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Full scale demonstration of air-purifying pavement

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HIGHLIGHTS

- The results of a demonstration project for photocatalytic pavement are shown.
- The photocatalytic performance was studied in a street as well as on lab scale.
- The outdoor monitoring was performed in different seasons and weather conditions.
- The NO_x concentration was in average 19% lowered by the photocatalytic street.
- Under ideal weather conditions the NO_x reduction reached up to 45%.

GRAPHICAL ABSTRACT



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ABSTRACT

Experiments concerning a full-scale demonstration of air purifying pavement in Hengelo, The Netherlands, are reported. The full width of the street was provided with concrete pavement containing TiO_2 over a length of 150 m (“De NO_x street”). Another part of the street, about 100 m, was paved with normal paving blocks (“Control street”). The outdoor monitoring was done during 26 days for a period exceeding one year, and measured parameters included traffic intensity, NO , NO_2 and ozone concentrations, temperature, relative humidity, wind speed and direction, and the visible and UV light irradiance. Prior and parallel to these field measurements, the used blocks were also measured in the lab to assess their performance. The NO_x concentration was, on average, 19% (considering the whole day) and 28% (considering only afternoons) lower than the obtained values in the Control street. Under ideal weather conditions (high radiation and low relative humidity) a NO_x concentration decrease of 45% could be observed.

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1. Introduction

Nitrogen oxides (NO_x) are the generic term for a group of highly reactive gases, most of them emitted in air in the form of nitric oxide (NO) and nitrogen dioxide (NO_2). They are mainly formed in combustion processes and cause a wide variety of health and environmental impacts. The NO_x compounds are responsible for

tropospheric ozone and urban smog through photochemical reactions with hydrocarbons. Furthermore, NO_x together with SO_x (sulfur dioxide and sulfur trioxide) is the major contributor to the “acid rain”.

The EU has taken important steps over the past decade leading to a decrease in the emissions to air and water of a number of pollutants. The directive 1999/30/EC [1] establishes limit values and, as appropriate, alert thresholds for concentrations of sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air intended to avoid, prevent or reduce harmful effects on human health and the environment. This directive imposes an annual limit value to NO_2 for the protection of human health of $40 \mu\text{g}/\text{m}^3$ (about 19.7 ppbv) and an annual limit value to NO_x for the protection of vegetation of $30 \mu\text{g}/\text{m}^3$ (about 17.9 ppbv). Some

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of the pollutant emissions have since become more or less manageable, although particulates, NO_x and smog are still problematic, especially due to the rapid rate of growth of the transport sector. In consequence of it the NO_x emissions from traffic must be reduced in order to meet European agreements.

Heterogeneous Photocatalytic Oxidation (PCO) represents an emerging environmental control option for the efficient removal of chemical pollutants. This process involves a solid semiconductor catalyst, most often anatase titanium dioxide (TiO_2), which is activated with ultraviolet light of the appropriate wavelength. To date, a number of researchers have investigated the dynamics of the photocatalysis of nitrogen oxides [2–8]. Photocatalytic oxidation of NO_x offers the following distinctive advantages: (1) no extra reactants are required and (2) NO_x is converted to nitrates, a significantly less harmful material.

The development of innovative materials that can be easily applied on structures, with both de-soiling and de-polluting properties, is a significant step towards improvements of air quality. The use of TiO_2 photocatalyst in combination with cementitious and other construction materials has shown a favourable effect in the removal of air pollutants [9]. In recent years, a wide number of laboratory scale tests have been performed, under different experimental conditions, in order to evaluate the NO_x degradation properties of TiO_2 photocatalytic materials [10–19].

So far some projects were working on innovative solutions for improving air quality employing photocatalytic materials in European roads: Air Quality Innovation Programme (IPL) in the Netherlands [20], the New Road Construction Concepts (NR2C) [21] and Photocatalytic Innovative Coverings Applications for Depollution (PICADA) [22]. Real scale studies in streets or canyons have proven significant reductions of NO_x in Belgium, in Italy and in France [15,23,24].

In the present paper, the results of the air quality measurements performed in the Castorweg street in Hengelo City (The Netherlands) before and after its modification (Fig. 1) are presented in order to evaluate the photocatalytic effect of pavement blocks containing titanium dioxide over the NO_x reduction.

2. Methodology

A new demonstration project about the air purifying pavement was performed in Hengelo, Province of Overijssel, The Netherlands. This project was executed from January 2008 till July 2011, with financial support from the Province of Overijssel (The Netherlands), and was jointly executed by the University of Twente, Eindhoven University of Technology, Hengelo Municipality and Struyk Verwo Infra. The street Castorweg in Hengelo was covered with the photocatalytic concrete blocks produced by Struyk Verwo Infra. With the purpose of evaluating the effect of the photocatalytic blocks over the degradation of nitrogen compounds, an air quality monitoring program was carried out in this street. The methodology for the air quality monitoring was established after consulting and by using advice from TNO (The Netherlands), Catholic University of Louvain (Belgium) and the RIVM (National Institute for Public Health and the Environment in The Netherlands) [25].

The modified street ("De NO_x street") covered with photocatalytic blocks over the entire width of the street (about 5 m) and approximately 150 m long was compared with a part of the street ("Control street") with normal blocks of about 100 m long with identical traffic volume and therefore pollution conditions (Fig. 2). The De NO_x blocks applied in the Castorweg consist of concrete double layer blocks with a 70 mm in height lower layer and with an active upper layer of 5 mm with TiO_2 . The size of the blocks applied in the street is 120 mm \times 220 mm. Periodically, the used concrete blocks in the street were tested in the lab according to ISO 22197-1:2007 [26] to assess their performance.



Fig. 1. Castorweg street in Hengelo (The Netherlands). a) Before modification. b) After modification.

Regarding the chronology of this research project, the 1st of December of 2006 the project proposal was submitted to the Province of Overijssel for its assessment and it was approved the 21st of December of 2007. The original plan forecasted the street to be rebuilt with the new concrete blocks by the end of 2008. However, due to some delays in the construction and encountered soil contamination, the remodelling of the street with the De NO_x blocks finished by the end of October 2009.

The outdoor air quality monitoring started before the precast concrete blocks were placed in December 2008 and continued till July 2011. After the applications of the De NO_x blocks in November 2009, the first monitoring in the street together with associated laboratory tests of the blocks did not show a significant decrease of the NO_x concentration. Therefore, in order to increase the performance of the photocatalytic activity of the blocks, a coating made with a suspension of TiO_2 was subsequently sprayed on the street. According to the supplier, the coating was prepared as 4% (w/w) TiO_2 water suspension, and 50 L of suspension were employed in 750 m² of street, giving 2.67 g/m² of TiO_2 . Carbon doped TiO_2 from Kronos International was used.

The first coating was applied in May 2010 during spring time giving good results in the lab as well in the field. However, after 2.5 months of normal outdoor exposition, the coating was lost due to normal wearing, vehicles, weather, etc. [27] or solids were deposited on the surface (e.g. dust or from tires) and the photocatalytic efficiency decreased to the original values before the coating. Then, a second coating was applied in September 2010 with an improved durability. After 1.5 months of exposition of the

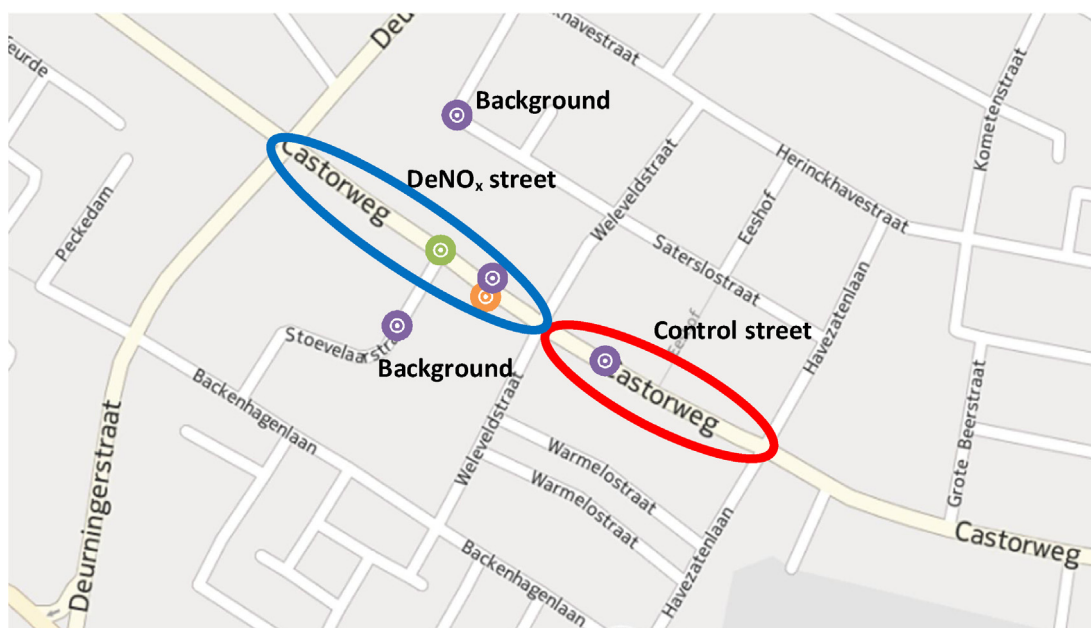


Fig. 2. Castorweg street in Hengelo (The Netherlands) and sampling places during outdoor air quality monitoring. ● NO_x and O₃ analyzer and radiometer. ● Weather station. ● Traffic volume counter. Sampling position in DeNO_x street: 52°16'31.99" N 6°48'21.29" E. Sampling position in Control street: 52°16'30.81" N 6°48'24.57" E.

second coating, still a good photocatalytic performance was found. However, almost 11 month after the application of the last coating the low original block photocatalytic performance was found again.

2.1. Laboratory experiments

Prior and parallel to the outdoor measurements, the used blocks in the street were tested at laboratory scale according to the standard ISO 22197-1:2007 [26] for the nitric oxide (NO) photocatalytic removal. The applied experimental device is composed of a planar reactor cell housing the concrete block sample, a suitable UV-A light source, a chemiluminescent NO_x analyzer, and an appropriate gas supply [28].

The testing conditions stated in the above mentioned standard were: 10 W/m² of UV irradiance, 50% of relative humidity, 3 l/min of flow rate, inlet NO concentration equal to 1 ppm, an exposed surface equal to 100 mm × 200 mm, and a reactor height of 3 mm, giving therefore a residence time of 1.2 sec. For more details of the experimental setup employed in this study see [28].

In addition, the upper layer of these blocks was analyzed with X-ray fluorescence (XRF).

2.2. Outdoor monitoring

The following parameters that could have effect over the photocatalytic performance of the blocks were measured in the street: temperature, wind speed, wind direction, air pressure, relative humidity, NO concentration, NO₂ concentration, irradiance (visible and UV light), traffic volume, and O₃ concentration.

The most important features of the used equipment are listed as follows: (i) Weather station *Wireless Vantage Pro2 Station*. The Vantage Pro2 Wireless Weather Station is suitable to measure temperature, wind speed, wind direction, pressure, relative humidity, solar radiation and among others weather parameters. (ii) Radiometer *UV-VIS Radiometer RM-12 Dr. Groebel UV-Elektronik GmbH*. The radiometer RM-112 can measure irradiances and illuminances in different UV and visible spectral ranges employing the respective sensors: UV-A sensor from 315 to 400 nm and Blue-Green visible light from 400 to 570 nm. (iii) NO_x analyzers *Ambient NO_x Monitor Horiba APNA-370 and APNA-360*. The Ambient NO_x Monitor Horiba APNA-370 and APNA-360 use the chemiluminescence principle

and the referential calculation method to measure continuously NO_x, NO, and NO₂. (iv) O₃ Analyzer *Aeroqual Series 500 Multi-Sensor Handheld Gas Monitor*. This gas sensor is a replaceable head system and it can measure ultra low ozone concentration from 0 to 0.15 ppm. (v) Traffic volume. The Municipality of Hengelo placed in some period of time a radar dispositive to count the traffic. This radar not only counts the number of vehicles per unit of time, but also can measure the speed, direction and size of the vehicles.

The air quality monitoring was performed in different seasons in order to obtain representative data during a year (in total 26 measurements). Some of these measurements were done before the street modification to obtain background information. According to the season, the weather conditions and the electric energy availability provided by the Castorweg residents, the experiments used to start between 8:30 and 9:30 am and they used to last till between 4:00 and 5:00 p.m.

The NO_x analyzer APNA-370 and the radiometer were placed mostly in the modified street during the measurement day (with the exception of few times when both NO_x analyzers were exchanged), changing the height sampling each one hour starting at 150 cm, then at 30 cm and finally at 5 cm (Fig. 2). Regarding the O₃ analyzer and the second NO_x analyzer APNA-360, in the course of the selected days their measurements were done in different places in the Control street at the same height as in the modified street. In the morning the O₃ and APNA-360 analyzers started to measure in one of the background streets (see Fig. 2). After half an hour they were moved to the Control street and then every one hour the O₃ analyzer was moved between the Control and DeNO_x street. The sampling in the Control street can be assumed with similar conditions to the sampling position in the modified street (direction, buildings height, street width, closeness, traffic volume). The sampling places were around 4 m from the centre of the traffic lane and at least 1.5 m from the nearest building [1]. At the end of the day either the background area was monitored again for half an hour or both NO_x analyzers were placed together to check the compatibility of both equipments.

As mentioned before, the NO_x samplings were placed at different heights: 5 cm (near the active surface), 30 cm (car exhaust height) and 150 cm (the breathing zone) in order to evaluate the decontamination effect for difference distance from the active

Table 1

Laboratory test results of different samples according to ISO 22197-1:2007, using UV and visible light.

Sample	$X_{\text{NO}_x, \text{UV}}$ [%]	$X_{\text{NO}_x, \text{UV}}$ [%]	$X_{\text{NO}_x, \text{vis}}$ [%]	$X_{\text{NO}_x, \text{vis}}$ [%]
Original stone	12.5	9.6	–	–
First coating	47.3	38.6	7.7	6.9
2.5 months exposition	13.9	4.1	–	–
Second coating	60.2	37.4	–	–
1.5 months exposition	43.9	19.1	–	–
11 months exposition	3.6	2.8	–	–

$$X = (C_{\text{inlet}} - C_{\text{outlet}}) / C_{\text{inlet}} \times 100.$$

surface. The radiometer measurement was performed over the concrete surface. The weather conditions (temperature, pressure, wind speed and direction, and relative humidity) were measured near the air sampling place of the DeNO_x street at 2 m above the ground (Fig. 2).

3. Results

3.1. Laboratory results

Table 1 shows the NO and NO_x (total of nitrogen oxides, predominantly NO + NO₂) conversion at laboratory scale employing different concrete blocks samples taken from the DeNO_x street. As mentioned before the original double layer block presented a low performance due to its low TiO₂ content. Nevertheless, the first coating applied in the street showed an overall NO_x degradation of 38.6% at laboratory scale. In addition, this coating has presented activity under visible light. However, 2.5 months later some samples from the street were removed and the original low degradation was found again during the lab test. Then, a second coating was applied in September 2010 increasing again the photocatalytic NO_x reduction to 37.6%, that after 1.5 months of its application was only reduced to 19.1%. In July 2011, after 11 months of outdoor exposition, almost no NO_x abating ability was found because of the ageing of the coating.

In addition, previous to the photocatalytic coating application, the upper layer of the original block was analyzed with X-ray fluorescence (XRF), showing a TiO₂ content of 0.59% by weight in the layer volume. According to experience with other photocatalytic blocks, this content is too low to achieve the necessary NO degradation of 40–50% in the lab [29].

3.2. Overall field results

The average weather conditions for each measuring day (average temperature, average relative humidity, average wind speed and average solar radiation) of the air monitoring in the Castorweg performed as from December 2008 till July 2011 are shown in Table 2. The UV-A irradiance measured by the radiometer was around 3% of the total solar radiation.

The traffic volume was determined in the Castorweg during three different times (in December 2008, February 2009 and June 2010) by the traffic counter radar. The average results for the number of vehicles per unit of time, speed, direction and size of the cars are shown in Table 3. An average of 110 ± 14 vehicles per hour was determined in the Castorweg.

In order to evaluate the NO_x reduction effect by the photocatalytic blocks in the Castorweg, the relative and absolute contamination reduction by the DeNO_x street can be defined:

$$\text{Relative Reduction [\%]} = \frac{C_{\text{NO}_x, \text{Control}} - C_{\text{NO}_x, \text{DeNO}_x}}{C_{\text{NO}_x, \text{Control}}} \times 100 \quad (1)$$

$$\text{Absolute Reduction [ppm]} = C_{\text{NO}_x, \text{Control}} - C_{\text{NO}_x, \text{DeNO}_x} \quad (2)$$

where $C_{\text{NO}_x, \text{Control}}$ and $C_{\text{NO}_x, \text{DeNO}_x}$ are the average concentrations of NO_x in ppm measured in the Control street and in the DeNO_x street, respectively.

Table 4 shows the average of absolute and relative NO_x reduction, and the average concentration of NO_x for every measuring day before the modification of the street and before the applications of the photocatalytic coatings, and including some measurements performed when the coatings lost their abating ability and during rainy and very windy days (26th of May, 15th of September and 21st of October, 2010). The same results are shown in Table 5 for the outdoor monitoring performed under the presence of a photocatalytic surface after the first and second coating applications in the Castorweg, respectively.

It is worthwhile to mention that before the street coating in May 2010, and including some days in July and August when the activity of the coating was lost according to lab test, the average NO_x concentrations in the DeNO_x street is about 3.5% higher than in the Control street. Including all the measurements when no photocatalytic effect can be considered (without photocatalytic coating and rainy and very windy days) the average NO_x difference between the both streets is -5.8% with a standard deviation σ equal to 22.26%, meaning that the concentration of NO_x in the DeNO_x street is 5.8% higher than in the Control street when no photocatalytic effect is present. If the outliers are taken out (26/05/2010 and 03/08/2010), this difference is reduced to -0.4% ($\sigma = 16.80\%$).

On the other hand, the measurements performed after the application of the coatings and when there was certainly photocatalytic activity in the street have shown that the concentration in the DeNO_x street is 19.2% ($\sigma = 17.81\%$) in average lower than in the Control street. However, if the average of the NO_x concentration is calculated only in the afternoon, this difference increased to 28.3% ($\sigma = 19.97\%$). This could be due to in the afternoon the solar radiation and temperature increases, leading the relative humidity becomes lower and the street drier than in the morning. This set of conditions will favour the NO_x reduction because when the blocks are dry the pollutants can be adsorbed over the active sites of TiO₂ and therefore can react. On the other hand, when the radiation is higher the activation of the photocatalyst is improved. And for a lower relative humidity in the atmosphere, the pollutants have less competition with water for the active sites, also increasing the NO_x reaction rate [28,30].

Nevertheless, it is hard to make conclusions about the different factors effects over the efficiency of the NO_x removal observing the reduction results of different measurement days. This is because from one day to the other, several parameters changed simultaneously and therefore it is not possible to analyze the effect of only one parameter. In order to predict the effect of different factors independently over the NO_x degradation a CFD model would be needed [31,32]. On the other hand, due to the application of the photocatalytic coating that is not very durable under normal outdoor exposition, the photocatalytic performance decreases with the ageing of the coating. Therefore, the street does not present constant photocatalytic efficiency from one measuring day to the other. In the next paragraph, some measurements results will be discussed in more detail.

Table 2
Average weather conditions during the outdoor monitoring.

Date	Solar radiation (W/m ²)	Temperature (°C)	Relative humidity (%)	Wind speed (m/s)	Wind direction	General weather condition
12/2/2009	252.05	2.4	80.8	1.53	NW	Sunny
13/3/2009	353.83	9.3	72.2	1.35	W	Partially cloudy
16/3/2009	142.46	6.7	86.6	0.68	SSW	Cloudy
17/3/2009	331.65	9.5	75.6	1.63	NNE	Partially sunny
2/12/2009	73.00	5.0	82.5	1.55	S	Cloudy
4/12/2009	44.02	4.3	85.7	2.19	SW	Cloudy
3/3/2010	348.35	3.1	81.7	0.60	WSW	Partially sunny
4/3/2010	337.55	2.0	77.9	1.24	NNW	Partially sunny
18/5/2010	402.07	12.8	63.2	0.87	NW	Partially cloudy
19/5/2010	348.35	3.1	81.7	0.60	WSW	Partially sunny
20/5/2010	707.38	17.6	50.7	1.90	NE	Sunny
21/5/2010	694.73	17.7	60.6	1.63	NNW	Partially sunny
26/5/2010	329.76	11.7	52.6	1.44	E	Cloudy/Rainy
3/6/2010	744.70	19.8	46.7	1.95	ENE	Sunny
4/6/2010	738.89	18.9	52.6	0.90	ENE	Sunny
8/7/2010	715.62	27.9	37.7	1.26	SW	Sunny
3/8/2010	376.12	17.8	78.3	0.95	WNW	Partially sunny/Rainy
6/8/2010	643.42	19.2	57.0	0.85	WNW	Partially sunny
6/9/2010	625.17	17.2	52.3	2.69	SE	Sunny
13/9/2010	384.16	16.2	75.7	0.93	WNW	Partially cloudy
15/9/2010	582.14	14.9	65.8	2.51	SW	Partially sunny/Windy
22/9/2010	502.65	18.3	72.2	1.18	S	Sunny
8/10/2010	133.47	15.0	86.7	1.23	ESE	Cloudy
11/10/2010	462.54	13.0	57.6	1.65	ENE	Sunny
21/10/2010	240.80	7.4	80.7	1.89	SW	Cloudy/Rainy
27/07/2011	509.20	20.0	70.8	0.60	NE	Partially sunny

Table 3
Traffic information in the Castorweg.

	Average number of vehicles/hour Direction: to Stoevelaarstraat	Average speed (km/h) Direction: to Stoevelaarstraat	Average number of vehicles/hour Direction: to Weleveldstraat	Average speed (km/h) Direction: to Weleveldstraat
Motorbikes	1.32	30.17	1.66	28.73
Light vehicles	54.43	34.80	48.63	34.10
Middle heavy vehicles	1.18	30.74	1.73	31.51
Heavy vehicles	0.34	31.26	0.26	30.11
Total	57.27	34.59	52.28	33.85

Table 4
Average NO_x concentration, absolute reduction and relative reduction for the measuring days without the presence of a photocatalytic effect: i) before street modification ii) after street modification and before the application of the first coating, iii) when the first and second coatings lost their abating ability, iv) rainy days (26/05/10 and 21/10/10) and v) very windy days (15/9/10).

	Date	C _{NO_x, DeNO_x} (ppm)	C _{NO_x, Control} (ppm)	Absolute reduction (ppm)	Relative reduction (%)
i	12/2/2009	0.0227	0.0188	−0.0039	−20.87
	13/3/2009	0.0149	0.0194	0.0045	23.28
	16/3/2009	0.0147	0.0156	0.0008	5.43
	17/3/2009	0.0140	0.0163	0.0023	13.97
ii	2/12/2009	0.0621	0.0611	−0.0011	−1.73
	4/12/2009	0.0225	0.0225	0.000	0.05
	3/3/2010	0.0375	0.0341	−0.0034	−10.09
	4/3/2010	0.0121	0.0137	0.0016	12.01
	18/5/2010	0.0189	0.016	−0.0029	−18.32
	19/5/2010	0.0076	0.008	0.0004	4.64
	20/5/2010	0.0093	0.0111	0.0018	16.39
iv	26/5/2010	0.019	0.0127	−0.0062	−49.1
iii	8/7/2010	0.0156	0.0149	−0.0006	−4.3
	3/8/2010	0.0135	0.0091	−0.0044	−48.08
	6/8/2010	0.0105	0.0126	−0.0022	−20.71
v	15/9/2010	0.0142	0.0106	−0.0036	−33.48
iv	21/10/2010	0.0386	0.0312	−0.0073	−23.50
iii	27/07/2011	0.0131	0.0152	0.0020	13.34
	Average	0.0200	0.0190	−0.0010	−5.82 (σ = 22.26)
	Average without outliers ^a	0.0205	0.0201	−0.0005	−0.42 (σ = 16.80)

^a 26/05/2010 and 03/08/2010.

Table 5

Average NO_x concentration, absolute reduction and relative reduction for the measuring days with the presence of a photocatalytic effect: i) after first coating application and ii) after second coating application, excluding rainy days (26/05/10 and 21/10/10) and very windy days (15/9/10).

	Date	C _{NO_x, DeNO_x} (ppm)	C _{NO_x, Control} (ppm)	Absolute reduction (ppm)	Relative reduction %	Relative reduction (afternoon) (%)
i	21/5/2010	0.0072	0.0109	0.0043	37.62	41.33
	3/6/2010	0.0061	0.0112	0.0051	45.52	47.57
	4/6/2010	0.0074	0.0102	0.0027	27.00	31.28
ii	6/9/2010	0.0084	0.0114	0.0029	25.94	54.95
	13/9/2010	0.0134	0.0131	−0.0003	−2.65	11.68
	22/9/2010	0.0270	0.0283	0.0013	4.57	4.84
	8/10/2010	0.0214	0.0272	0.0058	21.27	32.71
	11/10/2010	0.0181	0.0175	−0.0006	−3.32	2.11
	Average	0.0136	0.0162	0.0026	19.18 (σ = 17.81)	28.31 (σ = 19.97)

3.3. Specific field results

One of the measurements before the street modification was done on 17th of March 2009. This day was partially sunny, the average relative humidity was approximately 75.6%, and the average temperature was 9.5 °C.

In Fig. 3 the pollutants (NO, NO₂ and O₃) concentrations measured in the DeNO_x street are shown. These concentrations are compared with those measured by RIVM (National Institute for Public Health and the Environment in The Netherlands) in two regional stations near Hengelo, namely in Hellendoorn and Eibergen. The O₃ concentration in the street gradually increases during the day because of homogeneous reactions between oxygen and nitrogen oxides promoted by the solar radiation [33], and has approximately the same value as the O₃ concentrations measured by RIVM. It is worth to mention that O₃ can also accept electrons of

TiO₂ like O₂ and can be decomposed [34]. However, this cannot be observed directly from the measurements due combining effects of O₃ photogeneration and degradation by NO_x and TiO₂. The NO_x concentration in the street is higher than at the RIVM measuring points, with much higher peaks which can be contributed to passing traffic.

Fig. 4 shows the NO_x concentration measured in the DeNO_x street together with the NO_x concentration measured in the Control street (Fig. 4(a)) and in the background street (Fig. 4(b)). Because the background street is less busy than the Castorweg, the NO_x concentration is significantly lower there. On the other hand, the

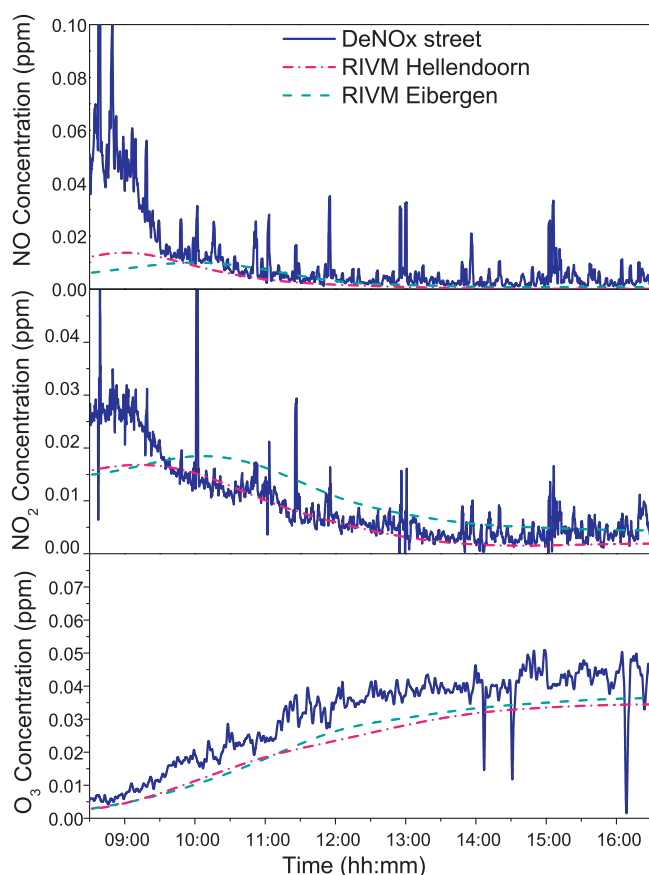


Fig. 3. NO, NO₂ and O₃ concentrations measured in the DeNO_x street compared with two RIVM station measurements, 17th of March, 2009, prior to street modification.

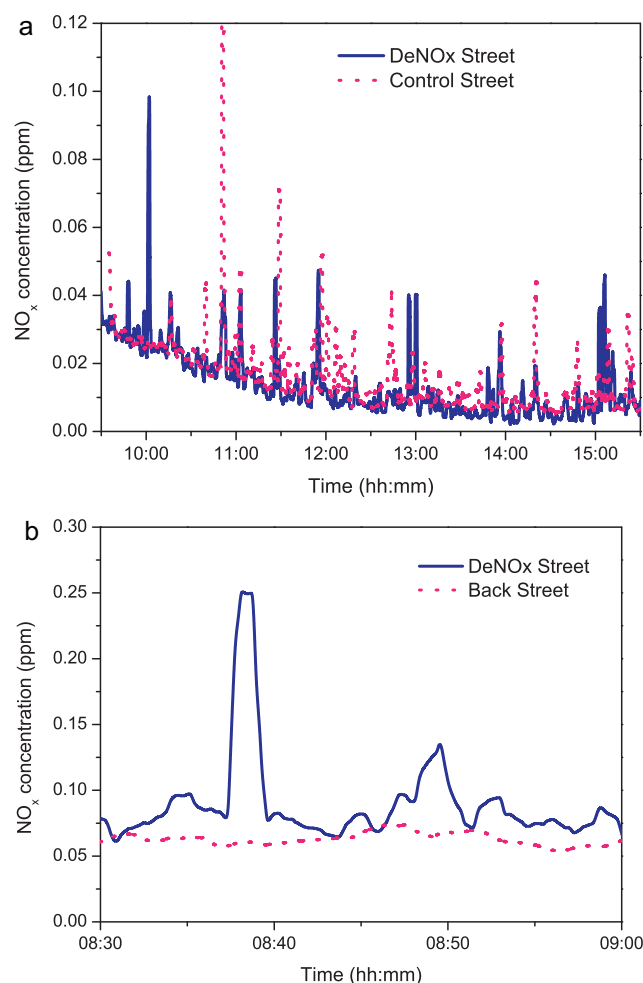


Fig. 4. NO_x concentration measured in the DeNO_x street compared with: (a) NO_x concentration measured in the Control street, (b) NO_x concentration measured in the background street, 17th of March, 2009, prior to street modification.

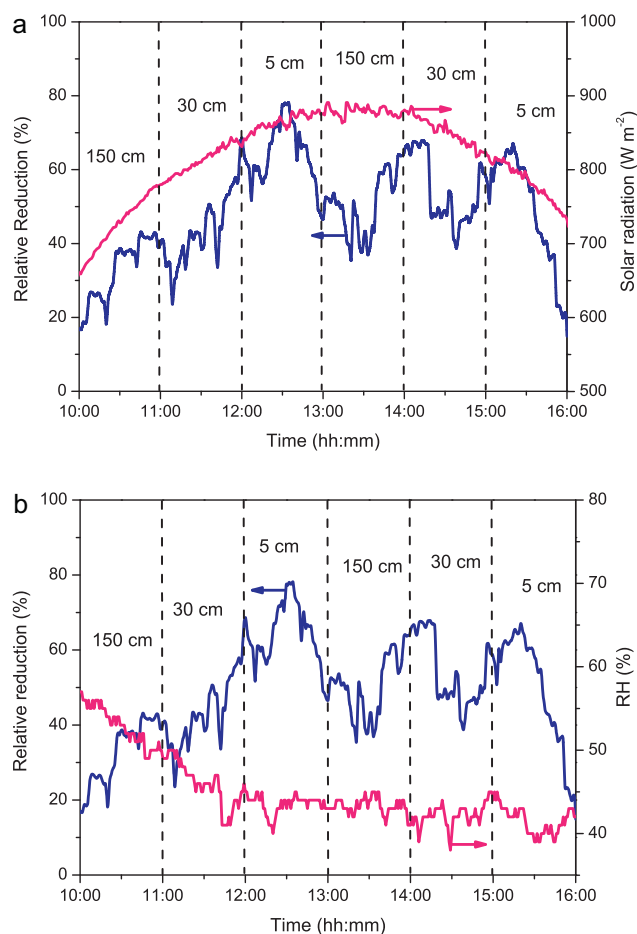


Fig. 5. Relative reduction for the NO_x concentration measured in the DeNO_x street and in the Control street at different height sampling versus: (a) the solar radiation, (b) the relative humidity, 3rd of June, 2010, after first coating.

NO_x concentration in the DeNO_x and in the Control street were similar, indicating that both street present similar conditions of pollution.

After the application of a first photocatalytic coating on 21st of May 2010, with a NO_x degradation performance at lab scale of 39%, another air quality measurement was performed the 3rd of June 2010. This day was perfectly sunny. The maximum irradiance registered around the solar noon (13:30 pm) was 890 W/m². The wind speed was approximately perpendicular to the Castorweg street, mainly from the ENE and NE, with gusts of 4 m/s and an average wind speed of 1.9 m/s. The relative humidity varied from 55% in the morning to 40% in the afternoon.

Fig. 5 shows the relative reduction calculated with the average NO_x concentration measured in the DeNO_x street and in the Control street. Both sampling positions, in the Control and in the DeNO_x street, were at 150, 30 and 5 cm height, starting at 150 cm and changing the height every hour. A reduction of approximately 45.5% for the NO_x concentration in the DeNO_x street can be seen here, but it changes according the sampling height. When the sampling height is closer to the photocatalytic pavement, the difference between the NO_x concentrations is higher. Measuring at 5 cm from the surface, the NO_x reduction is increased approximately 37% and 30% respect to the measurements done at 150 cm and at 30 cm respectively. In addition, in Fig. 5 (a) and (b) the solar radiation and relative humidity respectively are shown for that day. When the solar radiation increases along the day and the atmosphere becomes dryer, the NO_x reduction increases. This is in concordance

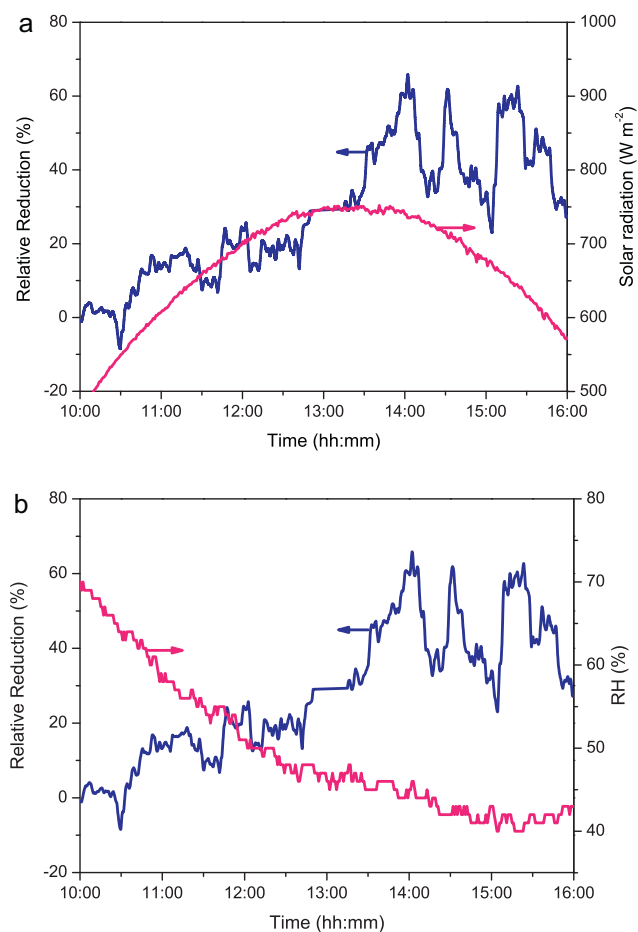


Fig. 6. Relative reduction for the NO_x concentration measured in the DeNO_x street and in the Control street versus: (a) the solar radiation, (b) the relative humidity, 6th of September, 2010, after second coating.

with the lab tests done by [28], where the effect of different parameters over the photocatalytic NO_x degradation was studied.

The 6th of September, immediately after the application of the second photocatalytic coating, was also a sunny day. The maximum irradiance registered was 750 W/m², because it was late in the summer. The wind speed was a little high, mainly from the SE, along the Castorweg, with gusts of 5 m/s. During this day the relative humidity was higher than in June, from 70% to 40%.

The NO_x reduction by the air purifying street that day can be observed in Fig. 6. The NO_x concentration difference is almost negligible in the morning, but it increases significantly in the afternoon. This can be explained observing Fig. 6(b), where the relative humidity in the morning was high and therefore the NO_x degradation rate was low, but also the DeNO_x blocks were probably wet because of the dew in the morning. In the afternoon, when the irradiance increased (Fig. 6(a)), the relative humidity became lower and most likely the blocks were dry, the NO_x reduction increased till almost 55%.

The other results performed after the first and second coatings are not shown in details here, although some general analysis can be made in order to understand the obtained results. The day of the coating application (21/05/2010) the NO_x concentration was measured with the NO_x analyzer, showing that when the coating was applied in front of the sampling place a significant NO_x reduction was observed. A few days after the coating application, 4/6/2010, again a significant NO_x decrease was found as on 3/6/2010. Two of this days were rainy (26/05/2010 and 21/10/2010) and therefore no positive results were found. During these two days the

NO_x concentration in the DeNO_x street was not reduced and was even higher than in the Control street because the surface was wet and the contaminants could not reach the active sites. On the other hand, the result on 15/09/2010 shows again a higher NO_x concentration in the DeNO_x street than in the Control street because this day was particularly and extremely windy (with gusts of 6.2 m/s) and the contamination probably came from other streets (e.g. Deurningerstraat, Fig. 2) as well as the residence time of the air over the surface was very short without the possibility to react [30]. On 13/09/2010 and on 22/09/2010 the relative humidity was very high (97%) in the morning and the street surface was wet. Especially on 22/09/2010, despite it was a sunny day and good results were expected, the relative humidity was pretty high preventing the NO_x reaction with the photocatalytic surface. Then, in the afternoon of both days, the results improved significantly when the relative humidity decreased and the surface dried. On 8/10/2010, despite it was a cloudy day, a very good degradation was found since that day the air sample was taken closer to the surface the whole day (at 30 cm). Finally, on 11/10/2010, the performance was again lower probably because the temperature dropped and also probably because after several days with sun the nitrates were accumulated over the surface reducing the photocatalytic efficiency [35].

The measurement data collected at all other days and their pertaining discussion can be found in a detailed report [36]. In this reference also more exhaustive specifications of the used equipment, measurements strategies, etc. can be found.

4. Conclusions

A demonstration project of the air purifying pavement was done in the city of Hengelo (The Netherlands) in the Castorweg street, where photocatalytic active blocks were applied in the road. The air quality monitoring was performed from the December 2008, so prior to the application of the photocatalytic surface to July 2011 after the application of two photocatalytic coatings. The NO_x (NO and NO₂) concentration in the modified street (DeNO_x street) and in a Control street was measured as well as weather parameters (temperature, solar radiation, UV radiation, relative humidity, wind speed) and the ozone concentration. The main conclusions are as follows:

- (1) The pavement was applied with blocks containing relatively little photocatalytic powder (0.59%, w/w), and the NO_x reducing effectiveness was poor (at lab scale and at street scale). After the application of the first coating the effectiveness was high, but this decreased in time. After the application of the second coating, the blocks performed well again. Also this second coating lost its abating ability in time.
- (2) Following point 1), a clear and direct relation between the NO_x abating ability of blocks in the lab (taken from the street and determined according to ISO 22197-1:2007 [26]) and the performance of the street could be observed. And this NO_x reducing ability is directly related to the amount of photocatalyst present on the surface of the block.
- (3) Just after the application of the first coating and later, after the application of the second coating, in the lab the blocks featured a NO_x reducing ability of around 38% according to ISO 22197-1:2007 [26] using a surface of 100 mm × 200 mm. In the DeNO_x street, the NO_x concentration was, on average, 19% (considering the whole day) and 28% (considering only afternoons) lower than the obtained values in the Control street. The pertaining standard deviations (σ) amount 18% and 20%, respectively. Under ideal weather conditions (high radiation and low relative humidity), a concentration decrease of 45% could be observed.
- (4) The measurements were done at heights of 5 cm, 30 cm and 150 cm, the same period of time at each height, and the reductions under point 3) constitute an average. At a height of 5 cm the NO_x reduction is about 1/3 higher than at 150 cm.
- (5) Measurements prior to the street modification (4 days), after the modification with the almost non-performing blocks (7 days), after the first and second coatings lost their abating ability (3 days), and when the weather conditions limited the photocatalytic action of the blocks (2 days) are all considered as the “non-active DeNO_x street”. These non-active situations reveal that the NO_x concentration in the DeNO_x street is almost the same, only 0.42% ($\sigma = 17\%$) higher, as in the Control street.¹

Though the number of measurements reported here is limited and the spreads in results large (reflected in the large σ), and that the project has been executed with relatively modest means; one can tentatively conclude that a photocatalytically active street can reduce NO_x concentrations tangibly. They also support the view to continue the measurements, and/or to set up a comparable new experiment in another street, but then employing continuously (all days and nights) air-monitoring stations during a period of one year or so. The valuable experiences gained with the set-up and execution of the Hengelo project, reported here, will serve such a new project.

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¹ When two outliers would be included, this number is 5.8% ($\sigma = 22\%$), so then DeNO_x street is substantially more contaminated in the zero situation. This percentage could be added to the reductions mentioned under point 4).

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