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RESEARCH ARTICLE

Real-life Field Studies of the NO_x Removing Properties of Photocatalytic Surfaces in Roskilde and Copenhagen Airport, Denmark

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ARTICLE HISTORY

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Abstract: ***Aims*:** To evaluate the real-life effect of photocatalytic surfaces on the air quality at two test-sites in Denmark.

***Background*:** Poor air quality is today one of the largest environmental issues, due to the adverse effects on human health associated with high levels of air pollution, including respiratory issues, cardiovascular disease (CVD), and lung cancer. NOx removal by TiO_2 based photocatalysis is a tool to improve air quality locally in areas where people are exposed.

***Objective*:** To demonstrate and quantify the NOx removal capacity of photocatalytic asphalt and concrete in real life.

***Methods*:** Two test sites were constructed in Roskilde and Copenhagen airport. In Roskilde, the existing asphalt at two parking lots was treated with TiO_2 containing liquid and an *in-situ* ISO 22197-1 test setup was developed to enable *in-situ* evaluation of the activity of the asphalt. In CPH airport, photocatalytic concrete tiles were installed at the "kiss and fly" parking lot, and NOx levels were continuously monitored in 0.5 m by CLD at the active site and a comparable reference site before and after installation for a period of 2 years.

***Results*:** The Roskilde showed high stability of the photocatalytic coating with the activity being largely unchanged over a period of 2 years. The CPH airport study showed that the average NOx levels were decreased by 12 % comparing the before and after NOx concentrations at the active and reference site.

***Conclusion*:** The joined results of the two Danish demonstration projects illustrate the high stability of the photocatalytic coating as well as a high potential for improvements in the real-life air quality in polluted areas.

Keywords: Photocatalytic surfaces, air purification, titanium dioxide, nitrogen oxides, field studies, asphalt, concrete.

1. INTRODUCTION

Poor air quality is today one of the largest environmental issues, due to the adverse effects on human health associated with high levels of air pollution, including respiratory issues, cardiovascular disease (CVD), and lung cancer [1-4]. A recent report from the Lancet Commission on Pollution and Health claims that exposure to contaminated air, water, and soil annually causes 9 million premature deaths, corresponding to 16 percent of all global deaths, predominantly in low-income countries. This is three times as many as are killed by AIDS, tuberculosis, and malaria collectively [5]. According to the World Health Organization (WHO), outdoor air pollution annually causes 4.2 million premature deaths, while 9 out of 10 breath air containing high levels of pollutants [6]. In 2010, the British Environment Audit Committee estimated that the cost of health impacts of air pollution in the UK alone was likely to exceed estimates of £8 to 20 billion [7], while the Lancet Commission concluded that air pollution control pays off £1-30 [5], underlining furthermore the economic incentives of improving the global air quality. Among the most important air pollutants are the NO_x gasses (NO and NO_2), which are mainly emitted from the combustion of fossil fuels, with car engines contributing 40 % of anthropogenic emissions in 2005 [8]. The health effects associated with increased levels of NO_2 are still being debated due to difficulties in separating the effects of NO_2 from those of other pollutants [9, 10]. Exposure has previously been linked to increased risks of mortality, lung cancer and respiratory problems in asthmatic children among other effects [10-12]. NO_x is furthermore involved in the formation of several other of the main atmospheric pollutants, as tropospheric NO_x chemistry mediates ozone formation and contributes to the formation of secondary organic aerosol (SOA), *via* oxidation of volatile organic compounds (VOCs) [13]. The only significant sink for tropospheric NO_x is the reaction of NO_2 with OH radicals, resulting in the formation

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of HNO_3, which is one of the main constituents of acid rain. The current EU Directive specifies a limit on ambient NO_2 of 32 mg/m^3 as the annual mean concentration, as well as an hourly limit of 140 mg/m^3 that must not be exceeded on more than 18 occasions a year [14], however, these limits are exceeded on regular basis in many European cities [15, 16]. Existing NO_x emission control technologies include both pre- and post-formation strategies [17]. The most widely used post-formation technology is selective catalytic reduction (SCR), in which exhaust gas mixed with ammonia is passed through a catalyst to facilitate the reaction between NO_x and ammonia to produce nitrogen and water [18]. Alternatively, NO_x can be removed post emission, *e.g*. in areas where human exposure is high. This principle is the basis of photocatalytic removal strategies, where sunlight, water and a titanium dioxide, TiO_2, catalyst are used to remove pollutants from ambient air. The basic principle of photocatalysis was first discovered four decades ago by Fujishima and Honda, and the possibilities for using TiO_2 based photocatalysis for removal of various pollutants have since been the subject of various studies [19-22]. Photocatalysis utilizes the semiconducting properties of TiO_2. Illumination of the catalyst by UV light induces transfer of electrons from the valence band to the conduction band, resulting in the formation of an electron/ whole pair. In the presence of water, the high reactivity of the hole, h^+, enables electron transfer from OH^- ions, resulting in the formation of hydroxyl radicals, OH, and deactivation of the TiO_2 catalyst:

$$OH^- + h^+ \rightarrow OH^{\cdot} \quad (1)$$

The following oxidation process at the catalyst surface closely resembles the tropospheric NO_x removal mechanism, in which NO_x is converted into nitrate, NO^-_3 by reaction with OH radicals:

$$NO + 2OH^{\cdot} \rightarrow NO_2 + H_2O \quad (2)$$

$$NO_2 + OH^{\cdot} \rightarrow NO_3^- + H^+ \quad (3)$$

The resulting nitrate is extremely soluble in water; hence, it is easily washed away. As OH radicals are strong oxidizing agents, the photocatalytic reduction is not limited to NO_x gases, but has the potential to remove also, *e.g*., VOCs and SO_2. Incorporation of photocatalysis into building materials, such as cement has gained interest due to its self-cleaning as well as air purifying properties [23-25]. The potential for removal of different airborne pollutants has been proven in a range of laboratory studies [26-29], and a recent report by the Environmental Industries Commission furthermore suggested that applying photocatalytic treatment to roads is amongst the cheapest options to reduce PM and NO_x pollution [30]. However, evaluating the real-life potential for air quality improvements, regardless of it is photocatalysis or any other NOx reducing technology, presents a great challenge due to the many parameters related to weather and traffic that significantly impact ambient NOx levels [31], [32]. A number of photocatalytic field studies have been conducted with overall promising results [33-49]. Here, we present the results from recent real-life field studies in Roskilde and Copenhagen Airport, Denmark, and compare them with preliminary results from a large-scale test site in Stuttgart, Germany. The joined studies show high stability of the photocatalytic surface as well as the promising potential for improvement of the air quality.

2. METHODS

In this section, we present the experimental approaches followed in the Roskilde and Copenhagen Airport studies.

2.1. Roskilde Field Study

The demonstration project in Roskilde was executed by Photocat A/S in collaboration with the Municipality of Roskilde. The project had a duration of three years and aimed to test the activity and durability of a photocatalytic treatment of asphalt, NOxOFF, which is developed by Photocat A/S. The project was divided into a laboratory and an *in-situ* part as described in the following section.

2.1.1. Photocatalytic Coating

The asphalt samples for the laboratory tests as well as the *in-situ* test site were treated with Photocat NOxOFF TC 400, which is a TiO_2 containing fluid with a particle size of 30 nm ± 10 nm. Material consumption is approximately 10 m^2/l [50].

2.1.2. Laboratory Tests

Prior to the construction of the test site, the photocatalytic activity of the photocatalytic coating was tested in the laboratory. Asphalt samples were collected from a renovation project in the municipality of Roskilde. The samples were cut in dimensions of 49 x 99 mm^2, washed with deionized water, and dried before application of the TiO_2 containing treatment (Photocat NOxOFF TC 400). After the application, they were finally left to dry overnight. The treated samples were afterward tested according to the ISO 22197-1 standard [51]. The light source was UVA-340 fluorescent tubes from Q-lab, the light detector was PMA2100 from Solar Light with UVA detector PMA2100 (320-400 nm) and the NO_x analyzer was a Horiba APNA NO_x analyzer model 370 (detection limit of 1 ppb). The test conditions were set according to the ISO standard and are given in (Table **1**). The samples were then subjected to an accelerated aging test according to the EN 1297-2004 procedure (QUV/Spray from Q-lab) [52]. Additional ISO tests were performed after 138, 300, and 586 hours of accelerated aging corresponding to an estimated time of 6 months, 1 year and approximately 2 years of aging in real-time. Finally, the amount of catalyst in the formulation is optimized to obtain maximum absolute activity.

2.1.3. In-situ Setup

For the *in-situ* activity measurements, a portable ISO 22197-1 setup was developed. An Eco Physics CLD NO_x analyzer (detection limit 1 ppb) was installed in a vertical rack, which is installed in a van along with two diaphragm pumps, gas cylinders, and flow meters. The main difference from the common ISO test setup is the construction of the test cell. In the *in-situ* setup, the cell was constructed without a bottom, so that it can be installed directly at the active surface, and with a UV transparent 5-8 mm polycarbonate lid. Two different test cells of 100 cm^2 and 532 cm^2 were used. Installing the cell without destroying the cell or the surface while ensuring that the setup is airtight presents a challenge,

which was here solved by using playdough as the sealing gasket. The diaphragm pumps collect ambient air which was then passed over the cell. The flow rate was monitored by a flow meter. The light intensity was measured by a PMA2100 analyzer. The setup is shown in (Fig. **1**). Three types of experiments were performed with the conditions given in Table (**2**).

Table 1. Test conditions for the ISO 22197-1 experiments.

Inlet Concentration	1.0 ppm NO
Air flow	3 L/min
Temperature	20°C ± 5°C
Relative humidity	50 ± 15 %
Light intensity	1.0 mW/cm^2 UVA

2.1.4. Construction of Test Site

Two parking lots located in the municipality of Roskilde, Denmark, (Bønnelyckes Plads and Skt. Peder./SKt Ols Stræde, hereafter referred to as PL1 and PL2) were chosen as the test sites (Fig. **2**). Both parking lots are located centrally in Roskilde close to busy streets. A total of 5000 m^2 of the photocatalytic surface was constructed with 3800 m^2 at PL1 and 1200 m^2 at PL2. The existing asphalt at both sites was treated with Photocat A/S NOxOFF fluid. The application of the photocatalytically active coating was done on September 29^{th,} 2014. Both locations were initially swept with a manual sweeping machine and the Photocat TC 400 coating was applied to the asphalt and left to dry for 120 minutes before the parking lot was re-opened to traffic.

2.1.5. Monitoring Campaign

The first *in-situ* measurements were conducted in March 2015, 5 months after the application. In total, three *in-situ* measurements were performed during the campaign on March 5th 2015, September 9th 2015, and April 20th 2016. All measurements were conducted in the afternoon. To estimate peak concentrations, one background measurement was initially performed at PL2 using the Eco Physics CLD NO_x analyzer.

2.2. Copenhagen Airport

In 2012 and 2013, a larger demonstration project was executed in Copenhagen Airport. The project was partly financed by Fornyelsesfonden and supported by Copenhagen Airport, IBF A/S and Photocat A/S. The project was presented on October 17, 2013, at the conference 'Fotokatalytiske Materialer i Byrummet'. The conference was arranged by Dansk Selskab for Materialeteknologi (DSM) and held at Ingeniør huset in Copenhagen [53]. The project had a duration of 2 years, where the first part was to demonstrate the efficiency in the lab, using the ISO 22197-1 standard. The second part was to design the best suited real-life experiment based on previous attempts made to demonstrate air quality improvement with photocatalysis [33, 34, 36, 38, 39]. The purpose of the project was to evaluate and demonstrate the air purifying properties of a photocatalytic concrete stone -

Fig. (1). The Roskilde *in-situ* monitoring setup (left panel) and one of the two *in-situ* test cells installed at the monitoring site (right panel). (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

Table 2. Test conditions for the *in-situ* experiments in Roskilde.

	Ambient Experiment	Model Experiment 1	Model Experiment 2
Temperature	Ambient	Ambient	Ambient
Relative humidity	Ambient	Ambient	Ambient
Light source	Ambient	Ambient	Artificial (3.0 mW/cm^2 UVA)
Initial NO concentration	Ambient	Model gas (100-500 ppb)	Model gas (100-500 ppb)

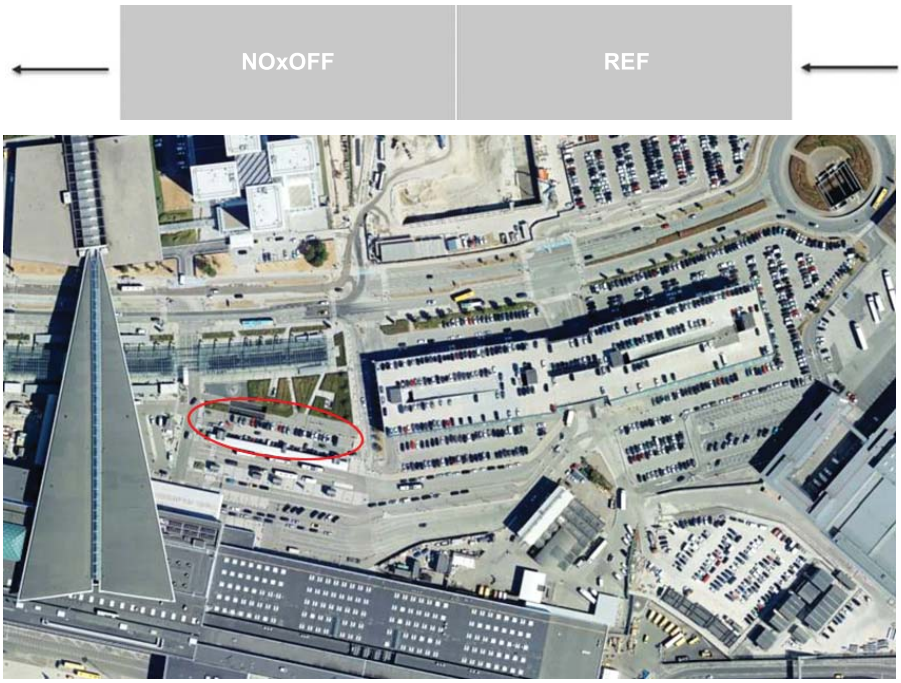

Fig. (2). Location of the test site in Copenhagen Airport (lower panel) and schematic representation of the test site design (top panel). The arrows indicate car flow direction. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

NOxOFF concrete. The technology behind the photocatalytic stone was developed by Photocat and the product was commercially launched by IBF Denmark.

2.2.1. Photocatalytic Concrete

The NOxOFF concrete technology is based on a waterborne solution containing small-sized TiO_2 with a particle size of 30 nm ± 10 nm consisting of approximately three aggregated crystals of anatase TiO_2 with a crystallinity of > 95 % [54, 55]. The solution further optimized to adhere to concrete as an inorganic binder was included as well as stabilizing agents resulting in the stability of this solution of more than 12 months. The NOxOFF solution was spray applied on the concrete pavement tiles after casting and can be applied either wet, directly after casting, or dry, more than 24 hours after casting. Here, it is applied dry. This ensures that the TiO_2 catalyst is located in the outermost surface of the concrete tiles, 1-2 mm depth, to optimize the activity and avoid additional cost by introducing catalytic TiO_2 in the matrix of the concrete where it has no photocatalytic effect. More than 100 g/m^2 product was applied. NOxOFF IBF Modulserie 30x10x10 cm (manufactured by IBF, Denmark) was produced and used to test in the lab as well as to test the real-life effect of produced photocatalytic concrete stones, in the following referred to as NOxOFF stones. The amount of photocatalytic dispersion was applied with an automatic spraying set-up. 150 g/m^2 of photocatalytic dispersion was applied to the stones with a hydraulic nozzle set-up.

2.2.2. Laboratory Tests

For that lab testing after ISO 22197-1 the product was cut into 5x10 cm^2 pieces and cleaned with deionized water and then dried for 24 hours in ambient air before the NO_x performance was evaluated according to ISO 22197-1. The samples were tested according to the following steps: 1) NO degradation tested according to ISO 22197-1 after the application of Photocatalytic dispersion and 24 hrs. ambient drying. 2) The samples tested in Step 1 were tested against outwashing by rainwater by dropwise application 900 ml deionized water to the 5x10cm^2 sample (appr. 30 min treatment). The sample was subsequently ambient surface dried and then dried at 105 °C for 24 hours. Dryness is confirmed when a constant mass is reached. Hereafter, the samples were tested for NO degradation according to ISO 22197-1, at conditions given in Table (**1**).

2.2.3. Field Study

After testing the NOxOFF stone in lab, 250 m^2 of NOxOFF stones were produced and dried before installing them on parking lot P8 at Copenhagen Airport, which was chosen as a testing site. P8 is a 'kiss-and-fly' payment parking lot, where the cars enter from one side and leave from the other side. The testing parking lot was divided into a reference site, which continued to be a reference site throughout the entire test period, and an active site, where the concrete tiles halfway through the study were changed to NOxOFF concrete tiles. Each of the sections on the parking lot was 250 m^2 (5x50 m) and all cars driving through the reference section have to drive through the NOxOFF section as well. In the basement next to the parking lot P8 an Eco Physics, CLD NO_x analyzer (detection limit 1 ppb) is mounted. The NO_x analyzer is installed with two solonoid valves for multiplexing controlled by data logger, so it will measure 30 sec. at the reference site and then switch to measure 30 sec. at the NOxOFF site. This procedure is continued for the entire measuring time. This ensures that no calibration issues between two apparatus occur. The NO_x analyzer is calibrated before the measuring campaign as well as halfway through the campaign by C.K. Environment A/S. Every night the NO_x data is transferred *via* the GSM network. The NO_x con-

centration was measured in heights of 0.5 m on both measuring sites. The reference site is expected to closely resemble the action in terms of weather and traffic conditions, however, even minimal differences have previously been shown to affect the NO_x levels [31]. To minimize this uncertainty, the relation between the NO_x concentrations of the two sites before installing NOxOFF stones (blank period) was then compared to the relation between NO_x concentration after the NOxOFF stones were installed. The blank measuring campaign took place from March 17 to April 28, 2013 (41 measuring days). Between April 29 to May 10, the NOxOFF stones were installed and from May 11 to July 4 (43 measuring days) the measuring campaign for the active site was done.

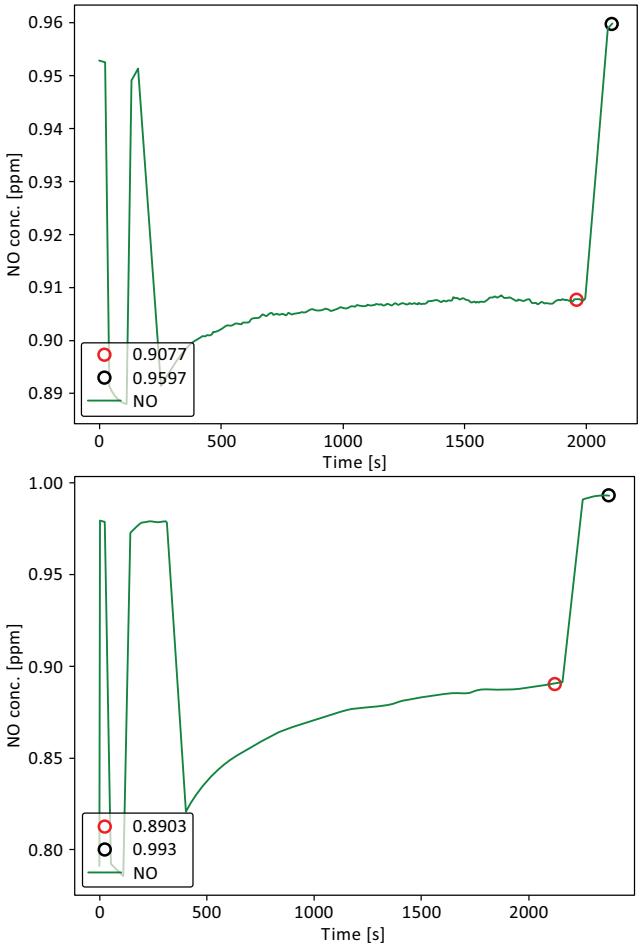

Fig. (3). ISO 22197-1 test results after 0 hours of aging before (top panel) and after (lower panel) optimization of absolute activity of the NOxOFF asphalt. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

3. RESULTS AND DISCUSSION

3.1. Roskilde Field Study

In this section, we present and discuss the results from the laboratory and *in-situ* measurements conducted in the Roskilde field study. In subsection 3.1.5, we further present an estimate of the potential savings related to decreased health costs.

3.1.1. Laboratory Tests

Fig. (**3**) shows the ISO test performance of the NOxOFF asphalt samples before and after optimization. The measured activities before and after optimization are 5.4 and 10.3 %, respectively. The relative activities after 0, 136, 300 and 586 hours of accelerated aging are given in (Table **3**). It is observed that the activity initially is reduced by 4 % after 138 hours and 17 % after 300 hours, however, after 586 hours the activity seems to have stabilized. The removal reaction follows a first-order reaction mechanism; hence the rate coefficient is dependent on the initial concentration of NO. Hence, small variations in the NO concentration may lead to uncertainties in the activity, which possibly explain why the activity seems to increase from 300 to 586 hours of aging.

Table 3. Activities relative to time=0 after 0, 138, 300 and 586 hours of accelerated aging of the NOxOFF asphalt samples from Roskilde.

Aging Time/ h	Relative Activity/ %
0	100
138	96
300	83
586	90

3.1.2. In-situ Measurements

Fig. **4** (left panel) shows the results of the first *in-situ* measurements conducted in March 2015 using a model gas simulating a maximum NO_x level of 500 ppb using ambient light and artificial light (3 mW/cm^2 UVA). This NO_x concentration is chosen based on the background measurement of the NO_x concentration at PL2 conducted prior to the first field measurement. The figure clearly shows a high abatement efficiency both for ambient and artificial light. The right panel of the figure shows the results of the experiments conducted at ambient conditions. As the day of measurement was cloudy in March, light intensities were expected to be low. Here, we measured an intensity below or equal to 0.9 mW/cm^2. The NO_x concentration was initially 35-40 ppb and the experiment demonstrated a NO_x removal of approximately 90 %. As the reduction capacity is highly dependent on the dimensions of the test cell, it is more sensible to consider the unitless uptake coefficient, which is independent on cell dimensions. In the following section, we calculate the rate coefficient and convert it to uptake coefficients to assess the comparability between laboratory and *in-situ* data.

3.1.3. Kinetic Model

The photocatalytic NO_x oxidation follows a first-order kinetic reaction mechanism [28] so that the NOx concentration is exponentially dependent on time. The reaction coefficient, $k_{rxn,}$ can be determined from Equation 4 [56].

$$k_{rxn} = -\frac{\ln\left(\frac{c_t}{c_0}\right)}{t_{rxn}} \quad (4)$$

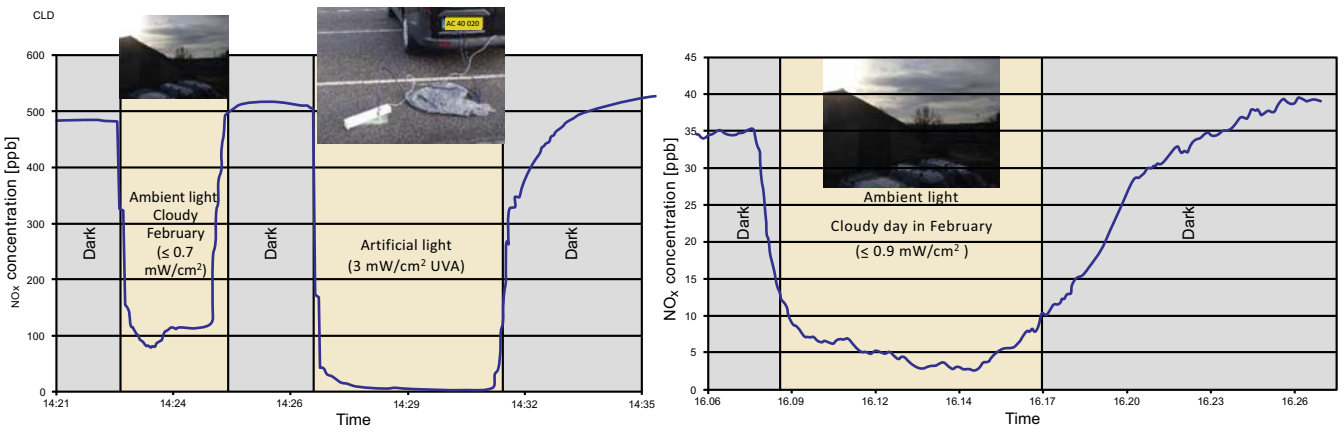

Fig. (4). *In situ* results from the Roskilde field study for model air (left panel) at ambient and artificial light conditions and for ambient air and light conditions (right panel). (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

Where t_{rxn} is the reaction time, here the time the gas is in the test cell, and c_t and c_0 are the final and initial NO_x concentrations, respectively. The rate coefficient gives a measure of the activity of the surface; however, the rate coefficient is dependent on the dimensions of the cell. To avoid this dependence, the activity can also be expressed as the unitless uptake coefficient, γ, which is expressed by Equation 5 [13].

$$\gamma = \frac{4k_{rxn} \cdot V}{v \cdot S_{active}} \quad (5)$$

Where S_{active} is the area of the active surface, V is the volume of the gas passing through the cell and v is the average molecular rate given by Equation 6.

$$v = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}} \quad (6)$$

Where R, T, and M are the ideal gas constant, the temperature, and the molar mass of the reactants respectively. It is important to note that while the uptake coefficient is independent on cell dimensions, it is still highly dependent on light intensity as well as the initial NO concentration, temperature, and relative humidity. In this section, the first-order rate coefficient for the reaction and the unitless uptake coefficient are calculated for 3 scenarios to compare laboratory activity with real-life activities. The 3 scenarios are: i) The laboratory ISO test conditions; ii) *in situ* measurements at high NO_x concentration (model air with an initial NO concentration of 510 ppb); and iii) *in situ* measurements at low NO_x concentration (ambient air with an initial concentration of 35 ppb). The *in-situ* scenarios use artificial light of 3 mW/cm^2. The results are given in (Table **4**) and show that uptake coefficients calculated for the 3 scenarios are similar. Surprisingly, the uptake coefficients calculated for *in-situ* conditions are 66 and 32 % higher than the laboratory coefficient. This result is unexpected as the *in-situ* measurements were conducted after 6 months of wearing, which could have decreased the activity compared to the laboratory test of the freshly applied coating. The difference is most likely due to the more favorable light conditions (3mW/cm^2) used in the *in-situ* measurements, which is expected to increase the activity [27]. Furthermore, the different initial NO concentrations will affect the activity. Other uncertainties include temperature and relative humidity, which were not measured in the *in-situ* experiments, but are expected to vary significantly between the three measuring days. The conditions in September are expected to closely resemble laboratory conditions, while the temperatures in early spring (March and April) are expected to be significantly different. The manual application procedure may also have caused irregularities in the amount of photocatalytic coating applied to the *in-situ* surface. Due to the many factors influencing the activities, as well as the many uncertain parameters, large uncertainties in the uptake coefficients are expected. Nevertheless, the calculated uptake coefficients for the three scenarios are in the same range, indicating that test results measured by the portable ISO-setup can be used to estimate the activity of a photocatalytic product *in-situ*.

Table 4. Rate coefficients and uptake coefficients (Equation 5) calculated for three different scenarios. The in-situ data is from the first measurement day, 03-05-2015 (Roskilde study).

Scenario	k_{rxn}/ s^{-1}	γ
Laboratory	0.219	9.6 10^{-6}
Low NO_x	0.229	15.9 10^{-6}
High NOx	0.180	12.6 10^{-6}

Uptake coefficients were furthermore calculated for all of the measurements conducted during the 2 years monitoring campaign. The results are shown in (Table **5**). The results show very high stability, with uptake coefficients being largely unchanged over time in the period of two years. Again, the measurements are associated with some degree of uncertainty due to differences in initial NO_x levels, weather parameters as well as irregularities in the asphalt surface and the potential uneven distribution of coating, as the measurements were not conducted at the exact same position each time. Interestingly, when comparing the two measurements from the 2th of September, a significantly decreased uptake coefficient is observed for the high-NO_x measurement. This

is in agreement with previous studies, who found that, although the absolute removal is increased, the degradation efficiency is decreased with increasing initial concentration of NO_x [27, 57].

Table 5. Initial and final NO concentrations and uptake coefficients (Equation 5) measured at the Pl1, Roskilde test site, at artificial light conditions (3 mW/cm^2).

Date	c_0/ppb	c_t/ppb	γ
03-05-15	688	47	2.2 10^{-5}
09-02-15	330	4	3.6 10^{-5}
09-02-15	1014	110	1.8 10^{-5}
04-20-16	1726	226	1.7 10^{-5}

3.1.4. Calculation of NO_x Abatement Potential

To assess the collective effect of the construction of the two photocatalytically active parking lots, we estimate in this section the total amount of NO_x removed. This is done based on the laboratory ISO test results, which were shown in Section 3.1.3 to reflect the real-life results with good approximation. The ISO test showed a NO_x removal efficiency of approximately 10 %. Considering the illuminated test area of 5 x 10^{-3} m^2 this corresponds to a removal rate of 4.83 $\frac{mg[NO]}{m^2 h}$ at the gas flow of 3 L/min (0.18 m^3/h). For the total area of 5000 m^2, this corresponds to a removal capacity of the two parking lots of 24.2 g/h. Utilizing that the experimental light intensity is 10 W/m^2, it is possible to obtain an abatement capacity in terms of the solar effect of 0.483 g/kWh. In Denmark, approximately 1000 kWh/m^2 is received per year, of which approximately 5 %, corresponding to 50 kWh/m^2, is in the UV region. [58]. This yields an estimate of NO removed per year of 24.2 g/m^2 per year, corresponding to 120 kg per year. Taking into account also the cumulative sky model, it is found that the sun will deliver 586 kWh/m^2 per year at street level giving a final estimate of 69 kg of NO removed per year by the two parking lots [59].

3.1.5. Economic Considerations

Recent guidelines (2019) from the Danish Centre For Environment and Energy (DCE) estimates regional societal costs of 34 euro per kg NO_x pollution in Denmark. Furthermore, they estimated an additional local cost of 9.7 - 47 euro per kg NO_x [60]. The distribution of health costs is outlined in Fig. **5**. Considering the DCE guidelines, 69 kg NO_x was removed each year by the photocatalytic parking lots in Roskilde, and 3,015-5,589 euros were saved each year. Assuming an installation cost of 11,000 euros, the payback time is between 2 and 3.5 years approximately.

3.2. Copenhagen Airport Study

3.2.1. Laboratory Tests

The NO_x degrading properties of the NOxOFF stones before installation were tested according to ISO 22197-1. The results are summarized in (Table **6**). The NOxOFF stone showed degradation of NO according to the ISO 22197-1 of 10 % directly after production which increased to 23 % after simulated rainfall, light activation and drying in an oven at 110ºC for 12 hours before testing, following the procedure proposed by Prof. Brouwers *et al.* [27], which agrees with the ISO 22197-1 standard that specifies that the sample "may be dried within a temperature range that does not cause physical or chemical changes to the test piece (max of 110 ºC)" Dryness is confirmed when a constant mass is reached.

3.2.2. Field Test

The NO_x levels before and after installation of the NOxOFF stones are shown in Fig. **6**. It is clearly seen that the

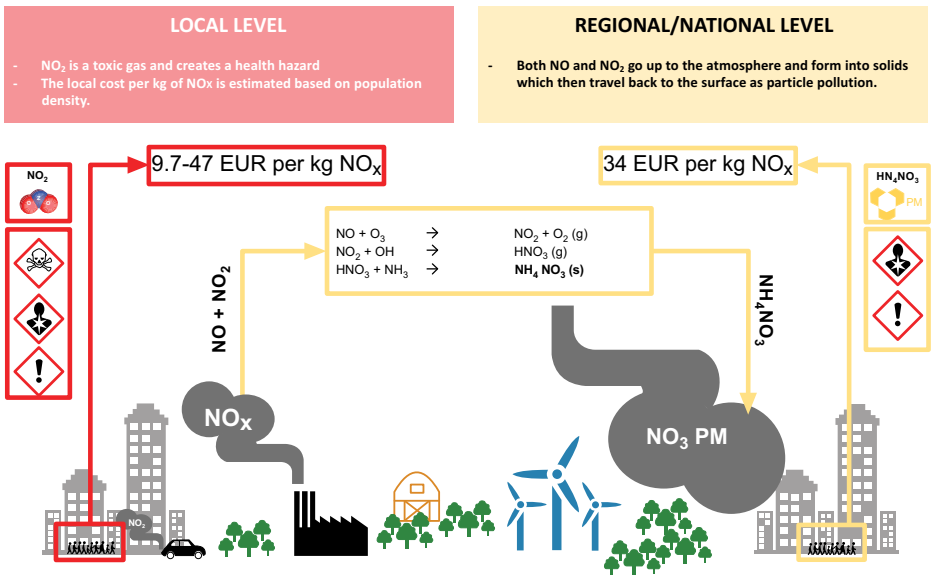

Fig. (5). Schematic overview of the health costs per kg of NOx according to the DCE recommendations. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

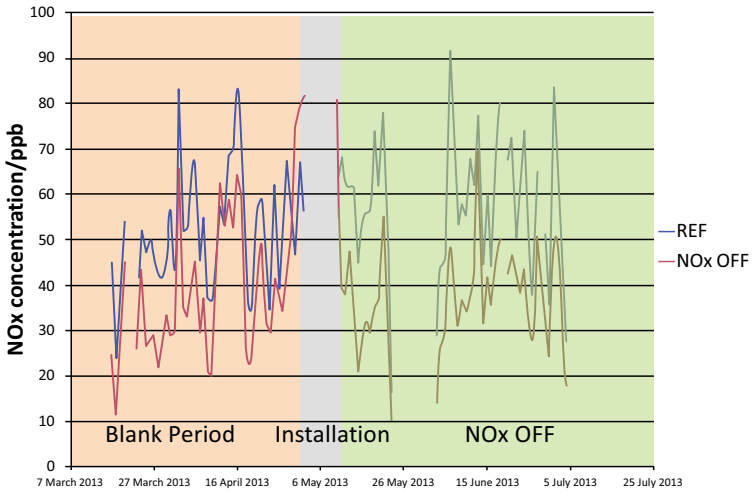

Fig. (6). Raw data from the Copenhagen Airport test site. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

NO_x level is higher at the reference site than the NOxOFF site, also in the blank period. This clearly underlines the importance of the blank period monitoring. In order to evaluate the effect of installing the NOxOFF stones, the average NO_x concentration at the reference site and the NOxOFF site in the blank period and the NOxOFF period are compared. The data is shown in (Table **7**). It is observed that from the blank period to the NOxOFF period, an increase in NO_x concentration at the reference site is observed, while the average concentration at the NOxOFF site is unchanged. The drop in relative difference between the two periods corresponds to a reduction of NO_x of 12 %. The 12 % reduction in NO_x is an average over the 43 measuring days, including night time, where there is no light intensity and thereby no photocatalytic activity. A measurement of the light intensity on the parking lot during the measuring campaign revealed that the light intensity on the parking lot is highest around noon and there is sufficient light to effectively drive the photocatalytic process from 10 am to 8 pm. Considering the NO_x level for a specific day during the blank period and comparing it to a specific day during the NOxOFF period reveals that during the blank period, the NO_x levels for the two sites have similar trends. However, during the NOxOFF period, the peak values seem to be cut off for the NOxOFF site compared to the reference site.

Table 6. NO degradation results after ISO 22197-1 (CPH Airport study) before (step 1) and after (step 2) simulated rainfall by the procedure explained in Section 2.2.2.

	Average of 6 NOxOFF Stones
Amount [ml/m^2]	150
% NO Degr. Step 1	10 ± 2%
% NO Degr. Step 2	23 ± 7 %
Uptake Coefficient	2.28 10^{-5}

3.2.3. Theoretical Reduction

As recommended by Kleffmann [61], we here present the theoretical NO_x removal potential calculated by the model applied by Gallus *et al.* [42], where the test site is treated as a laboratory flow reactor experiment. In the study by Gallus *et al.*, this is a quite good approximation, as the study was conducted in a tunnel where a constant wind direction parallel to the tunnel is expected. Here, we make the same assumption, but it should be noted that the wind direction, in reality, is most likely not constant, hence assuming that flow reactor conditions are a rough approximation. We use the following parameters for the test site: width=5m, length=50m, height=0.5 m, average wind speed=4.5 m/s, average humidity= 30 % and average irradiance= 16.1 W/m^2, corresponding to the irradiance measured a specific day in July 2018 in Copenhagen. At these parameters, a theoretical reduction of 14.5 % is obtained, which is in very good agreement with the observed 12 %. The height of 0.5 m is chosen for the modeling as this is the monitoring height at the test site. Increasing the height in the model to 1.5 m, which corresponds well to the height of breathing, a reduction of 6.7 % is obtained.

3.3. Discussion of Preliminary Results from Stuttgart

In a large-scale field study conducted in Stuttgart, Germany, 6,300 m^2 of asphalt at "Am Neckartor" was replaced with photocatalytic TiO_2 containing asphalt from ClAir® [62]. The construction began on the 14th of April 2019 and finished on the 18th of April. NO_2 levels were monitored continuously at an altitude of 2.5 m above the street monitoring station at Am Neckartor 18-22. Air quality is publicly available [63]. Here, we analyzed this data to estimate the effect of the photocatalytic asphalt. The daily average NO_2 concentration in 2018 and 2019 is shown in Fig. **7**. Interpretation of the data is greatly complicated by the lack of reference data, in particular, because the city of Stuttgart has implemented several other initiatives to improve the air quality during the same period of time including a traffic prohibition for all vehicles with diesel motors with the emission standard 4 / IV and lower, initiated from 1st of January 2019 [64]. Here, we roughly estimate the effect of this initiative by

Table 7. Average NO_x concentration in the blank period and the NOxOFF period from the Copenhagen Airport test site.

Measuring Period	Reference Site [ppb]	NOxOFF Site [ppb]	Relative Difference [Ref/NOxOFF]
Blank (41 days)	51	37	0.73
NOxOFF (43 days)	58	37	0.64

comparing the average NO_2 concentration from January to March 2018 (before diesel prohibition and before photocatalytic asphalt) with that of the same period in 2019 (after diesel prohibition and before photocatalytic asphalt). Comparing the average concentration in the period from May to October 2019 (after diesel prohibition and before photocatalytic asphalt) with that of the same period in 2019 (after photocatalytic asphalt), a significant reduction of 30 % is observed. Taking into account the effect of diesel prohibition, an actual reduction of 21 % is obtained. It should be noted, that due to the lack of reference and monitoring of meteorological and traffic-related data, this number serves only as a very rough estimate of the upper limit of effect of the photocatalytic asphalt.

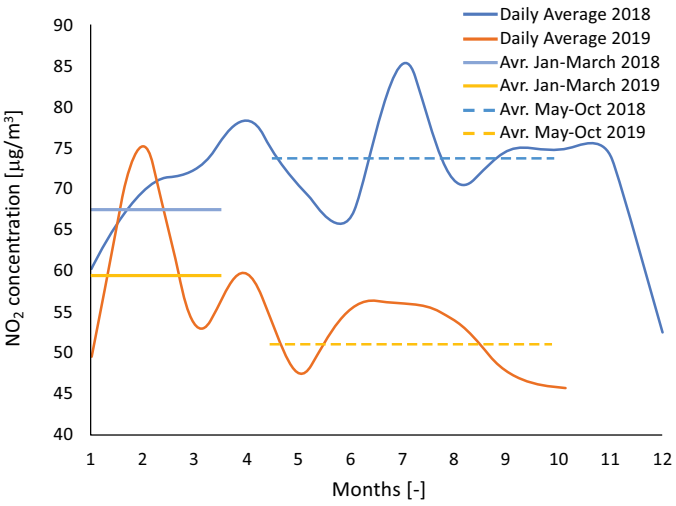

Fig. (7). Publicly available air quality data from Am Neckartor, Stuttgart. Photocatalytic asphalt was installed in March 2019. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

CONCLUSION

Air pollution is a global problem causing considerable harm to human health and the environment. TiO_2 based photocatalysis can be implemented at a relatively low cost in various road materials, such as asphalt or concrete to remove pollutants in areas where people are exposed. In this paper, we presented the results from two real-life demonstration projects in Roskilde and Copenhagen Airport, Denmark, aiming to evaluate the effect of photocatalytic asphalt and concrete stones on the ambient NO_x concentration. At the Roskilde test site, photocatalytic fluid was applied to the existing asphalt on two parking lots covering a total area of 5,000 m^2 in Roskilde, Denmark. A portable test setup was developed to transfer the standardized ISO 22197-1 test from laboratory conditions to *in situ* conditions. Comparison of unitless uptake coefficients calculated from laboratory test results and *in situ* results showed good agreement, despite many uncertainties associated with the *in-situ* measurements. This demonstrates that laboratory activities can be directly used as an estimate for *in-situ* activities and the opposite. Furthermore, the uptake coefficients were largely unchanged over time, during the 2 years monitoring period, demonstrating high stability of the photocatalytic treatment. The ISO test results showed an activity of 0.483 g/kWh. Considering the effect of UV light delivered by the sun in Denmark, this corresponds to an estimated removal of a total of 69 kg NO per year as a result of the photocatalytic asphalt applied to the two parking lots. At the Copenhagen Airport test site, 250 m^2 of photocatalytic concrete tiles, NOxOFF stones, were installed at the "kiss and fly" parking lot, P8. NO_x levels were monitored at the NOxOFF site as well as at the other half of the parking lot, which was left as the reference before and after installation of the NOxOFF stones. A reduction in NO_x concentration of 12 % was found, which is in good agreement with a theoretical upper limit reduction of 14.5 %, which was calculated by a flow reactor model. Due to the limited size of the test site, we expect a larger observed effect for a larger test site, where mixing with surrounding air is less significant. Promising preliminary results from a large-scale field study in Stuttgart, 6,300 m^2 photocatalytic asphalt, indicate an upper limit of 21 % reduction measured in 2.5 m. The joined results of the two Danish demonstration projects and the study in Stuttgart illustrate high stability of the photocatalytic coating as well as a high potential for improvements of the real-life air quality in polluted areas.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The authors confirm that the data supporting the findings of this study are available within the article.

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CONFLICT OF INTEREST

This study was conducted by researchers associated with Photocat A/S.

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