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Construction of a photocatalytic de-polluting field site in the Leopold II tunnel in Brussels

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ABSTRACT

Within the framework of the European Life+-funded project *PhotoPAQ (Demonstration of Photocatalytic remediation Processes on Air Quality)*, which was aimed at demonstrating the effectiveness of photocatalytic coating materials on a realistic scale, a photocatalytic de-polluting field site was set up in the Leopold II tunnel in Brussels, Belgium. For that purpose, photocatalytic cementitious materials were applied on the side walls and ceiling of selected test sections inside a one-way tunnel tube. This article presents the configuration of the test sections used and the preparation and implementation of the measuring campaigns inside the Leopold II tunnel. While emphasizing on how to implement measuring campaigns under such conditions, difficulties encountered during these extensive field campaigns are presented and discussed. This included the severe de-activation observed for the investigated material under the polluted tunnel conditions, which was revealed by additional laboratory experiments on photocatalytic samples that were exposed to tunnel air. Finally, recommendations for future applications of photocatalytic building materials inside tunnels are given.

1. Introduction

The de-pollution performance of photocatalytic cement-based materials containing titanium dioxide (TiO_2) has been assessed in numerous studies over the past decade, e.g. (Ângelo et al., 2013; Boonen and Beeldens, 2013; Maggos et al., 2008; Maury-Ramirez et al., 2010; Ohama and Van Gemert, 2011), illustrating their potential for urban pollution control. However, in addition to application on outdoor building façades and road surfaces, these materials – irradiated by artificial UV light to activate them – might also contribute to a significant reduction of air pollution in road tunnels. Although road tunnels in urban areas are usually well ventilated with regular air renewal inside, previous research has shown that they suffer from strongly elevated concentrations of air pollutants such as nitrogen oxides (NO_x), volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs); these are associated with emissions from road traffic, especially during rush hours (Indrehus and Vassbotn, 2001; Larsson et al., 2007; Vanderstraeten et al., 1991). Moreover, air from tunnels is often ventilated to the ambient atmosphere without effective de-

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pollution measures and, therefore, contributes to a large extent to air pollution in the areas nearby the ventilation exit. Hence, by cleaning the air inside the tunnel using e.g. TiO_2 photocatalysis technology, not only a significant improvement for tunnel users could be obtained, but also a better air quality for the outside surroundings. So far, to the authors' best knowledge only one study has been conducted on this topic and it was limited to one type of pollutant, i.e. NO_x (Guerrini, 2012).

The European Life + project PhotoPAQ, *Demonstration of Photocatalytic remediation Processes on Air Quality* (PhotoPAQ, 2010–2014), was aimed at demonstrating the usefulness of photocatalytic construction materials for air purification purposes in the urban environment. Eight partners from five different European countries formed the consortium that undertook this project. For the needs of the project, and in view of the aforementioned findings, an extensive three-step field campaign was organized in the Leopold II tunnel in Brussels, Belgium during the period June 2011–January 2013. In particular, two different photocatalytic cementitious coating materials were applied on the side walls and the ceiling of selected sections in the tunnel branch running along the Basilica–Midi axis. The air-purifying surfaces were activated by a dedicated UV lighting system installed inside the tunnel. During the associated field campaigns, the effect of the photocatalytic coatings on air pollution (including NO_x, VOCs, particulate matter, etc.) in the tunnel section was rigorously assessed. In the present article, the construction of the photocatalytic de-polluting field site and the implementation of the field campaigns are elaborated in detail. In addition, the results of some supplementary laboratory experiments are presented; these were performed on photocatalytic samples exposed to tunnel air, in order to investigate possible surface passivation phenomena under the prevailing tunnel conditions. The actual results for NO_x abatement are discussed in more detail elsewhere (Gallus et al., 2015).

2. Setup and requirements for the tunnel field campaigns

Carrying out a monitoring campaign in a tunnel environment has the advantage that local pollution and meteorological conditions are far less variable than in an outdoor environment, thus allowing an easier interpretation of the collected data. For the location of the test site in the tunnel, some general prerequisites had to be met:

- the site should provide the maximum measurable effect of the photocatalytic material;
  - high surface-to-volume ratio of the photocatalytically active test area,
  - high traffic volumes to obtain reasonable pollution levels,
  - limited impact of the tunnel entrances, exits and cross section on the dilution of the air in the test section,
  - limited impact of the ventilation system both on the main environmental parameters like temperature and relative humidity and on the dilution of the tunnel air,
  - limited impact of the traffic flow on the dilution of the tunnel air;
- the aerology of the site should be implementable into numerical models for an assessment of pollution abatement.

In addition to these "experimental" constraints some practical issues had to be considered for the choice of a proper tunnel field site, like the mandatory approval from local authorities to build up a photocatalytic test section, safety issues especially towards the drivers, related to the application of additional UV-lighting to activate the air-purifying products, and, finally, the availability of space to accommodate air monitoring instruments.

2.1. Selection of the field site

Bearing in mind the above-mentioned constraints, the Leopold II tunnel in Brussels (Fig. 1) was selected as the most appropriate field site. The tunnel carries high traffic volumes regularly reaching a few thousands of vehicles per hour (Table 1), which generate a sufficient level of pollutants. Based on the existing air pollution measurements (NO_x and CO) carried out continuously in the tunnel over several years, the section could be described as highly polluted with annual average half-hour concentrations of around 1000 and 400 $\mu g/m^3$ for NO and NO_2, respectively.

The Leopold II tunnel is a two-way tunnel connecting the motorway coming from Ghent and Bruges with the central business district in Brussels. The 2.5 km long city tunnel runs underground along the Basilica–Midi axis, within a densely built urban environment (Fig. 1).

Air quality is currently controlled by a ventilation system through multiple inlets (injectors) and outlets (extractors) over the entire length of the tunnel. As a result, the tunnel is divided into several sections with similar air properties and with lengths varying from 100 to 200 m. The tunnel geometry is highly complex and consists of two segments (one for each direction) separated by a wall, with varying cross-sectional areas along each direction and the presence of several entrances and exits along its length (Fig. 1). However, about 300 m upwind of the selected field site section, at the entrance "Basilique", the tunnel tubes are separated by regular concrete pillars only, allowing effective mixing of the pollutants from both tunnel tubes. This fact, though, did not influence the field experiments and only caused additional emissions to the tunnel air of the selected site.

A section of about 200 m with a relatively uniform cross section was identified here. This section had the advantage of the presence of a technical room above the tunnel, which allowed accommodation of the large set of scientific instruments to be deployed for air pollution monitoring. Direct connections to the tunnel were provided by holes in the ceiling of the tunnel, in order to position the sampling lines and cables needed for the measurements. The selected section is located between the entrance "Basilique" and the entrance "Sainte-Anne" in the direction to the city centre, as shown in Fig. 1, and it has a surface-to-volume ratio of about 0,4 m^{-1}.

2.2. Field testing strategy in the tunnel

The basic principle of the field campaigns was to compare the air purification effect of photocatalytically active surfaces with that of "normal" non-active surfaces in very similar environments. Furthermore, the study focused on combining two important strategic objectives: testing in realistic circumstances on the one hand, and gathering very precise measurement data on the pollutant concentrations inside the tunnel on the other hand.

Three field testing strategies were extensively discussed:

1) Carrying out measurements *before and after the application* of the material, so that the efficiency of the material can be assessed by comparing the differences in air quality obtained during the two periods. This approach, which has already been chosen in one other study (Guerrini, 2012), has the advantage of being applicable to both indoor and outdoor sites. In addition, it is readily understood by non-scientists and hence easily transferable to decision-makers.

On the other hand, considering the extremely high variability of the concentrations of atmospheric pollutants and/or the meteorological conditions, it would require extremely careful and difficult

Fig. 1. Plan view of the Leopold II tunnel in Brussels—In red the segment chosen as field site [Google maps]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Typical peak hour traffic loads in the Leopold II tunnel in Brussels.

Tunnel direction	Traffic load [vehicles/hour]	Peak hours [h:mm]
Basilica to Centre	2250–2300	7:00–9:00
Centre to Basilica	2300–2400	15:00–19:00

interpretation of the experimental data as the emission of pollutants might change substantially in between, e.g. owing to a changing vehicle fleet. In addition, this strategy implies deployment of the air quality monitoring equipment during longer periods of time. In our case, a small pre-campaign with just a few instruments (NO_x and CO_2) was carried out to have an indication of the pollutants concentrations under normal conditions.

2) The second approach ("*upwind/downwind*") consists of deploying two identical sets of scientific instruments in two measurement stations: one measuring the "normal" air, the other measuring the air which has been in contact with the active surfaces, with similar air masses passing both sites to allow comparison. Very important with this approach is the preliminary intercalibration of the identical instruments. This second strategy was adopted for the tunnel campaign(s), since the latter provides a more meaningful approach to the characterization of the possible air pollution abatement as measurements on both sites are made under strictly similar conditions, unlike in the "*before/after*" strategy.

In this respect, two heavily instrumented monitoring stations were set up (Fig. 2). The first one – defined here as "site 1" – is the first to probe an air mass entering the test section. It therefore defines the initial air pollution levels in the tunnel section. Under normal conditions, i.e. when the flow of cars induces sufficient air movements, this site is "upwind" of the active section. Consequently, measurements at this point were considered not to be affected by photocatalysis during most of the time. The second one – referred to as "site 2" – is generally fed with air which has been in contact with the photocatalytic materials ("downwind" under normal traffic conditions).

3) A third approach is to monitor air pollution at the downwind site modulated by the UV lamps (*"on/off" approach*), to discriminate further between "active" and "non-active" periods of the photocatalytic materials. No further measurement point is necessary for that approach.

In addition, not only the absolute levels of harmful pollutants were compared, but also ratios of the pollutants (e.g. NO_x) to the inert emission tracer CO_2 were considered. In the absence of photocatalytic remediation, this ratio (e.g., NO_x/CO_2) - determined from plots of the pollutants (e.g. NO_x) against the CO_2 data - is independent of the variable dilution and of additional emissions between the two sites and thus simplifies the data evaluation (Gallus et al., 2015).

On both sites gaseous pollutants were sampled through 7 m long and 0.95 cm inner diameter sampling lines of polytetrafluoroethylene (PTFE) at a height of 20–40 cm below the tunnel ceiling (Fig. 2). In addition, meteorological parameters such as wind speed, wind direction, temperature and relative humidity were measured using two weather stations installed adjacent to the inlets of the gas sampling lines below the tunnel ceiling. More details on the specific detection methods can be found in (Gallus et al., 2015).

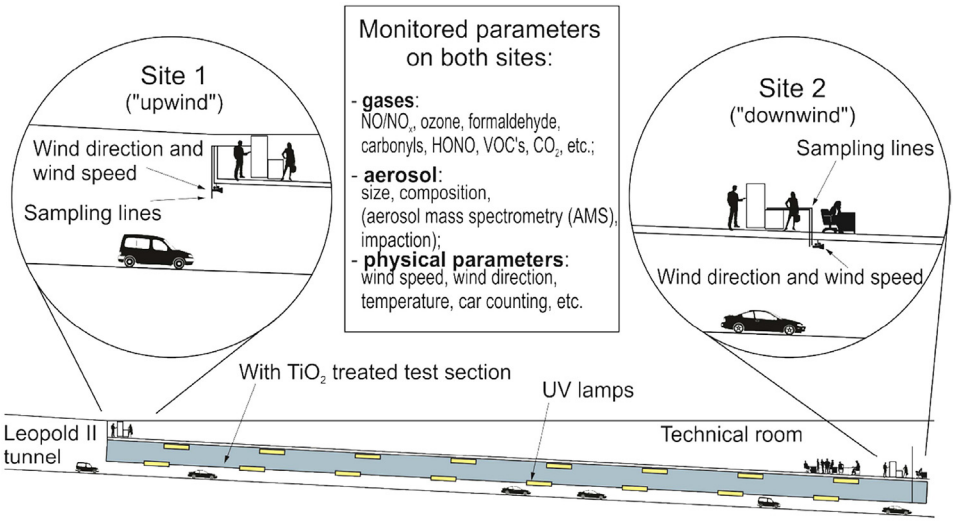

Fig. 2. Schematic representation of the test sites in the Leopold II tunnel during the PhotoPAQ campaigns.

3. First tunnel campaign

During the first main field campaign organized in the Leopold II tunnel the selected test section (Fig. 3) was located between security recesses 43 and 49, with a length of about 90 m measured on the road surface. It starts at a discontinuity in the tunnel ceiling (site 1), after which the cross section remains fairly constant (about 4.8 m × 8.4 m) and ends just before an extraction point (site 2, "first campaign"), to avoid the influence of air renewal on the measurements.

3.1. Preliminary measuring campaign – ante operam (June 2011)

A preliminary measuring campaign (*ante operam*) was performed in June 2011 in order to better prepare the actual field campaign of September 2011. Routine measurements of NO_x and CO_2 were conducted from 15/6 through 23/6/2011 on the two sampling sites shown in Fig. 3. This way, the expected pollution levels (NO_x/CO_2 ratios) and differences between the two measurement sites could be assessed with a view to evaluate the depollution effectiveness after the application of the photocatalytic materials in the test section (see approach 1).

3.2. Application of the photocatalytic material

The photocatalytically active material was the commercially available TX Active® white *i.active COAT* cement-based coating (hereafter: *TX*) provided by the industrial partner CTG Italcementi Group. It is a white fine-grained cementitious skim coat for spray application, coming in a powder form and based on the TX Active® technology, featuring de-polluting and self-cleaning properties (Italcementi, 2012). A "boosted", photocatalytically more active version was used in a second phase of the project (hereafter: *TX-Boosted*) – see Section 4.

During the PhotoPAQ project the material was extensively investigated in lab scale experiments for its photocatalytic activity; the results will be presented in forthcoming publications. This product is intended for spray-finishing large interior or exterior vertical surfaces, including tunnel vaults. It is prepared by intensively mixing the product with clean water (mean water/powder

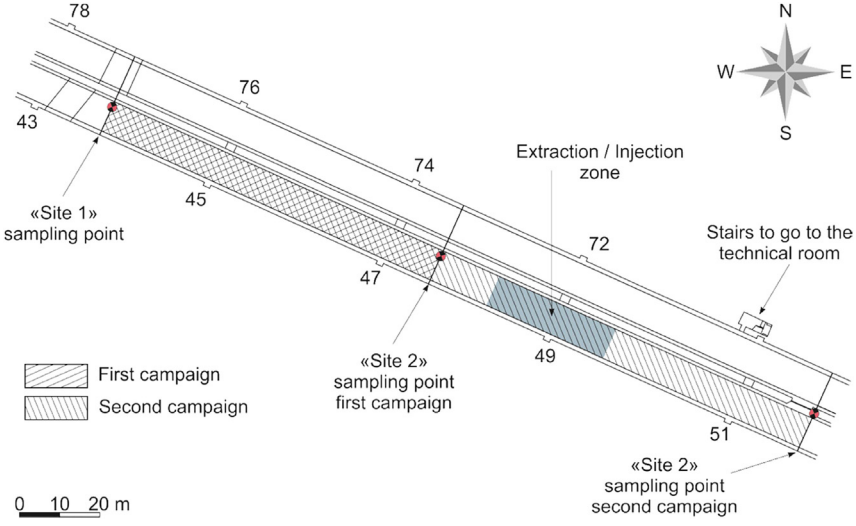

Fig. 3. Plan view of the tunnel test section for the first and second tunnel campaign.

ratio of 0.24), using an electric drill mixer until a smooth, lump-free batch is obtained. The application in the Leopold II tunnel was done with specific spraying devices (pumps) and adequate equipment (guns, nozzles), see Fig. 4a.

The complete implementation of the field site included the following tasks:

- cleaning of the tunnel vaults by washing;
- application of the TX coating by spray technology;
- installation of the UV lighting system;
- setting and hardening of the TX coating;
- set-up of the instruments in the technical room.

The photocatalytic cement-based TX material was sprayed on the ceiling and upper parts of the side walls of the tunnel over a total length of 70 m and in two layers, in order to obtain a homogeneous covering. Under normal circumstances the TX coat does not require any activation phase and is photoactive just after hardening. Furthermore, it should be noted that the substrate surface consisted mainly of very rugged "shotcrete" (sprayed concrete) walls, which had an impact on the final roughness of the coated tunnel surfaces as shown in Fig. 4b (middle).

3.3. Installation of the UV lighting

The application of photocatalytic materials in a closed environment makes special demands, as neither natural sunlight nor rain is present for natural activation or cleaning of the surface. Therefore an additional dedicated UV lighting system had to be installed in the tunnel. Special care was taken not to interfere with the users of the tunnel.

The artificial UV lighting was provided by Disano Illuminazione S.P.A, an Italian company which already had the necessary experience from the installation of a similar lighting system in a tunnel in Rome (Guerrini, 2012). Simulation design studies were performed to assess the UV lighting levels in connection with the tunnel geometry and the activation of the photocatalytic material, and in accordance with road traffic safety in the tunnel, in order to avoid the risk of interference with the tunnel users. Finally, a lighting system consisting of two rows of 13 and 14 armatures – including two 80-W PHILIPS type 'TL80W/10–R' light bulbs per lamp armature – each with an inter-distance of 7.5 m was attached to the side walls and the ceiling of the test section, respectively (see Fig. S1 of Supplementary materials). Thus, a total of 54 UV lamp armatures were used to provide an average UV-A irradiance of about 1.6 W/m^2 for the side walls and around 1.7 W/m^2 for the ceiling.

The final installation of the UV lighting was completed in September 2011 1 week after the application of the photocatalytic cementitious coating, to allow some time for setting and hardening. However, measurements performed in the tunnel revealed that the actual irradiance level (range: 315–420 nm) was much lower than expected, 0.6 ± 0.3 W/m^2 on average, which also impacted the final results as discussed below and in (Gallus et al., 2015).

3.4. First tunnel campaign – post operam (September 2011)

Using the strategy and types of pollutant reported in Section 2.2, the first main tunnel campaign took place between the 9th and 23rd of September 2011. The first two days were spent on the intercalibration of the duplicate instruments for sites 1 and 2 (cf. Fig. 2), by placing them on one site sampling the same air from the tunnel. Considering the complexity of the scientific instruments used, it is clear that such an extensive field campaign requires a thorough logistic organization.

Measurements were performed day and night during the two-week campaign, taking into account all kinds of traffic conditions including the maximum and minimum traffic volumes (*i.e.*, congestion or no traffic at all). In addition to air pollution measurements at the two stations also selected meteorological parameters were recorded, namely temperature, relative humidity, and wind speed and direction (Section 2.2).

As discussed before, a triple strategy was adopted to assess the de-polluting effect by:

i) Before/after approach
ii) Upwind/downwind strategy
iii) Lamps on/off analysis

Detailed results using all three strategies to investigate possible photocatalytic NO_x de-pollution in the tunnel are presented and discussed in (Gallus et al., 2015).

However, some difficulties arose during the implementation of the first campaign:

Fig. 4. a) Typical equipment needed for the preparation and application of the photocatalytic cementitious coating material used in the Leopold II tunnel, and b) spraying and associated surface finish on shotcrete and concrete blocks, respectively.

- the test section was not coated entirely, only about 70 m of the initially planned 90 m;
- the UV-A irradiance level was lower than expected (0.6 versus 1.6 W/m^2);
- de-activation in terms of photocatalytic activity of the TX material used.

These issues contributed to the fact that the measurable photocatalytic reduction of major pollutants in this first field campaign was below the precision errors (about 2%) of the instruments used (Gallus et al., 2015). Actually, a severe surface passivation of the photocatalytic coating mortar was identified under these tunnel conditions (see the section below). It is possible that the low level of UV irradiation together with the roughness of the surface and the highly polluted tunnel conditions provoked an accelerated build-up of dirt and grime on the photocatalytic coat, thereby dramatically reducing its efficiency.

To verify this hypothesis, sample plates sprayed with the TX product from the first tunnel campaign were tested for their photocatalytic activity before and directly after being stored in the tunnel, using a bed flow photoreactor similar to the ISO 22197-1 approach (Boonen and Beeldens, 2013; ISO, 2007). The reduction in nitrogen oxides NO_x (= NO + NO_2) concentration was measured at the outlet of the reactor for an initial inlet concentration of 1 ppm NO, a relative humidity of 50%, an air flow rate of 3 l/min, an active surface area of 200 cm^2 in combination with an air volume of 100 cm^3, and an UV-A irradiance of 4 W/m^2. Analysis of the data showed that the commercial product used in the tunnel campaign was rapidly deactivated owing to the high pollution in the tunnel, leading to significant NO_x emissions measured directly after the exposure in the tunnel (Table 2: *1 week in tunnel*). Such emissions were also observed in other laboratory studies performed on irradiated TiO_2/SiO_2 films, as a consequence of photocatalytic decomposition of adsorbed nitrate (Monge et al., 2010). In addition, the NO_x emissions observed for the cementitious material may also be explained by the desorption of adsorbed nitrogen oxides originating from the tunnel.

Subsequent treatment of the surface in the lab for several days with even stronger UV-A than in the tunnel (*after tunnel + 121 h UV-A treatment at 4 W/m^2*) and/or washing of the sample (*after tunnel + 121 h UV-A + washing*) was not enough to regain sufficient photocatalytic activity of the passivized samples (Table 2). This observation is explained by the limited ability of the applied surfaces to efficiently oxidize and remove adsorbed pollutants (e.g., semi-volatile VOCs, “grime”, etc.) from the surface, even at 4 W/m^2 irradiance level. In view of these results and the knowledge gained during an intermediate laboratory campaign (see Section 4.1 and Supplementary material S2), it was decided to perform a second main measuring campaign in order to respond to the difficulties and problems met in the first one, mainly the low efficiency of the investigated material under the tunnel conditions and the low irradiance levels obtained.

Table 2
Reduction in the initial NO_x level due to the photocatalytic reaction, measured in a bed flow photoreactor similar to the one specified in ISO 22197-1 (ISO, 2007) on test plates with TX material from the September 2011 campaign, before and directly after being kept in the tunnel for 1 week, and after subsequent UV-A treatment and/or washing of the surface. Negative figures indicate a production of pollutants.

Sample	Reduction NO_x [%]
Before tunnel	33
1 week in tunnel	−40
After tunnel +121 h UV-A treatment at 4 W/m^2	1
After tunnel + 121 h UV-A + washing	7.5

4. Second tunnel campaign

During the second main campaign a similar strategy was followed as in the September 2011 campaign, with the following differences:

- increased length of the test section (160 m instead of 70 m);
- higher UV-A irradiance, with a targeted level of at least 4 W/m^2;
- use of a more active material newly prepared by Italcementi (TX Active Skim Coat Boosted, defined here as *TX-Boosted*) to provide a higher photocatalytic activity, and much less subject to de-activation at 4 W/m^2 (see below).

In addition, prior to the execution of the second campaign some preliminary testing on a laboratory scale was performed to see whether the “new” photocatalytic surfaces could be activated with the planned UV irradiance levels under the tunnel conditions.

4.1. Intermediate laboratory campaign

The main objective of this intermediate laboratory study was to see if the rate of activation (under UV lighting) was faster than the rate of deactivation (under the polluted tunnel conditions), to be sure to have a photocatalytically active product in the tunnel during the second campaign. More details and test results can be found in Supplementary material S2.

The main conclusions that could be drawn from this intermediate laboratory campaign were that:

- de-activation initially occurred for all samples and even resulted in emission of pollutants for the cementitious coatings after one week of storage in the tunnel;
- all samples could be reactivated under UV after being inside the tunnel, although not always to the original level of activity;
- the TX-Boosted product performed better than the commercial TX product tested in the measuring campaign of September 2011. The reactivation rate was reasonable (about 60% of the activity for NO regained) and the NO_2 yield during the laboratory test was lower than with the other samples, although significantly higher than with TX samples not exposed to the tunnel air, see Table S2 in Supplementary material S2;
- application by brush or trowel makes no significant difference in photocatalytic activity. A higher activity is expected from application by spraying, although it is also likely that more dirt and dust will be deposited in that case;
- washing of the samples with demineralized water could have an additional effect for reactivation, as confirmed by other studies (Strini et al., 2014).

In view of these tests, and in order not to completely change the surface properties investigated (i.e., cementitious versus polymeric materials), the PhotoPAQ consortium decided to continue in the second tunnel campaign with the TX-Boosted cementitious coat produced by the PhotoPAQ industrial partner.

Finally, an additional test was performed to check if reactivation under UV could also take place in the presence of the polluted tunnel air. The experimental set-up and corresponding results of this last test are explained in more detail in Supplementary material S3. This final test (see Fig. S3a and b in Supplementary material S3) led us to conclude that the TX-Boosted material should be able to work under the tunnel conditions and a second main campaign inside the Leopold II tunnel would be feasible.

4.2. Preparation of the second tunnel campaign

Besides increasing the irradiance level to at least 4 W/m^2 so as to match the irradiance applied in the laboratory, and in addition to using the aforementioned more active TX-Boosted material, it was decided to extend the test section in order to increase the expected pollution remediation. As a result, besides the original site 1 a new sampling site 2 needed to be identified at a significantly longer distance. During the first main campaign the two sampling sites were separated by approximately 70 m. After thorough inspection, it was decided to keep the first sampling site used in September 2011 (site 1) and to select a new sampling site 2 some 90 m away from the "former" site 2, leading to an active test section of around 160 m – see Fig. 3.

However, unlike in the first measurement campaign one extraction/injection zone of the ventilation system was located at approximately three quarters of the distance between these new sampling points. As the overall duration of the ventilation periods was rather short (only during morning rush hours), in accordance with the results from the September 2011 campaign, it was considered nonetheless that neglecting these periods would have a minor impact on the demonstration of the final de-polluting effect.

The new TX-Boosted material was applied in this extended test section after high-pressure water cleaning of the surface of the tunnel vault. This cleaning step was repeated after the application of the material, just before the start of the measurements (Section 2.2).

As an increased UV-A irradiance of the order of at least 4 W/m^2 was planned, a large number (212) of more powerful 400-W Supratec 'HTC 241 R7s' UV lamps from Osram were used (Fig. 5) for this second main tunnel campaign. In addition, it was decided to create a 40-m transition zone behind the test section (160 m) with extra, "normal" visible light lamps, in order to overcome the so called "blinding effect". This effect is known to arise from the sudden transition from the highly illuminated test zone to the "darker" zone in the rest of the tunnel. With this new UV lighting system – consisting of two rows of 64 and 42 armatures with a distance of 2.5 and 3.75 m in between for the side walls and the ceiling, respectively – it was expected that the average irradiance levels on the side walls and ceiling of the extended test section would be of the order of 4.15 and 4.70 W/m^2 UV-A, respectively. The installation of these new lamps started in December 2012, one week after the application of the photocatalytic material.

Unfortunately, a severe problem occurred when switching on these powerful UV lamps after installation. Several glass covers broke some time after the ignition of the lamps. For safety reasons, the installation was temporarily stopped to discuss and assess alternative options. Finally, it turned out that the lighting armatures used were not entirely adapted to the shorter UV light causing punctual heating by the glass cover, due to the absorption of a significant fraction of UV light <350 nm. This led to problems with the structural integrity of the glass and ultimate breaking when switching on the UV lights. As a solution, metallic deflectors were installed inside the lamp holder to reduce the direct UV intensity and the punctual heating of the glass cover, as shown on the inset of Fig. 5.

It was decided to delay the implementation of the second main campaign for a few weeks, to fix the problems with the UV lighting and to conclude the final installation (Fig. 5). As a result, the actual measuring campaign started only in January 2013 and these "special" circumstances also partially affected the final results of the second tunnel campaign, as discussed below and in (Gallus et al., 2015).

4.3. Implementation of the second tunnel campaign (January 2013)

Using the same strategy as for the September 2011 campaign, a second main measurement campaign was conducted from 21st of January through 1st of February 2013. This included the installation of all instruments on both sampling sites, the calibration and harmonization of the analysers, the actual measuring campaign, and the removal of the instruments afterwards.

Once again, the results from this second tunnel campaign indicated *no observable reduction in pollution level*, in contrast to first estimations based on the laboratory studies (e.g. Section 4.1, and Supplementary materials S2 and S3). More detailed results and an elaboration on the NO_x measurement data can be found in (Gallus et al., 2015).

The reason for the low NO_x abatement should be sought in the unfortunate coincidence of several adverse events during the implementation phase. First of all, the problems with the new UV lighting system and the corresponding delay in the installation (cf. Section 4.2) led to the fact that after application the photocatalytic coating material was left inside the tunnel for six weeks without UV activation, instead of the initially planned one week. As a result, severe deactivation of the TX-Boosted material was observed in the

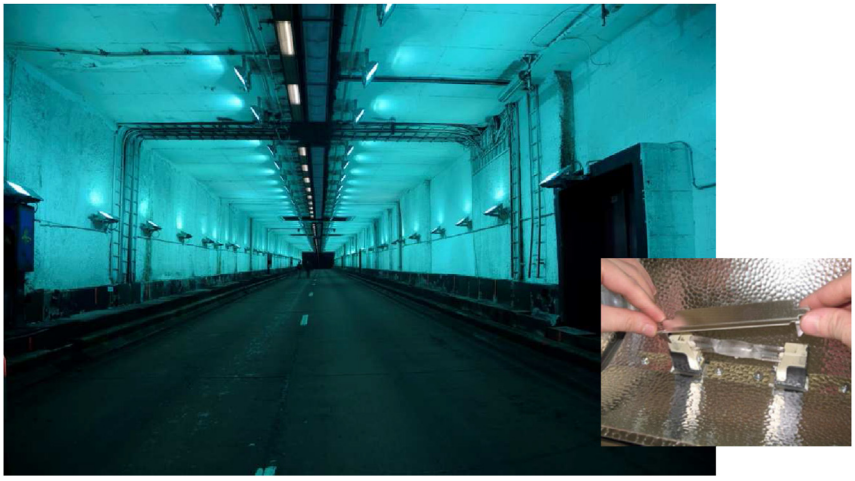

Fig. 5. Final installation of the UV lighting in the Leopold II tunnel during the second main campaign (January 2013). Inset: metallic shutters used to solve the problem of glass heating and subsequent breaking.

highly trafficked and heavily polluted Leopold II tunnel. In conjunction, owing to the metallic shutters (cf. inset of Fig. 4) and the UV-absorbing glass plates used for the lamps, the final average irradiance (between 315 and 420 nm) dropped to 1.6 ± 0.8 W/m^2 (see Figure S4 in Supplementary material S4); this was below the target values (above 4 W/m^2) and insufficient for proper activation in the polluted tunnel environment. Another adverse condition was the high wind speed (up to 3 m/s) in the tunnel –which is, however, typical of a one-way road tunnel –, limiting the contact time between pollutants and the active surface. Finally, January 2013 was marked by an unusually wintry period causing cold and humid conditions in the tunnel, with relative humidity ranging from 70 to 90 % which also reduced the activity of the photocatalytic material, as illustrated in Fig. 6.

To study the influence of these changed conditions on the experimental results, measurements were once again performed on photocatalytic sample plates using the ISO-type bed flow reactor discussed before. These samples were produced concurrently with the application of the material in the second campaign, and stored in the tunnel during the entire field campaign (approximately 6.5 weeks) prior to the laboratory experiments. Upon testing, a significantly reduced photocatalytic activity compared to the clean reference samples was observed at the low irradiance and high humidity levels of the tunnel study, as indicated in Fig. 6. Photocatalytic activity is presented here in terms of the deposition velocity of NO [cm/s], as defined in equation (S2a) of Supplementary material 2 and in (Ifang et al., 2014).

Thus, the combination of the adverse effects of the individual parameters discussed above resulted in a significant reduction of the activity of the photocatalytic surfaces in the harsh environment of the Leopold II tunnel, by a factor of 6 for NO compared to the theoretical expectations based on the reactivated lab samples of Table S2 in Supplementary material S2 (cf. "prelim" in Fig. 6). In comparison with fresh original samples as typically used in standardization tests, even a reduction in NO reactivity by a factor of 12 was observed. In addition, a 50% higher NO_2 yield was observed for the de-activated tunnel sample, which increased the de-activation problem even further if the total NO_x reduction is considered.

Based on the observations from the tunnel and the lab experiments of Fig. 6, it is concluded that the de-activation of the used photocatalytic mortar surfaces is caused, at least in part, by a) observed sticking of particles, for example, soot, brake dust, etc., and b) by adsorption of low/semi-volatile organic hydrocarbons ("organic grime") on the surfaces, blocking the active sites for the photocatalytic NO_x oxidation. Adsorbed organics are proposed here since the tunnel samples showed higher photocatalytic formaldehyde (HCHO) emissions compared to freshly prepared surfaces (Gallus et al., 2015).

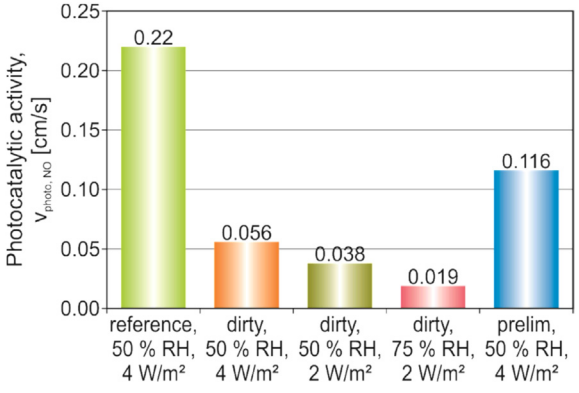

Fig. 6. Photocatalytic activity expressed as deposition velocity $v_{photo,NO}$ [cm/s](see Supplementary material S2 and [Ifang et al., 2014]) and determined on different samples before (= "reference") and after (= "dirty") exposure to the tunnel environment, for different testing conditions (RH = relative humidity, UV light intensity in W/m^2) and based on the preliminary testing (see Section 4.1 and Table S2 of Supplementary material S2) for the preparation of the second tunnel campaign (= "prelim").

Nevertheless, by combining the knowledge gained during the tunnel campaigns and the laboratory investigations performed by the PhotoPAQ consortium numerical simulations were performed in order to estimate the possible best-case abatement of pollutants and to provide a tool for extrapolating the PhotoPAQ field results to other urban tunnel sites (Gallus et al., 2015; PhotoPAQ, 2010–2014). Using these calculations, optimized (experimental) boundary conditions – in terms of UV lighting intensity level, meteorological conditions (wind speed, humidity, etc.), and the geometrical configuration of the tunnel including the ratio between the active surface and volume of air to be treated – were proposed under which photocatalysis technology might be applicable in road tunnels.

Finally, in view of the results from the present study it is recommended that future users should test photocatalytic materials for possible de-activation under the exact tunnel conditions, for example as explained in detail in Supplementary materials S2 and S3. Ideally, comparative measurements should be performed using the same photoreactor as in the laboratory for testing in the polluted tunnel. The photo-reactor should be fed with polluted tunnel air while simultaneously being irradiated by the UV lamps to be installed in the tunnel with the expected tunnel irradiance level. Subsequently, by using two NO_x monitors at the in- and outlet of the reactor, respectively, the photocatalytic deposition velocity should be measured from the average difference between the input and output concentrations. This data could then be used in the PhotoPAQ fast calculation tunnel tool (PhotoPAQ, 2010–2014), to calculate the expected upper limit of pollution reduction under the prevailing tunnel conditions (wind speed, relative humidity, tunnel geometry, etc.). With this procedure it could be checked if a specific "photocatalytic tunnel application" makes sense or not.

5. Conclusions and perspectives

The Leopold II field campaigns conducted by the *PhotoPAQ* team proved to be a unique real-world and fully comprehensive assessment of the effect of photocatalytic air-purifying materials on air pollution inside a tunnel environment. Although the final results were not as expected, a lot of useful information was gathered on air pollution dynamics in tunnels and the setting up of a tunnel field campaign.

Furthermore, recommendations for the proper use of photocatalytic materials can be made, such as:

- optimized application of the photocatalytic coating on a regular substrate, in order to obtain a low surface roughness minimizing dust adsorption;
- high UV light intensity levels ideally around 10 W/m^2, to avoid surface passivation;
- adequate design of the illumination system (visible plus UV light), to reach acceptable investments in terms of cost-benefit ratio (Ravesloot, 2012);
- low average relative humidity of tunnel air (≤60%);
- high photocatalytic activity of the de-polluting material, with a photocatalytic deposition velocity for NO of at least 0.1 cm/s measured under tunnel conditions;
- low average tunnel wind speed, for increased reaction time of pollutants;

- two-way tunnels, for increased reaction time and turbulent mixing;
- high active surface-to-volume ratio (smaller-sized tunnel tubes); in absolute terms, the length of the tunnel should be adequate to have an appreciable de-pollution effect.

Based on the extensive experimental data set gathered and the numerical model calculations performed, a valuable tool for extrapolation can be provided to estimate an upper limit of the pollution reduction to be expected on future road tunnel sites (PhotoPAQ, 2010–2014). This tool could also be used by non-experts to check the feasibility of applying photocatalytic materials for air purification purposes in an urban environment.

However, it should be highlighted that potential users should test the photocatalytic material under "real tunnel conditions" to check for possible de-activation issues, in order to correctly quantify the expected pollution reduction and thus to enable a complete cost-benefit analysis, before setting up a "photocatalytic tunnel".

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2015.03.001.

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