

Supplementary materials

Of

**Investigation of the effect of aerosolized TiO₂ nanoparticles on NO₂ concentrations under
UVA exposure**

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The effect of UVA exposure on the NO₂ concentration

The time series of NO, NO₂ and NO_x concentration under UVA exposure for different numbers of UV-lamps in the absence of TiO₂ nanoparticles is presented in Fig. S1. The reduction of NO₂ to NO in the presence of UVA light takes place according to the following reaction:



And also, the second chemical reaction in the presence of oxygen:



When no lamp was active, the initial mixing ratio of NO and NO₂ measured at the inlet of the reactor were 8 ppbv and 123 ppbv, respectively. By turning on a single lamp, the NO₂ ratio decreased from 123 ppbv to 102 ppbv, while the NO mixing ratio increased to 24 ppbv at the outlet. The initial reaction of NO₂ was very quick but due to the low UVA exposure, as a source of energy, the reaction needed longer time to reach the steady state condition. However, by increasing the UVA exposure, the time to reach the steady state decreased due higher energy input.

To investigate the effect of UVA exposures on the NO₂ concentration, six different UV intensities of 351.6, 703, 1055, and 2109 W s m⁻² were used which correspond to 1, 2, 3 and 6 active UVA lamps, respectively. The reduction for each applied UVA exposure was calculated by using the difference of inlet and outlet concentration in comparison to the inlet concentration. The concentrations at the inlet and outlet were only considered for steady state conditions (the variation of NO, NO₂ and NO_x concentration under UVA exposure for different numbers of UV-lamps is presented in Fig. S1). The reduction of NO₂ concentration increases by increasing the number of lamps. This reduction is 8%, 17.6%, 20.1% and 27.9% for the number of 1, 2, 3 and 6 lamps, respectively.

By increasing the number of lamps in each step, the illuminate energy increases. Experimental results express that by increasing the UVA exposure, more energy is emitted to the NO₂ molecules which leads to increase the reduction of NO₂ (RS1). Besides, the higher UVA

exposure leads to an increase of the free oxygen atoms which accelerate the reduction of NO₂. Fig. S1 clearly shows the conversion between NO₂ and NO while the amount of total NO_x (NO₂ + NO) remains constant.

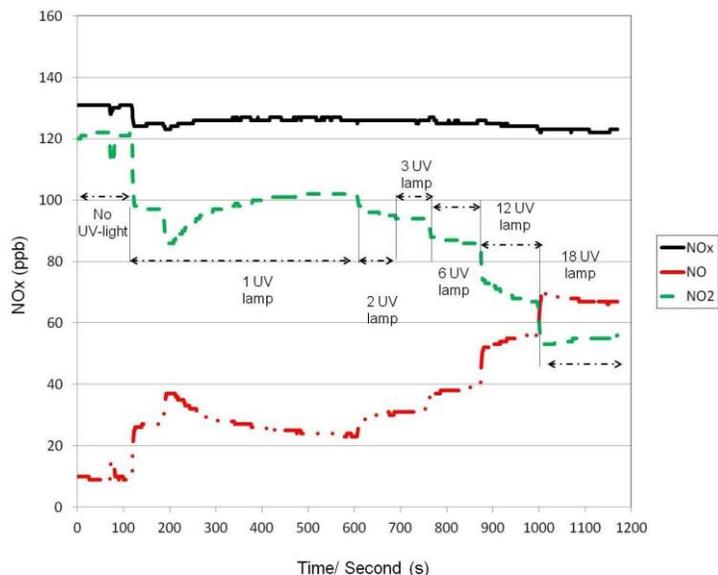


Figure S1. Time series of NO, NO₂ and NO_x concentration under UVA exposure for different numbers of UV-lamps.

Calculation of reactive surface area concentration

Engineered nanoparticles by definition have a size range of 1–100 nm; however, during production and handling, as well as during the atmospheric transport, they grow due to agglomeration, resulting in a particle sizes up to 1000 nm. By using SMPS, the number size distribution is measured and the (external) surface area concentration can be calculated under the assumption of spherical particles. In contrast, it is the reactive surface area concentration ($\text{m}^2 \text{m}^{-3}$) (Uekawa et al., 2003), which also includes the internal surface area of pores, that determines the photocatalytic reaction (Lin et al., 2006).

To calculate the reactive surface area, it is necessary to first determine the total mass concentration. Initially the mass size distribution was calculated for the measured number size distribution for each size channel i , using the effective particle density of P25 (1.236 g cm^{-3}) (Yusoff et al., 2018)):

$$C_m(d_{pi}) = C_N(d_{pi}) \frac{\pi}{6} \rho_{\text{eff}} d_{pi}^3 \quad (\text{S1})$$

The resulting mass size distribution (the normalized average of mass concentration is presented in Fig. S2.) was then integrated to obtain the total mass concentration:

$$C_{m,\text{tot}} = \sum_i C_m(d_{pi}) \quad (\text{S2})$$

The specific reactive surface area, also known as BET surface area, of P25 P25 (Evonik AG, Germany) is known to be $(50 \pm 10 \text{ m}^2 \text{ g}^{-1})$ (Gustafsson et al., 2006; Zein and Bedjanian 2012; Chen et al., 2014; Yusoff et al., 2018; Kebede et al., 2013). The total reactive surface concentration was hence calculated as follows for the generated particle concentrations.

$$A_s = C_{m,\text{tot}} \times \text{BET} \quad (\text{S3})$$

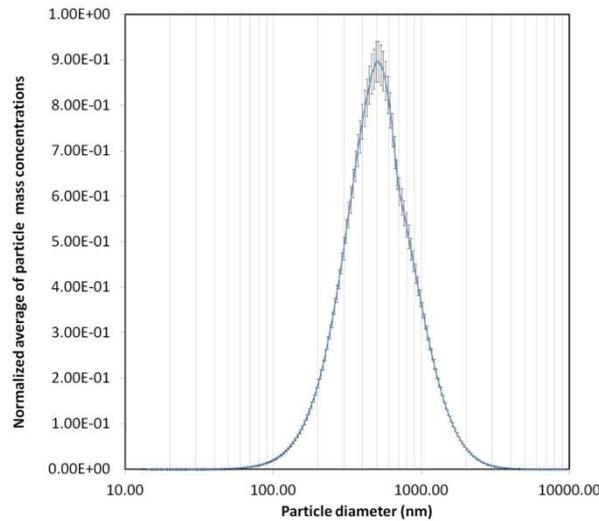


Figure S2. average normalized particle mass size distribution of TiO_2 nanoparticles

The effect of UVA exposure on the photocatalysis reaction

To express the effect of UVA exposure in the presence of TiO₂, it should be noted that when the UVA exposure is greater than a certain value, the photogenerated carriers can be excited, so the electrons and holes generated by TiO₂ move to the surface of the nanoparticles and a photocatalytic reaction occurs (Dalton et al., 2002). The possible photochemical reactions of NO₂ with TiO₂ under UVA light are presented in supplementary file in the section of “Governing photochemical reaction inside the reactor”. Increasing the UVA exposure increases the energy of the excitation photocatalyst, so the number of photogenerated holes and electrons increases which leads to an increase of the photocatalytic reaction. Therefore, the reduction as well as uptake coefficient increased (Fig. 5).

The effect of UVA exposure for different TiO₂ reactive surface area concentrations on the first order reaction rate is presented in Figure S3. Our experimental results show that by increasing the UVA exposure, the trend of the first order reaction rate is increasing for every reactive surface area concentration, except in the case of 2.89 m² m⁻³ where the effect of the reactive surface area is dominant and the variation of the UVA exposure is negligible. For instance, an increase of the UVA exposure from 351.6 W s m⁻² to 2109 W s m⁻², for reactive surface area concentrations of 0.38, 0.79, and 2.89 m² m⁻³ resulted in an increase of the first order reaction rate by the factor of 4, 2.26, and 1.05, respectively. Increasing the reactive surface area concentration leads to a higher number of electrons and holes generated even under low UVA exposure. Therefore, by increasing the reactive surface area concentration, the role of UVA exposure decreases.

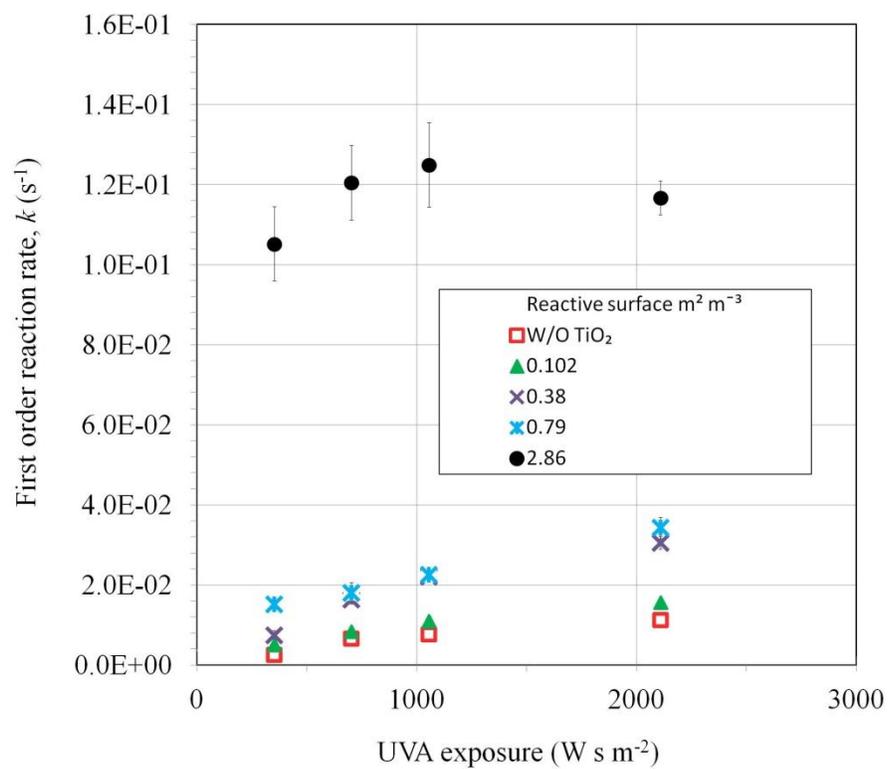


Figure S3. First order reaction rate (1/s) as a function of UVA exposure for different TiO₂ reactive surface area concentrations.

Governing photochemical reaction inside the reactor

The following equations describe the reaction that occurred in the present experimental setup.

TiO₂ nanoparticles under UVA light produce electrons and holes.



The electron hole initiates reaction with H₂O to produce hydroxyl radicals



In the presence of O₂, an electron transfer occurs to produce oxygen activated species.



The produced active oxygen and hydroxy radicals react with NO₂ and NO as follows:

NO and NO₂ reaction with hydroxyl radicals (OH[•]):



NO reaction with active Oxygen (O₂⁻):

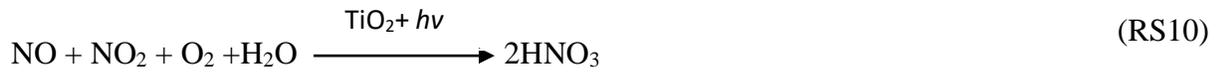


NO₂ reaction with surface hydroxyl:



By considering the above equations, it can be found that the photochemical reaction between NO₂ and NO with TiO₂ nanoparticles under UVA exposure form nitrates (NO₃⁻) (Dalton et al.,

2002; Monge et al., 2010; Laufs et al., 2010). Laufs et al. (2010) concluded that NO and NO₂ as nitrogen species are photocatalytically oxidized leading to nitrate NO₃⁻. Laufs et al. (2010) proposed an equation which explains a photocatalytic net reaction between NO and NO₂ with TiO₂ under UVA light.



The effect of TiO₂ on uptake coefficient:

This inverse dependence is consistent with the concept of the uptake coefficient which is expressed as the rate of effective collisions between TiO₂ nanoparticles and NO₂ gas molecules to the rate of all collisions. Although adding TiO₂ reactive surface area provides a higher number of effective collisions between gas molecules and nanoparticles, which leads to higher NO₂ reduction and reaction rate, this increase is not large enough compared to the total added TiO₂ surface area which appears in the denominator of the uptake coefficient equation (Eq. 6). The reason for less effective collisions can be due to the low initial NO₂ concentration in the current experimental condition compared with the high UVA exposure and TiO₂ reactive surface area concentration. For instance, in the experimental condition used in the present experiment, the reduction of NO₂ at the UVA exposure of 2109 W s m⁻² for the TiO₂ reactive surface area concentration of 0.102 m² m⁻³ and 0.38 m² m⁻³ were 36.7% and 59%, respectively. However, by considering the reactive surface area concentration of 2.86 m² m⁻³ (which is 28 and 7.5 times higher, respectively), the reduction changed to 96.7%. Since the high UVA exposure by itself has a strong impact on the reduction of the NO₂ concentration, the addition of TiO₂ nanoparticles had no major influence. However, at low UVA exposure the effect of the reactive surface area is dominant and thus the uptake coefficient larger for higher reactive surface area concentrations. It could be interpreted that illuminating a large reactive surface area with a low UVA intensity leads to more electrons and holes generated by TiO₂ and therefore increase the photochemical reaction rate.

The effect of increasing reactive surface area for different UVA exposures on the uptake coefficient factor is presented in Figure S4. Our experimental results show that by increasing the reactive surface area concentration, the trend of the uptake coefficient factor is decreasing for every UVA exposure. For instance, by increasing the reactive surface area concentration from 0.102 to 0.79 m² m⁻³ for the UVA exposure of 351.6, 703, 1055, and 2109 W s m⁻² resulted in a decrease of the uptake coefficient by the factor of 2.6, 3.7, 3.6 and 3.5, respectively. As explained, increasing the reactive surface area concentration leads to an increase of the photocatalytic reaction of NO₂. However, in comparison with an increase of the reactive surface area concentration, this reduction was small. It appears that due to the low NO₂ concentration (120 ppb), increasing the reactive surface area concentration did not provide more effective collisions between NO₂ molecules with TiO₂ nanoparticles. For a reactive surface area

concentration of $2.89 \text{ m}^2 \text{ m}^{-3}$, the uptake coefficients for all UVA exposures are similar which explains the dominant role of high reactive surface area compared to UVA exposure.

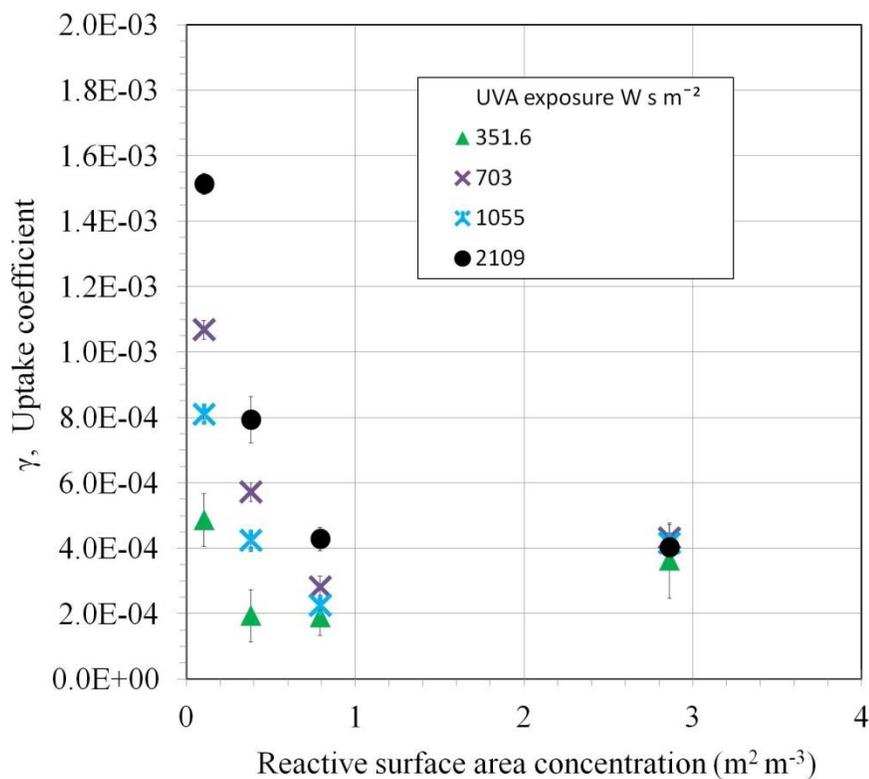


Fig S4 Uptake coefficient as a function of TiO_2 reactive surface area concentration for different UVA exposures at 5% relative humidity.

Experimental results for different UVA exposures and TiO₂ concentrations

The details of NO₂ reduction, first order reaction rate (k) and uptake coefficients (γ) of the reported results are presented in Table S1.

Table S1. Experimental results for different UVA exposures and TiO₂ concentrations.

No. Lamp		1 lamp	2 lamp	3 lamp	6 lamp
UAV exposure (W s m ⁻²)		351.6	703	1055	2109
Particle number concentration #/cm ³	Reactive surface area concentration (m ² m ⁻³)	Reduction %			
0	0	7.3	16.6	20.1	27.9
4.67E+05	0.102	13.7	21.7	27.6	36.7
1.03E+06	0.38	19.6	40.7	48.8	59
1.72E+06	0.79	35.8	40.8	48.2	63
3.23E+06	2.66	95.3	96.6	97.3	96.7

No. Lamp		1 lamp	2 lamp	3 lamp	6 lamp
UAV exposure (W s m ⁻²)		351.6	703	1055	2109
Particle number concentration #/cm ³	Reactive surface area concentration (m ² m ⁻³)	1 st order reaction rate (1/s)			
0	0	0.00259	0.00665	0.00769	0.0112
4.67E+05	0.102	0.00503	0.00837	0.0110	0.01565
1.03E+06	0.38	0.00750	0.0179	0.0229	0.0305
1.72E+06	0.79	0.0152	0.0182	0.0225	0.0342
3.23E+06	2.66	0.105	0.121	0.125	0.117

No. Lamp		1 lamp	2 lamp	3 lamp	6 lamp
UAV exposure (W s m ⁻²)		351.6	703	1055	2109
Particle number concentration #/cm ³	Reactive surface area concentration (m ² m ⁻³)	Uptake coefficient factor			
4.67E+05	0.102	0.000487	0.000810	0.00107	0.00151
1.03E+06	0.38	0.000194	0.000467	0.000596	0.000794
1.72E+06	0.79	0.000189	0.000225	0.000281	0.000428
3.23E+06	2.66	0.000363	0.000415	0.000431	0.000402

Arrangement of UVA lamp and exposure time:

The arrangements of lamps for investigating the effect of exposure time are presented for one, two, three and six lamps in Figure S5 and S6, respectively.

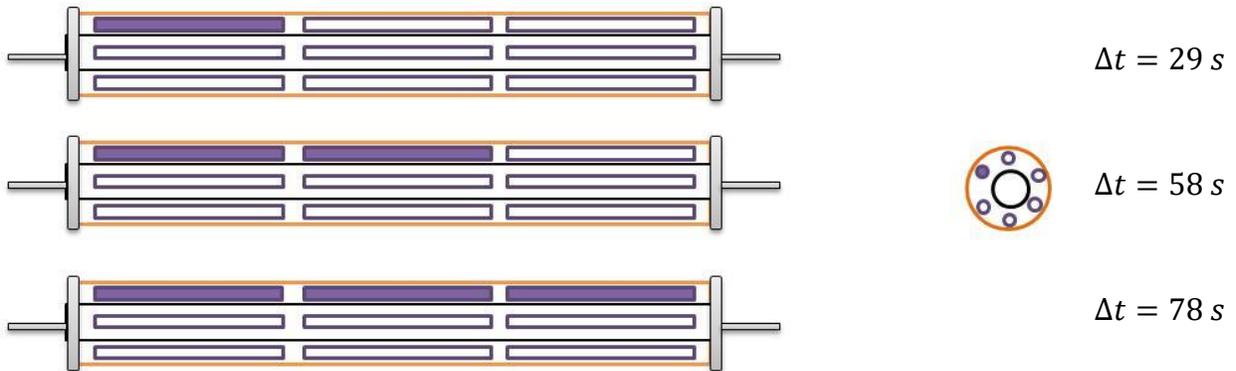


Figure S5 The arrangement for constant intensity of 12 Wm^{-2}

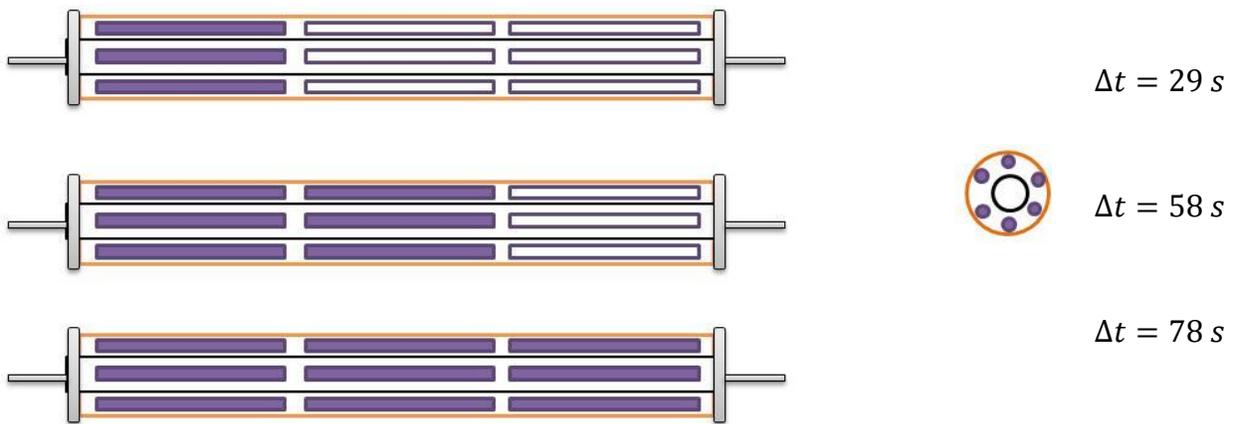


Figure S6 The arrangement for constant intensity of 72 Wm^{-2}

The effect of exposure time on the rate of NO₂ reduction

The produced nitrate, as explained in the section “Governing photochemical reaction inside the reactor”, covered the surface of TiO₂. This nitrate on the surface acts as an inhibitor of the photochemical reaction (Zein and Bedjanian, 2012; Kebede et al., 2013). The amount of generated nitrate increases with exposure time and leads to a decrease of the reaction rate (Fig. S7) until a steady state condition is reached. Zein et al (2012) reported that the rate of the photochemical reaction reduced to 10% of the initial reaction rate.

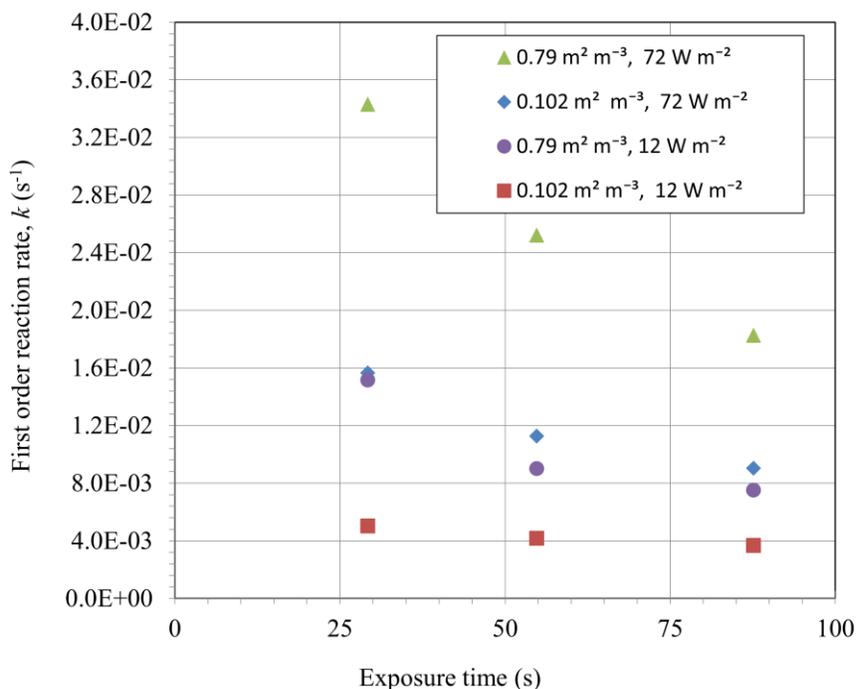


Fig. S7. First order reaction rate (s⁻¹) of reactive surface area concentrations of 0.102 and 0.79 m²m⁻³ versus exposure time for two different intensities of 12 Wm⁻² and 72 Wm⁻².

The effect of exposure time on the first order reaction rate for four different conditions is presented in Figure S7. Our experimental results show that increasing the exposure time as expected decreases the reaction rate. It was explained that this reduction is due to increasing nitrate production (which is an inhibitor for photochemical reactions) over the TiO₂ surface. For a better comparison, the slope of the reaction rate was considered. Our results show that the slope in the case of a reactive surface area concentration of 0.79 m² m⁻³ under UVA exposures of 72 W s m⁻² is highest. This was expected as this condition showed higher NO₂ reduction which means

stronger photochemical reaction. On the other hand, the lowest slope was related to the case of $0.102 \text{ m}^2 \text{ m}^{-3}$ under a UVA exposure of 12 W s m^{-2} which showed the lowest NO_2 reduction. For the other two conditions the results are very similar, because of similar NO_2 reduction.

The effect of humidity on the rate of NO_2 reduction:

Tang et al. (2014) investigated the effect of relative humidity on the photochemical reaction of N_2O_5 with TiO_2 nanoparticles. Tang et al. (2014) explained that the pollutant gas was adsorbed and solved in the water covered over the TiO_2 nanoparticles, followed by hydrolysis of gas by surface-adsorbed water to form HNO_3 . They showed that increasing the water layer over the TiO_2 nanoparticle surface caused an increase of the uptake coefficient. Their experiments, which were carried out with reactive surface area concentrations below $0.049 \text{ m}^2 \text{ m}^{-3}$, showed that the trend of the uptake coefficient for relative humidity levels below 40% is decreasing or constant. However, for higher relative humidity levels, they reported an increasing trend. A similar trend was reported by Pradhan et al. (2010) who investigated the effect of humidity on the photochemical reaction between Gobi and Saharan aerosolized dust and H_2O_2 . Their experiment was carried with a reactive surface area concentration of $0.01 \text{ m}^2 \text{ m}^{-3}$ showed that for both dusts the uptake coefficients were almost constant up to a relative humidity of 35% and started to increase at a relative humidity level of 40%.

A similar trend of the reaction rate was observed in our experiments with a reactive surface area concentration of $0.102 \text{ m}^2 \text{ m}^{-3}$ as shown in Figure S8. The reaction rates at 5% and 35% rh were nearly identical, but those at 70% were clearly higher. However, during experiments with a reactive surface area concentration of $0.79 \text{ m}^2 \text{ m}^{-3}$, the reaction rates at humidity levels of 5% and 35% were already quite different. This difference could be due to relatively large reactive surface area which made it possible to adsorb more water and thus led to a higher uptake coefficient. Our experimental results also showed that the reaction rate increased for a relative humidity of 70% for both reactive surface area concentrations of 0.102 and $0.79 \text{ m}^2 \text{ m}^{-3}$. For the UVA exposure of 6328 W s m^{-2} (72 W m^{-2} with exposure time of 87.6 s), the reaction rate for all three relative humidity cases showed similar results for both reactive surface area concentrations of 0.102 and $0.79 \text{ m}^2 \text{ m}^{-3}$, because the high UVA exposure led to a steady state condition.

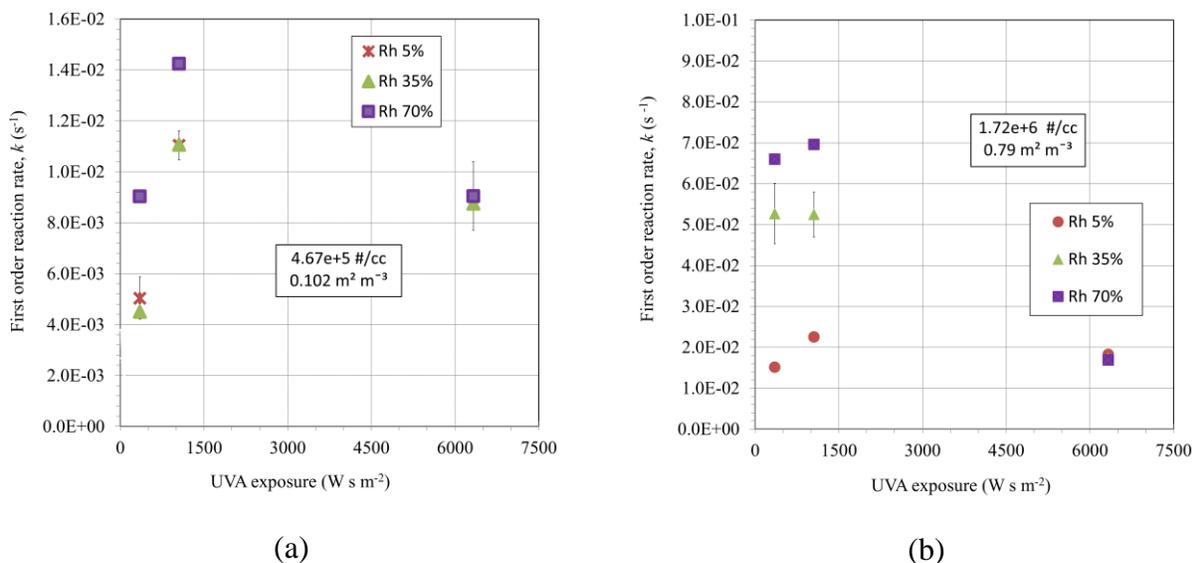


Fig. S8. First order reaction rate as a function of UV exposure at different relative humidity levels for reactive surface area concentrations of 0.102 (a) and 0.79 $\text{m}^2 \text{m}^{-3}$ (b).

For calculating the reaction rate for UVA exposure 6328 W s m^{-2} , the Δt which appears in the dominator (Eq. 6), is 3 times higher than in the case of 1055 W s m^{-2} . Therefore, the reaction rate shows a decreasing trend although the degradation of NO_2 for a UV exposure of 6328 W s m^{-2} is higher than in the case of 1055 W s m^{-2} (Fig. 8a and b). The details of the lamp arrangement are presented in Fig. S9.

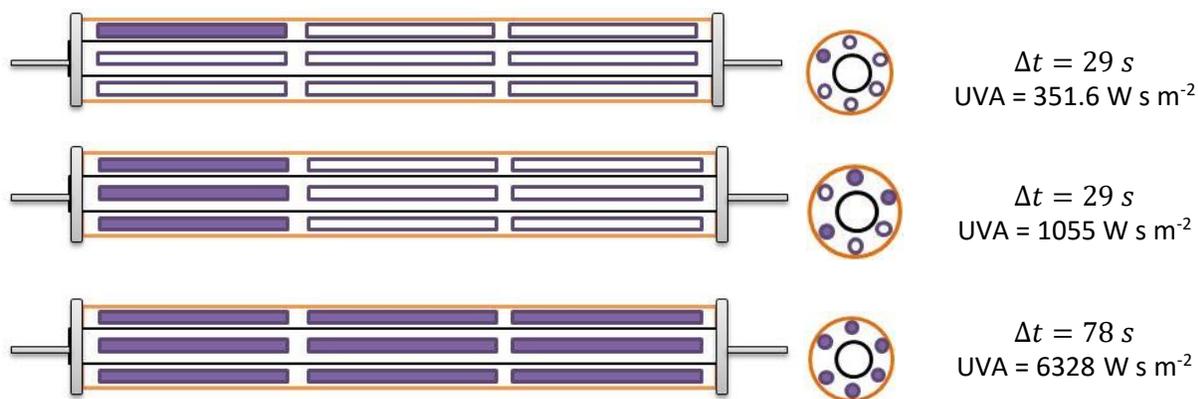


Fig. S9 Lamp arrangement with corresponding UVA exposure and exposure time