



## Can photocatalysis help to improve urban air quality? Results from the LIFE+-project PhotoPAQ

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### Abstract

During the European PhotoPAQ project (Demonstration of Photocatalytic Remediation Processes on Air Quality), using photocatalytic cementitious coatings, the remediation of nitrogen oxides, ozone, volatile organic compounds, formaldehyde and particles was studied both, in a traffic tunnel at Brussels, and in an artificial street canyon near Bergamo. In contrast to former field studies, no significant remediation was observed. For NO<sub>x</sub> an upper limit remediation of ≤2% was derived for both studies. For the tunnel experiments this is explained by strong deactivation of the photocatalytic materials applied under the highly polluted tunnel conditions. For the canyon study the low reduction is explained by transport limitations.

### 1. Introduction

Urban air quality is of high importance for human health since the majority of the world's population lives inside metropolitan areas. With respect to still significant exceedances of threshold limit values for important pollutants (e.g., nitrogen oxides, NO<sub>x</sub>) further improvement of the urban air quality is necessary. Here, over the last decades, titanium dioxide (TiO<sub>2</sub>) based photocatalytic surfaces have been developed and tested, both, at a laboratory scale and in the open atmosphere as an alternative technical means for the remediation of NO<sub>x</sub> [1-5], VOCs [5-8], O<sub>3</sub> [8], and particles [8-10].

While typically high remediation is obtained in the laboratory, controversial results exist concerning the extent of NO<sub>x</sub> reduction in the real urban atmosphere ranging from 0 to 80% [1,11-17]. Reasons for these contradictory results are

still under discussion and further field studies are necessary to better account for the total impact of this technology on air quality.

In addition to the application on outdoor surfaces, photocatalysis might also contribute to air quality improvement inside road tunnels, but requires the photocatalytic tunnel surfaces to be irradiated by UV light. However so far, only one tunnel study has been conducted with a NO<sub>x</sub> abatement of 20% [18]. Thus, further studies are necessary to quantify the impact of photocatalytic air remediation inside road tunnels.

The European Life+ project PhotoPAQ (*Demonstration of Photocatalytic remediation Processes on Air Quality*) [19] was aimed at demonstrating a possible usefulness of photocatalytic construction materials for air purification purposes in the urban environment. Both, tunnel [20,21] and street canyon studies [22] were performed to test photocatalytic cementitious coating materials in the real atmosphere.

### 2. Experimental

#### 2.1. Tunnel Study

The tunnel study was performed in a section of the Leopold II tunnel, at Brussels, Belgium, which is explained in detail elsewhere [20,21]. A pre-campaign in the untreated tunnel and two campaigns with two photocatalytically active mortars (CTG) in tunnel sections of 70 and 160 m were conducted in 2011 and 2013, respectively. Surfaces were irradiated with switchable UV lighting systems with average irradiance levels (range 315-420 nm) on the active surfaces of 0.6±0.3 and 1.6±0.8 W m<sup>-2</sup>, respectively (see Fig. 1). From the various

measured gas and particle phase pollutants only results on  $\text{NO}_x$ , HCHO and  $\text{CO}_2$  are presented here.

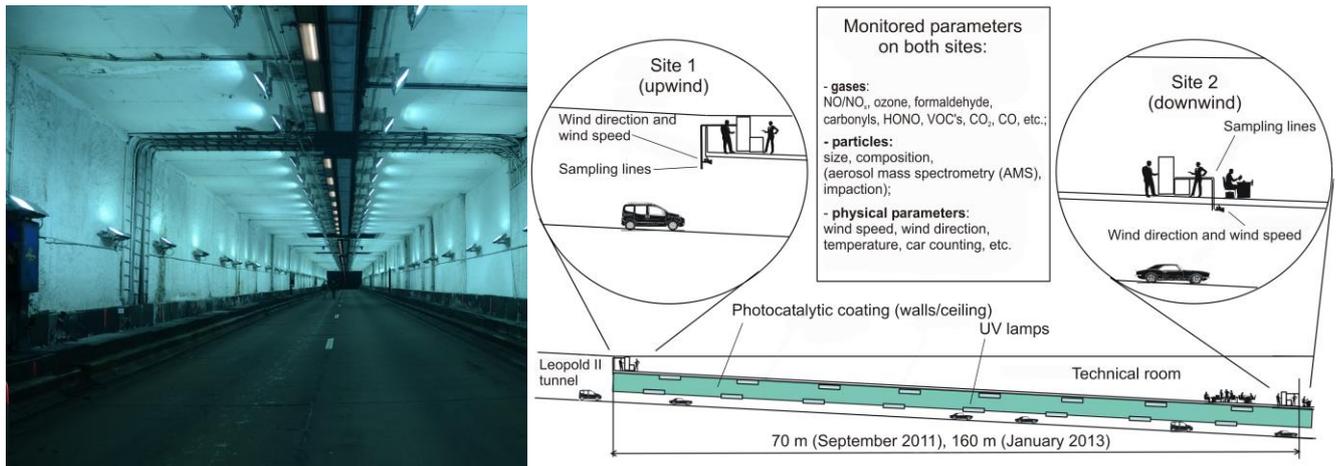


Fig. 1: Experimental set-up in the Leopold II tunnel in Brussels, Belgium.

## 2.2. Canyon Study

Measurements were performed in 2013 in two artificial street canyons of the dimensions 5x5x53 m (widthxheightxlength) at an industrial site in Petosino – Sorisole, a few kilometres north of Bergamo, Italy, which is explained in detail elsewhere [22]. To create conditions as similar as possible in both canyons, the walls were constructed with fibre cement boards mounted on metal scaffoldings in front of the original buildings

(see Fig. 2). During the first campaign the surfaces of both untreated canyons were photocatalytically inactive, while during the main campaign walls and ground surfaces only of the active canyon were coated with a photocatalytically active mortar (CTG). The other reference canyon was not modified. Various gas and particle phase pollutants were quantified from which here only results on  $\text{NO}_x$ , HCHO, VOCs,  $\text{O}_3$  and particles are presented.



Fig. 2: Experimental set-up of the model street canyon site in Petosino, Italy.

## 3. Results and Discussion

### 3.1. Tunnel Study

Based on a) laboratory data, b) corresponding model calculations [20] and c) results from another tunnel study [18], significant  $\text{NO}_x$  remediation was initially expected under UV irradiation. To test this hypothesis the lamps were periodically switched on and off in the tunnel, which however, did not result in any systematic steps in the concentration difference between the upwind and downwind sites (see Fig. 3 as an example).

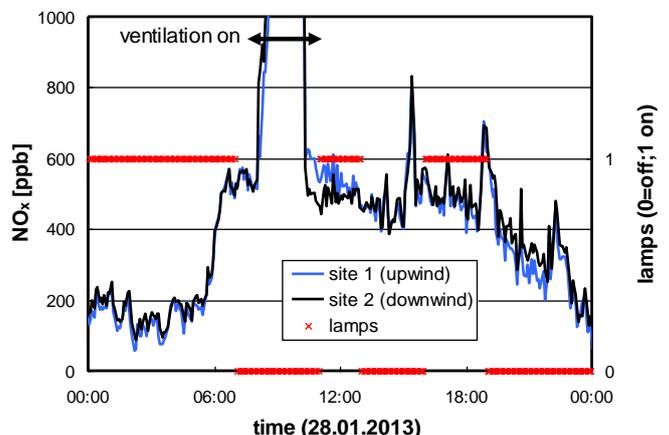


Fig. 3: Plot of the 10 min  $\text{NO}_x$  and lamps on/off data at the two sites during one day of the 2013 campaign.

To improve the significance of the data evaluation and eliminate dependencies from the variable pollution level in the tunnel, the photocatalytic remediation was evaluated from average  $\text{NO}_x/\text{CO}_2$  ratios using three approaches i.e., before/after application; upwind downwind the active site and with lamps on/off. However in none of the approaches any significant photocatalytic reduction could be identified. As an upper limit, taking into account the precision errors of the data analysis, a value of  $\leq 2\%$  has been estimated for the photocatalytic remediation in the longer more active tunnel section investigated in 2013.

To understand the low  $\text{NO}_x$  remediation, additional laboratory experiments were performed using samples collected from the tunnel (for details see [21]). These experiments showed a serious deactivation of the photocatalytic activity of the samples with uptake coefficients [23] at least one order of magnitude lower compared to untreated fresh samples. Based on these results simple model calculations indicate an upper limit  $\text{NO}_x$  remediation in the tunnel of only 0.4 %, clearly below the experimental errors.

In contrast to most measured tunnel pollutants for which no significant photocatalytic impact was observed, undesired photocatalytic formation of formaldehyde (HCHO) was detected in the irradiated tunnel.

### 3.2. Canyon Study

Fig. 4 shows all 10 min averaged  $\text{NO}_x$  and UVA data from the main measurement campaign in 2013 with the photocatalytically active surfaces. During the first part of the campaign (1st – 4th May) the weather was typically good with only partial cloud coverage, high UVA irradiance of up to  $40 \text{ W m}^{-2}$  and low wind speed (WS) of  $< 1 \text{ m s}^{-1}$  inside the canyon, favouring photocatalytic remediation. However, from the difference of the 10 min averaged  $\text{NO}_x$  data between both canyons, on average no significant remediation is visible (see Fig. 4). Caused by the different UVA levels, the period 1st-4th May with a higher expected photocatalytic remediation was separately evaluated. All 10 min averaged  $\text{NO}_x$  data from the active canyon were plotted against corresponding data from the reference canyon for day- and night-time separately. From the identical slopes an upper limit  $\text{NO}_x$  remediation of  $\leq 2\%$  was derived.

Subsequent laboratory studies using samples directly collected from the canyon after the field campaign showed no deactivation of the reactivity in the open atmosphere in contrast to the tunnel study. Thus, potential fast deactivation of the photocatalytic surfaces as observed in other field studies [13, 20, 21] cannot explain the low photocatalytic remediation results from the present field trial, which is explained here by transport limitations. Similar results were obtained for almost all other pollutants with the following upper limit reductions: VOCs  $\leq 5\%$ ;  $\text{O}_3$   $\leq 3\%$ ; particle mass and composition  $\leq 5\%$ .

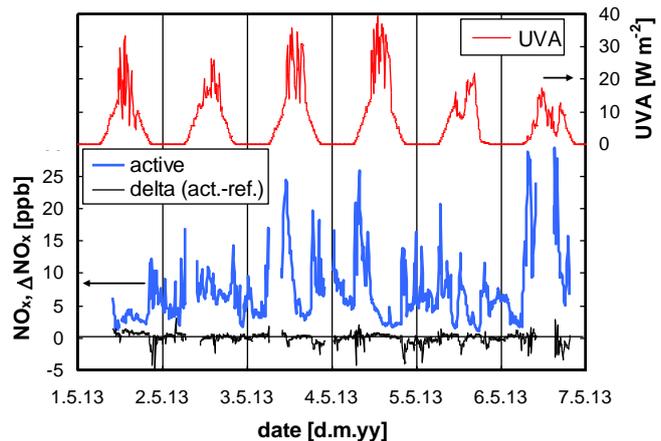


Fig. 4: 10 min averaged  $\text{NO}_x$  concentration in the active canyon, difference between both canyons and UVA irradiance during the main field campaign in Petosino.

Similar to the tunnel study, also in the canyon undesired photocatalytic formation of formaldehyde (HCHO) was observed on the photocatalytic surfaces used in PhotoPAQ which was scaling with the UV irradiance. This result was also confirmed in separate laboratory studies in which emission fluxes of HCHO were determined for untreated samples and those directly collected from the canyon and from the tunnel. These HCHO emission fluxes were significant and e.g., one order of magnitude higher compared to theoretical deposition fluxes of  $\text{NO}_x$  under the prevailing atmospheric canyon conditions. Further laboratory experiments demonstrated that HCHO was formed at least in part by photocatalytic degradation of organic additives in the cementitious materials used. Although the emissions were found to decrease with irradiation time, they were still significant after ca. 1000 h under irradiation. Thus for the future, photocatalytic materials should be optimized not only for high reactivity against atmospheric pollutants, but also for minimum emissions of harmful reaction products.

#### 3.2.1. Discussion Canyon Study

In the present canyon study no significant photocatalytic remediation of  $\text{NO}_x$ , VOCs,  $\text{O}_3$  and particles could be derived under atmospheric conditions at an urban background site. For  $\text{NO}_x$  only an upper limit of  $\leq 2\%$  could be derived from comparison of day- and night-time correlation plots. For VOCs and particles the non-significant reductions could be expected caused by a) slower photocatalytic uptake kinetics of VOCs, typically one order of magnitude smaller compared to  $\text{NO}_x$  [24], b) resulting also in a limited impact on secondary aerosol (SOA) formation by VOC oxidation and c) obviously, no direct influence of heterogeneous photocatalysis on primary airborne particles (e.g. soot) as proposed recently [8], since only adsorbed particles can be photocatalytically oxidized.

However, at least for  $\text{NO}_x$  much higher remediation was originally expected based on most other field trials in the open atmosphere [1,11-14] in which reductions in the range 19-80% were detected. In contrast, non-quantifiable  $\text{NO}_x$  reductions were observed at two motorways [15,16] and at an

urban street site [17] in agreement with the present study. As explanations for these very different field results the following reasons were identified:

- Different surface to volume ratios (Sactive/V) in the considered studies, varying from small model street canyon sites to open structured motorways with only photocatalytically active noise protection walls;
- Different time periods investigated. In all former experiments in which significant photocatalytic remediation was observed [1,11-14] only daytime data were evaluated, while in the three other studies with non-measurable NO<sub>x</sub> reduction [15-17], the whole diurnal data were considered.
- Different sampling heights ranging from a few cm to 3 m, with a clear tendency of higher measured reductions for lower sampling heights [13];
- General differences in the pollution level and micro-meteorology between the active and reference sites for which similarity was assumed to quantify the photocatalytic reduction. E.g., in a recent model study [25,26] significant differences were identified for the two sites of a street canyon study [14], resulting in an expected upper limit photocatalytic remediation during daytime in the range of only 4-14%, compared to the published values of 26-66% [14].

In conclusion, when considering all these 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<sub>x</sub> remediation by photocatalysis can be drawn. Based on the differences listed above and considering results from different field and modelling studies, a realistic annual averaged NO<sub>x</sub> reduction of ~2% can be estimated when photocatalytic active surfaces are used in main urban street canyons, in which the annual NO<sub>2</sub> threshold limit value of 40 µg m<sup>-3</sup> is typically exceeded.

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 or implementations of low emission zones showed only small reductions of the urban NO<sub>2</sub> levels by a few percent at maximum. Hence, a complete cost-benefit analysis of all discussed measures is highly recommended, for which photocatalysis may be still 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.

#### 4. Conclusions

During the European PhotoPAQ project, photocatalytic remediation of NO<sub>x</sub>, O<sub>3</sub>, VOCs and particles were studied both, in a traffic tunnel in Brussels, and in an artificial street canyon in Bergamo using photocatalytic cementitious

coatings. In contrast to former field studies, no significant remediation was observed, with an upper limit NO<sub>x</sub> reduction of ≤2%. For the tunnel experiments this is explained by strong deactivation of the photocatalytic materials applied under the highly polluted tunnel conditions. Thus, it is recommended to test possible deactivation in small scale experiments under the prevailing atmospheric conditions before application of photocatalytic materials in larger field sites. This is also of importance with respect of the observed undesired formation of HCHO. For the canyon experiment the low reduction is explained by transport limitations. When considering also results from other field studies a realistic average NO<sub>x</sub> reduction by photocatalysis in a typical urban environment of only a few % is expected. This low reduction has to be compared on a cost-benefit basis with other measures aimed to improve urban air quality, for which also only low NO<sub>2</sub> reductions were observed in the past.

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