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1	Key parameters influencing the uptake of m-xylene on photocatalytic paints
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1 ABSTRACT

Given the toxic nature of many volatile organic compounds (VOCs) present within indoor 2 3 environments, it is necessary to develop new materials to eliminate them. Photocatalytic paints represent a promising technology to remove the indoor pollutants but they are not 4 5 optimised yet. Here we evaluate the capacities of one conventional white-wall paint, three photocatalytic paints containing 3.5, 5.25 and 7% of nano-TiO₂ PC 500, and two 6 photocatalytic paints with a hybrid cellulose nanocrystals-nano-TiO₂ (CNC-nano-TiO₂) to 7 8 eliminate *m*-xylene from the indoor environment. In particular, we assess the impact of nano-9 TiO₂ content, light intensity, relative humidity (RH), surface temperature (288-320 K) and pigment volume concentration (PVC) on uptake of *m*-xylene. Uptake coefficients of *m*-xylene 10 increase by a factor 3, 5 and 3, respectively, as a function of nano-TiO₂ content, irradiance 11 and PVC. In contrast, uptakes of *m*-xylene decrease for a factor of 2 and 3, as a function of 12 RH, and surface, suppressing the photocatalytic activity. The addition of CNC-nano-TiO₂ in 13 14 the binder induces limited binder degradation. These are very promising results which may help to improve the performances of indoor photocatalytic paints aimed to eliminate indoor 15 airborne pollutants. 16

Keywords: Indoor Air; Photocatalysis; Uptake coefficient; Cellulose Nanocrystals; Flow
Tube; PTR-MS

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1 **1. INTRODUCTION**

2 Volatile organic compounds (VOCs) represent ubiquitous indoor air pollutants [1,2]. Some VOCs are known to cause human health effects and VOC compounds, such as formaldehyde, 3 benzene, dichloromethane, have been identified as carcinogens [3]. The indoor sources of 4 5 VOCs are numerous and include emissions from building itself, decorative material (paints, vanishes...), furniture, inhabitants' activities (cooking, smoking...) and domestic cleaning 6 7 products, among others. Recent studies carried out in France [4] and in Europe [5] shown a 8 VOCs indoor-to-outdoor environment concentration ratios up to 14.3. In occidental countries, 9 humans spend on average over 90% of their lifetime within indoor settings [6]. Based on these two observations, it is necessary to develop methods to reduce VOCs levels in order to 10 improve indoor air quality. This approach include different techniques such as biofiltration, 11 12 adsorption, condensation, incineration and photocatalytic oxidation (PCO) [7-9]. The photocalytic system allows to oxidize, as well as reduce, air pollutants adsorbed on 13 semiconductor surface. PCO is intensively studied and considered as a promising technology 14 [10] to improve indoor air quality. 15

Benzene, Toluene, Ethylbenzene and *o-m-p* Xylenes also called BTEX have been extensively
studied in indoor air because of their toxicity [11–14] and their high measurements frequency.
For instance, Hazrati *et al* .[15] summarized house BTEX concentrations in different
countries. Their concentrations range as 1-5 ppb, 3-10 ppb, 1-5 ppb and 2-15 ppb for benzene,
toluene, ethylbenzene and xylenes, respectively. The main sources of xylenes are vehicles
exhaust [16].

The degradation of *m*-xylene has been studied on different supports as a function of Relative Humidity (RH) [17–20], irradiance [21] and nano-TiO₂ content [21]. To the best of our knowledge, there is no previous studies focused on the influence of surface temperature, aging and Pigment Volume Concentration (PVC) of photocatalytic materials on the *m*-xylene

degradation. The study of Strini et al. [21] has shown the increase of the photocatalytic 1 activity with increase of light intensity. The improved photocatalytic ability was also observed 2 with increase of nano-TiO₂ content [21]. Jo et al. [19] observed no impact of RH on 3 photocatalytic activity whereas two other studies showed an influence of RH on 4 photocatalytic efficiency. At low concentration of *m*-xylene (46 ppb) [18] a decrease of 5 photocatalytic activity has been observed with increase of RH. At high concentration 6 (460 ppb) of *m*-xylene [18] an increase between 0 and 45% of RH and a decrease above 45% 7 of RH; of photocatalytic activity have been observed. These different studies have been 8 performed on photocatalytic thin films [19], glass fibers [17] and cement mortars [18,21] but 9 never on photocatalytic paints. Tryba et al. [22] have studied the degradation of 10 benzo[a]pyrene by photocatalytic paints but they have not assessed the impact of different 11 environmental and physical parameters on photocatalytic efficiency to eliminate indoor 12 13 VOCs. Additional studies are recommended to improve the knowledge o, this matter.

In this study we have chosen *m*-xylene as a model compound because: 1) it is commonly observed in indoor environment [15], 2) it is not emitted by the studied paints [23] thus avoiding experimental artefacts, 3) it presents hazardous effects on human health (neurologic effects, digestive disorder, irritation...) [14] and 4) it is not an easily degradable compound due to the relative stability of aromatic rings with respect to its oxidation and reduction process.

In the present work, the uptake coefficients of *m*-xylene on various paints (non-photocatalytic, hereafter, reference paint and photocatalytic paints) were determined under different experimental conditions in presence of UV irradiation. The influence of key parameters driving the reaction was evaluated by the comparative approach. The influence of environmental parameters (surface temperature, RH, irradiance intensity) as well as paint

physical parameters (photocatalyst type and content, paint aging and paint porosity) on *m* xylene degradation have been examined.

3 2. MATERIALS AND METHODS

4 **2.1.Experimental study**

A double wall flow tube photoreactor was connected to High Sensitivity-Proton Transfer
Reaction-Mass Spectrometry (HS-PTR-MS) (IONICON Analytik, Austria). The operational
procedure of flow tube photoreactor has been described in detail by Gandolfo *et al.* [24] and
Morin *et al.* [23]. The schematic diagram of the experimental setup is presented in Figure 1.
Experimental details that are particularly relevant to this work are given below.



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The flow tube is made of borosilicate glass with an internal volume of 131 cm^3 and was coupled to a temperature-controlled circulating bath (RC6 LAUDA, Germany) which allows to perform the experiments at different surfaces temperatures between 288 and 320 K (±1 K). Experiments were carried out at 1 atm total pressure of synthetic air (Linde Gas, France, >99.999 stated purity). The glass plate recovered by the paint was introduced into the flow tube reactor with the painted side upward oriented. Inside the flow tube, a glass made

<sup>Figure 1: Schematic illustration of the experimental setup. Permeation oven (a), mass flow
controller (b), on/off valve (c), needle valve (d), relative humidity system (e), reactor + glass
paint (f), UV-lamps (g), RH probe + hygrometer (h).</sup>

movable injector was inserted into the flow tube to inject *m*-xylene and vary the residence
time and thus asses the kinetics of the heterogeneous reactions.

The flow tube reactor was placed in a stainless steel box with four UV fluorescent lamps (Philips TL-D 18W Actinic BL, 340-400 nm, $\lambda_{max} = 368$ nm, length = 60 cm) mounted side by side on the upper part of the box above the flow tube photoreactor. The UV-lamps simulated UV solar irradiation and could be operated individually. The spectral irradiance of the UV lamps used in this work had been determined previously [25]. The integrated spectral irradiance (340< λ <400 nm) was estimated to be 4.9, 8.8, 13.5 and 18.6 W m⁻² for 1, 2, 3 and 4 lamps, respectively.

Gaseous *m*-xylene was generated using a gas-phase generator (PUL 200, Saint Chamas, 10 France). A sealed permeation cell consisting of a Teflon tube (perfluoroalkoxy, 4.0×6.4 mm, 11 8 cm long) filled with pure *m*-xylene (Sigma-Aldrich, \geq 99.5%) was used to generate gas-12 phase *m*-xylene. The permeation cell was placed in the oven chamber of the gas-phase 13 generator. At the exit of the oven, a constant flow of 10 sccm (Brooks SLA, Series mass flow 14 controller, in the range 0–10 sccm, $\pm 1\%$ stated accuracy) of gaseous *m*-xylene was allowed to 15 16 enter the injector. A sheath synthetic air flow of 190 sccm (Brooks SLA, Series mass flow 17 controller, in the range 0–500 sccm, $\pm 1\%$ stated accuracy) was allowed to enter the flow tube to dilute the *m*-xylene flow. To better simulate realistic indoor concentration, all experiments 18 were carried out at ~ 50 ppb of m-xylene. 19

Relative humidity was adjusted by splitting the sheath synthetic air flow into a dry flow and a
humidified flow. For all the experiments, the RH was measured online at the exit of reactor by
a hygrometer "Hygrolog NT2" (Rotronic) with "HygroClip SC04" probe and ranged from 2
to 70% with accuracy of ±1.5%.



protonated molecular pic (m/z, 107). Formaldehyde (m/z, 31), acetaldehyde (m/z, 45) and 1 acetone (m/z 59) were also monitored as intermediates by-products. The HS-PTR-MS high 2 time resolution (10 seconds) allows us to measure rapid changes in gas phase concentrations. 3 The drift temperature, drift voltage and a pressure were fixed at 333±1 K, 500±1 V and 4 2.02±0.01 mbar respectively, that corresponded to the E/N value of 124 Townsend 5 (1 Townsend = 10^{-17} V cm²), where E is the electric field (V cm⁻¹) and N is the ambient air 6 number density within the drift tube (cm^{-3}) . The calculation of VOCs mixing ratio and surface 7 8 emission fluxes is described in detail by Morin et al. [23].

9

2.2. Preparation of paints

10 Paints were formulated and produced by the paint manufacturer ALLIOS (Marseille, France). TITANE PC 500 in anatase form with 85% of TiO₂ nanoparticle was used as a photocatalyst. 11 TITANE PC 500 represents ultrafine TiO₂ powder with specific area of $350 \text{ m}^2 \text{ g}^{-1}$ and 12 particle size between 3 and 5 nm. A mixture of ground additives (slurry) was prepared with 13 35% (w/w) active nanosized TiO₂. Then, other paint constituents (architectural constituent of 14 15 paints, i.e., CaCO₃ and micrometric TiO₂) were mixed with 10, 15 and 20% of the slurry to reach 3.5, 5.25 and 7% (w/w) of photocatalytic active TiO₂ nanoparticles, respectively. The 16 TiO₂ nanoparticles are not present in the reference paint. The prepared paint is applied on the 17 glass plate by dint of a spiral film applicator. This methodology allows to obtain controlled 18 and reproducible wet paint thickness of 100 µm. Then, the paints were dried in an oven 19 ventilated by clean air during 21 days at 296 K and 55% of RH resulting in a uniform 20 thickness film of 40 µm. 21

To investigate the impact of porosity on the degradation rates, three paints with different porosities were developed. To assess the paint porosity, it was necessary to introduce the Critical Pigment Volume Concentration (CPVC). CPVC is a specific Pigment Volume Concentration (PVC) in which the voids between the solid particles (structural agents and pigments) are just filled with the binder [26]. The PVC and CPVC are linked to the paint
porosity as follows:

$$porosity (\%) = 1 - \frac{CPVC}{PVC}$$
(Eq.1)

4 The value of CPVC is not clearly known but it can be estimated between 50-60% 5 (manufacturer information). For this study, three paints with PVC of 53, 72 and 80% were 6 considered. The calculation of PVC were shown previously by Gandolfo *et al.* [26].

7 In another series of paints, the standard nano-TiO₂ (PC 500) was replaced by a hybrid cellulose nanocrystals-nano-TiO₂ (CNC-TiO₂) in the paint preparation to increase nano-TiO₂ 8 dispersion in the slurry. This addition allowed to form hybrid CNC-TiO₂ nanoparticles which 9 may improve the photocatalytic activity of TiO_2 . The aim of this hybrid nanoparticle was to 10 reduce the quantity of nano-TiO₂ embedded in the paint and keeps high photocatalytic 11 efficiency. In this work, two photocatalytic paints with 0.16 and 0.23% (w/w) of nano-TiO₂ 12 have been studied. Photocatalytic paints with hybrid CNC-nano-TiO₂ and the photocatalytic 13 paint with 3.5% of nano-TiO₂ PC 500 have been aged in a accelerated weathering chamber 14 15 for 500 hours and 1000 hours according to the ISO norm 16474-3 [27,28]. Aging of 500 hours correspond to an important aging of paint and an aging of 1000 hours correspond to a paint of 16 end-of-life. 17

The paints, except CNC paints, were applied on one side of glass plates that were 29 cm long and 1.9 cm wide according to a standard operating procedure developed by the manufacturer ALLIOS [29]. The CNC paints were applied on Leneta supports that were 29 cm long and 1.9 cm wide. To assure proper fit of the Leneta surface into the reactor, the later were fixed on a glass plate with wire to both ends prior to kinetic experiments.

23 **2.3.Kinetic measurements**

24 The aim of this study was to evaluate the uptake coefficients (γ) of *m*-xylene on reference

paint and on photocatalytic paints. The uptake coefficients were determined using thefollowing equation [30]:

3
$$\gamma = \frac{4k_{1st}}{\omega} \frac{V}{S}$$
(Eq.2)

4 where k_{1st} is the pseudo-first order rate constant of *m*-xylene loss (s⁻¹), ω is the mean 5 molecular velocity (cm s⁻¹) and V/S represents the ratio of the volume of the reactor to surface 6 of the glass plate (cm).

 k_{1st} was determined by the slope of $ln(C_0/C_x)$ plotted as a function of the residence time (t). C_0 7 8 is the initial concentration of *m*-xylene in position P_0 . In this case, gaseous *m*-xylene is not 9 exposed to the paint. C_x is the concentration of *m*-xylene at different positions from P₁ to P₄ (Table 1). The difference of concentrations between C₀ and C_x corresponds to amount of *m*-10 xylene consumed by its reaction with the paint surface. Each position was hold during about 11 30 min to get stabilized signal and reliable measuring points. After each position change, the 12 13 injector was pushed in position P_0 to go back to the initial conditions. The variation of the concentration in function of the injector position enabled to calculate the pseudo-first order 14 rate constant [25,26,31,32]. 15

16	Table 1 : Distance to the end of reactor (cm), exposed paint surface (cm ²) and contact time (s)
17	between gaseous <i>m</i> -xylene and paint as a function of movable injector position.

Position	Distance (cm)	Exposed surface (cm ²)	Contact time (s)
\mathbf{P}_0	0	0	0
P_1	4	7.6	5.4
P ₂	8	15.2	10.9
P ₃	15	28.5	20.4
P_4	22	41.8	29.9

¹⁸

A typical experiment and the assessment of pseudo-first order rate constant of *m*-xylene are
presented in SI (Figure S1-S2). Blank experiments have been performed to ensure that no wall
loss occurs during experiments and corrections have been applied to the obtained results.

- 1 The Cooney-Kim-Davis (CKD) method was used to correct the uptake coefficients from
- 2 diffusion limitation in the flow tube [33,34]. Under the applied experimental conditions, the
- 3 estimated correction by CKD was less than 10%.
- 4 The experimental conditions are given in Table 2.
- 5 **Table 2**: Experimental conditions

Experiments	Nano-TiO ₂ content w/w (%)	Surface temperature (K)	RH (%)	Irradiance (W m ⁻²)	PVC (%)
1	0, 3.5, 5.25 and 7	296	40	8.8	72
2	0 and 7	298	40	0-18.6	72
3	7	295	0-70	8.8	72
4	7	288-320	37	8.8	72
5	7	296	40	8.8	53-80
6	NCC : 0.16, 0.23	298	40	8.8	NA*
	PC 500 : 3.5				

6 * Not available

7 **3. RESULTS AND DISCUSSION**

8 **3.1.Nano-TiO₂ content**

9 The influence of the quantity of nano-TiO₂ on the uptake coefficients of m-xylene is presented

10 in Figure 2.



Figure 2: The effect of nano-TiO₂ content on uptake coefficients of *m*-xylene. *m*-xylene
mixing ratio: 50 ppb, temperature: 296 K, RH: 40%, light intensity: 8.8 W m⁻², PVC: 72%,
aging: 0 hour, nano-TiO₂ PC 500. The line represents the linear regression. The errors bars are
derived from uncertainties associated to uptake coefficient.

6

7 The uptake coefficient for the reference paint is $(7.3\pm2.3)\cdot10^{-7}$ and increases up to 8 $(2.0\pm0.5)\cdot10^{-6}$ for the photocatalytic paint at 7% of nano-TiO₂. The linear relation between 9 uptake coefficient and nano-TiO₂ content is described as follows:

10
$$\gamma = (1.8 \pm 0.2) \times 10^{-7} \times nanoTiO_2 content + (7.1 \pm 0.7) \times 10^{-7}$$
 (Eq.3)

11 When the nano-TiO₂ quantity increases, the quantity of OH radicals produced increases [35] 12 on the paint surface which accelerates the degradation of *m*-xylene. For this reason, the 13 increase of quantity of TiO₂ nanoparticles from 0 to 7%, improves the removal of *m*-xylene 14 by a factor of 3 which is in agreement with the reported factor of 4 in a previous study 15 focused on removal of *o*-xylene [21] on cementitious photocatalytic materials.

16 Due to improved removal efficiency towards *m*-xylene, the photocatalytic paint containing 17 7% of nano-TiO₂ was used to assess the impact of RH, surface temperature, light intensity and 18 pigment volume concentration.

19 **3.2.UV irradiation intensity**

1 The effect of light intensity on the uptake coefficients of *m*-xylene on reference paint and on





3

Figure 3: The effect of light intensity on uptake coefficients of *m*-xylene. *m*-xylene mixing
ratio: 50 ppb, temperature: 298 K, RH: 40%, PVC: 72%, aging: 0 hour. Photocatalytic paint:
7% nano-TiO₂ PC 500 (filled triangle) and reference paint (empty triangle). The line
represents the linear regression of the plotted data. The errors bars are derived from
uncertainties associated to uptake coefficient.

9

The uptakes of *m*-xylene on a reference paint only slightly increase with the variation of spectral irradiance from $(5.7\pm1.0)\cdot10^{-7}$ in dark up to $(9.7\pm1.4)\cdot10^{-7}$ at 18.6 W m⁻². In contrast, the uptake of *m*-xylene on a photocatalytic paint with 7% TiO₂ nanoparticles increases for a factor of 3, from $(1.2\pm0.4)\cdot10^{-6}$ in dark up to $(3.5\pm0.4)\cdot10^{-6}$ under maximum light irradiation of 18.6 W m⁻². The linear relation depicted in plot is described by the equation (Eq.4):

15
$$\gamma = (1.3 \pm 0.1) \times 10^{-7} \times Irradiance (W m^{-2}) + (1.1 \pm 0.1) \times 10^{-6}$$
 (Eq.4)

16 The increase of light intensity leads to enhanced formation of OH radicals formed on the paint

17 surface which in turn leads to accelerated degradation of *m*-xylene [36].

A similar trend of linear increase of the degradation of toluene on glass fiber as a function of
light intensity was observed by Palau *et al.* [17] and the degradation of *o*-xylene on

cementitious material by Strini *et al.* [21]. In their work, an increase by a factor 2.5 was
 observed that is in agreement with the factor 2 measured here.

3 These results show that the experiments were performed under light unsaturation and that the

4 surface chemical reaction is the rate-determining step.

5 **3.3.Relative humidity**

6 The impact of the RH on the uptake coefficients is shown in Figure 4.



7

Figure 4: The effect of RH on uptake coefficients of *m*-xylene. *m*-xylene mixing ratio: 50 ppb. Photocatalytic paint: 7% nano-TiO₂ PC 500 (filled square) and reference paint (empty square), light intensity: 8.8 W m⁻², temperature: 295 K, PVC: 72%, aging: 0 hour. The line represents the linear regression. The errors bars are derived from uncertainties associated to uptake coefficient.

13

The uptake coefficient of *m*-xylene is $(2.8\pm0.4)\cdot10^{-6}$ at 2% RH and decreased up to (1.4±0.5)·10⁻⁶ at 70% RH. The linear relation is described by the following mathematical equation (Eq.5):

17
$$\gamma = -(1.7 \pm 0.2) \times 10^{-8} \times RH \,(\%) + (2.7 \pm 0.1) \times 10^{-6}$$
 (Eq.5)

The decrease of the uptake by a factor 2 is in good agreement with the observed decreasing 1 conversion ratio (46 ppb of *m*-xylene) by a factor of 1.5 as the RH increased from 0 to 70% 2 [18]. This phenomenon can be ascribed to a competitive adsorption between water and m-3 xylene molecules on the paint surface. At low humidity, the adsorption competition on 4 semiconductor surface is limited which allowed the more efficient degradation of *m*-xylene. 5 As the humidity increases, absorbed water molecules on nano-TiO₂ competes with the m-6 xylene adsorption. Consequently, the photocatalytic heterogeneous reactivity is reduced at 7 8 high relative humidity [8].

9 At very high mixing ratio of *m*-xylene (460 ppb), Martinez *et al.* [18] observed an increased 10 removal efficiency of *m*-xylene at 45% RH which further decreased for RH between 45 and 11 80%. Such increase of removal efficiency of xylene (230 ppb) on photocatalytic materials has 12 also been observed by Palau *et al.* [17] for RH comprised between 4 and 70%.

13 **3.4.Surface temperature**

To the best of our knowledge, the impact of surface temperature on the uptake coefficients of *m*-xylene has not been studied previously. The surface temperature varied between 288 and
320 K (Figure 5).



1

Figure 5: The effect of surface temperature on uptake coefficients of *m*-xylene. *m*-xylene mixing ratio: 50 ppb. Photocatalytic paint: 7% nano-TiO₂ PC 500 (filled lozenge) and reference paint (empty lozenge), light intensity: 8.8 W m⁻², RH: 37%, PVC: 72%, aging: 0 hour. The line represents the linear regression. The errors bars are derived from uncertainties associated to uptake coefficient.

Figure 5 shows that the uptake coefficients of *m*-xylene decreased significantly as the temperature increases followed by a saturation effect. At 288 K; the uptake coefficient is $(2.8\pm0.4)\cdot10^{-6}$ and decreased up to $(7.6\pm2.9)\cdot10^{-7}$ at 308 K. At higher temperatures than 308 K, the uptakes of *m*-xylene remain stable. For the range of temperatures between 288 and 308 K, the solid line in Figure 5 represents the regression line which corresponds to the following equation (Eq.6):

14
$$\gamma = -(1.0 \pm 0.1) \times 10^{-7} \times T (K) + (3.3 \pm 0.2) \times 10^{-5}$$
 (Eq.6)

The reduced removal efficiency of photocatalytic paint with 7% TiO_2 nanoparticles at higher temperatures can be ascribed to the reduced contact time between gaseous *m*-xylene and the paint surface. Namely, as the surface temperature increases *m*-xylene desorb more rapidly and thus decrease the contact time with the paint surface. In that way, the contact time becomes not sufficient to achieve the degradation process [37]. The uptakes of *m*-xylene for temperature range between 308 and 320 K, (7.6±2.9)·10⁻⁷, fall in the same range as the uptake of *m*-xylene on a reference paint, (7.3±2.3)·10⁻⁷. Hence, the observed plateau in Figure 5 indicates that at higher temperature than 308 K, the removal of *m*-xylene is not driven by the photocatalytic process.

5 **3.5.Effect of pigment volume concentration (PVC)**

6 The removal of *m*-xylene was also evaluated on photocatalytic paints containing 7% of nano7 TiO₂ with PVC of 53%, 72% and 80% (Figure 6).



Figure 6: The effect of PVC on uptake coefficients of *m*-xylene. *m*-xylene mixing ratio:
50 ppb. Photocatalytic paint: 7% nano-TiO₂ PC 500 (filled triangle) and reference paint
(empty triangle), temperature: 296 K, light intensity: 8.8 W m⁻², RH: 37%, aging: 0 hour. The
errors bars are derived from uncertainties associated to uptake coefficient.

13

14 The uptake coefficients of *m*-xylene increase from $(8.6\pm2.4)\cdot10^{-7}$ to $(2.3\pm0.3)\cdot10^{-6}$ as the PVC

15 increases from 53 to 80%.

This increase of photocatalytic efficiency towards the removal of m-xylene can be ascribed to the fact that the increase of the porosity allows gaseous m-xylene to penetrate more easily

through the paint and increase the contact time with the OH radicals which are generated by

19 the irradiation of TiO_2 nanoparticles [35]. Similarly, the increase of porosity on a commercial

⁸

paint induced faster degradation of methyl ethyl ketone [38]. Jansson *et al.* [39] observed
 accelerated degradation of formaldehyde by zeolite/TiO₂.

3 3.6.CNC and aging

The aging of three photocatalytic paints with various photocatalysts namely PC 500, CNC 0.5 and CNC 0.72 have been examined (Figure 7). The PC 500 represents the photocatalytic paint with 3.5% of nano-TiO₂ and CNC 0.5 and CNC 0.72 paints contain 0.5 and 0.72% of hybrid cellulose nanocrystals (CNC) embedded in that paint that correspond to 0.16% and 0.23% of nano-TiO₂, respectively. At first sight, the three paintings are identical in term of color and appearance regardless of the aging.



10

Figure 7: The effect of aging and photocatalyst on uptake coefficients of *m*-xylene. *m*-xylene: mixing ratio: 50 ppb, temperature: 296 K; light intensity: 8.8 W m⁻², RH: 37%, paint PC 500 (circle), paint CNC 0.5 (lozenge) and paint CNC 0.72 (square). The errors bars are derived from uncertainties associated to uptake coefficient.

15

16 As shown on Figure 7, the uptake coefficients of *m*-xylene prior to aging of paints are similar

for all the considered photocatalytic paints, (1.7 ± 0.3) - (2.0 ± 0.3) · 10^{-6} . The addition of CNC in

the paint formulation allowed to obtain similar effect on *m*-xylene degradation with 15 and 22

19 times lower nano-TiO₂ quantity.

The uptake coefficient of *m*-xylene on the paint PC 500 increased with the aging. After 500 or 1 1000 hours of aging, uptake coefficients are 3 times higher than for the fresh dry paint. On the 2 other hand, the aging has no effect on paint containing CNC-TiO₂ hybrid nanoparticles. The 3 effect of aging on the binder of the paint was previously observed by Truffier-Boutry et al. 4 [28]. Once the binder was degraded, nano-TiO₂ became more accessible to interact with m-5 xylene; hence, increased the removal efficiency. This hypothesis is confirmed by the results 6 7 presented in Figure 7 for the paint PC 500. However, the consumption of m-xylene is not altered anymore after 500 hours of aging. This can be explain by the fact that after 500 hours 8 the paint binder is completely degraded and cannot further influence the photocatalytic 9 10 process.

For CNC paints, the uptake coefficients of *m*-xylene are independent of the aging process.
Thus, the hybrid CNC-nano-TiO₂ plays a protective role of the binder, limiting the contact
between the OH radicals and *m*-xylene.

14

3.7. By-products formation

In theory, the photocatalytic oxidation (PCO) should lead to the total mineralization of 15 pollutants in CO₂ and H₂O [35]. Unfortunately, the PCO is known to produce volatile 16 aldehydes and other partially oxidized by-products that can be released back to indoor air 17 [24,40]. Formaldehyde, acetaldehyde, acetone, formic acid et acetic acid were produced due 18 to the incomplete mineralization [41]. Formaldehyde and acetaldehyde have been observed as 19 by-products during *p*-xylene degradation [42], whereas formaldehyde, acetaldehyde and 20 acetone during toluene degradation [43]. The mixing ratios of *m*-xylene, formaldehyde, 21 22 acetaldehyde and acetone in position P_0 and P_4 are shown in Figure 8.



Figure 8: Temporal profile of formaldehyde (red line), acetaldehyde (green line), acetone
(blue line) and *m*-xylene (dark line) mixing ratio (ppb) at temperature: 296 K, RH: 37%, light
intensity: 18.6 W m⁻², aging: 0 hour, photocatalytic paint: 7% of nano TIO₂ PC500. In the part
(A), injector is in position P₀ and in part (B) in position P₄.

In this experiment approx. 13 ppb of m-xylene has been degraded in position P₄. If 100% of 7 this compound is converted, a $2.55 \cdot 10^{10}$ molecules cm⁻² s⁻¹ of VOCs would have been formed. 8 In order to compare *m*-xylene consummation and by-products formation, we normalized 9 10 observed mixing ratio to exposed paint surface area and reaction time to obtain the surface 11 emission fluxes. For the mixing ratio and surface emission fluxes calculation, we used the method presented in detail by Morin et al. [23]. The surface emission fluxes of formaldehyde, 12 acetaldehyde and acetone due to the reaction between molecules present in the binder and 13 radical species produced by the photocatalyst (nano-TiO₂) is $1.77 \cdot 10^{11}$, $9.33 \cdot 10^{10}$, 14 $1.07 \cdot 10^{10}$ molecules cm⁻² s⁻¹, respectively. The sum of surface emissions fluxes for these three 15 compounds is $2.81 \cdot 10^{11}$ molecules cm⁻² s⁻¹. The additional emission of VOCs due to *m*-xylene 16 degradation would correspond to an increase of about 9% of the surface emission flux. 17 Moreover, a part of degraded *m*-xylene is mineralized to CO₂ and H₂O [43,44]. Debono *et* 18 al. [43] observed a mineralization up to 76% for toluene that decreased the quantity of VOCs 19

potentially formed at 2% or $5.81 \cdot 10^9$ molecules cm⁻² s⁻¹ which represents the uncertainly of the measurements. For this reason, no difference has been observed in the mixing ratios of this by-product between the position P₀ and P₄ (Figure 8); hence, the formed by-products cannot be determined in this study.

To identify and quantify the formed products due to the degradation of *m*-xylene, the same approach as Debono *et al.* [43] should be applied based on pure nano-TiO₂. This method will allow to determine the formed by-product but it will not be relevant from environmental point of view. Surely, many efforts are needed to optimize the photocatalytic paints and establish as a safe option for removal of indoor pollutants.

10 **4. CONCLUSION**

The influence of nano-TiO₂ content, relative humidity, light intensity, surface temperature, pigment volume concentration, type of nanoparticles and aging, on the degradation of mxylene on photocatalytic paints have been assessed under UV irradiation. The obtained results contribute to improve the knowledge on a poorly documented area that is the removal of VOCs by photocatalytic paints in indoor air. The results are crucial for the development of an optimal formula for photocatalytic paint as a function of environmental and physical parameters.

The increase of nano-TiO₂ content and the PVC improve the removal of *m*-xylene by a factor of 3. The application of innovative CNC nanoparticles do not impact significantly the photocatalytic activity of the paint in comparison of widely used TiO₂ nanoparticles. Paint aging has no influence on removal of *m*-xylene by paint containing CNC photocatalyst but the removal efficiency increased for the paints containing PC 500 nano-TiO₂. However, the aging of the paint implies environmental problem because of the emission of nanoparticles in the air. This subject is out of the scope in this study but deserves an attention from a healthcare
 point of view.

3 The increase of light intensity improved the removal efficiency of *m*-xylene by a factor 5. In
4 contrast, high surface temperature and RH slowed down the degradation of *m*-xylene.

In order to assess the impact of photocatalytic paints on indoor air quality, we suggest a 5 simple calculation to compare the lifetime of *m*-xylene through the major removal pathways 6 7 in an indoor environment [45]. The consumption of m-xylene by photocatalytic paint is considered for a model room of 50 m^3 with a constant irradiated wall surface of 3 m^2 . From 8 the experimental results from this study, the removal rate of *m*-xylene is estimated to be 9 $7.3 \cdot 10^{-6}$ s⁻¹ for a non-aged photocatalytic paint containing 7% of nano-TiO₂ with a PVC of 10 72% at 40% of RH under a spectral irradiation intensity of 8.8 W m⁻² and a surface 11 12 temperature of 298 K. The lifetime associated to this removal pathway is approximatively 38 hours while the lifetime due to the oxidation by gas-phase OH radicals (assuming a mean 13 OH concentration of $5 \cdot 10^5$ radicals cm⁻³ [46] and bimolecular rate constant of k_{OH+m}-14 $xy_{lene} = 2.3 \cdot 10^{-11}$ molecules cm⁻³ s⁻¹ [47]) is 24 hours, and 2 hours for a typical air exchange 15 rate of 0.5 h^{-1} [48]. Under these conditions, the main removal pathway of *m*-xylene is air 16 exchange rate which account for more than 99% of its elimination. The photocatalytic 17 degradation and OH oxidation account only minor contribution to the removal of *m*-xylene 18 from the indoor air. 19

The future formulation of an optimized photocatalytic paint should consider the influence of the physical (quantity of TiO_2 nanoparticles, type of photocatalyst, and PVC), and environmental (RH, light intensity, surface temperature) parameters on the degradation of indoor air pollutants. In the future, photocatalytic oxidation must be studied under visible irradiation because 45% of solar irradiation is in visible region (400-700 nm) against only 4% for in the UV region of wavelengths.

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6 ASSOCIATED CONTENT

7 Supporting Information

- 8 Typical experiment of m-xylene degradation (Figure S1), loss of gas phase m-xylene as a
- 9 function of exposure time (Figure S2).

10 Notes

11 The authors declare no competing financial interest.

12 **REFERENCES**

- 13 (1) Bolden, A. L.; Kwiatkowski, C. F.; Colborn, T. New Look at BTEX: Are Ambient
- 14 Levels a Problem? *Environ. Sci. Technol.* **2015**, *49* (9), 5261–5276.
- 15 https://doi.org/10.1021/es505316f.
- 16 (2) Salthammer, T.; Mentese, S.; Marutzky, R. Formaldehyde in the Indoor Environment.
- 17 *Chem. Rev.* **2010**, *110* (4), 2536–2572. https://doi.org/10.1021/cr800399g.
- 18 (3) Thepanondh, S.; Varoonphan, J.; Sarutichart, P.; Makkasap, T. Airborne Volatile
- 19 Organic Compounds and Their Potential Health Impact on the Vicinity of
- 20 Petrochemical Industrial Complex. *Water, Air, Soil Pollut.* **2011**, *214* (1), 83–92.
- 21 https://doi.org/10.1007/s11270-010-0406-0.
- 22 (4) Verriele, M.; Schoemaecker, C.; Hanoune, B.; Leclerc, N.; Germain, S.; Gaudion, V.;

1		Locoge, N. The MERMAID Study: Indoor and Outdoor Average Pollutant
2		Concentrations in 10 Low-Energy School Buildings in France. Indoor Air 2015, 26 (5),
3		702–713. https://doi.org/10.1111/ina.12258.
4	(5)	Geiss, O.; Giannopoulos, G.; Tirendi, S.; Barrero-Moreno, J.; Larsen, B. R.; Kotzias,
5		D. The AIRMEX Study - VOC Measurements in Public Buildings and
6		Schools/Kindergartens in Eleven European Cities: Statistical Analysis of the Data.
7		Atmos. Environ. 2011, 45 (22), 3676–3684.
8		https://doi.org/https://doi.org/10.1016/j.atmosenv.2011.04.037.
9	(6)	Roberts, J., Nelson, W National Human Activity Pattern Survey Data Base. United
10		States Environ. Prot. Agency 1995.
11	(7)	Sattler, M. L.; Liljestrand, H. M. Method for Predicting Photocatalytic Oxidation Rates
12		of Organic Compounds. J. Air Waste Manage. Assoc. 2003, 53 (1), 3-12.
13		https://doi.org/10.1080/10473289.2003.10466119.
14	(8)	Zhong, L.; Haghighat, F.; Blondeau, P.; Kozinski, J. Modeling and Physical
15		Interpretation of Photocatalytic Oxidation Efficiency in Indoor Air Applications. Build.
16		<i>Environ.</i> 2010 , <i>45</i> (12), 2689–2697.
17		https://doi.org/https://doi.org/10.1016/j.buildenv.2010.05.029.
18	(9)	Zhong, L.; Haghighat, F. Photocatalytic Air Cleaners and Materials Technologies –
19		Abilities and Limitations. Build. Environ. 2015, 91, 191–203.
20		https://doi.org/https://doi.org/10.1016/j.buildenv.2015.01.033.
21	(10)	Zhao, J.; Yang, X. Photocatalytic Oxidation for Indoor Air Purification: A Literature
22		Review. Build. Environ. 2003, 38 (5), 645–654.
23		https://doi.org/https://doi.org/10.1016/S0360-1323(02)00212-3.

1	(11)	INRS.	Benzène,	Fiche	Toxicole	ogique	<i>N°49</i> ; 2009.
	· ·					0.1	,

- 2 (12) INRS. Toluène, Fiche Toxicologique N°74; 2012.
- 3 (13) INRS. *Ethylbenzène*, Fiche Toxicologique $N^{\circ}266$; 2018.
- 4 (14) INRS. *Xylènes, Fiche Toxicologique N°77*; 2009.
- (15) Hazrati, S.; Rostami, R.; Farjaminezhad, M.; Fazlzadeh, M. Preliminary Assessment of
 BTEX Concentrations in Indoor Air of Residential Buildings and Atmospheric
- 7 Ambient Air in Ardabil, Iran. *Atmos. Environ.* **2016**, *132*, 91–97.
- 8 https://doi.org/https://doi.org/10.1016/j.atmosenv.2016.02.042.
- 9 (16) INERIS. Exposition Par Inhalation Au Benzène, Toluène, Éthylbenzène, et Xylènes
 10 (BTEX) Dans l'air; 2004.
- 11 (17) Palau, J.; Penya-Roja, J. M.; Gabaldón, C.; Javier Álvarez-Hornos, F.; Sempere, F.;

12 Martínez-Soria, V. UV Photocatalytic Oxidation of Paint Solvent Compounds in Air

- 13 Using an Annular TiO2-Supported Reactor. J. Chem. Technol. Biotechnol. 2011, 86
- 14 (2), 273–281. https://doi.org/10.1002/jctb.2515.
- Martinez, T.; Bertron, A.; Escadeillas, G.; Ringot, E.; Simon, V. BTEX Abatement by
 Photocatalytic TiO2-Bearing Coatings Applied to Cement Mortars. *Build. Environ.*
- 17 **2014**, *71*, 186–192. https://doi.org/https://doi.org/10.1016/j.buildenv.2013.10.004.
- 18 (19) Jo, W.-K.; Park, K.-H. Heterogeneous Photocatalysis of Aromatic and Chlorinated
- 19 Volatile Organic Compounds (VOCs) for Non-Occupational Indoor Air Application.
- 20 *Chemosphere* **2004**, *57* (7), *555–565*.
- 21 https://doi.org/https://doi.org/10.1016/j.chemosphere.2004.08.018.
- 22 (20) Ao, C. H.; Lee, S. C.; Mak, C. L.; Chan, L. Y. Photodegradation of Volatile Organic
- 23 Compounds (VOCs) and NO for Indoor Air Purification Using TiO2: Promotion versus

1		Inhibition Effect of NO. Appl. Catal. B Environ. 2003, 42 (2), 119–129.
2		https://doi.org/https://doi.org/10.1016/S0926-3373(02)00219-9.
3	(21)	Strini, A.; Cassese, S.; Schiavi, L. Measurement of Benzene, Toluene, Ethylbenzene
4		and o-Xylene Gas Phase Photodegradation by Titanium Dioxide Dispersed in
5		Cementitious Materials Using a Mixed Flow Reactor. Appl. Catal. B Environ. 2005, 61
6		(1-2), 90-97. https://doi.org/10.1016/J.APCATB.2005.04.009.
7	(22)	Tryba, B.; Homa, P.; Wróbel, R. J.; Morawski, A. W. Photocatalytic Decomposition of
8		Benzo-[a]-Pyrene on the Surface of Acrylic, Latex and Mineral Paints. Influence of
9		Paint Composition. J. Photochem. Photobiol. A Chem. 2014, 286, 10–15.
10		https://doi.org/https://doi.org/10.1016/j.jphotochem.2014.04.012.
11	(23)	Morin, J.; Gandolfo, A.; Temime-Roussel, B.; Strekowski, R.; Brochard, G.; Bergé, V.;
12		Gligorovski, S.; Wortham, H. Application of a Mineral Binder to Reduce VOC
13		Emissions from Indoor Photocatalytic Paints. Build. Environ. 2019, 156, 225-232.
14		https://doi.org/10.1016/J.BUILDENV.2019.04.031.
15	(24)	Gandolfo, A.; Marque, S.; Temime-Roussel, B.; Gemayel, R.; Wortham, H.; Truffier-
16		Boutry, D.; Bartolomei, V.; Gligorovski, S. Unexpectedly High Levels of Organic
17		Compounds Released by Indoor Photocatalytic Paints. Environ. Sci. Technol. 2018, 52
18		(19), 11328–11337. https://doi.org/10.1021/acs.est.8b03865.
19	(25)	Bartolomei, V.; Sörgel, M.; Gligorovski, S.; Alvarez, E. G.; Gandolfo, A.; Strekowski,
20		R.; Quivet, E.; Held, A.; Zetzsch, C.; Wortham, H. Formation of Indoor Nitrous Acid
21		(HONO) by Light-Induced NO2 Heterogeneous Reactions with White Wall Paint.
22		Environ. Sci. Pollut. Res. 2014, 21 (15), 9259-9269. https://doi.org/10.1007/s11356-
23		014-2836-5.

24 (26) Gandolfo, A.; Bartolomei, V.; Truffier-Boutry, D.; Temime-Roussel, B.; Brochard, G.;

1		Bergé, V.; Wortham, H.; Gligorovski, S. The Impact of Photocatalytic Paint's Porosity
2		on Indoor NOx and HONO Levels. Phys. Chem. Chem. Phys. 2019.
3		https://doi.org/10.1039/C9CP05477D.
4	(27)	ISO. 16474-3:2013, Paints and Varnishes- Methods of Exposureto Laboratory Light
5		Sources-Part 3: Fluorescent UV Lamps. 2013.
6	(28)	Truffier-Boutry, D.; Fiorentino, B.; Bartolomei, V.; Soulas, R.; Sicardy, O.; Benayad,
7		A.; Damlencourt, JF.; Pepin-Donat, B.; Lombard, C.; Gandolfo, A.; Wortham, H.;
8		Brochard, G.; Audemard, A.; Porcar, L.; Gebel, G.; Gligorovski, S. Characterization of
9		Photocatalytic Paints: A Relationship between the Photocatalytic Properties - Release
10		of Nanoparticles and Volatile Organic Compounds. Environ. Sci. Nano 2017, 4 (10),
11		1998-2009. https://doi.org/10.1039/C7EN00467B.
12	(29)	Gandolfo, A.; Bartolomei, V.; Gomez Alvarez, E.; Tlili, S.; Gligorovski, S.;
13		Kleffmann, J.; Wortham, H. The Effectiveness of Indoor Photocatalytic Paints on NOx
14		and HONO Levels. Appl. Catal. B Environ. 2015, 166–167, 84–90.
15		https://doi.org/https://doi.org/10.1016/j.apcatb.2014.11.011.
16	(30)	Finlayson-Pitts, B. J.; Pitts, J. N. Chemistry of the Upper and Lower Atmosphere :
17		Theory, Experiments, and Applications; Academic Press, 2000.
18	(31)	George, C.; Strekowski, R. S.; Kleffmann, J.; Stemmler, K.; Ammann, M.
19		Photoenhanced Uptake of Gaseous NO2 on Solid Organic Compounds: A
20		Photochemical Source of HONO? Faraday Discuss. 2005, 130 (0), 195–210.
21		https://doi.org/10.1039/B417888M.
22	(32)	El Zein, A.; Bedjanian, Y. Interaction of NO ₂ with TiO ₂ Surface under UV Irradiation:
23		Measurements of the Uptake Coefficient. Atmos. Chem. Phys. 2012, 12 (2), 1013-
24		1020. https://doi.org/10.5194/acp-12-1013-2012.

1	(33)	Behnke, W.; George, C.; Scheer, V.; Zetzsch, C. Production and Decay of ClNO2 from
2		the Reaction of Gaseous N2O5 with NaCl Solution: Bulk and Aerosol Experiments. J.
3		Geophys. Res. Atmos. 1997, 102 (D3), 3795-3804. https://doi.org/10.1029/96JD03057.
4	(34)	Cooney, D. O.; Kim, SS.; James Davis, E. Analyses of Mass Transfer in
5		Hemodialyzers for Laminar Blood Flow and Homogeneous Dialysate. Chem. Eng. Sci.
6		1974 , 29 (8), 1731–1738. https://doi.org/https://doi.org/10.1016/0009-2509(74)87031-
7		4.
8	(35)	Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental
9		Applications of Semiconductor Photocatalysis. Chem. Rev. 1995, 95 (1), 69–96.
10		https://doi.org/10.1021/cr00033a004.
11	(36)	Toor, A. P.; Verma, A.; Jotshi, C. K.; Bajpai, P. K.; Singh, V. Photocatalytic
12		Degradation of Direct Yellow 12 Dye Using UV/TiO2 in a Shallow Pond Slurry
13		Reactor. Dye. Pigment. 2006, 68 (1), 53-60.
14		https://doi.org/https://doi.org/10.1016/j.dyepig.2004.12.009.
15	(37)	Barakat, N. A. M.; Kanjwal, M. A.; Chronakis, I. S.; Kim, H. Y. Influence of
16		Temperature on the Photodegradation Process Using Ag-Doped TiO2 Nanostructures:
17		Negative Impact with the Nanofibers. J. Mol. Catal. A Chem. 2013, 366, 333-340.
18		https://doi.org/https://doi.org/10.1016/j.molcata.2012.10.012.
19	(38)	Giosuè, C.; Belli, A.; Mobili, A.; Citterio, B.; Biavasco, F.; Ruello, M.; Tittarelli, F.
20		Improving the Impact of Commercial Paint on Indoor Air Quality by Using Highly
21		Porous Fillers. Buildings 2017, 7 (4), 110. https://doi.org/10.3390/buildings7040110.
22	(39)	Jansson, I.; Suárez, S.; Garcia-Garcia, F. J.; Sánchez, B. Zeolite–TiO2 Hybrid
23		Composites for Pollutant Degradation in Gas Phase. Appl. Catal. B Environ. 2015, 178,
24		100-107. https://doi.org/https://doi.org/10.1016/j.apcatb.2014.10.022.

1	(40)	Auvinen, J.; Wirtanen, L. The Influence of Photocatalytic Interior Paints on Indoor Air
2		Quality. Atmos. Environ. 2008, 42 (18), 4101-4112.
3		https://doi.org/https://doi.org/10.1016/j.atmosenv.2008.01.031.
4	(41)	Hodgson, A. T.; Destaillats, H.; Sullivan, D. P.; Fisk, W. J. Performance of Ultraviolet
5		Photocatalytic Oxidation for Indoor Air Cleaning Applications. Indoor Air 2007, 17
6		(4), 305—316. https://doi.org/10.1111/j.1600-0668.2007.00479.x.
7	(42)	Farhanian, D.; Haghighat, F. Photocatalytic Oxidation Air Cleaner: Identification and
8		Quantification of by-Products. Build. Environ. 2014, 72, 34-43.
9		https://doi.org/10.1016/J.BUILDENV.2013.10.014.
10	(43)	Debono, O.; Hequet, V.; Le Coq, L.; Locoge, N.; Thevenet, F. VOC Ternary Mixture
11		Effect on Ppb Level Photocatalytic Oxidation: Removal Kinetic, Reaction
12		Intermediates and Mineralization. Appl. Catal. B Environ. 2017, 218, 359–369.
13		https://doi.org/10.1016/J.APCATB.2017.06.070.
14	(44)	Binas, V.; Stefanopoulos, V.; Kiriakidis, G.; Papagiannakopoulos, P. Photocatalytic
15		Oxidation of Gaseous Benzene, Toluene and Xylene under UV and Visible Irradiation
16		over Mn-Doped TiO2 Nanoparticles. J. Mater. 2019, 5 (1), 56-65.
17		https://doi.org/10.1016/J.JMAT.2018.12.003.
18	(45)	Manoukian, A.; Quivet, E.; Temime-Roussel, B.; Nicolas, M.; Maupetit, F.; Wortham,
19		H. Emission Characteristics of Air Pollutants from Incense and Candle Burning in
20		Indoor Atmospheres. Environ. Sci. Pollut. Res. 2013, 20 (7), 4659–4670.
21		https://doi.org/10.1007/s11356-012-1394-y.
22	(46)	Carslaw, N. A New Detailed Chemical Model for Indoor Air Pollution. Atmos.
23		Environ. 2007, 41 (6), 1164–1179.
24		https://doi.org/https://doi.org/10.1016/j.atmosenv.2006.09.038.

1	(47)	Kramp, F.; Paulson, S. E. On the Uncertainties in the Rate Coefficients for OH
2		Reactions with Hydrocarbons, and the Rate Coefficients of the 1,3,5-Trimethylbenzene
3		and m-Xylene Reactions with OH Radicals in the Gas Phase. J. Phys. Chem. A 1998,
4		102 (16), 2685–2690. https://doi.org/10.1021/jp9732890.
5	(48)	Murray, D. M.; Burmaster, D. E. Residential Air Exchange Rates in the United States:
6		Empirical and Estimated Parametric Distributions by Season and Climatic Region. Risk
7		Anal. 1995, 15 (4), 459–465. https://doi.org/10.1111/j.1539-6924.1995.tb00338.x.
8		