, when photocatalysis should be active. In addition, all campaign data, but separately also all daytime (6:00–20:30 local time) and nighttime (20:30–6:00 local time) data of NO , NO_2 and NO_x were averaged, respectively (see Table 1).

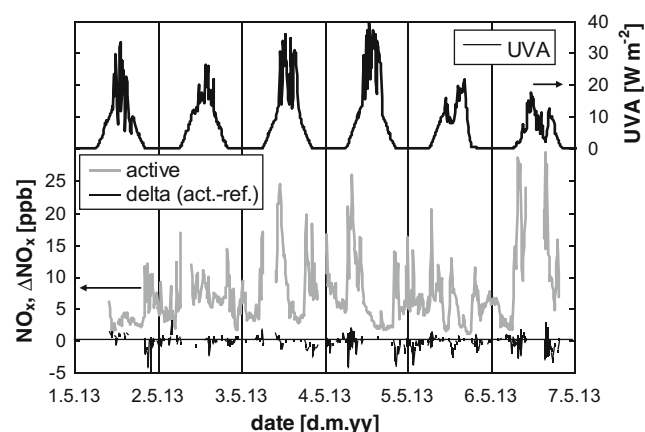


Fig. 2 10 min averaged NO_x concentration in the active canyon, difference between both canyons and UVA irradiance during the main field campaign in Petosino

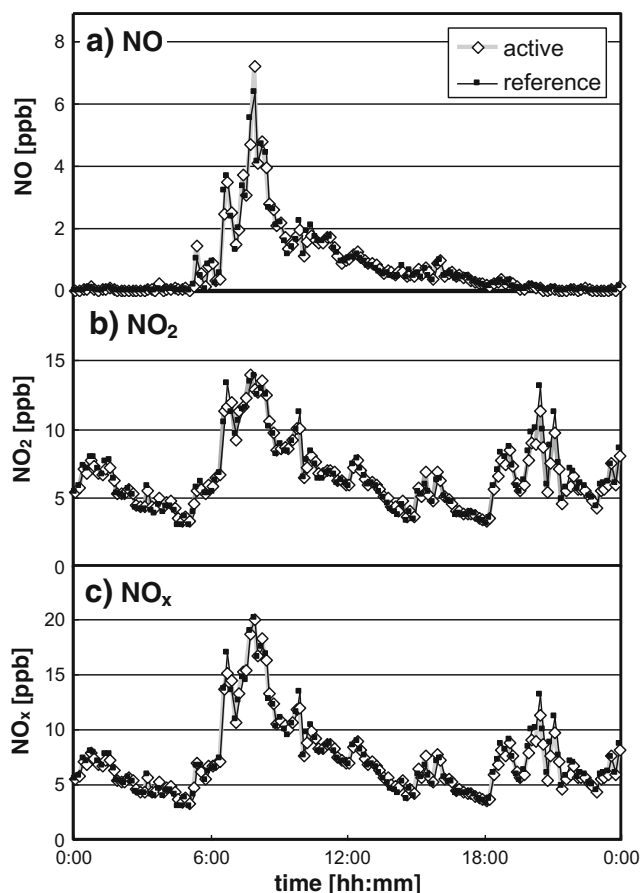


Fig. 3 Diurnal averaged profiles of NO, NO₂, and NO_x in both canyons in Petosino

Within the experimental errors, all the corresponding concentrations are similar in both canyons, and thus, the corresponding average relative differences ((1-reference/

Table 1 Campaign averaged concentrations of NO, NO₂ and NO_x in both canyons and relative concentration differences. For the latter, negative values imply a remediation in the active canyon. Errors reflect only the 2σ precision of the instruments

	NO	NO ₂	NO _x
All data			
Active [ppb]	0.77±0.10	6.55±0.30	7.32±0.32
Reference [ppb]	0.76±0.08	6.59±0.27	7.35±0.30
(1-reference/active)×100 [%]	2±17	-0.7±6.1	-0.4±6.0
Daytime (6:00 – 20:30 local time)			
Active [ppb]	1.21±0.11	7.11±0.32	8.33±0.36
Reference [ppb]	1.21±0.09	7.10±0.29	8.31±0.34
(1-reference/active)×100 [%]	0.6±11.5	0.2±6.1	0.3±6.0
Nighttime (20:30 -6:00 local time)			
Active [ppb]	0.09±0.10	5.68±0.24	5.77±0.24
Reference [ppb]	0.07±0.07	5.82±0.24	5.89±0.25
(1-reference/active)×100 [%]	23±150	-2.4±5.9	-2.0±5.9

active)×100) cannot be distinguished from zero. More interestingly, the relative changes between both canyons—which may also result from general differences in the pollution levels or from systematic differences between the two instruments' responses—were not becoming more negative when the daytime was compared with the nighttime data. From the combined precision errors of the instruments, an upper limit for NO_x remediation of ≤6 % can be derived (see Table 1).

The weather during the last 2 days of the main campaign was partially rainy and compared to the first days much lower UVA levels were observed (see Fig. 2). Therefore, the period 1st–4th May 2013 with a higher expected photocatalytic remediation was separately evaluated. All 10 min averaged NO, NO₂ and NO_x data from the active canyon were plotted against the corresponding data from the reference canyon for daytime and nighttime separately (see Fig. 4), the resulting slopes of which are listed in Table 2. While deviations of the individual slopes from unity may again be explained by (a) systematic differences between the instruments' responses and (b) potential general pollution differences between both

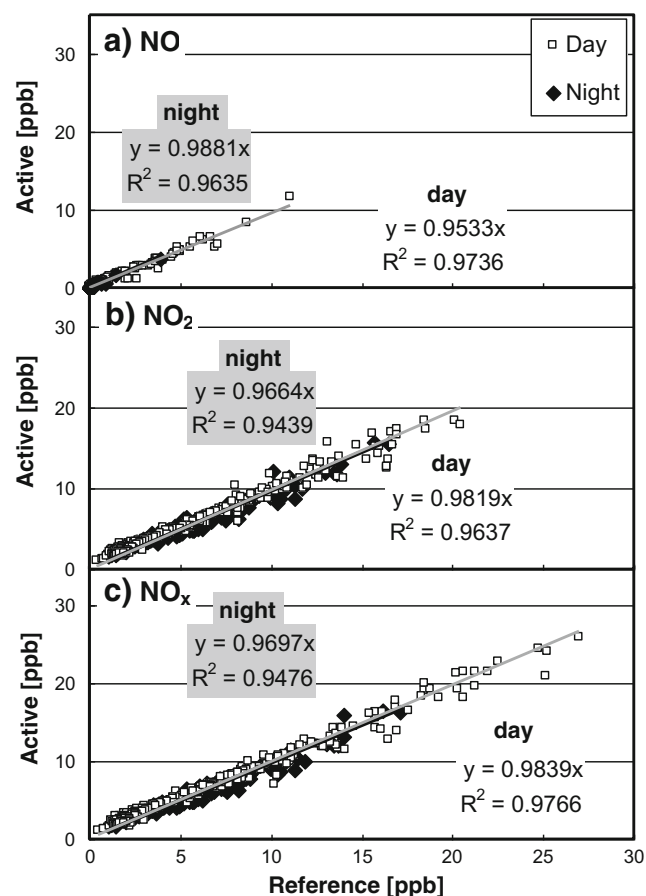


Fig. 4 Correlation plots of the active against the reference site for NO, NO₂ and NO_x during nighttime and daytime of the period 1st–4th May 2013

Table 2 Slopes from the correlation plots of the active against the reference canyon for NO, NO₂ and NO_x during nighttime and daytime derived from Fig. 4

Pollutant	Daytime	Nighttime	(Day-night)×100 [%]
NO	0.953±0.016	0.988±0.029	- 3.5±3.3
NO ₂	0.982±0.013	0.966±0.014	+1.6±1.9
NO _x	0.984±0.011	0.970±0.014	+1.4±1.8

Errors reflect only 2σ precisions from the correlations. The differences of the slopes between daytime and nighttime are considered here as the average changes induced by the photocatalytic surfaces, for which negative values imply a photocatalytic remediation

canyons, the comparison of the slopes between daytime and nighttime should only reflect the photocatalytic effect independent of the artificial differences (a) and (b). However, even when using this more precise correlation data, the remediation of NO₂ and NO_x cannot be distinguished from zero within the measurement precision errors. It is only for NO that a small photocatalytic remediation can be inferred (ca. -3.5 %, see Table 2). In conclusion, when comparing daytime and nighttime correlation data, an even lower upper limit NO_x remediation of ≤2 % can be derived from the present field data.

Volatile organic compounds (VOCs)

Figure 5 shows correlation plots of the sum of the VOC concentrations from both canyons obtained during the control and main campaign. For the control campaign with nonactive surfaces, the measurements reveal no significant difference between the two sites (slope active against reference: 0.966±0.028) confirming the expected general similarity of the two collocated canyons. However, similar results were also obtained for the main measurement campaign with the active canyon

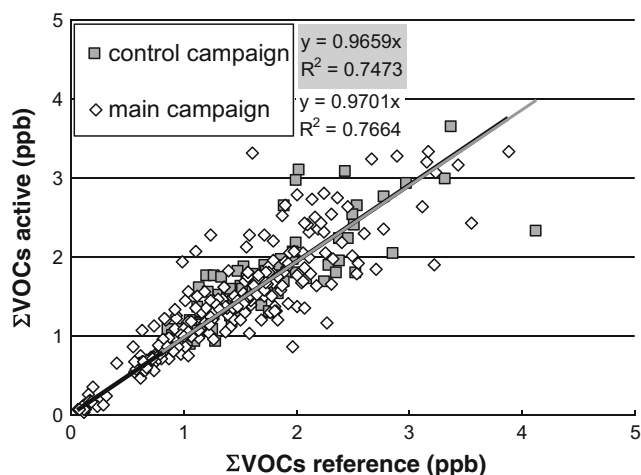


Fig. 5 Correlation plots of the sum of selected VOCs between both canyons for the control (14th–16th of April) and main campaign (3rd–7th of May). VOCs considered: butene, pentene, benzene, toluene, xylene, trimethylbenzene, diethylbenzene, acetone and propanol

(slope active against reference, 0.970±0.029) indicating no significant degradation of the selected VOCs by the photocatalytic material. Within the experimental errors, the same results were also obtained when single VOCs were considered. From the combined 2σ precision errors of the correlation data and of the PTR-TOF-MS, an upper limit for the photocatalytic remediation of the selected VOCs of ≤5 % was derived.

Ozone (O₃)

The correlation of the O₃ data from both canyons collected during the control campaign shows that the two artificial street canyons was comparable also with respect to the ozone levels. When all the campaign data were used, only a small difference between the two sites was discernible, with slightly higher values in the active canyon (slope active against reference, 1.046±0.016, see Fig. 6). When only the daytime data was considered, an even smaller difference was observed (slope, 1.026±0.024). Due to the fast Leighton equilibrium between O₃ and NO_x during daytime (Finlayson-Pitts and Pitts 2000), it can be concluded that both canyons were under the influence of similar pollutant sources. Thus—although not directly measured—this indicates also similar NO_x levels in both canyons in the absence of photocatalysis, in good agreement with the nighttime NO_x results from the main campaign (see Sect. “Nitrogen Oxides (NO_x = NO + NO₂)”).

During the main campaign with active surfaces again, no remediation of O₃ was observed. The correlation using all the campaign data resulted in exactly the same slope as obtained in the control campaign (slope active against reference, 1.038±0.021, see Fig. 6). When using only daytime data, the correlation slope was even higher compared to the control campaign (slope active against reference, 1.067±0.030), with the difference being, however, within the combined measurement precision errors. Higher O₃ levels in the active canyon during

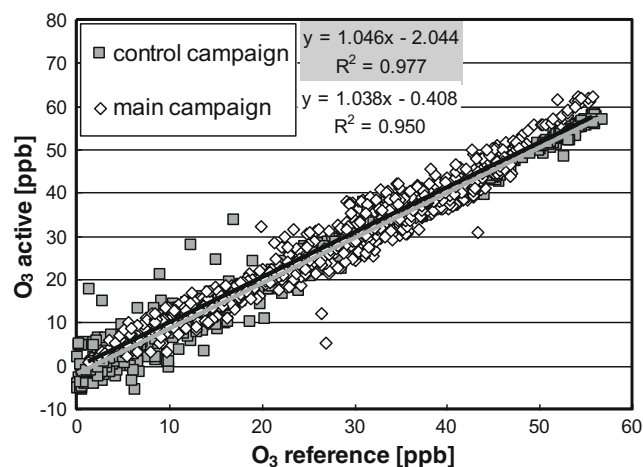


Fig. 6 10 min averaged O₃ data in both canyons during the control and main campaign

daytime may be explained by photocatalytic degradation of adsorbed nitrate (Monge et al. 2010b).

The present study shows that the impact of the photocatalytic material at the first order (direct emission/abatement of O_3) or at the second order (emission/abatement of NO_x or other O_3 precursors) was negligible. No improvement of the air quality with respect to the O_3 level was thus obtained with an upper limit average photocatalytic remediation of $\leq 3\%$ derived from the combined 2σ precision errors of the correlation data.

Particles

During the control campaign, no significant differences in the particle number, mass, size distribution, and chemical composition between the two canyons were observed indicating again the general similarity of the two sites also with respect to the particles characteristics (Table 3). However, similar results were also found during the main campaign when the active material was applied, as shown exemplarily for the AMS data in Fig. 7. Correlations of the obtained data between the two canyons for organics, nitrate, sulfate, and ammonium result in slopes indistinguishable from unity for all the compounds (see Table 3). In conclusion, the impactor, SMPS and AMS results indicate no significant impact of the used photocatalytic material also on the particle concentrations and composition.

Laboratory experiments on NO_x

In an effort to explain the unexpected low remediation of NO_x , original samples from the field site were tested in the laboratory after the campaign. Two PhotoPAQ laboratory actions focused on photocatalytic reactions of different pollutants (NO_x , HONO, VOCs, formaldehyde) on the surfaces used in the canyon study, the results of which will be presented in forthcoming publications. Here, only the uptake kinetics of NO and NO_2 on samples used in the field campaign were investigated in a bed flow photoreactor. Details on the experimental setup used are given elsewhere (Ifang et al. 2014). Reactor independent photocatalytic uptake coefficients and deposition velocities (Ifang et al. 2014) were determined from

Table 3 Summary of the slope of the correlation plots (active versus reference canyon) for different AMS particle components from the two campaigns

Compound	control campaign: slope (R^2)	main campaign: slope (R^2)
Organics	0.99 (0.88)	0.99 (0.96)
Nitrate	0.99 (0.94)	1.01 (0.98)
Sulfate	0.98 (0.92)	0.99 (0.98)
Ammonium	0.99 (0.94)	1.01 (0.98)

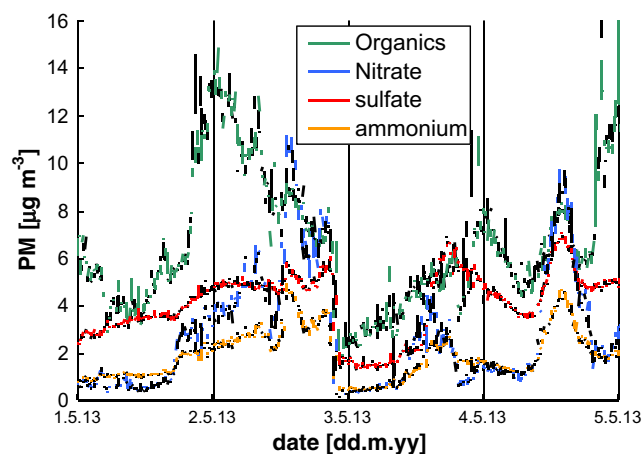


Fig. 7 AMS time series of the main aerosol components (organics, nitrate, sulfate, ammonium) during the main campaign. The colored data refer to measurements made in the active canyon and the black one in the reference canyon

the difference between dark and light-induced uptake of NO and NO_2 on the photocatalytic samples.

The laboratory measurements revealed a significant photocatalytic activity of NO and NO_2 for the TX-Boosted samples (see Table 4). However, in a recent tunnel study in Brussels, strong deactivation of similar surfaces was observed under highly polluted conditions (Gallus et al. 2015; Boonen et al. 2015). Because of the low NO_x remediation observed in the present canyon study, possible deactivation of the surfaces was investigated on samples directly cut from the walls of the active canyon after the main field campaign.

In contrast to the results from the tunnel studies (Gallus et al. 2015; Boonen et al. 2015), no deactivation of the photocatalytic NO_x uptake was observed for the samples used in the street canyon (see Table 4). This may be explained by the much lower pollution level and the much higher UV irradiance during the field campaign under the urban background conditions in the canyon compared to the highly polluted tunnel situation. Thus, (a) less pollutants that may potentially block active sites (e.g., “urban grime”) will stick to the surfaces, and (b) the pollutants will be faster oxidized by the photocatalytic self-cleaning effect. In addition, in the tunnel (Gallus et al. 2015; Boonen et al. 2015), the cementitious surfaces were curing in the dark for several days, whereas here, they were directly exposed to significant UV sunlight, thus reducing the accumulation of pollutants on the surfaces.

The present laboratory studies show that potential fast deactivation of the active surfaces as observed in other field studies (Ballari and Brouwers 2013; Gallus et al. 2015; Boonen et al. 2015) cannot explain the low remediation results from the present field trial (see Sect. “Nitrogen Oxides ($NO_x = NO + NO_2$)”). However, it should be highlighted that only possible fast deactivation of samples exposed for 3 weeks to an urban background situation was considered. In contrast, deactivation over longer time scales (e.g., several months)

Table 4 Photocatalytic uptake coefficients and deposition velocities (Ifang et al. 2014) of NO and NO₂ on TX-Boosted samples used only in the laboratory (*laboratory*) and collected after the street canyon campaign in Petosino (*canyon*)

TX-Boosted	$\gamma(\text{NO})_{\text{photo}}$	$\nu(\text{NO})_{\text{photo}}$	$\gamma(\text{NO}_2)_{\text{photo}}$	$\nu(\text{NO}_2)_{\text{photo}}$
Laboratory	$(3.3 \pm 0.3) \times 10^{-5}$	$0.38 \pm 0.03 \text{ cm s}^{-1}$	$(3.2 \pm 0.5) \times 10^{-5}$	$0.29 \pm 0.05 \text{ cm s}^{-1}$
Canyon	$(3.0 \pm 0.4) \times 10^{-5}$	$0.34 \pm 0.05 \text{ cm s}^{-1}$	$(3.3 \pm 0.6) \times 10^{-5}$	$0.31 \pm 0.06 \text{ cm s}^{-1}$

Experimental conditions: NO/NO₂:~100 ppb, UVA: ~8 W m⁻², r.h.: ~40 %

and under more polluted conditions may still be possible, which should be investigated in future studies.

Discussion

In the present field study, no significant photocatalytic remediation of NO_x, VOCs, O₃, and particles could be observed under atmospheric conditions at an urban background site in Petosino near Bergamo, Italy. For NO_x, only an upper limit of ≤ 2 % could be derived from a comparison of daytime and nighttime correlation plots. The only moderate pollution level observed during the present model canyon study compared to a real urban kerbside situation can be excluded as reason for the general low remediation, since relative reductions (%) are independent of the concentration for the first order kinetics observed in PhotoPAQ laboratory studies for the TX-Boosted material used. In addition, the analytical instrumentation applied was highly sensitive, enabling the detection even of small absolute concentration differences. For VOCs, the nonsignificant reductions could be due to slower photocatalytic uptake kinetics of VOCs, which are typically one order of magnitude lower compared to NO_x (Chen et al. 2011). This would also result in a limited impact on secondary aerosol (SOA) formation by VOC oxidation. In addition, no direct influence of heterogeneous photocatalysis on primary airborne particles (e.g., soot) is expected as proposed recently (De Richter and Caillol 2011), since only adsorbed particles can be photocatalytically oxidized.

However, at least for NO_x, much higher remediation was originally expected based on the results from most other field trials in the open atmosphere (PICADA 2006; Guerrini and Peccati 2007; Maggos et al. 2008; Fraunhofer 2010; Ballari and Brouwers 2013). In contrast, nonquantifiable NO_x reductions were also observed at two motorways (Tera 2009; IPL 2010) and at an urban street site (Jacobi 2012). The latter results may be explained by the low surface to volume ratios (S_{active}/V) of the open structured motorway field sites with only photocatalytically active noise protection walls (Tera 2009; IPL 2010) or where only the sideways of a street were active (Jacobi 2012). However, in other studies in real (Guerrini and Peccati 2007; Ballari and Brouwers 2013) or model street canyons (PICADA 2006; Maggos et al. 2008; Fraunhofer 2010) similar to the present study, much higher

NO_x reductions in the range of 19–80 % were reported. The much lower reduction of the present study compared to these former field trials can neither be explained by potential deactivation of the studied surfaces (see Sect. “Laboratory experiments on NO_x”) as observed in other investigations (Ballari and Brouwers 2013; Gallus et al. 2015; Boonen et al. 2015), nor by the geometry of the present canyon site which has an even higher S_{active}/V ratio (0.6 m^{-1}) compared to other photocatalytic field experiments (Guerrini and Peccati 2007; Fraunhofer 2010; Ballari and Brouwers 2013). In contrast, the unrealistically high S_{active}/V ratio during the PICADA model canyon experiments using only 2.4 m wide canyons is one potential reason for the reported high NO_x reductions of up to 80 % (PICADA 2006; Maggos et al. 2008). As recently discussed (Laufs et al. 2010), the S_{active}/V ratio of a field site is one important parameter limiting heterogeneous uptake. Thus, high remediation results from experiments in smaller model sites (PICADA 2006; Maggos et al. 2008; Fraunhofer 2010; and present study) have to be scaled down to real urban street canyon conditions. In the former study (Laufs et al. 2010), extrapolation of results obtained in small canyons (PICADA 2006; Maggos et al. 2008; Fraunhofer 2010) resulted in an estimated reduction of only ~5 % in a typical main urban street.

Besides the unrealistic geometries used in some previous field trials, in all former experiments in which significant remediation was observed (PICADA 2006; Guerrini and Peccati 2007; Maggos et al. 2008; Fraunhofer 2010; Ballari and Brouwers 2013), only daytime data were evaluated. In contrast, in three other studies where nonmeasurable NO_x reduction was reported (Tera 2009; IPL 2010; Jacobi 2012), the whole diurnal data were considered. Since photocatalytic remediation is considered as one of several potential measures to reach the European annual threshold limit for NO₂ of $40 \mu\text{g m}^{-3}$, results from studies in which daytime data is used should only be considered as upper limits. NO_x levels during nighttime are often comparable to those during daytime (higher emissions are compensated by stronger convective vertical dilution during daytime), see, e.g., Fig. 3c. Hence, relative reductions observed in studies using only daytime data can be roughly divided by a factor of two to estimate the average reduction in an urban environment. For example, since the estimated 5 % reduction (see above and Laufs et al. 2010) is still based on daytime data, an annual NO_x reduction of only ~3 % is expected in a typical main urban street.

In addition to the sampling intervals considered, also the distance of the sampling inlet to the active surface is of particular importance when trying to understand the differences in the published NO_x remediation results. While a measurement height of 3 m is recommended for urban network stations in which annual NO_2 threshold limit exceedance is verified, photocatalytic remediation was typically measured much closer to the active surfaces in most previous studies. For example, in PICADA (PICADA 2006; Maggos et al. 2008), samples were taken only a few cm away from the active canyon walls, which presents another potential reason for the exceptionally high NO_x reduction results obtained in this study. Also, in the other field trials in which high NO_x remediation was observed, the sampling heights above the active surfaces were much less than 3 m (0.05–1.5 m in Ballari and Brouwers 2013; 0.3–1 m in Guerrini and Peccati 2007; 0.5 m in Fraunhofer 2010). Because of the expected and also observed gradients (Ballari and Brouwers 2013) of the photocatalytic reduction, the high remediation results of these previous studies again have to be considered as upper limits. Unfortunately, extrapolation to the recommended 3 m sampling height is only possible using, at the least, 1D model calculations to realistically describe the turbulent vertical mixing. In contrast, in the present study samples were directly collected at 3 m above ground level, resulting in a more reasonable estimate of the expected reductions at urban measurement stations. Lower sampling heights may still be important for specific environmental issues, e.g., health effects for pedestrians or entrainment of pollutants to indoor air via air-exchange through windows mounted on the active walls. However, as far as the urban NO_2 problem is concerned, remediation should be quantified at 3 m height.

Another potential reason for the high reductions observed in some former field studies are general differences between the active and reference sites used. In all studies, similarity was presumed to quantify the photocatalytic remediation (PICADA 2006; Guerrini and Peccati 2007; Maggos et al. 2008; Tera 2009; Fraunhofer 2010; IPL 2010; Jacobi 2012; Ballari and Brouwers 2013), which may not always be the case, for example, in model street canyon experiments in which NO_x was artificially injected into the active and reference canyons (PICADA 2006; Maggos et al. 2008; Fraunhofer 2010). In contrast, in the present study the homogeneous urban NO_x background was investigated, for which the similarity between both canyons is more reasonable. In addition, in real street canyon experiments in which the two sites are located at a significant distance from each other (Guerrini and Peccati 2007; Ballari and Brouwers 2013), different emission strength and pollutant dispersion may cause high uncertainties in the remediation results. For example, in a recent model study (Flassak 2012; Bolte and Flassak 2012) results from an experimental street canyon campaign in Bergamo (Guerrini and Peccati 2007) were re-evaluated,

resulting in an expected upper limit for photocatalytic remediation during daytime in the range of only 4–14 %, compared to the published values of 26–66 % (Guerrini and Peccati 2007). Reasons for this discrepancy were suggested to be (a) strong differences in the vehicle NO_x emissions at the active and reference sites with much higher vehicle fleet density at the reference site and (b) different dispersion conditions (geometry of the sites, micrometeorology). Even these model results can be considered as an upper limit, since transport limitations represented by the turbulent and quasi laminar resistances (VDI 2006) were neglected in the model. Thus, the calculated NO_x reduction during daytime of, e.g., 4 % for a reasonable average wind speed of 1 m s^{-1} and when using a realistic photocatalytic deposition velocity of 0.3 cm s^{-1} during daytime (Bolte and Flassak 2012; compare also with values in Table 4) will in reality be reduced to <2 % using (a) diurnal averages and (b) considering also transport limitations. This result is in excellent agreement with present and other studies (Tera 2009; IPL 2010; Jacobi 2012) highlighting the necessity of careful interpretation of field data.

In conclusion, when considering all the differences in the geometry of the field sites, in sampling positions, in sampling periods and general differences between the active and reference sites, a much more consistent picture of the expected NO_x remediation by photocatalysis can be drawn. Based on the discussion presented above and considering results from different field and modeling studies, a realistic annual averaged NO_x reduction of ~2 % can be estimated when active surfaces are used in main urban street canyons, in which the European annual NO_2 threshold limit value of $40 \mu\text{g m}^{-3}$ is typically exceeded.

However, even this number has to be considered as an upper limit since (a) often commercially available surfaces show lower photocatalytic deposition velocities than the 0.3 cm s^{-1} used in the model described above (Bolte and Flassak 2012) and (b) deactivation of the surfaces after longer use in the field may further reduce the remediation (Ballari and Brouwers 2013; Gallus et al. 2015; Boonen et al. 2015). Consequently, on the one hand, high threshold photocatalytic activities against NO_2 should be defined in future CEN (European Committee for Standardization) and ISO (International Organization for Standardization) standards to test active surfaces, in which presently only NO is considered (Ifang et al. 2014). On the other hand, potential deactivation should be studied at the field site of interest in small scale experiments, before application of larger surfaces (Gallus et al. 2015; Boonen et al. 2015). Only when surfaces show high activity towards NO_2 and when no strong deactivation under the specific field conditions is observed, should photocatalysis be recommended as a measure to reduce urban NO_2 levels.

The low reduction by photocatalysis may be considered as a disappointing result; however, it should be compared with

other measures used to improve urban air quality. Here, also improved emission standards (Velders et al. 2011; Carslaw et al. 2011; Melkonyan and Kuttler 2012; Carslaw and Rhys-Tyler 2013) or implementations of low emission zones (LANUV 2009; Panteliadis et al. 2014) showed only small reductions in the urban NO₂ levels of a few percent at maximum. Hence, a complete cost-benefit analysis of all discussed measures is highly recommended, for which photocatalysis may still be more attractive compared to other expensive methods if extra costs for photocatalytic surfaces compared to the application of normal urban surfaces (roads, paints, roof tiles, etc.) are minimized by industry in the future and when photocatalytical materials are applied when urban surfaces are renewed anyway.

Summary

In the present field study photocatalytic remediation of nitrogen oxides (NO_x), ozone (O₃), volatile organic compounds (VOCs) and particles was studied in an artificial street canyon in comparison to a similar collocated reference site. No significant remediation could be observed for the investigated trace species, with an upper limit NO_x remediation of ≤ 2 %. This result cannot be explained by potential deactivation of the used surfaces as observed for other studies, but is due to transport limitations of the pollutants towards the active surfaces. The high photocatalytic NO_x remediation results from some previous studies can be explained by differences in the geometry of the field sites, in sampling positions, in sampling periods and by general differences between the active and reference sites. If all these factors are considered and results from different studies are extrapolated to realistic urban conditions, a diurnal averaged NO_x reduction in the same range as the upper limit of the present study is estimated (~2 %), leading to a consistent picture of the possible urban air pollution remediation by photocatalysis. Thus, this technique alone will not solve the urban NO₂ problem in European cities and should be considered only as one measure besides the others. The lower remediation obtained in the present study should not be considered as a stop criterion for this innovative technique, but should be compared to other measures aimed at improving urban air quality on a cost-benefit analysis basis. Here, in the past, also more modern combustion technologies (e.g., EURO standards) or implementations of low emissions zones has resulted in a reduction of the urban NO₂ levels by only a few percent at maximum.

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