Journal of Environmental Chemical Engineering 11 (2023) 109758

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

The role of flow structures in the effective removal of NO_x pollutants by a TiO_2-based coating in a street canyon

Štěpán Nosek [a,*], Tomáš Ducháček [b], Pavol Magyar [b], Jan Procházka [b]

[a] Institute of Thermomechanics AS CR, v.v.i., Dolejškova 1402/5, Prague 18200, Czech Republic
[b] Advanced Materials, JTJ s.r.o., Kamenné Žehrovice 27301, Czech Republic

ARTICLE INFO

Editor: Dr. G. Palmisano

Keywords:
Photocatalysis
NO_x
Street canyon
Air purification
Urban air pollution
Turbulence

ABSTRACT

Photocatalytic titanium dioxide (TiO_2) coatings are known to effectively remove harmful nitrogen oxides (NO_x) in so-called laminar flow reactors (LFRs). However, their effectiveness in turbulent flow environments, such as street canyons, is not well understood. In this study, we applied physical modelling principles to simulate NO_x photocatalysis on the walls of a street canyon polluted by idealised traffic, and compared the results of this modelling with those of experiments in a standard LFR. The results show that the LFR is partially able to simulate photocatalysis in such a turbulent environment, but with about 18 times higher flow rate than recommended in the standards (3 l min^{-1}). However, the results from the street canyon experiment show that the performance of the photocatalyst is spatially dependent due to the mean flow structures that develop in the canyon. The mean vertical recirculation transports the NO_x pollutants from the line source first to the leeward wall and then to the windward wall, making the windward wall more favourable for pollutant removal. The secondary corner vortices that form at the bottom of the canyon increase the reaction time, so that NO_x pollutants are removed more effectively (up to 33%) than at other locations in the canyon. In contrast, the lowest removal efficiencies were found at the leeward wall (6%), where pollutants are mainly advected from the traffic and have less contact with the wall. These results provide valuable insights into the effectiveness of photocatalytic coatings in turbulent flow environments and may be useful for the development and implementation of these coatings in realistic urban pollution scenarios.

1. Introduction

Urban air pollution from automobile traffic by nitrogen oxides ($NO_x = NO + NO_2$) continues to pose a significant threat to human health [1]. The highest NO_x pollution is observed in the so-called street canyons as buildings obstruct the penetration of fresh wind [2,3]. Because of this poorer ventilation, there is also a greater conversion of nitrogen oxide (NO) into the more dangerous nitrogen dioxide (NO_2) and ozone (O_3) during the day [4–7]. Therefore, it is of utmost importance to reduce NO_x in urban street canyons.

One of the promising and cost-effective technologies to reduce NO_x in street canyons is painting the building facades with a photocatalytic semiconductor material, such as titanium dioxide (TiO_2) [8,9]. TiO_2 is a white, powdery substance used in a variety of products, including building materials and facades. When TiO_2 is added to paint, it acts as a pigment and UV stabiliser, helping to protect the painted surface from fading and discolouration caused by sunlight. TiO_2 is also used as an ingredient in some types of concrete and other building materials where it can improve the strength and durability of the material. It is also well known that after the application of ultraviolet (UV) light ($\lambda < 380$ nm) to TiO_2 surfaces, the formation of electron-hole pairs promotes a variety of oxidation-reduction reactions by exciting electrons from the valence to the conduction band [10]. Numerous laboratory studies in flow reactors have shown that both NO and NO_2 are efficiently oxidised to nitrates, with this efficiency depending primarily on the crystal structure and active surface area of TiO_2, as well as on parameters of the contaminated air such as velocity and relative humidity [11–14]. However, the tests in flow reactors are too idealised from the flow conditions in street canyons, as the recommended flow velocities are laminar.

Since only a few in situ experiments [15,16] have been conducted on real street canyons, the effect of photocatalysis for NO_x remediation in urban streets remains unclear. The study by Folli et al. [15] in Copenhagen shows on 200 m long pavements, half of which consisted of concrete blocks with TiO_2 as photocatalyst and the other 100 m of

* Corresponding author.
E-mail address: nosek@it.cas.cz (Š. Nosek).

https://doi.org/10.1016/j.jece.2023.109758
Received 27 January 2023; Received in revised form 18 March 2023; Accepted 20 March 2023
Available online 22 March 2023
2213-3437/© 2023 Elsevier Ltd. All rights reserved.

concrete blocks without TiO_2 (reference area), that the monthly average concentration NO near the photocatalytic area was about 22% lower than in the reference area. However, the authors of this study admit that the blank tests were not conducted over a sufficiently long period of time (two months) to obtain statistically significant data for comparing the results with the reference area. Brattich et al. [16] presented in situ experiments on two full-scale street canyons, but with different geometry and location. Concentration measurements were taken three days before application of the photocatalyst and another three days after application. The authors developed three independent methods to determine the removal efficiency of the photocatalyst. All three methods showed photocatalytic NO_x reduction in the range of 14%–21%. On the other hand, studies [17,18] conducted on models of street canyons (i.e. smaller than the real street canyon) reported contradictory results. The study by Maggos et al. [17] shows NO_x removal efficiencies of 37–82%, while the study by Gallus et al. [18] reports negligible efficiency in the uncertainty range of the experiment.

The main reason for the ambiguity in the field studies is that the dispersion of pollutants in a street canyon is determined not only by the morphology of the canyon and its surroundings, but also by atmospheric flow processes whose time and length scales are larger than those of the urban canopy. The interaction of these different turbulence scales means that data averaged over 30 min are not ergodic, even under the same conditions. Schatzmann and Leitl [19] have shown that only observations repeated over very long periods (at least half a year) can be sufficiently representative. To overcome the difficulties associated with in-situ measurements, researchers have relied on physical modelling of these processes in wind tunnels [20]. In a wind tunnel, controlled, repeatable and statistically steady conditions prevail, which is of utmost importance for the dispersion of pollutants in turbulent flows. It is well known that the criteria for the similarity of the flow between the modelled and the real case can only be fulfilled to a limited extent due to the geometric reduction of the area of interest. However, if the length and time scales are appropriately modelled, the flow will resemble that observed under real conditions, provided the Reynolds number is sufficiently high [21].

The reproducibility of small-scale experiments, including those conducted in flow reactors, has been questioned because the surface-to-volume ratio is unrealistically high [12,22]. However, it should be emphasised that the conversion to full-scale conditions includes not only the geometric scale, but also the temporal scale. The standardised flow reactor has a surface-to-volume ratio that is three orders of magnitude (200 m^{-1}) higher than that of a typical street canyon (0.1 m^{-1}). Similarly, the reaction time in the flow reactor is three orders of magnitude faster when the results are converted to full scale. The conversion of flow reactor or wind tunnel experiments to full scale is thus independent of the surface/volume ratio when the time scale of the reaction times is considered. However, the boundary conditions in the standardised flow reactor do not correspond to those in the street canyon (including the position of the pollutant source), and it is therefore unclear whether the results from the flow reactor are representative under these conditions.

The aim of this study is to improve our understanding of the effectiveness of photocatalytic coatings in turbulent flow environments such as street canyons. It also aims to determine whether standard flow reactors are suitable for simulating photocatalysis in such environments. To achieve these goals, we will use a method that involves physical modelling of atmospheric dispersion processes in wind tunnels and compare the results with those obtained using a standard laminar flow reactor. By comparing these two approaches, we can gain valuable insights into the performance of photocatalytic coatings under different but controlled conditions. Furthermore, by extrapolating our results to the scale of real street canyons, we can gain further insight into the potential use of photocatalytic coatings on building facades to remove NO_x emissions from vehicle traffic in urban streets.

2. Methods

2.1. Wind-tunnel experiment

2.1.1. Street-canyon model

To investigate the performance of NO_x removal by a photocatalytic coating applied on the walls of the street canyon, we used an idealised urban model that we have routinely tested in previous studies [23,24]. The model was based on the centres of several European cities (e.g. Prague, Paris, Vienna) and contained an evenly distributed 8 × 4 grid of courtyard buildings with pitched roofs of the same height ($H = 6.25$ cm) at a scale of 1:400 (i.e. $H = 25$ m at full scale) (Fig. 1a). All buildings were produced with a 3-D printer using the plastic ABS. Because the width (W) of the streets was 5 cm (i.e. 20 m at full scale), the aspect ratio (H/W) of all street canyons was 1.2. However, the aspect ratio related to the height ($0.8H$) of the building facades corresponds to 1. The examined street canyon was in the middle of the urban model (with respect to the flow direction), where a sufficiently developed atmospheric boundary layer (ABL) was present.

We applied a commercial photocatalytic coating FN NANO®2 to the leeward and windward walls of the studied street canyon up to the eaves height, i.e. $H = 5$ cm, and along the entire length of these walls ($L = 30$ cm), accounting for a total of 300 cm^2 of the coated area (Fig. 1b). The FN NANO®2 was developed and manufactured by Advanced Materials-JTJ (Czech Republic) and consists of approximately 74% Aeroxide TiO_2 P25; the remaining portion is an inorganic binder. In the liquid form, the solids content was 10 wt% in the deionised water suspension. The physicochemical properties of the photocatalyst were described in detail in [14]. The ratio of the coated area to the volume of the street canyon was 40 m^{-1} (see Table 1), i.e. 400 time larger than in the full scale.

2.1.2. Wind tunnel

We positioned the urban model in the middle of the wind tunnel (Fig. 1c and d). The tunnel was constructed as an open tunnel with a constant cross-section of 1.5 × 1.5 m^2. The fan drew in the outside air through the inlet openings of the stilling chamber, which was 6 × 6 × 12 m^3 and had a chamber area of 64 m^2. This chamber eliminated the influence of external conditions (e.g. air fluctuations due to wind and air pollution due to dust particles). The outside air was then sucked out of the chamber into a development section of 1.5 × 1.5 × 23 m^3. At the beginning of the development section, the air parameters (temperature, relative humidity, air pressure) were measured with the humidity–temperature probe Comet DSRH/C. Five metres downstream, the corresponding ABL was developed over a length of 12 m to the entrance of the test section with Irwin towers (a set of three towers, 1.4 m hight) and a staggered arrangement of roughness elements (thin plates of 5 cm width and height).

2.1.3. Modelled atmospheric boundary layer

The main parameters of ABL (roughness length, $z_0 = 1.87$ m; displacement height, $d_0 = 3$ m; and friction velocity, $u_* = 0.43$ m s^{-1}; all to scale) and turbulent properties (turbulence intensity in the flow direction and vertical direction of $I_u = 35\%$ and $I_w = 25\%$, respectively, and turbulence spectra at different heights) modelled in the wind tunnel were measured with a laser Doppler anemometer at the entrance of the test section. These parameters followed the recommendations for atmospheric flow and dispersion modelling and are presented in detail in [23]. Based on the mean height of the buildings and the free-stream velocity $U_{ref} = 6.2$ m s^{-1} (measured continuously with a Prandtl tube) in the wind tunnel, the experiment was conducted at a sufficiently high Reynolds number (i.e. $Re_{ref} = HU_{ref}/\nu \approx 24{,}400$, where ν is the kinematic viscosity of the air) [21]. However, the more comparable Re value to the flow reactor experiments is the one based on the flow velocity at the height of the building ($Re = HV_B/\nu \approx 4580$). This Re value was also sufficiently far above the critical value ($Re_c = 3400$) recommended for

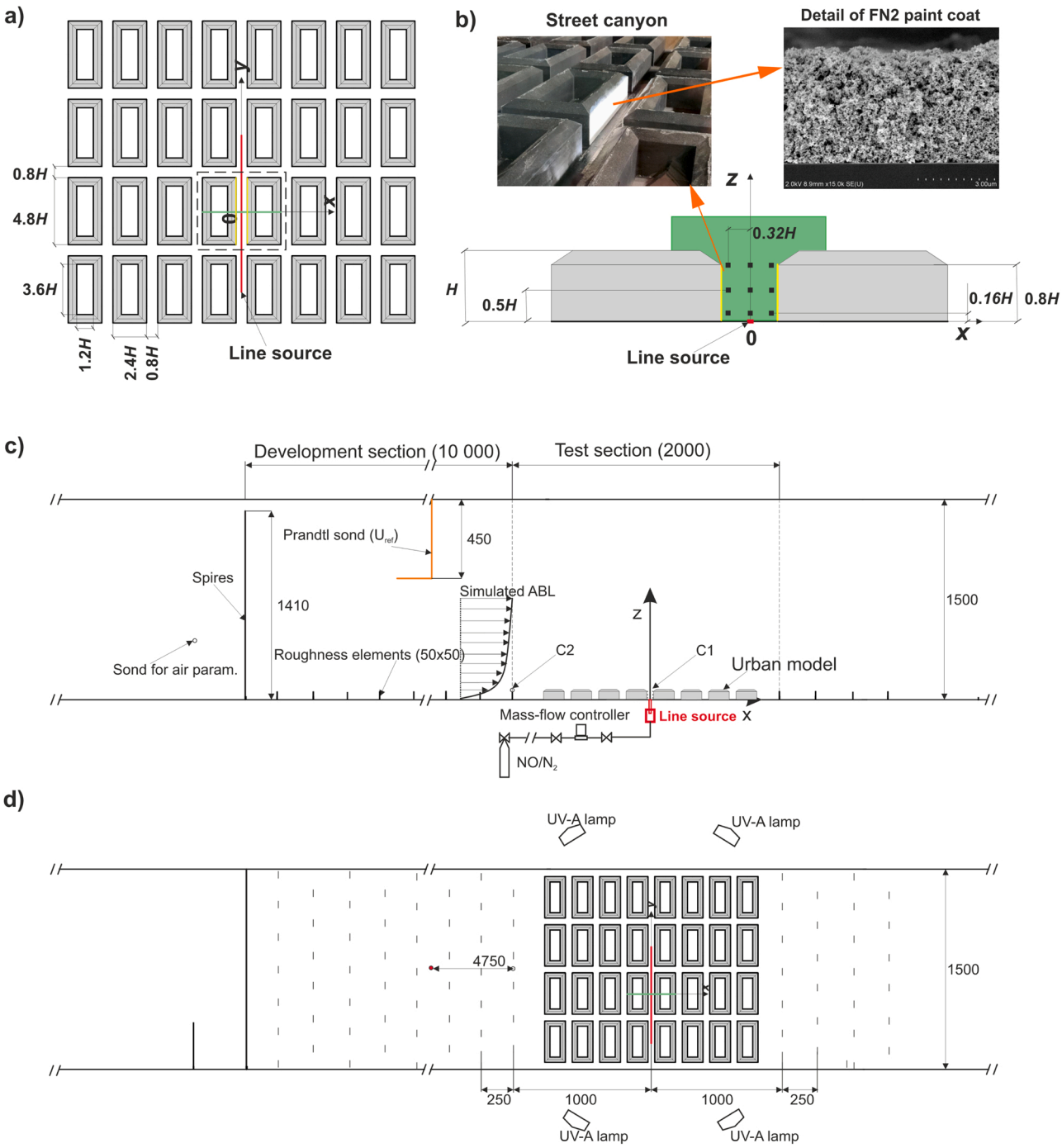

Fig. 1. Schematic representation of the experimental setup in the wind tunnel in relation to the wind-tunnel coordinates (x, y, z): a) urban model, b) detail of the investigated street canyon, c) top and d) side view of the wind tunnel. The red line represents the ground-level line source and the green line is the measured plane in the investigated street canyon. The black dots in (b) represent the positions of the NO_x concentration measurements. All dimensions are in mm.

Table 1
Essential parameters and conditions in the experiments the street canyon and ISO flow reactor.

Experiment	Volume (cm^3)	Irradiated area (cm^2)	Area/Volume (m^{-1})	Ref. velocity ($m\ s^{-1}$)	RH (%)	Irradiation ($W\ m^{-2}$)	NO_{in} (ppm)
Street canyon	750	300	40	6.2	20 – 30	5 – 20	50
ISO reactor	25	50	200	0.20 – 0.73	0.1 – 95	0.1 – 50	0.1

modelling flows and pollutant dispersion in street canyons [25]. We also confirmed the independence of the sufficiently high turbulent flow within the street canyon by several visualisation and statistical tests (not shown here).

2.1.4. *Pollution source model*

We used a ground-level line source model that simulated local pollution by NO within a street canyon by idealised traffic with a constant volume flow rate ($Q = 9$ ml s^{-1}) and concentration (50 ppm). Such

flow rate was established in flow-rate independence tests. To achieve the continuous flow rate of NO, we used an ALICAT MC-10SLPM, which automatically regulated the prescribed flow rate from the vessel NO (Fig. 1c). The line source was 0.5 m long and consisted of 252 evenly spaced stainless steel tubes arranged flat side by side along the transverse axis of the studied street canyon and adjacent intersections (see the red line in Fig. 1a and d). The tubes had an inner diameter of 0.3 mm and a length of 100 mm and were installed in a pressure chamber under the floor of the wind tunnel. The entire length of the tubes was below the floor of the city model, with the outlets aligned with this level. The pressure drop between the plenum and the bottom of the wind tunnel was such that the flow was not affected by local pressure variations within the street canyon. We tested the homogeneity of the line source and the negligible effect of the gas outflow velocity within the street canyon by comparing the gas concentrations and air velocities measured with and without the line source.

2.1.5. Measuring techniques

We used two Horiba APNA-370 analysers to simultaneously monitor concentrations of NO_x at one of nine selected points in the canyon (C1 in Fig. 1c) and at a point at the entrance to the test section (C2 in Fig. 1c). At each point, analysers were used to measure the concentrations of NO and NO_2 at a frequency of 0.2 Hz. The sampling time for each point was 30 mins for simulating pollution from the ground-level line source. This long sampling time was necessary because of the flow turbulence, the low sampling frequency of the analysers and the time needed to reach a quasi-equilibrium of the chemical reactions of NO_x. We observed that the dispersion of reactive pollutants in the street canyon reached a quasi-equilibrium state within a few minutes. To simulate photocatalytic oxidation, we installed four UV-A lamps around the measurement section of the tunnel. We measured a concentration response after the activation light was turned on/off. This arrangement ensured that the irradiance of the coated surfaces of the canyon under investigation varies between 5 and 20 W m^{-2}, which corresponds to the average intensity of UV-A radiation in the outdoor environment. This variation was mainly due to the height, and thus the lowest irradiance value (5 W m^{-2}) was measured near by the bottom of the street canyon, while the highest value was at the eaves (20 W m^{-2}). The concentrations of NO_x were measured on two days. On the first day, the concentrations were measured without UV-A irradiation to simulate dark conditions. On the second day, the concentrations of NO_x were measured at the same points as on the first day, but with the UV-A irradiation to simulate the photocatalysis. On this second day, the average relative humidity varied between 20% and 36%.

To observe and measure the spatiotemporal evolution of flow in the studied street canyon, we used a 2-D time-resolved Particle Image Velocimetry (TR-PIV) system from Dantec Dynamics in addition to concentration measurements. We positioned a 1.5-mm-thick DualPower 30–100 laser sheet to illuminate flow-supported passive seeding particles in the plane where NO_x concentrations were previously measured (green line and plane in Fig. 1a and b, respectively). The 1 μm diameter particles were seeded using a Smoke Factory Tour Hazer 2 upstream of the Irwin towers. A SpeedSense VEO 410 CMOS camera was positioned outside the wind tunnel and captured 6227 consecutive double-frame images during a 12 s acquisition time. This time was sufficiently long to obtain time-independent mean flow statistics. The instantaneous velocity vector fields were computed using the adaptive PIV method of DynamicStudio software. The size of the interrogation area was set to 32 × 32 pixels with 50% overlap, resulting in a spatial resolution of the velocity vector fields of 2.5 mm (0.04 *H*). We estimated the relative measurement error of the mean velocities and turbulent kinetic energy to be less than 5% from four repeated TR-PIV runs.

2.2. Experiments in a flow reactor

We used a flow reactor that was designed according to the standard ISO 22197–1:2016 to test the air purification performance of semi-conducting photocatalytic materials (as shown in Fig. 2). The reactor featured an irradiated photocatalytic surface of 50 cm^2 with a 0.5 cm high gap above it to guide the airflow over the surface. The FN NANO®2 suspension was applied onto glass plates (5 × 10 cm^2) with an airbrush spray gun to ensure homogeneous distribution of the photocatalyst. Several layers were applied to achieve the final sample weight of 50 mg (10 g m^{-2}). The volume of the polluted air above the photocatalytic surface was 25 cm^3, resulting in a ratio of the irradiated area to this volume of 200 m-1, which is five times higher than in the wind tunnel experiment (as shown in Table 1) and corresponds to a scale of 1:2000 when compared to full-scale street canyon dimensions.

2.2.1. Flow velocity tests

Since the mean velocities and thus the reaction times vary spatially within the street canyon, we tested five (3, 5, 7, 9 and 11 L min^{-1}) flow rates of the polluted air in the flow reactor. Depending on the cross-section of the reactor, these flow rates corresponded to 0.2, 0.33, 0.47, 0.6 and 0.73 m s^{-1}, respectively. We calculated the Reynolds number (Re) for each velocity using the hydraulic diameter of the reactor and the kinematic viscosity of air at 25 °C and found that all Re values were significantly below the critical value of 2300, indicating that the flows were laminar. The concentrations of NO_x were measured using a Horiba APNA-370 chemiluminescence analyser at the outlet of the flow reactor for 10 min with the UV-A light off and another 10 min with the light on, at each flow rate. The total inlet concentration of NO was kept at 0.1 ppm_v, as recommended by [13]. The UV-A irradiance was set at 10 W m^{-2} throughout the experiment.

2.2.2. UV irradiance and relative humidity tests

We also investigated the effects of UV-A light intensity (using lamps from Philips, type BLB, 15 W) and the percentage of relative humidity on the performance of the photocatalyst tested. We tested five intensities (0.5, 5, 15 and 50 W m^{-2}) and five relative humidities (0.1%, 25%, 50%, 75% and 95%) for the NO inlet concentrations of 0.1 ppm. During the UV-A irradiance tests the relative humidity was kept at 50%. During the relative humidity tests, the UV-A irradiance was set at 10 W m^{-2}. The peak intensity of the UV lamps was at 365 nm.

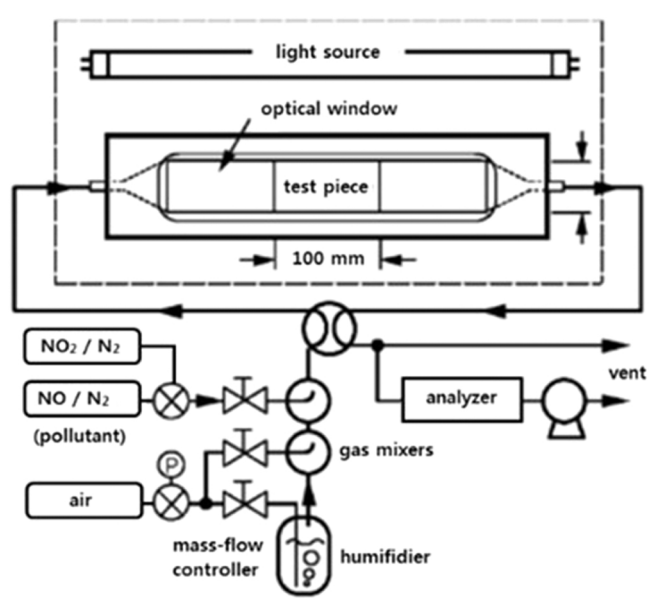

Fig. 2. Scheme of the experimental setup for testing the air-purification performance of the photocatalytic coating in the flow reactor according to ISO 22197–1:2016 [14].

2.3. Analysis of the kinetics and removal efficiency

To compare the kinetics between the street-canyon and flow reactor experiments, we used the reactive uptake coefficient (J) according to [13]:

$$J = \frac{4 \bullet k}{\bar{v} \bullet \frac{S}{V}} \tag{1}$$

where k (s^{-1}) is the first-order rate coefficient, $\bar{v}$ (m s^{-1}) is the mean molecular velocity of NO_x, S (m^2) is the active surface area of the photocatalyst, and V (m^3) is the active volume of the pollutant in the photoreactor or street canyon. We calculated the rate coefficient as follows:

$$k = -\frac{\ln \frac{C}{C_0}}{t} \tag{2}$$

where C (ppm) is the mean NO_x concentration measured at the outlet of the photoreactor or at the given position in the street canyon when the UV-A lights were on, C_0 (ppm) is the mean NO_x concentration at the inlet of the photoreactor or at the same position in the street canyon when the UV-A lights were off, t (s^{-1}) is the reaction time, which we calculated as:

$$t = \frac{V}{\dot{V}} \tag{3}$$

where V (m^3) is the volume above the active surface in the flow reactor or the volume of the street canyon, and $\dot{V}$ (m^3 s^{-1}) is the volumetric flow rate in the flow reactor or in the street canyon. Thus, for the street canyon, the residence time is equal to H/U_{2D}, where U_{2D} is the resulting two-components velocity at the point. The mean molecular velocity of NO_x in Eq. (1) was calculated as:

$$\bar{v} = \sqrt{\frac{8 \bullet R \bullet T}{\pi \bullet M}} \tag{4}$$

where R is the ideal gas constant ($R = 8.314$ J mol^{-1} K^{-1}), T is the absolute temperature (K) and M is the molecular mass of the reactant (kg mol^{-1}).

Ifang et al. [26] defined the uptake coefficient as the ratio of the number of collisions that lead to reaction over all collisions of the gas-phase reactant with a reactive surface. Considering the first-order kinetics, the uptake coefficient is independent of the reaction time, the pollutant level, and the surface/volume of the reactor or street canyon. Therefore, recalculating the values of the uptake coefficient on the full scale (with respect to both the temporal and spatial scales) gives the same results, and the removal efficiency of NO_x can be calculated as follows:

$$R = 1 - e^{(-k \bullet t)} = 1 - \frac{C}{C_0} \tag{5}$$

We estimated the absolute error of the calculated NO_x removal efficiency to be no more than 0.01.

3. Results

3.1. Street-canyon dispersion characteristics in the darkness

Knowledge of the flow characteristics and dispersion processes within the street canyon is critical to understanding the potential for photocatalytic removal. In our case, the mean flow field is characterized by the vertical recirculation (Fig. 3a). The flow velocity is lowest in the centre of this recirculation, while it is highest at the edges, i.e. at the windward and leeward walls and the top of the street canyon. Since this is a highly developed turbulent flow, the instantaneous flow field, which is crucial for photocatalytic oxidation, differs considerably from the mean flow field. The mean recirculation and turbulent kinetic energy (*TKE*), as shown in Fig. 3b, provide insight into the dynamics of the instantaneous flow within the street canyon. The *TKE* is a measure of the kinetic energy associated with the velocity fluctuations that can be caused either by the chaotic motion of the flow or by organised flow structures such as vortices. Here we have used the 2D form of the *TKE*, calculated as ¾ of the sum of the mean variances of the longitudinal ($\overline{(u')^2}$) and vertical ($\overline{(w')^2}$) velocity fluctuations. The higher *TKE* on the roof and on the windward wall of the street canyon is due to the eddies detaching from the edge of the upstream roof and are either ejected into the flow above the roof or swept along the windward wall into the street canyon. On the other hand, the lower *TKE* on the leeward wall of the street canyon shows the upward advection of the flow to the top of the street canyon.

The dispersion of pollutants in the canyon in the dark (i.e. with the UV-A light switched off) is determined by the properties of turbulent flow described above. However, the position of the pollutant source is

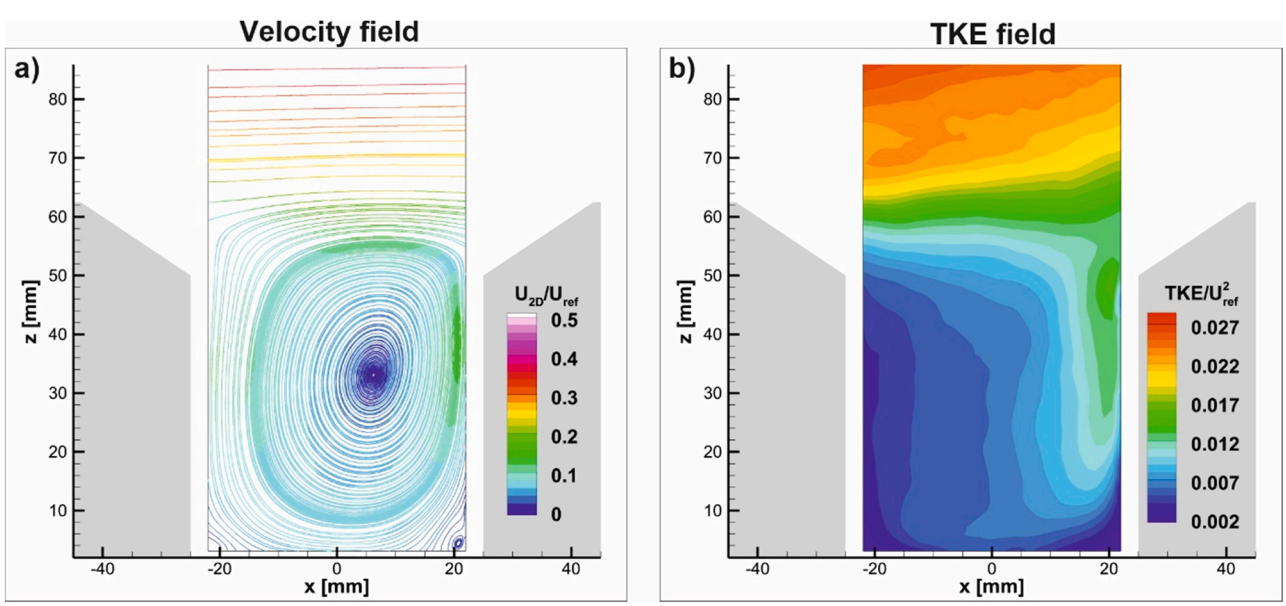

Fig. 3. Normalised a) streamlines (U_{2D}/U_{ref}) and b) turbulence kinetic energy (TKE/U_{ref}^2) in the street canyon and above the roofs, determined with the PIV system. The wind is from the left to the right.

essential. Sampling over a sufficiently long period shows that, on average, the highest NO_x concentrations form at the bottom and along the leeward wall (Fig. 4a). The lowest concentrations are reached near the windward eaves and the windward wall, where fresh air is drawn in from the canopy flow. Converting the NO_x concentration into the dimensionless form ($C^* = CU_{ref}HL/Q$, where L is the length of the line source and Q is the volume flow rate from the source) yielded the same values (within experimental error) as those observed in our previous study [27] for a passive pollutant (ethane). Relative to the time scale of the primary recirculation, which is 14 T (where $T = H/U_{ref}$ is the reference time scale), and the average residence time (52 T) of the NO_x in the street canyon, the pollutant rotates about four times between the leeward and windward walls before being removed through the top opening. This number of rotations is consistent with the observations of Liu et al. [28] for a street canyon with flat roofs. If we convert the average concentration in the street canyon to the full scale by using the average residence time of the pollutant in the street canyon for the emission intensity of NO_x from traffic (120 μg m^{-1} s^{-1}, [29]), we get 65 μg m^{-3}, a typical value for real street canyons with similar geometry.

3.2. The effect of photocatalysis on the NO_x dispersion in the street canyon

The effect of photocatalysis is first illustrated using the time series of the concentrations of NO_x, NO and NO_2 at the windward (Fig. 5a) and leeward (Fig. 5b) wall and at the centre (Fig. 5c) of the street canyon. For each case, the time series obtained in the darkness (dashed lines) and with the UV-A light switched on (solid lines) are superimposed.

In Fig. 5, we can observe the oscillation of the concentrations around the mean values, which represent the turbulent flow under steady-state conditions. More importantly, the NO_x concentrations (green lines) decrease significantly at the windward wall (Fig. 5a) and in the middle

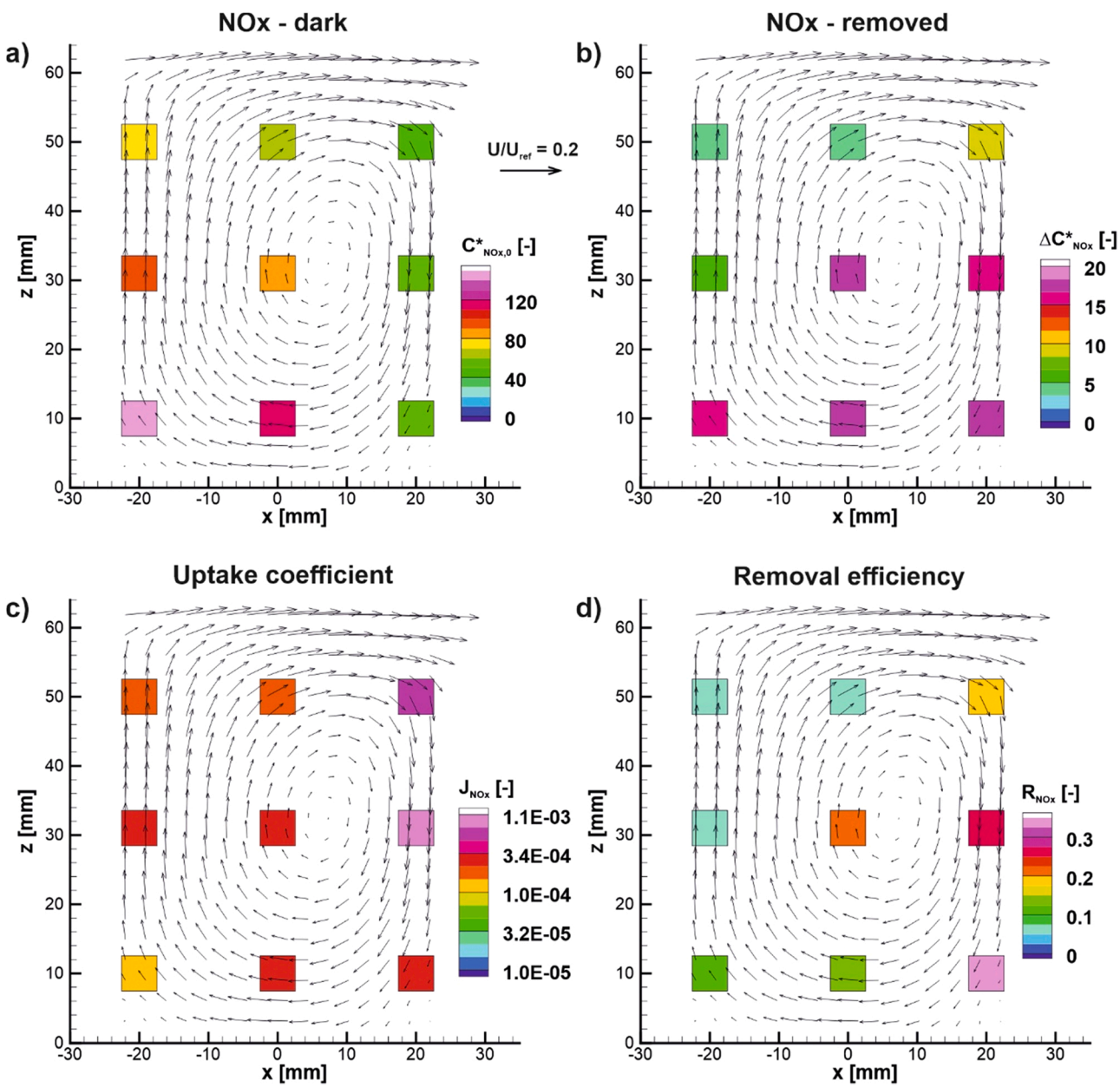

Fig. 4. Spatial distribution of mean dimensionless a) NO_x concentrations in the dark ($C^*_{NOx,0}$) and the mean dimensionless b) removed concentrations (ΔC^*_{NOx}), c) uptake coefficients (J_{NOx}) and d) removal efficiencies (R_{NOx}) of NO_x because of photocatalysis in the street canyon. The arrows represent the 2-D velocity vector field in the measured plane.

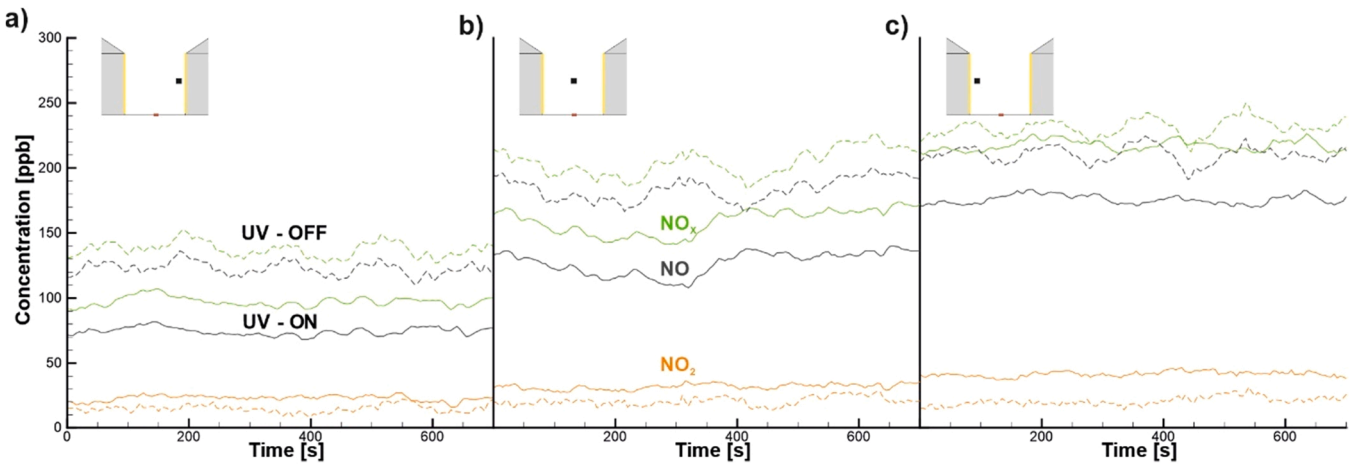

Fig. 5. Time series of NO_x (green lines), NO (grey lines) and NO_2 (orange lines) concentrations at the a) windward wall, b) middle of the street canyon and c) leeward wall in the dark (dashed lines) and with UV-A lights switched on (solid lines).

(Fig. 5b) of the street canyon, while the NO_x concentrations at the leeward wall (Fig. 5c) decrease less due to weaker photocatalysis. The main reason for this smaller decrease in NO_x concentration at the leeward wall is twofold. First, the NO_x pollutants are transported along the leeward wall exclusively by advection, which leads to fewer reactive collisions with the photocatalyst at this wall than at the windward wall. Secondly, the part of the already cleaned air at the leeward wall is transported to the windward wall by the flow recirculation within the canyon. This combined effect of NO_x removal from the street canyon leads to a greater decrease in the concentrations of NO and NO_2 at the windward wall than at the leeward wall and in the middle of the canyon, as shown in Fig. 4b, confirming that more NO_2 is removed than formed in the street canyon.

The effect of turbulence on NO_x photocatalysis in the street canyon is evident from the NO_x uptake coefficients calculated for each measurement point (Fig. 4c). The uptake coefficients are highest on the windward wall, especially at mid-height (x = 20, z = 31 mm, Fig. 4c) and at eaves height (x = 20, y = 50 mm, Fig. 4c). The main reason for these high values is the high turbulence level (see Fig. 6a), which allows for more intensive contact of NO_x with the coated wall with less reaction time. On the other hand, the uptake coefficient at the mean height of the leeward wall (x = −20, z = 31 mm, Fig. 4c) is about five times lower, although the reaction time is similar to that at the windward wall. This is due to the aforementioned advection of the pollutant, which reduces the contact with the wall.

Fig. 4d shows that the NO_x removal efficiency correlates with the uptake coefficient only in some places (Fig. 4c). Instead, the removal efficiency inversely reflects the distribution of pollutants within the street canyon along the z-axis under dark conditions (Fig. 4a). Thus, the efficiency is mainly determined by the flow structures within the street canyon and not by the turbulence (Fig. 6b). The highest efficiency of 33% is reached at the end of the recirculation near the corner of the windward wall, where *TKE* is relatively very low (see number 7 in Fig. 6b). Here a secondary small counter-rotating vortex forms (Fig. 3a) and the NO_x concentration decreases the most due to the prolonged reaction time (Fig. 4b). Similarly, the effect of flow recirculation is also observed in the middle of the street canyon, where the efficiency of 20% is still achieved, although it is further away from the coated walls and the NO_x concentration is relatively high (Fig. 4a). The lowest removal efficiencies of about 7% are observed at the leeward wall and in the

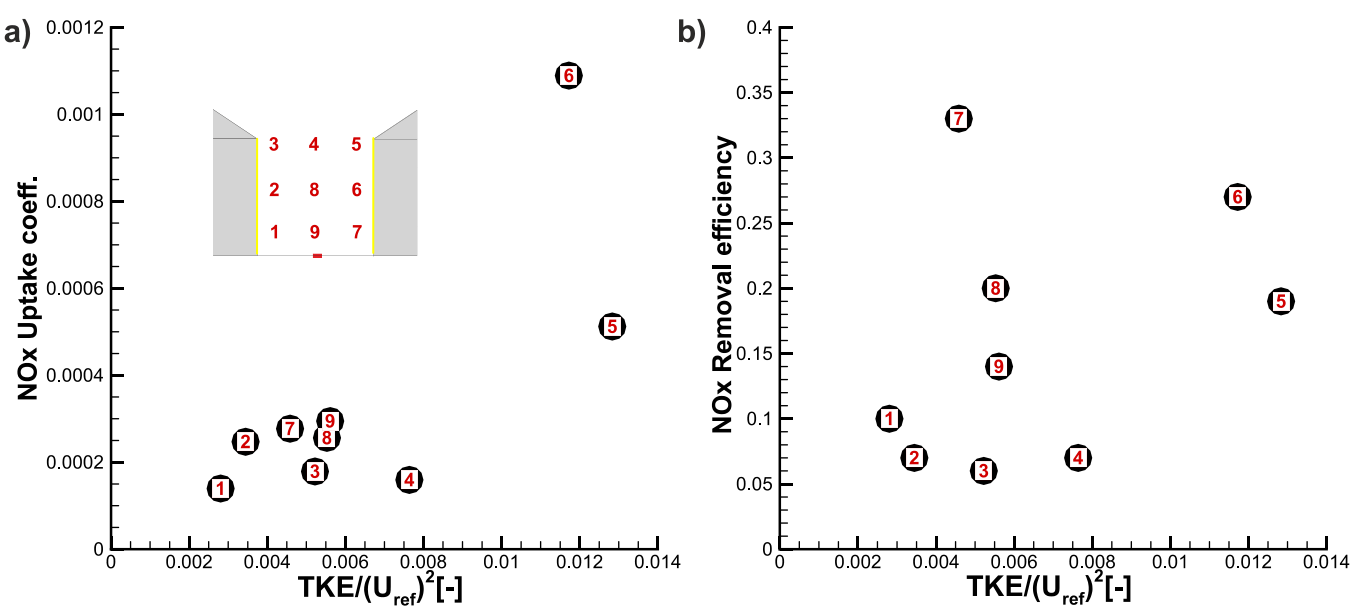

Fig. 6. Dependence of a) NO_x uptake coefficient and b) NO_x removal efficiency on the dimensionless turbulence kinetic energy (TKE/U_{ref}^2) within the street canyon. The positions within the street canyon are indicated by the numbers.

upper middle of the street canyon, which can be attributed to the lower contact with the coated walls due to the vertical advection of the pollutant or to the high velocity fluctuations (*TKE*) that transport the pollutant away into the flow above (see also number 4 in Fig. 6b). Spatial averaging of the removal efficiencies over the measured area yields a value of 16%.

3.3. The comparison between the street canyon and the flow reactor

Before we compare the results of the wind tunnel experiment, we first explain the conditions under which the experiment was conducted. In particular, we will show the effects of the UV light intensity and the percentage of relative humidity in the polluted air on the effectiveness of the photocatalyst. These effects were determined in earlier experiments in the flow reactor.

As can be seen in Fig. 7a, the efficiency of the photocatalyst is very sensitive to UV light intensity (*I*), with a decrease of about 40% at intensities of 10 W m^{-2} and below. However, at intensities above 10 W m^{-2}, the efficiency of the photocatalyst remains constant regardless of the UV-A intensity. Accordingly, the UV light intensity range used in the wind tunnel experiments (5–20 W m^{-2}) had no influence on the experimental results and can be compared with the results from the laminar flow reactor at a UV-A light intensity of 10 W m^{-2}.

Concerning the relative humidity (*RH*) of the polluted air, Fig. 7b shows that the efficiency of the photocatalyst decreases significantly at *RH* above 75%, but still has a relatively high efficiency (37%) at *RH* = 95%. At a relative humidity of less than 75%, the effects on the efficiency of the photocatalyst are less pronounced and range between 55% and 68%. The highest efficiency (68%) is achieved at *RH* = 25%, which corresponds to the average value of *RH* during the wind tunnel experiment. In the following, the results of the experiments in the flow reactor at the same relative humidity are compared with the wind tunnel experiment results.

Fig. 8 compares, at full scale, the dependence of the NO_x uptake coefficient (Fig. 8a) and the NO_x removal efficiency (Fig. 8b) on the reaction time between the street canyon and the flow reactor. Since the ratio between the photocatalytic surface area and the volume of the reactant is 2000 times higher in the flow reactor than in the full scale, the lowest reaction time (273 s) is too high compared to the highest reaction time (143 s) observed in the full-scale street canyon. Such long reaction times lead to unrealistically low uptake coefficients and high reaction rates. Assume that the experiment is carried out in the flow reactor with a sufficiently high flow rate and thus reaction time. Rough calculations show that such a flow rate should be about 18 times higher than the recommended flow rate (3 l min^{-1}) and that at this high flow rate the flow in the flow reactor is turbulent. In this case, the uptake coefficients are similar to those in the street canyon, but only where advection of the pollutant dominates (i.e. at the leeward wall). However, the local performance of the photocatalyst in the street canyon cannot be modelled due to the different boundary conditions in the flow reactor.

4. Discussion

Using the principles of physical modelling, we have shown that the performance of the photocatalyst in a street canyon is spatially dependent and that this performance cannot be modelled in standard laminar flow reactors. The spatial dependence of the performance is mainly due to the vertical recirculation of the pollutant within the street canyon and two small corner vortices. Therefore, the highest removal efficiencies of NO_x are found at mid-height (27%), where turbulence prevails, and at the bottom of the windward wall (33%), where recirculation ends and reaction times are high. Interestingly, this area of the highest removal efficiency receives the lowest UV light intensity (5 W m^{-2}) than higher areas of the street canyon. The lowest efficiencies (about 6%) were found at the leeward wall and street canyon top. The spatial average of the removal efficiency within the street canyon yielded 16%. Assuming an emission rate of 120 μg m^{-1} s^{-1} of NO_x from traffic and about 2044 h of sunshine per year, the photocatalyst roughly removes 17.1 kg of NO_x per year in the case of the investigated street canyon, relative humidities and wind direction. However, in real cases, the wind direction changes, and so does the pollution of the street canyon. For winds blowing obliquely or parallel to the axis of the street canyon, NO_x concentrations are lower because the pollutant is more effectively advected from the street canyon, making the performance of the photocatalyst less effective but also less important.

The results of the present study also indicate that the performance of the photocatalyst depends on the street-canyon aspect ratio. For deep street canyons, the reaction times are higher, which increases the removal efficiency. For shallow, better ventilated street canyons, the efficiency is minimal. On the other hand, deep street canyons are less

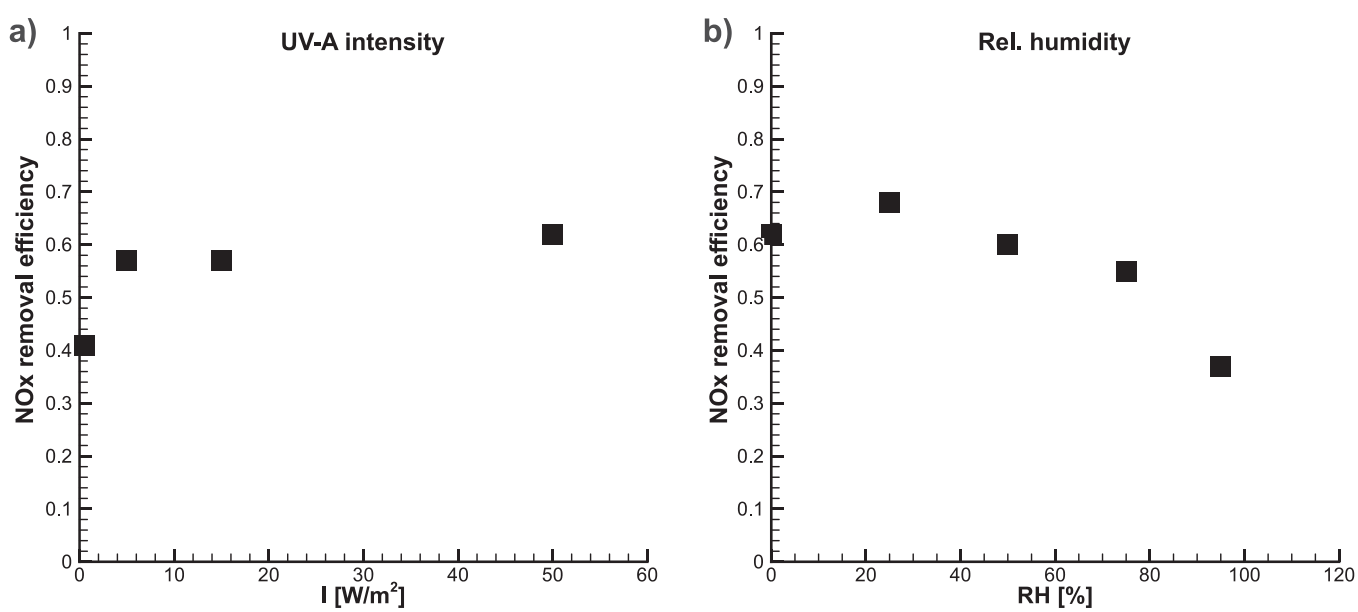

Fig. 7. Dependence of NO_x removal efficiency on a) UV light intensity (*I*) and b) relative humidity (*RH*) of the photocatalytic coating in the ISO flow reactor at an input concentration of 0.1 ppm and a flow rate of 3 L min^{-1}. The *RH* was 50% during the UV intensity tests, and the UV light intensity during the *RH* tests was 10 W m^{-2}. The size of the symbols is larger than that of the error bars.

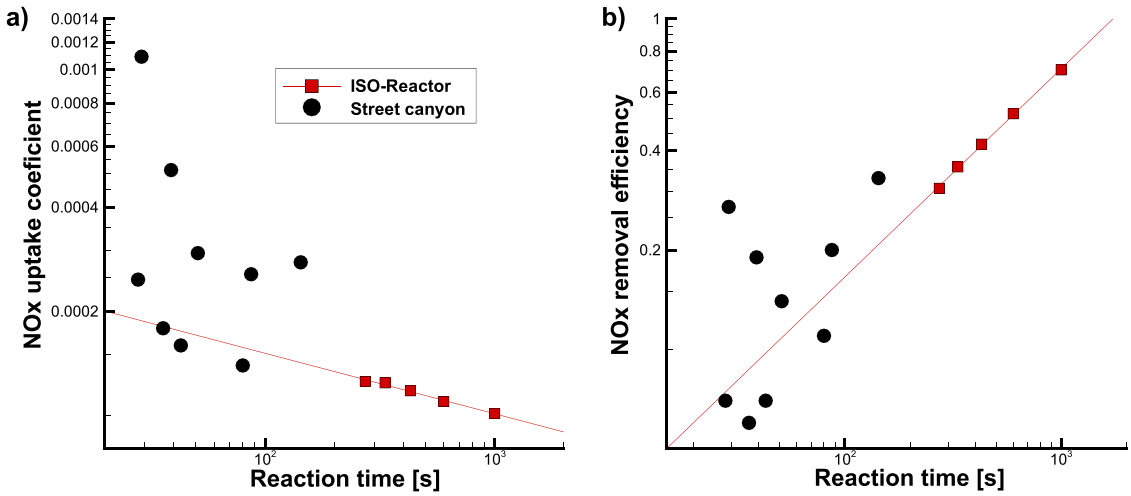

Fig. 8. Comparison of NO_x a) uptake coefficient and b) removal efficiency between the street canyon (circles) and the ISO flow reactor (red squares) at full scale. Exp. conditions for ISO reactor: 3 L min^{-1}, 10 W m^2, $RH = 25\%$, 0.1 ppm NO.

favourable for solar radiation, so the photocatalyst efficiency might be lower than expected. The results of the UV-A light intensity tests conducted for the laminar flow reactor indicate that this decrease would be about a factor of 1.5. However, the effects of the aspect ratio as well as the UV light intensity distribution within the street canyons on the photocatalysis performance need to be further investigated.

Another limitation of the present study is that narrow range (20 – 30%) of relative humidity has been investigated for the model of the street canyon. The tested photocatalyst show relatively stable removal efficiency up to 75% of relative humidity in the laminar flow reactor. However, the effect of relative humidity on the photocatalytic performance in flow reactors with turbulence is worth of another future investigation.

5. Conclusions

In this paper, we present the results of a controlled wind tunnel experiment on the photocatalysis of nitrogen oxides (NO_x) in a street canyon using a method for physical modelling of atmospheric dispersion. We also compare the results with those of a standardised flow reactor. The street canyon was polluted by a ground-level line source simulating idealised traffic. A commercial photocatalytic coating was used as a photocatalyst and applied to both walls of the street canyon. Under conditions independent of the Reynolds number, we measured the decrease in NO_x concentration due to photocatalysis in the street canyon.

The results show that the NO_x concentration decreases significantly in contact with the windward wall and in the middle of the street canyon. However, the decrease in NO_x concentration is lower on the leeward wall. The main reason for this is that the NO_x pollutants along the leeward wall are mainly transported by advection, which leads to less reactive collisions with the photocatalyst at this wall, and because some of the already cleaned air at the leeward wall is transported to the windward wall by the flow recirculation within the street canyon. The effect of turbulence on NO_x photocatalysis is evident in the street canyon, with the highest uptake coefficients at the windward wall, especially at mid-height and eaves height, due to the high turbulence values that allow more intense contact of NO_x with the coated wall in a shorter time. We also show that the NO_x removal efficiency is mainly determined by the mean pollutant recirculation and two corner vortices, with the highest removal efficiency of 33% observed at the end of the recirculation near the corner of the windward wall and the lowest removal efficiencies of about 7% observed at the leeward wall and the upper middle of the street canyon.

The comparison with the flow reactor shows that the recommended flow rate and thus the flow velocity is too low to adequately simulate the photocatalysis performance under the turbulent conditions observed in the street canyon. Increasing the flow velocity only partially solves the problem, as the flow structures and the position of the source in the flow reactor cannot be modelled.

This study also provided a preview of future work to better understand photocatalysis of NOx pollutants in street canyons. Studies on the effects of the aspect ratio of street canyons (especially those forming deep street canyons) or micrometeorological parameters such as relative humidity and the distribution of UV light intensity within street canyons on NOx remediation are of interest.

CRediT authorship contribution statement

Štěpán Nosek: Conceptualization, Methodology, Investigation, Writing – original draft. **Tomáš Ducháček:** Investigation, Writing – review & editing. **Pavol Magyar:** Investigation, Writing – review & editing. **Jan Procházka:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

The authors gratefully acknowledge funding by the Ministry of Industry and Trade of the Czech Republic (Grant No. FV40209), the Czech Science Foundation GACR (Grant No. GA22-14608S), and the institutional support RVO:61388998. The authors also would like to thank Jan Kozohorsky for his valuable support during the experiments. We also would like to express our thanks to the anonymous reviewers whose constructive comments and helpful suggestions have improved the presented paper substantially.

References

[1] WHO, Urban population growth, (2018). ⟨http://www.who.int/gho/urban_health/situation_trends/urban_population_growth_text/en/⟩.

[2] T.R. Oke, Street design and urban canopy layer climate, Energy Build. 11 (1988) 103–113, https://doi.org/10.1016/0378-7788(88)90026-6.
[3] J. Fenger, Urban air quality, Atmos. Environ. 42 (2008) 3909–3910, https://doi.org/10.1016/j.atmosenv.2007.09.035.
[4] S.K. Grange, A.C. Lewis, S.J. Moller, D.C. Carslaw, Lower vehicular primary emissions of NO2 in Europe than assumed in policy projections, Nat. Geosci. 10 (2017) 914–918, https://doi.org/10.1038/s41561-017-0009-0.
[5] J. Hang, J. Liang, X. Wang, X. Zhang, L. Wu, M. Shao, Investigation of O3–NOx–VOCs chemistry and pollutant dispersion in street canyons with various aspect ratios by CFD simulations, Build. Environ. 226 (2022), 109667, https://doi.org/10.1016/j.buildenv.2022.109667.
[6] K. Zhang, G. Chen, Y. Zhang, S. Liu, X. Wang, B. Wang, J. Hang, Integrated impacts of turbulent mixing and NOX-O3 photochemistry on reactive pollutant dispersion and intake fraction in shallow and deep street canyons, Sci. Total Environ. 712 (2020), 135553, https://doi.org/10.1016/j.scitotenv.2019.135553.
[7] J. Liu, S. Cui, G. Chen, Y. Zhang, X. Wang, Q. Wang, P. Gao, J. Hang, The influence of solar natural heating and NOx-O3 photochemistry on flow and reactive pollutant exposure in 2D street canyons, Sci. Total Environ. 759 (2021), 143527, https://doi.org/10.1016/j.scitotenv.2020.143527.
[8] M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S. M. Dunlop, J.W.J. Hamilton, J.A. Byrne, K. O'Shea, M.H. Entezari, D.D. Dionysiou, A review on the visible light active titanium dioxide photocatalysts for environmental applications, Appl. Catal. B Environ. 125 (2012) 331–349, https://doi.org/10.1016/j.apcatb.2012.05.036.
[9] J. Chen, C. sun Poon, Photocatalytic construction and building materials: from fundamentals to applications, Build. Environ. 44 (2009) 1899–1906, https://doi.org/10.1016/j.buildenv.2009.01.002.
[10] M.A. Henderson, A surface science perspective on TiO2 photocatalysis, Surf. Sci. Rep. 66 (2011) 185–297, https://doi.org/10.1016/j.surfrep.2011.01.001.
[11] M.M. Ballari, Q.L. Yu, H.J.H. Brouwers, Experimental study of the NO and NO2 degradation by photocatalytically active concrete, Catal. Today 161 (2011) 175–180, https://doi.org/10.1016/j.cattod.2010.09.028.
[12] S. Laufs, G. Burgeth, W. Duttlinger, R. Kurtenbach, M. Maban, C. Thomas, P. Wiesen, J. Kleffmann, Conversion of nitrogen oxides on commercial photocatalytic dispersion paints, Atmos. Environ. 44 (2010) 2341–2349, https://doi.org/10.1016/j.atmosenv.2010.03.038.
[13] F. Mothes, S. Ifang, M. Gallus, B. Golly, A. Boréave, R. Kurtenbach, J. Kleffmann, C. George, H. Herrmann, Bed flow photoreactor experiments to assess the photocatalytic nitrogen oxides abatement under simulated atmospheric conditions, Appl. Catal. B Environ. 231 (2018) 161–172, https://doi.org/10.1016/j.apcatb.2018.03.010.
[14] R. Zouzelka, J. Rathousky, Photocatalytic abatement of NOx pollutants in the air using commercial functional coating with porous morphology, Appl. Catal. B Environ. 217 (2017) 466–476, https://doi.org/10.1016/j.apcatb.2017.06.009.
[15] A. Folli, M. Strøm, T.P. Madsen, T. Henriksen, J. Lang, J. Emenius, T. Klevebrant, Å. Nilsson, Field study of air purifying paving elements containing TiO2, Atmos. Environ. 107 (2015) 44–51, https://doi.org/10.1016/j.atmosenv.2015.02.025.
[16] E. Brattich, F. Barbano, B. Pulvirenti, F. Pilla, M. Bacchetti, S. Di Sabatino, The effect of photocatalytic coatings on NOx concentrations in real-world street canyons, Build. Environ. 205 (2021), 108312, https://doi.org/10.1016/j.buildenv.2021.108312.
[17] T. Maggos, A. Plassais, J.G. Bartzis, C. Vasilakos, N. Moussiopoulos, L. Bonafous, Photocatalytic degradation of NOx in a pilot street canyon configuration using TiO2-mortar panels, Environ. Monit. Assess. 136 (2008) 35–44, https://doi.org/10.1007/s10661-007-9722-2.
[18] M. Gallus, R. Ciuraru, F. Mothes, V. Akylas, F. Barmpas, A. Beeldens, F. Bernard, E. Boonen, A. Boréave, M. Cazaunau, N. Charbonnel, H. Chen, V. Daële, Y. Dupart, C. Gaimoz, B. Grosselin, H. Herrmann, S. Ifang, R. Kurtenbach, M. Maille, I. Marjanovic, V. Michoud, A. Mellouki, K. Miet, N. Moussiopoulos, L. Poulain, P. Zapf, C. George, J.F. Doussin, J. Kleffmann, Photocatalytic abatement results from a model street canyon, Environ. Sci. Pollut. Res. 22 (2015) 18185–18196, https://doi.org/10.1007/s11356-015-4926-4.
[19] M. Schatzmann, B. Leitl, Issues with validation of urban flow and dispersion CFD models, J. Wind Eng. Ind. 99 (2011) 169–186, https://doi.org/10.1016/j.jweia.2011.01.005.
[20] A. Robins, Wind tunnel dispersion modelling some recent and not so recent achievements, J. Wind Eng. Ind. Aerodyn. 91 (2003) 1777–1790, https://doi.org/10.1016/j.jweia.2003.09.025.
[21] W. Snyder, Guideline for fluid modeling of atmospheric diffusion, 1981.
[22] P. Pichat, A brief survey of the practicality of using photocatalysis to purify the ambient air (indoors or outdoors) or air effluents, Appl. Catal. B Environ. 245 (2019) 770–776, https://doi.org/10.1016/j.apcatb.2018.12.027.
[23] Š. Nosek, L. Kukačka, R. Kellnerová, K. Jurčáková, Z. Jaňour, Ventilation processes in a three-dimensional street canyon, Bound. Layer. Meteor. 159 (2016) 259–284, https://doi.org/10.1007/s10546-016-0132-2.
[24] Š. Nosek, L. Kukačka, K. Jurčáková, R. Kellnerová, Z. Jaňour, Impact of roof height non-uniformity on pollutant transport between a street canyon and intersections, Environ. Pollut. 227 (2017) 125–138, https://doi.org/10.1016/j.envpol.2017.03.073.
[25] R.N. Meroney, M. Pavageau, S. Rafailidis, M. Schatzmann, Study of line source characteristics for 2-D physical modelling of pollutant dispersion in street canyons, J. Wind. Eng. Ind. Aerodyn. 62 (1996) 37–56, https://doi.org/10.1016/S0167-6105(96)00057-8.
[26] S. Ifang, M. Gallus, S. Liedtke, R. Kurtenbach, P. Wiesen, J. Kleffmann, Standardization methods for testing photo-catalytic air remediation materials: Problems and solution, Atmos. Environ. 91 (2014) 154–161, https://doi.org/10.1016/j.atmosenv.2014.04.001.
[27] Š. Nosek, Z. Kluková, M. Jakubcová, Z. Jaňour, The effect of courtyard buildings on the ventilation of street canyons: a wind-tunnel study, J. Wind Eng. Ind. Aerodyn. 220 (2022), https://doi.org/10.1016/j.jweia.2021.104885.
[28] C. Liu, D. Leung, M. Barth, On the prediction of air and pollutant exchange rates in street canyons of different aspect ratios using large-eddy simulation, Atmos. Environ. 39 (2005) 1567–1574, https://doi.org/10.1016/j.atmosenv.2004.08.036.
[29] X. Xie, C. Hao, Y. Huang, Z. Huang, Influence of TiO2-based photocatalytic coating road on traffic-related NOx pollutants in urban street canyon by CFD modeling, Sci. Total Environ. 724 (2020) 1–11, https://doi.org/10.1016/j.scitotenv.2020.138059.