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# In situ NO abatement by photocatalysis – study under continuous NO injection in a 10-m<sup>3</sup> experimental chamber

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#### 9 Abstract

Air pollution is a serious public health concern in France and many other countries. Nitrogen oxides  $(NO_x)$ 10 include nitrogen monoxide (NO) and nitrogen dioxide (NO<sub>2</sub>). They are mainly outdoor pollutants 11 produced during combustion of fossil fuel. These gases can easily infiltrate buildings and thus increase 12 indoor pollution. The recommended guideline values for NO<sub>2</sub> are 200  $\mu$ g/m<sup>3</sup> (short-term exposure) and 13 14 40  $\mu$ g/m<sup>3</sup> (long-term exposure). Although no guideline values exist for NO, this gas can be oxidized by atmospheric ozone and thus produce NO<sub>2</sub>. This paper studies the depollution efficiency of photocatalysis 15 towards indoor NO. Experiments were conducted at real scale, in a 10-m<sup>3</sup> experimental chamber 16 developed at the LMDC and used as a reactor. The interior walls of the chamber were equipped with 17 18 painted plasterboards treated with photocatalytic coating (3 g/m<sup>2</sup> of TiO<sub>2</sub>). Gas was continuously 19 injected into the chamber according to a specific procedure: (1) pollutant injection at high flow rate to 20 reach 200 ppb of NO, (2) pollutant injection at low flow rate in order to keep the NO concentration 21 constant at 200±10 ppb, and (3) photocatalysis activation by switching on the light. Typical indoor 22 lighting systems (fluorescent tubes, LED and halogen bulbs) were tested and UV fluorescent tubes were 23 also used to optimise the photocatalytic efficiency. Results showed that NO indoor concentration was 24 reduced by photocatalysis in real-world conditions. Significant NO degradation was obtained under 25 visible light. In addition, using the experimental procedure presented in this paper, a new method for evaluating air depollution efficiency by photocatalysis at real scale is proposed. 26

27 Keywords: Photocatalysis, NO<sub>x</sub>, in situ, experimental chamber, TiO<sub>2</sub>, visible light, indoor air quality

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- 31 measurement and control.

#### 32 **1** Introduction

Improving air quality has been a major concern in industrial countries for some years (Solomon 2012; Li et al. 2016; World Health Organization 2016). A considerable number of studies have dealt with the subject from various points of view: socio-economic impacts (General & Kopp 2014), substances qualified as pollutants (Colls 2002), political decisions concerning air pollution reduction (Fenger 2009) and so on. Improvement of air quality has relied on two types of action: (1) limiting pollution production as much as possible by effective production control (EU 2008), and (2) using techniques to treat already existing air pollutants.

40 This paper focuses on nitrogen oxides (NO<sub>x</sub>). This group of gaseous pollutants includes nitric oxide (NO) 41 and nitrogen dioxide (NO<sub>2</sub>). In urban areas, combustion processes release large amounts of NO<sub>x</sub>, the 42 main sources being traffic and industries. Indoors, NO<sub>x</sub> are produced by chimneys, gas burners, cooking 43 devices and tobacco smoke. Furthermore NO<sub>x</sub> can infiltrate from outdoors (Blondeau et al. 2005). Since 44 over 80% of our time is spent in an indoor environment (Klepeis et al. 2001), it is primordial to increase 45 the understanding of indoor pollution, identify the types of pollutants, and evaluate, control and reduce 46 their concentrations. Nowadays, guideline values exist to help public authorities to combat air pollution. 47 They were established by organisations such as the World Health Organization (WHO) and the French 48 Indoor Air Quality Observatory (OQAI) (Mosqueron & Nedellec 2005; World Health Organization 2006; Krzyzanowski & Cohen 2008; General & Kopp 2014). For example, NO<sub>2</sub> guideline values are: 200  $\mu$ g/m<sup>3</sup> 49 for short-term exposure and 40  $\mu$ g/m<sup>3</sup> for long-term exposure. Limit values for NO have not been 50 51 defined yet (Mosqueron & Nedellec 2004; Mosqueron & Nedellec 2005) even though NO and NO<sub>2</sub> 52 concentrations are directly related. In fact, while most car exhaust systems produce mainly NO, part of it 53 can react with the atmospheric ozone and form NO<sub>2</sub> (Mills & Elouali 2015).

54 For a few decades, photocatalysis has been put forward as a means to fight air pollution (Fujishima et al. 55 2000). Studies on the use of semi-conductors such as  $TiO_2$  or ZnO are abundant in the literature 56 (Fujishima et al. 2008; Yu & Brouwers 2009; Lin et al. 2013; Zhong & Haghighat 2015; Ren et al. 2017). 57 Most experimental studies have been performed under laboratory conditions at different reactor scales 58 (Horgnies et al. 2015; Toro et al. 2016a; Ifang et al. 2014; Horgnies et al. 2012; Ren et al. 2017; Martinez 59 et al. 2011; Hot, Topalov et al. 2017; Hernández Rodríguez et al. 2016; Hüsken et al. 2009; Aïssa et al. 60 2011). Often, photocatalytic oxidation (PCO) efficiency is estimated using international standards and 61 recommendations (ISO 22197-1 2016; CEN/TS 16980-1 2016). However, experiments carried out under 62 such conditions are not very realistic representations of actual applications, where photocatalytic 63 coatings are applied on large existing surfaces, and some authors have worked on this problem. Assessing PCO efficiency towards air pollution under real-world conditions is a tricky task and only a few 64 65 studies on this subject have been published so far (Maggos et al. 2007; Maggos et al. 2008; Gallus et al. 66 2015; Hot, Martinez, et al. 2017; Chen & Chu 2011; Crain et al. 2016; Horgnies et al. 2015; Guerrini 67 2012). Moreover, only a handful of them are related to indoor air. In this paper, PCO of NO under realworld conditions is described, where "real-world conditions" should be understood as those existing in 68 69 an actual house, built from common materials and enabling natural exchanges with the ambient 70 environment. In the work reported here, a specific experimental procedure was used to evaluate the 71 reduction of NO indoor concentration under different lighting systems over a few hours. Two different methods are also proposed for evaluating photocatalytic depollution efficiency from availableexperimental data.

# 74 **2** Materials and methods

#### 75 2.1 Materials

#### 76 2.1.1 Experimental house

The air depollution efficiency of photocatalytic materials towards NO was evaluated under real-world conditions by using a small experimental house designed by the LMDC (Laboratory of Materials and Durability of Constructions, UPS/INSA, Toulouse, France). A schematic representation and some photographs of this experimental house are shown in Figure 1.



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Figure 1 – Experimental house developed at the LMDC for photocatalytic assessment - (a) Outside view (South wall), (b)
 Photograph of the photocatalytic material (North wall), (c) Schematic representation of inside (viewed from above)

The isolated house was a simple metal framework structure composed of four walls, a rectangular floor and a flat roof. Inside, a wall divided the house into two chambers: (1) the experimental chamber (used as a photocatalytic reactor), and (2) the control chamber (used for equipment storage and experiment devices). The interior walls were covered by chipboard and each room had an external door and a window. Two stainless tubes (6 mm in diameter) connected the chambers through the internal wall: one
was used for gaseous pollutant injection, the other for air sampling.

90 The experimental chamber (roughly 10 m<sup>3</sup>) was used as a vast photocatalytic reactor. Gaseous pollution 91 was injected into it from the control chamber and was then diluted with indoor air. Some of this air was 92 sampled. The experimental chamber was equipped with an air fan to improve pollution homogenisation 93 and repeatability. No other mechanical ventilation was installed and the door and window were kept 94 closed. However, indoor/outdoor exchanges occurred due to natural leakage. Thus, a standardised air 95 tightness test was conducted (NF EN ISO 9972 2016). For an overpressure and underpressure of 4 Pa, total air leakage was 33-37 m<sup>3</sup>.h<sup>-1</sup> and, for 50 Pa, leakage was 160-180 m<sup>3</sup>.h<sup>-1</sup>.The Q4<sub>Pa-surf</sub>, which is the 96 main indicator of air-tightness, was 1.32-1.44 m<sup>3</sup>.h<sup>-1</sup>.m<sup>-2</sup>. The experimental chamber was therefore 97 98 qualified as class D (A being the best and E the worst). This chamber was designed to assess 99 photocatalytic activity occurring on the walls. Rather than treating existing interior wall surfaces directly, 100 we applied the photocatalyst to removable plasterboards covering the walls, which enabled various 101 photocatalytic materials to be tested. Aluminium U profiles were fixed on the internal walls to allow 102 plasterboard plates be mounted and removed easily. On the ceiling, artificial lighting systems were 103 installed to test various illumination conditions. Window shutters were kept closed to ensure that there 104 was no interference with natural light and to allow tests to be carried out in the dark without activating 105 the photocatalytic material. Temperature, relative humidity and indoor/outdoor pressure variations 106 were not controlled (see Figure 1c); these parameters were influenced by the weather conditions and 107 were constantly measured by probes (KIMO). During tests, the interior of the experimental chamber 108 could be observed from the monitoring chamber via a camera.

109 The monitoring chamber was used to supervise experiments. As can be seen in Figure 1c, a gas cylinder 110 (Air Liquide – 45 ppm of NO stabilised in  $N_2$ ) was connected to a mass flow controller (MFC from M+W 111 Instrumentation). The flow rate of pollution was thus controlled before its injection into the 112 experimental chamber through the first stainless tube. Using the second stainless tube, polluted air was 113 sampled at 1 ln/min without affecting the pollution level inside the experimental chamber. A NO<sub>x</sub> 114 analyser (HORIBA APNA-370) in the monitoring chamber measured  $NO_x$  (NO and  $NO_2$ ) concentrations in 115 the sampled air. This apparatus gave instantaneous results and enabled continuous monitoring and 116 recording (one mean value every 5 min). The analyser was connected to a PC to store data and the 117 evolution of pollution was observed graphically in real time. A camera was also connected to the PC. To 118 preserve equipment service life, temperature and relative humidity (RH) were controlled by air 119 conditioning (20°C and 30-40% RH). Finally, artificial lighting was also switched on/off from the 120 monitoring room.

#### 121 2.1.2 Photocatalytic material

The photocatalytic material consisted of painted plasterboards (used as the substrate) coated with a TiO<sub>2</sub> aqueous solution (used as the photocatalyst). Standard plasterboards (Placoplatre<sup>®</sup> BA 13) were purchased and cut into pieces with specific dimensions to fit the indoor walls of the experimental chamber (100x50 cm<sup>2</sup>, 75x50 cm<sup>2</sup>, 50x50 cm<sup>2</sup> and 50x25 cm<sup>2</sup>). The edges of each piece were covered with an adhesive tape. Then, each plasterboard plate was painted with orange water-based acrylic paint containing natural pigment (provided by LRVision Company). Two layers were applied to plasterboard

- surfaces using a paint roller. The photocatalytic dispersion was prepared by diluting a water-based commercial product (CristalACTiV<sup>M</sup> S5-300B, TiO<sub>2</sub> content: 18 wt%) to obtain an aqueous solution
- 130 containing 6 wt% of dry TiO<sub>2</sub>. Three layers of this dispersion were applied to the plasterboard surfaces
- 131 with the help of a brush. The total quantity of  $TiO_2$  (dry matter) on substrate surfaces was 2.9±0.1 g/m<sup>2</sup>.
- 132 This quantity was controlled and determined by weighing the recipient containing the  $TiO_2$  dispersion
- and the brush before and after coating each plasterboard sample. The targeted value of 3  $g/m^2$  of
- 134 photocatalytic product on the surface was chosen according to previous research work carried out by the
- same authors (Hot, Topalov et al. 2017). Finally, each photocatalytic plasterboard sample was mounted
- 136 on the walls inside the experimental chamber. An area of 9.3 m<sup>2</sup> of plasterboards was used to cover
- 137 about half of the total indoor surface (ceiling, floor, door and window excluded).

#### 138 2.1.3 Lighting conditions

139 Photocatalysis requires light and its activity is strongly dependent on light wavelengths and intensities. 140 As the literature shows, UV-A lighting systems with wavelengths between 370 and 380 nm are very 141 suitable for  $TiO_2$  activation (Rajeshwar 2007; Ohama & Van Gemert 2011; Gaya & Abdullah 2008; 142 Mamaghani et al. 2017). However, these illumination conditions are very limited in indoor environments. 143 The objective of this paper was to study PCO under real-world conditions, so experiments were carried 144 out under typical indoor lighting conditions. Three different types of visible light lamps were used: (1) 145 four fluorescent tubes (Sylvania Luxline T8, 30 W, 2400 lm), (2) twelve LED bulbs (GE Energy Smart, 40 W, 146 470 lm), and (3) twelve halogen bulbs (Lumipro Eco, 55 W, 630 lm). Experiments were also conducted 147 under UV light provided by four fluorescent tubes (Narva Blacklight blue LT-T8, 30 W) to observe the 148 results under optimal conditions. During an experiment, the light was controlled from the monitoring 149 chamber. The lamps were turned on or off by switches and light amplitude (brightness) could be 150 adjusted by a dimmer. Here, the dimmer was always set to its brightest position in order to obtain 151 optimal illumination. Thus, in this study, lighting conditions were characterised by the type of lamp, its 152 wavelength and the irradiation intensity on the plasterboard surfaces.

153 Light intensity was measured with a radiometer (Gigahertz-Optik X1.1 Optometer) equipped with two 154 detectors: a UV-A detector for wavelengths between 315 and 400 nm (model UV-3717) and a visible 155 detector for wavelengths between 400 and 800 nm (model RW-3703). Firstly, the light intensity received 156 by the surface of the photocatalytic material was investigated. Measurements were made at around 100 157 selected points to map the light intensity distribution on the walls. The map obtained under UV, 158 illustrated in Figure 2, shows that light was able to reach every corner of the photocatalytic material. 159 However, its intensity was dependent on the distance from the light source and ranged from 50 mW/m<sup>2</sup> 160 (at floor level, 3 m from source) to 2,000 mW/m<sup>2</sup> (at approximately 2 m height, 1 m from source). 161 Furthermore, at the same heights, the light appeared to be quite evenly distributed over the three walls 162 (slightly lower on the North wall), and it was thus possible to quantify the received irradiation using a 163 single mean value. Therefore, each lighting condition was expressed by the mean intensity value 164 obtained at three different heights. The results are summarised in Table 1. The intensities of visible 165 wavelengths under UV light or UV wavelengths under visible light were negligible.

To get an idea of a typical indoor light magnitude, a prior measurement campaign was carried out at the
 LMDC. Three rooms were targeted (office, lab room and classroom). Inside each room, light intensity was

168 recorded at different times of day over several days. Detectors were placed at 100 cm from the floor and were not exposed to direct sunlight. Visible and UV light intensity were measured under a combination 169 170 of natural and artificial lighting. More details can be found in Hot, Topalov et al. (2017). The lowest mean UV intensity was 50 mW/m<sup>2</sup> and the highest was 260 mW/m<sup>2</sup>, depending on the room location and 171 172 aspect. These values were slightly lower than the ones obtained in the experimental chamber. 173 Concerning visible light intensity, the lowest and highest mean values were respectively  $2,200 \text{ mW/m}^2$ and 7,680 mW/m<sup>2</sup>: much higher than the values in the experimental chamber (from 300 to 6,100 174 175 mW/m<sup>2</sup> depending on the kind of lamps used). This was mostly due to the absence of natural light in the 176 experimental chamber. In all cases, the experimental lighting conditions tested were considered to be 177 representative of indoor environments.



178

179Figure 2 – Light mapping: irradiation received on photocatalytic material surfaces in the experimental chamber: (a) UV180lighting system (in mW/m²), (b) Fluorescent lighting system (in mW/m²)



	UV lighting 315<λ<400 nm		Visible lighting 400<λ<800 nm	
Height (cm)	Fluorescent	Fluorescent	LED	Halogen
20	40±20	400±100	300±100	900±100
100	300±50	1,000±200	800±200	1,700±300
180	1,200±300	2,500±500	2,300±300	6,100±500

183

184 According to the UV lamp data sheet, its distribution spectrum varies between 350 and 400 nm with a 185 peak around 365 nm. In the case of visible lighting, the emission wavelengths of each system were 186 investigated using a spectro-radiometer (Jeti specbos 1201) and the distribution spectrum of each lamp was obtained between 380 and 780 nm. The results are given in Figure 3. The fluorescent lamp showed a 187 188 discontinuous spectrum with the luminous intensity focused on three major peaks: 436 nm, 544 nm and 189 612 nm. The halogen lamp had a rising, continuous spectrum with no dominant wavelengths. The LED 190 lamp had a first peak around 450 nm and a second one around 605 nm, which were wider than the peaks 191 of fluorescent light.





193

Figure 3 – Spectrum distribution between 380 and 780 nm: (a) Fluorescent, (b) Halogen, (c) LED

## 194 2.2 Experimental procedure

The experimental procedure consisted of injecting NO at a high flow rate until its concentration inside the experimental chamber reached 200 ppb. NO flow rate was then lowered to keep a constant level of pollution in the chamber (sufficient continuous NO injection to compensate for air leakage). PCO was then activated by switching on the light. The four steps listed below, illustrated in Figure 4, summarize this procedure:

Step 1: Background NO<sub>x</sub> level assessment (30 min). Before NO pollutant injection, NO<sub>x</sub> levels existing in
 the experimental chamber due to infiltration (outdoor pollution) were evaluated.

Step 2: NO injection until 200 ppb was reached (30 min). During this step, NO was injected at a high flow rate (1.5 ln/min for approximately 30 min) in order to reach 200 ppb of pollution inside the experimental chamber.

Step 3: NO concentration kept constant at 200 ppb (180 min). Once the concentration of 200 ppb was
 reached in the experimental chamber, the flow rate was lowered (0.3±0.02 ln/min) in order to maintain
 a constant NO pollution level over 180 min (± 2 ppb after 20 min and ± 10 ppb after 180 min).

Step 4: Photocatalysis activation (160 min). After observing pollution stability for 20 min, the light was switched on to activate photocatalysis. Depollution efficiency was evaluated with different lighting systems by following the NO concentration for up to 160 min.





Figure 4 – A theoretical step by step diagram of the experimental procedure followed

In order to validate this experimental procedure, especially steps 2 and 3, a series of blank tests were first conducted in the dark (light OFF). For these tests, a constant pollution level was kept for more than 3h with a tolerance of ± 2 ppb after 20 min and ± 10 ppb after 180 min. In some cases, during the first few minutes of the pollution stabilisation step, it was necessary to adjust the flow rate (0.3±0.02 ln/min). Moreover, it was observed that maintaining a constant pollution level was harder on windy days. Photocatalytic tests were carried out three times to ensure a good repeatability.

#### 219 3 Results and discussion

#### 220 3.1 Background NO<sub>x</sub> levels

221 The first step of the study was to collect data on NO<sub>x</sub> background levels in the experimental chamber. As 222 reported in the literature (Laurence 2015; Baukal 2005; Ao et al. 2003), NO<sub>x</sub> are atmospheric gaseous 223 pollutants that can easily infiltrate indoor air, so their levels and evolutions are strongly dependent on the surrounding environment. However, pollution levels also depend on the air exchange rate, which 224 225 varies according to the building materials, insulation and ventilation (Blondeau et al. 2005). In this study, 226 the NO<sub>x</sub> analyser was used to monitor NO and NO<sub>2</sub> concentrations in outdoor air before the tests were 227 carried out in the experimental chamber. The results revealed that outdoor air pollution was relatively 228 low, probably because the experimental house was located on Toulouse university campus, surrounded 229 by green spaces, far from boulevards and roadways.

Background pollution levels measured in the experimental chamber for a few days in March and April 2017 are illustrated in Figure 5. During March, pollution was relatively low and no peaks were observed for the 4-day period investigated. The background pollution level of NO<sub>x</sub> was thus estimated from this measurement campaign: NO was between 10 and 20 ppb and NO<sub>2</sub> was below the analyser detection value of 3 ppb. During April, three NO peaks were observed in the 5 day investigation period: NO rose from a background level of 10-12 ppb to 50 ppb for the first peak and to 30 ppb for the other two. Each peak lasted for a few hours. In contrast, NO<sub>2</sub> level remained under 3 ppb even when NO peaks appeared.

237 Tests in the experimental chamber were thus carried out only if the NO initial background concentration

(step 1) before injection was less than 30 ppb. Otherwise, tests were held over to a later date to ensureno initial pollution.



Figure 5 – NO<sub>x</sub> concentrations in the experimental chamber coming from outdoor pollution - (a) 25-28 March 2017, (b) 20-24
 April 2017

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#### **3.2** NO<sub>x</sub> concentrations without photocatalysis

The second step was to continuously inject NO into the experimental chamber without light (light OFF) to ensure that a constant pollution level could be reached and maintained for at least 180 min. This blank test in the dark was conducted in the presence of photocatalytic plasterboards on the walls. In fact, no significant difference was noticed between tests carried out with and without photocatalytic material on the walls. This observation is in accordance with research work reported in the literature showing that NO has no adsorption properties (Maggos et al. 2007; Maggos et al. 2008; Hot, Martinez et al. 2017). The NO and NO<sub>2</sub> concentrations obtained over 240 min in the dark are given in Figure 6.





253 Figure 6 – Blank test: NO and NO<sub>2</sub> concentrations in the chamber in the dark before and during continuous NO injection

254 From t=0 min to t=30 min (step 1), NO<sub>x</sub> concentration monitoring showed the expected NO and NO<sub>2</sub> 255 background levels: around 15-20 ppb of NO and 0-5 ppb of NO<sub>2</sub>. Starting at t=30 min, NO was 256 continuously injected at 1.5 ln/min for about 28-30 min to reach 200 ppb (step 2). The pollution 257 increased linearly, at a rate of 6.3±0.2 ppb/min. During this step, NO<sub>2</sub> concentration remained between 0 and 3 ppb. Just before 200 ppb was reached, the flow rate was lowered to 0.3 ln/min in order to 258 259 maintain pollution at a constant level (step 3). NO pollution stabilized after only 5 min and lasted for 3 260 hours. Here again, NO<sub>2</sub> concentration remained low, (close to 0 ppb), which highlighted the absence of 261 reaction between NO and NO<sub>2</sub> under these experimental conditions, especially in the dark. Therefore, 262 steps 1 and 2 above allowed an NO concentration of 200 ppb to be reached rapidly in the experimental 263 chamber and maintained it constant over 3 hours.

#### **3.3** NO<sub>x</sub> concentrations with photocatalysis

#### 265 3.3.1 Under UV light

Figure 7 shows the variation of NO concentration in the experimental chamber when the UV light was switched on after step 2 (i.e. when NO pollution level had become constant).

268





Figure 7 – NO photocatalytic degradation in the experimental chamber under UV light

271 Steps 1 and 2 were identical to the blank test conducted without light. After the pollution injection flow 272 rate was lowered (at t=60 min), NO concentration was monitored in the dark for an extra 20 min to 273 ensure it remained constant. At t=80 min, UV light was switched on to initiate photocatalytic oxidation. It 274 can be seen in Figure 7 that, under UV light, photocatalysis had a significant depolluting effect with 275 respect to NO. After only 20 min of photocatalytic activity (at t=100 min), NO concentration had fallen to 276 39.7 ppb. After 40 min (at t=120 min), the NO rate had returned to its minimum value, i.e. the 277 background value (cf. part 3.1). The test was finally stopped after 70 min of UV illumination (at t=150 278 min) because NO and NO<sub>2</sub> concentrations remained constant.

279 Regarding NO<sub>2</sub>, generation of this gas was observed during the first 10 min of photocatalytic activity (from t=80 min to t=90 min). While NO decreased from 200 to 80 ppb, NO<sub>2</sub> increased from 0 to about 20 280 281 ppb. Then, when the NO concentration stabilised at 20 ppb,  $NO_2$  also decreased but remained at 8 ppb, 282 which was higher than the background level (cf. part 3.1). Here, a mechanism of NO photocatalysis over 283  $TiO_2$  is highlighted;  $NO_2$  formed as a by-product at first but then some of it was destroyed. This 284 observation is consistent with results reported by Hot, Martinez et al. (2017) in the case of NO static 285 injection. More generally, NO<sub>2</sub> generation has always been observed in tests carried out at laboratory 286 scale using photocatalytic reactor (Martinez et al. 2011; Martinez et al. 2013; Hot, Topalov et al. 2017; 287 Karapati et al. 2014; Hernández Rodríguez et al. 2016; Crain et al. 2016; Ifang et al. 2014).

Results obtained in this study proved that our experimental chamber constituted a pertinent tool for assessing PCO at real scale and in real time. It was very remarkable that the entire injected NO was destroyed, showing that the depollution efficiency was almost 100% for the experimental conditions used here.

#### 292 3.3.2 Under visible light

The photocatalytic degradation of NO under three visible lighting systems was assessed. The results are shown in Figure 8.

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296

297 298

Figure 8 – Typical NO photocatalytic degradation in the experimental chamber under various visible lighting systems: Fluorescent, Halogen and LED

299 As expected, photocatalysis efficiency was dependent on the lighting systems used. The best 300 photocatalytic degradation was obtained with fluorescent tubes. With this system, the NO concentration 301 had fallen to 65.4 ppb after 20 min (at t=100 min) and the minimal value was reached after a further 50 302 min (at t=150 min). NO concentration remained constant and low, at a value around 25 ppb, which was 303 slightly higher than the background pollution level. In this case, efficiency was nearly 98%. Halogen lamps 304 led to lower degradation kinetics as the steady state was reached after 140 min of irradiation, with a 305 final NO concentration of 64 ppb. Efficiency was thus around 78%. With LED used as lighting system, the 306 photocatalytic activity was clearly less effective. In fact, NO concentration was around 159 ppb after 140 307 min of irradiation. The efficiency was only 22%. These results show that photocatalysis could be highly 308 effective under visible light if a suitable lighting system was used. According to Table 1, halogen bulbs 309 produced the highest light irradiation but the photocatalytic oxidation was not as effective as that 310 observed with fluorescent tubes. In the case of LED, NO degradation was minimal although the light 311 irradiation (intensity) was almost identical to that of fluorescent tubes. These results stress the influence 312 of the light spectrum.

313



Figure 9 – NO<sub>2</sub> concentrations during NO oxidation by photocatalysis under different visible lighting systems: Fluorescent,
 Halogen and LED

Figure 9 shows NO<sub>2</sub> concentration variations obtained during tests carried out under visible light. NO<sub>2</sub> production was observed with fluorescent light. Because of the uncertainty on the NO<sub>2</sub> measurement (±5 ppb), the production of NO<sub>2</sub> under halogen and LED lamps was not clearly quantified. With visible fluorescent tubes, NO<sub>2</sub> production was maximal during the first 20 min of the photocatalytic reaction and then fell as has previously been observed with UV fluorescent tubes. With halogen and LED bulbs, NO<sub>2</sub> production lasted longer at a lower level.

#### 323 3.4 Photocatalysis efficiency with respect to NO

NO photocatalytic depollution was assessed by two different methods. Firstly, the PCO slope and the lowest NO concentration values were determined as shown in Figure 9. The intersection of these two lines gave the time needed by the PCO to reach more than 85% of its maximum reaction efficiency. Secondly, the depollution rate was evaluated by comparing the quantity of NO obtained after PCO to the quantity without PCO (blank test).

#### 329 3.4.1 PCO potential: slope & lowest NO level

The PCO potential was a method suggested by the authors to estimate the photocatalysis efficiency. This also allowed the efficiency of different lighting systems to be classified according to photoactivity. Two values were assessed: (1) the slope of NO decrease under PCO, and (2) the lowest NO concentration recorded after a maximum of 3 hours' illumination. The uncertainty on the slope was also estimated from the different measurements. Experiments were stopped earlier if a steady state was reached. The results are summarised in Table 2 and a graphical illustration of this method is given in Figure 10.





Figure 10 – Graphical illustration of PCO potential method



Table 2 – Values and uncertainties obtained to assess PCO potential under UV and visible light.

Lighting system	UV	Fluo	Halo	LED
Slope (ppb/min)	7.7±1.2	5.9±0.8	1.9±0.4	0.3±0.1
Lowest NO level (ppb)	20±5	25±5	64±5	160±5

#### 340 3.4.2 PCO depollution rate

The PCO depollution rate was a second method suggested by the authors to evaluate photocatalysis efficiency. It consisted of assessing the mass of NO degraded by a square metre of photocatalytic material over a period of one minute. The mass of NO injected after t=80 min (light OFF) was first calculated for each test using equation (1):

345 
$$M_{NO Blank} = M_{NO gc} * \frac{1}{V} * \phi * t$$
 (1)

346 where  $M_{NO Blank}$  is the mass of NO injected (in µg) during the blank test,  $M_{NO gc}$  is the mass of NO in the gas 347 cylinder (45 ppm or 55 215 µg/m<sup>3</sup>), V is the chamber volume (10 m<sup>3</sup>),  $\phi$  is the injection flow rate (0.3 348 ln/min) and t is the injection time (min).

Then, the area under the blank test curve was calculated from t=80 min to the end of the test ( $A_{Blank}$ ). In the same way, the area under each curve obtained with PCO was calculated ( $A_{PCO}$ ). This allowed the area of NO removed ( $A_{NO rem}$ ) - given in equation (2) and illustrated in Figure 11 - to be assessed.

$$352 A_{Blank} - A_{PCO} = A_{NO \ rem} (2)$$

353 This area was used to determine the mass of NO removed (M<sub>NO rem</sub>) according to equation (3).

354 
$$M_{NO \ rem} = \frac{A_{NO \ rem}}{A_{blank}} * M_{NO \ Blank}$$
(3)

Finally, equation (4) was used to obtain the depollution rate, DR ( $\mu$ g.min<sup>-1</sup>.m<sup>-2</sup>). S<sub>PC</sub> was the total area covered by the photocatalytic material (m<sup>2</sup>) and t<sub>PC</sub> was the total time of light irradiation (min). Results are presented in Table 3.

$$DR = \frac{M_{NO \ removed}}{S_{PC} * t_{PC}}$$
(4)

A<sub>Blank</sub>

A<sub>NO rem</sub>

140

120

160

180

200

A<sub>PCO</sub>

360

220

200

180 160

0

0

Pollution (ppb)



362

Figure 11 – Graphical illustration of PCO depollution rate method

100 Time (min)



40

20

NO background level

60

-NO without PCO

NO with PCO

Lighting	mass of NO injected	NO injection time	NO mass	Depollution rate
system	(after t=80min)	(after t=80min)	removed	
UV	1 160 µg	70 min	1 100 µg	1.60 μg.min <sup>-1</sup> .m <sup>-2</sup>
Fluorescent	1 325 μg	80 min	1 230 µg	1.55 μg.min <sup>-1</sup> .m <sup>-2</sup>
Halogen	2 650 μg	160 min	1 700 µg	1.08 μg.min <sup>-1</sup> .m <sup>-2</sup>
LED	2 650 µg	160 min	400 µg	0.26 µg.min <sup>-1</sup> .m <sup>-2</sup>

80

363

A similar method was used by Maggos et al. to evaluate the depollution rate of a  $TiO_2$  photocatalytic paint in a 917 m<sup>3</sup>, artificially closed car park (Maggos et al. 2007). The paint contained 10%  $TiO_2$  and was applied over the total surface area of the ceiling (322 m<sup>2</sup>). These authors reported a DR between 3 and 7.8 µg.min<sup>-1</sup>.m<sup>-2</sup> under UV light. A total of 20 UV lamps were used to provide 1 W/cm<sup>2</sup> on the surface of the photocatalytic material. However, the pollution was generated from the exhaust gases of a running vehicle and different pollutants were thus present simultaneously (NO<sub>x</sub>, VOCs, CO, CO<sub>2</sub>). Also, the NO concentrations tested were much higher (between 650 ppb and 1 300 ppb). Under these experimental conditions, Maggos et al. estimated the global photocatalytic removal of NO at around 20%. This value is
lower than the ones obtained in this study: almost 100% and more than 95% were respectively reached
under UV and visible light provided by fluorescent tubes. Therefore, care is needed when dealing with
DR as its value could be over- or under-estimated if other information, such as initial or final pollutant

375 concentration (the lowest value reached), is not specified.

# 376 **4 Conclusions**

377 Studies aimed at assessing PCO efficiency are mainly conducted at laboratory scale using a reactor and 378 most of them are inspired by ISO 22197. However, this standard is not suitable for real-world 379 applications. For example, the controlled experimental conditions, such as the small reactor volume, the 380 residence and contact time of the pollutant, or the lighting system (UV and high intensity), are not 381 representative of tests in situ and cannot be simply extrapolated to a larger scale. In this paper, a new, 382 simple method for assessing PCO of gaseous air pollutants under real-world conditions has been 383 presented. The targeted pollutant was NO. Its degradation by photocatalysis was studied using a specific 384 procedure in an experimental chamber developed at the LMDC. Various lighting systems were tested to 385 compare PCO efficiency under UV and visible light. The results clearly showed that the lighting systems 386 played an important role in the photocatalytic efficiency. Under UV, nearly 100 % of NO was removed by 387 PCO. Moreover, this study highlighted the reduction of NO concentration under visible light, especially 388 from fluorescent tubes. Results showed 97 % degradation under visible light from fluorescent tubes, 78 389 % under visible light from halogen bulbs and 30 % under visible light from LED bulbs. LED lighting is 390 gaining in popularity because of its light output coupled with its low energy consumption. The 391 abatement reaction rate with this lighting is lower than those obtained with other systems. 392 Nevertheless, the abatement remains significant and could even be improved by doping the 393 photocatalyst as shown by several authors (Zhou et al. 2007; Todorova et al. 2013; Hu et al. 2015).

The experimental procedure proposed here allowed PCO to be tested at larger scale, under realistic conditions, such as chamber volume, pollutant injection flow rate and lighting condition. In a future publication, the authors will propose a simple numerical model that describes the pollutant evolution observed during the different stages of the experiment. Then, an attempt will be made to link results obtained in this experimental chamber and in a reactor at a lab scale in order to suggest a numerical model able to predict real scale results from those found using a reactor.

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