



**HAL**  
open science

## Emission of titanium dioxide nanoparticles from building materials to the environment by wear and weather

Neeraj Shandilya, Olivier Le Bihan, Christophe Bressot, Martin Morgeneyer

### ► To cite this version:

Neeraj Shandilya, Olivier Le Bihan, Christophe Bressot, Martin Morgeneyer. Emission of titanium dioxide nanoparticles from building materials to the environment by wear and weather. *Environmental Science and Technology*, 2015, 49 (4), pp.2163-2170. 10.1021/es504710p . ineris-01855008

**HAL Id: ineris-01855008**

**<https://hal-ineris.archives-ouvertes.fr/ineris-01855008>**

Submitted on 25 Sep 2018

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Emission of Titanium Dioxide Nanoparticles from Building Materials to the**  
2 **Environment by Wear and Weather**

3  
4 *Neeraj Shandilya, Olivier Le Bihan, Christophe Bressot, Martin Morgeneyer\**

5  
6 Neeraj Shandilya, Dr. Olivier Le Bihan, Dr. Christophe Bressot  
7 Institut National de l'Environnement Industriel et des Risques (INERIS), Parc Technologique  
8 Alata BP 2, 60550 Verneuil-en-Halatte, France

9  
10 E-mail: [martin.morgeneyer@utc.fr](mailto:martin.morgeneyer@utc.fr)

11  
12 Neeraj Shandilya, Dr.-Ing. Martin Morgeneyer  
13 Université de Technologie de Compiègne (UTC), rue Roger Coutollenc, 60200 Compiègne,  
14 France

15  
16  
17 **Abstract**

18 In the present work, we investigate the effect of the weathering duration on a commercial  
19 photocatalytic nanocoating on the basis of its nanoparticles emission tendency into the two  
20 media - air and water. It is found that the increase in the weathering duration results into the  
21 stepwise structural deterioration of the nanocoating which, in turn, decreases the nanocoating  
22 life, changes the nanocoating removal mechanism and increases the particle emission  
23 concentration. The emission of the free TiO<sub>2</sub> nanoparticles is found to be weathering duration  
24 dependent. Three quantities- Emission Transition Pace (ETP), Stable Emission Level (SEL)  
25 and Stable Emission Duration (SED) are introduced. By linearly extrapolating these quantities  
26 from short weathering durations, the complete failure of the nanocoatings can be predicted  
27 and moreover the potential increase of nanoparticles release into the air.

28 **Keywords:** Weathering, Emission, Nanocoating

29  
30 **Abstract Art**

## 34 **1. Introduction**

35 Photocatalytic nanocoatings are readily being applied on the external walls of buildings for  
36 their anti bacterial and self cleaning properties.<sup>1, 2</sup> These properties are ensured by the  
37 presence of embedded manufactured photocatalytic titanium dioxide (TiO<sub>2</sub>) nanoparticles in  
38 the coating matrix. Resting on the external surfaces, these nanocoatings are frequently  
39 subjected to various mechanical solicitations and environmental weathering in real life  
40 conditions.<sup>3, 4, 5</sup> As a result, the consequent loss in their structural integrity leads to their  
41 disintegration which, in turn, may lead to the exposure of embedded nanoparticles<sup>6</sup> and thus  
42 their possible release too. Depending upon the type of medium in contact, this release can be  
43 into air as well as into ground waters. For a durable development, understanding their  
44 ecological and human health effects is important. In the last decade, slowly though, this  
45 concern has started gaining attention.<sup>6-19</sup> In this context, various toxicological and  
46 ecotoxicological studies have also demonstrated toxic effects of some types of TiO<sub>2</sub>  
47 nanoparticles.<sup>20-25</sup>

48 Here, the nanoparticles release from a commercial photocatalytic nanocoating is evaluated as  
49 a function of the duration of its weathering. Whilst the nanoparticles emission into air is  
50 studied via abrasion tests, their emission into water is studied via the microscopy and leaching  
51 tests of runoff samples. Through microscopic studies of the intermediate degraded states of  
52 the coated surfaces, the particles emission is shown to be weathering duration dependent.

53

## 54 **2. Materials and Methods**

### 55 **2.1. Samples**

56 For the study, a commercially available photocatalytic nanocoating, PHOTOCAL  
57 MASONRY, was chosen. It is manufactured by NANOFRANCE Technologies, France. It  
58 consists of anatase titanium dioxide nanoparticles having a primary size of <8 nm and a

59 volume percentage of 1.1%. Other material properties are as follows- Coagulation Index: ~2;  
60 Appearance: white; Dispersant: Polymethylmethacrylate (PMMA). This type of nanocoating  
61 is fabricated specifically for the applications on porous surfaces like brick, concrete etc. The  
62 substrate chosen for the nanocoating application was a masonry brick (11 cm x 5 cm x 5 cm;  
63 Leopard brick, Ref: 901796, Castorama, France). It is basically an alumino-silicate brick  
64 which is frequently used in constructing façades, house walls, stairs etc. The microscopic  
65 analysis of the nanocoating and the substrate were carried out using Optical Microscope  
66 (Model Imager.M1m; Carl Zeiss MicroImaging GmbH; Germany), Energy Dispersion  
67 Spectroscopy (EDS; Model X-max; Oxford Instruments UK) and Transmission Electron  
68 Microscope (TEM; Model CM12; Philips, The Netherlands). Information on the microscopic  
69 analysis results are provided in the separately available *supplementary part* of this paper. Four  
70 coating layers with a total thickness of 80 µm approx. were applied on the brick substrates.  
71 The substrate surfaces were prepared and the nanocoating was applied following the  
72 guidelines in the technical data sheet recommended by the nanocoating manufacturer (i.e.  
73 degreased using brush and ethanol soaked paper, dry and dust free surfaces; use of a High  
74 Volume Low Pressure spray during coating; 25°C of ambient temperature).

75

## 76 **2.2. Artificial weathering**

77 The artificial weathering tests were performed with the nanocoated and the uncoated  
78 reference brick samples in a weathering chamber (Model Suntest XLS+; Atlas; Germany).  
79 The artificial weathering consisted of maximum 2658 cycles (which corresponds to 7 months)  
80 of 2 hours each (120 min of UV light, 102 min dry, 18 min water spray). A xenon arc lamp  
81 (300–400 nm; 60 W/m<sup>2</sup>; Model NXE 1700; Ametek SAS; France) with an optical radiation  
82 filter was used as the UV source. Such a system is a representative of natural sunlight.<sup>20</sup> The  
83 temperature during UV exposure was monitored and averaged at 38 °C. The conditions were

84 chosen on the basis of an international standard.<sup>26</sup> De-ionized and purified water  
85 (conductivity < 1  $\mu\text{S}/\text{cm}$ ) was used for the water spray onto the nanocoated samples. The  
86 runoff water was collected in a reservoir, mounted at the bottom of the climate chamber. The  
87 whole weathering process was intervened at selected times (2, 4, 6 and 7 months) for  
88 analyzing the in-process condition of the test samples and sampling the collected runoff water  
89 for its leaching analysis.

90

### 91 **2.3. Leaching**

92 To quantify the  $\text{TiO}_2$  content in the leachate water, fixed amounts of samples (100 ml) were  
93 collected at selected times (as indicated earlier) and analyzed by using Inductively Coupled  
94 Plasma Mass Spectrometry (ICP-MS; Model 7500cx; Agilent Technologies; USA). The  
95 operating conditions of the ICP-MS were as follows- Sample volume: 2 ml; RF Power: 1550  
96 W; RF Matching: 1.78 V; Carrier Gas: 0.85 l/min; Makeup gas: 0.2 l/min; Nebulizer:  
97 Micromist; Nebulizer pump: 0.1 r/s; S/C temperature: 15  $^\circ\text{C}$ ; He flow rate: 5 ml/min;  $\text{H}_2$  flow  
98 rate: 2 ml/min; Integration time: 0.1 s; Chamber & Torch: Quartz; Cone: Ni; Element  
99 detection threshold limit: 0.5  $\mu\text{g}/\text{l}$ .

100

### 101 **2.4. Abrasion**

102 A modified Taber<sup>TM</sup> linear abrasion apparatus (Model 5750; Taber Inc. USA)<sup>27</sup> was used for  
103 the abrasion of the nanocoated samples. The standard form of this apparatus is referenced in  
104 numerous internationally recognized test standards.<sup>28-30</sup> This apparatus is already being used  
105 in industries for analyzing the performance of products like paint, coating, metal, paper,  
106 textile etc., during the application of a mechanical stress.<sup>31</sup> The normal stress of the abradant  
107 of about 15 – 500 kPa, being applied through Taber, also corresponds to the typical normal-  
108 and thus tangential- stress levels applied to surface coatings in a domestic setting, e.g. walking

109 with shoes, displacement of different furnishings etc.<sup>3, 32</sup> It incorporates a motor driven  
110 horizontal arm (bar) that displaces an abradant in a back and forth linear motion over the test  
111 sample. The abrasion is caused by the friction at the contact surface between the surfaces of  
112 the abradant and the sample. Via a vertical shaft, a known weight is mounted on the top of the  
113 abradant which shall be referred to as the *Normal Load* in the following text. The Taber™  
114 H38 non-resilient vitrified clay-carborundum abradant was used during the abrasion of the  
115 nanocoated samples. This abradant comes in a cylindrical shape (6 mm diameter, 2 cm length)  
116 and comprises of very fine abrasive particles (~4 μm) of carborundum that provide mild  
117 abrasion. For reproducing the domestic stress conditions, a normal load of 6 N was chosen.  
118 An abrasion stroke length of 76 mm, abrasion speed of 60 cycles/min and abrasion duration of  
119 10 min were other selected parameters.

120

## 121 **2.5. Experimental set-up**

122 Figure 1 shows the scheme of the complete experimental set-up. Particle free air is passed  
123 through a nanosecured work post (HPPE 10, Erma Flux S.A., France) containing the Taber  
124 abrasion apparatus. Already been successfully employed in various nanoparticles' dustiness  
125 tests,<sup>33</sup> this work post has a particle filter efficiency of 99.99%. The air flow rate inside this  
126 work post is equal to 31000 l/min. The test sample is placed inside a self designed *Emission*  
127 *Test Chamber* (0.5 m x 0.3 m x 0.6 m).<sup>34</sup> A small fraction of the air circulating inside the  
128 nanosecured work post passes through the emission test chamber before starting the abrasion  
129 tests in order to make it free from background particles. As soon as the chamber becomes  
130 particle free, it is sealed completely. A slot is also provided on one of the walls of this  
131 chamber allowing the horizontal arm of the abrasion apparatus passing through and operating  
132 the motor unit placed externally. A radial symmetric sampling hood with a volume of 713 cm<sup>3</sup>  
133 provides an encapsulation of the sampling suction zone around the abradant. Such sampling

134 hood has also been employed in other studies with varying volumes, such as 1500 cm<sup>3</sup> by  
135 Vorbau et al.<sup>3</sup> and 60 cm<sup>3</sup> by Gohler et al.<sup>35</sup>. Its use minimizes particle loss to the emission  
136 test chamber's walls or other surfaces. Furthermore, the aerosol concentration remains  
137 relatively high due to the low volume of the sampling hood and the fixed total sample flow  
138 that amounts to 6.8 l/min. The Taber apparatus along with the emission test chamber  
139 constitute the Aerosol Generation Section (*AGS*). The *AGS* is connected to an Aerosol  
140 Measurement Section (*AMS*) using anti-static electrically conductive tubes (6 mm diameter)  
141 where the generated aerosol particles are characterized in terms of their number concentration  
142 and size distribution. The particle number concentration (*PNC*) can be defined as the number  
143 of particles present in a unit centimeter cube of air at a given instant of time. The particle size  
144 distribution (*PSD*) is the classification of the *PNC* according to their size. The instruments  
145 used to measure these two quantities were: Condensation Particle Counter (*CPC*), Scanning  
146 Mobility Particle Sizer (*SMPS*), Aerodynamic Particle Sizer (*APS*) and a Mini Particle  
147 Sampler (*MPS*<sup>®</sup>; Ecomesure Inc. France).<sup>36</sup> The details on these instruments and their  
148 operation conditions are shown in figure 1. Whilst the *CPC* measures the emitted aerosol  
149 particles number concentration (*EAPNC*), the *PSD* is measured using *SMPS* and *APS*. A  
150 *MPS* is used for the particle collection through filtration technique on copper mesh grids  
151 which can be used later in *TEM* for various qualitative analyses of the emitted aerosol  
152 particles without any limitation on the aerosol size. Therefore, the whole aerosol measurement  
153 section, quantifying the particle emission, can measure aerosol particles having sizes ranging  
154 from 4 nm to 20 μm.

155

## 156 **2.6. Background and particle loss**

157 Three empty test runs were done before the main abrasion experiment to measure the  
158 concentration of the background particles and those generated by the motor in abrasion

159 apparatus. Without the test sample present in the chamber, the average concentration, detected  
160 by CPC within the sampling hood, was  $\sim 0.7 \text{ cm}^{-3}$  with a standard deviation of  $0.2 \text{ cm}^{-3}$ .  
161 Therefore, the concentrations of all the background particles and those generated by the  
162 abrasion apparatus were insignificant. The calculations on the loss of particle concentration,  
163 due to their deposition on the walls of the chamber, have shown a loss of 4% in number  
164 during 10 min (i.e. the duration of the abrasion process).  
165 For the present experimental set-up, the particle loss in the connecting tubes (i.e. losses due to  
166 their gravitational settling, inertial deposition etc.) has been calculated by Shandilya et al.<sup>37</sup>  
167 on the basis of system of equations enlisted by Brockmann et al.<sup>38</sup> Shandilya et al.<sup>37</sup> found it  
168 to be 17% for particles having size less than or equal to 10 nm. For the 100 nm sized particles  
169 or bigger, the loss reduces to mere 1%.

170

### 171 **3. Results and Discussion**

#### 172 **3.1. Structural deterioration of nanocoated sample surfaces**

173 In figure 2 (a) to (e), the evolution in the surface deterioration of the nanocoated sample can  
174 be observed with the increase in weathering duration. The optical microscopic image of a  
175 non-weathered sample (figure 2 (a)) shows a continuous and intact form. With 2 months of  
176 weathering (figure 2 (b)), *ridges* and *valleys* start to appear on the surface. If the weathering  
177 continues, they develop into the cracks by 4 months of weathering (figure 2 (c)). After 6  
178 months, these cracks start to broaden up with branching at different parts (figure 2 (d)). By 7  
179 months, the nanocoating is no longer continuous but reduced in the form of *lumps* (figure 2  
180 (e)). On the contrary, for an uncoated reference sample, no such effect of weathering was  
181 observed throughout the whole process. In the literature, the cracking of water based  
182 nanocoatings (as in present case) has been attributed mainly to two factors: drying stress due  
183 to water content evaporation<sup>39-42</sup> and gradual embrittlement of the polymeric binder present



184 in the nanocoating during its interaction with UV rays.<sup>43</sup> Moreover, the cracking is often  
185 accompanied by the shrinking or compaction of the nanocoating on the surface due to the  
186 evaporation of the water content, as observed by Murray<sup>40</sup> and Dufresne et al.<sup>41</sup>  
187 The nanocoating's shrinking and cracking may result in the exposure of the brick surface,  
188 lying underneath. In order to confirm this hypothesis, EDS analysis of the weathered  
189 nanocoated sample surfaces was done to create an elemental map between Ti (contributed by  
190 the nanocoating) and Ca (contributed by the brick). This would show the change in completely  
191 exposed surfaces of the brick substrate. The results are shown in figure 2 (f) to (j). One may  
192 see that while the Ti content on the surface remains approximately the same throughout the  
193 weathering (average value ~16.1%), the Ca content and the exposed surface increase  
194 proportionately. It directly implies the shrinkage of the nanocoating with weathering. If  
195 continued further, the increased shrinking may even lead to the increase in Ti % density in the  
196 nanocoating lumps.

197

### 198 **3.2. Particles emission into water by leaching**

199 For measuring the emission of TiO<sub>2</sub> nanoparticles in the water, 100 ml of leachate samples  
200 were taken from the collected runoff water at selected times from a reservoir which was kept  
201 beneath the nanocoated samples. For a detection threshold of 0.5 µg/l of an element, Ti was  
202 found to be always below this threshold in the sample volume whereas the leached amount of  
203 Ca (contributed by the brick) was found to be proportionally increasing with the weathering  
204 duration. The TEM and EDS analysis of various droplets from the leachate samples (test  
205 methodology and results described in supplementary information) showed irregularly shaped  
206 *microsized* particle agglomerates.

207 In coherence with the ICP-MS measurements, the EDS analysis of these particle agglomerates  
208 also showed an overall increasing Ca content, from 3 to 17% (by mass), with weathering. A

209 meager Ti content (0.2-1%, by mass) was observed in all particle agglomerates. The C content  
210 (from nanocoating copolymer) was found to be varying from 3 to 10 % by mass. The other  
211 dominating elements were Si (~32%, by mass) and Al (~20%, by mass). An increased water  
212 conductivity (from <1 to 13  $\mu\text{S}/\text{cm}$ ) was also observed in the leachate samples which is  
213 supposed to be a consequence of the increased presence of Si, Al and Ca.  
214 This concludes that despite the deterioration by weathering, the nanocoated sample surfaces  
215 are still strong enough to resist the leaching of the constituent nanoparticles in the runoff  
216 water. Infact, it is the brick that obviously leaches its constituents in the runoff water. These  
217 results seem to be consistent with Al-Kattan et al. <sup>10</sup> which studied the release of Ti, from  
218 paints containing TiO<sub>2</sub> nanoparticles, into runoff water under the effect of artificial  
219 weathering. They showed a close to background release of Ti, indicating that TiO<sub>2</sub>  
220 nanoparticles are strongly bound in the paint.

221

### 222 **3.3. Particles emission into air by abrasion**

223 Both uncoated reference and nanocoated samples were abraded after they were exposed to  
224 weathering with varying durations. In figure 3 (a) and (b), TEM images of the emitted aerosol  
225 particles are shown which were sampled and collected on mesh grids during the first 2  
226 minutes of abrasion of the 4 and 7 months weathered nanocoated samples, respectively, under  
227 the same sampling conditions. More aerosol particles get deposited on the mesh grids when  
228 the weathering duration is increased from 4 to 7 months. When zoomed, irregularly shaped  
229 polydispersed aerosol particles with no specific evolution in the shape, over the variation of  
230 the weathering duration, were observed. Most importantly, for 7 months weathered  
231 nanocoated samples, the presence of a considerable amount of free nanoparticles of TiO<sub>2</sub> (Ti  
232 mass > 90%) was observed (figure 3 (c) & (d)). Since this result is in contrary to the findings  
233 of numerous studies <sup>4, 31, 35, 44</sup>, it is of more particular interest as these studies show that a large

234 fraction of the emitted nanomaterial is present in the matrix-bound form and not in the free  
235 state. The increase in the relative % density of Ti, during the shrinking of the nanocoating  
236 with the weathering, (as hypothesized earlier) may lead to the generation of these free TiO<sub>2</sub>  
237 nanoparticles.

238 The results on the chemical composition of the aerosol particles, generated from the abrasion  
239 of 4 and 7 months weathered nanocoated samples, are shown in figure 3 (e). In this figure, the  
240 average mass percentages of 3 elements- C (essentially coming from the nanocoating's  
241 copolymer), Ti (essentially coming from the nanocoating) and Ca (essentially coming from  
242 the brick)- are shown. One can observe a sharp drop in the relative C content (from 56% to  
243 12%) while a sharp rise in the relative Ti content (from 7% to 55%) when the weathering  
244 duration increases from 4 months to 7 months. Also, the relative Ca content, which is absent  
245 in the case of 4 months weathered nanocoated samples, starts appearing and attains a value of  
246 6% with 7 months of weathering. Hence, a direct impact of the weathering duration on the  
247 size and chemical composition of the aerosol particles can be observed from these results.

248 Moreover, the chances of the exposure of free TiO<sub>2</sub> nanoparticles are much higher in the case  
249 of 7 months weathered nanocoated samples.

250 The results on the EAPNC and PSD, measured within the volume of the sampling hood, are  
251 shown in figure 4. In figure 4 (a) and (b), the abrasion test starts at t=120 s and ends at t= 720  
252 s. Before and after this time interval (i.e. t=0 to 120 s and t=720 to 840 s), the abrasion  
253 apparatus is at rest. For the uncoated reference samples, a constant EAPNC (~500 cm<sup>-3</sup>; std.  
254 deviation: 5 to 16 cm<sup>-3</sup>; repeated thrice) is observed, regardless the weathering durations.

255 Hence, the artificial weathering has no apparent effect on the emitted aerosol particles from  
256 the uncoated reference sample. However, for the nanocoated samples, the EAPNC increases  
257 with the weathering duration. Except for 6 and 7 months, the nature of its variation with time

258 is also strikingly similar i.e. ascends initially, becomes constant, ascends again and becomes  
259 constant at last (the PSD, during the first constant phase, is shown in figure 4(d)).

260 For 6 and 7 months weathered nanocoated samples, we observe a rise in the EAPNC curves  
261 during their initial phases ( $t= 120$  s to  $t= 360$  s) beyond the maximum level observed for the  
262 shorter weathering durations. After  $t= 360$  s, these curves tend back to the same level as that  
263 of the uncoated reference and their counterparts. Such a behavior can be explained on the  
264 basis of the nanocoating removal mechanism during the abrasion of the weathered nanocoated  
265 samples. In case of non-weathered, 2 and 4 months weathered nanocoated samples, the  
266 dominant material removal mechanism is assumed to be *abrasion wear* of the nanocoating  
267 due to its continuous and stable form. But for 6 and 7 months weathered nanocoated samples,  
268 it is hypothesized that the dominant material removal is rather *uprooting* of the nanocoating  
269 lumps (or soon to be lumps) by the abradant. Since these lumps are loosely attached to the  
270 surface, their uprooting is faster and easier. As a result, the EAPNC reaches its highest level  
271 as soon as the abrasion starts and comes back to the same level, later, as that of the uncoated  
272 reference, when all the nanocoating lumps have been uprooted and the brick surface is  
273 completely exposed. The PSD, shown in figure 4 (c) and (d) for uncoated reference and  
274 nanocoated samples respectively, vary in a different manner with respect to each other. Whilst  
275 for the uncoated reference samples, there is no significant change in the size mode (alternating  
276 between 250 nm to 350 nm) and maximum PNC (lying around  $375 \text{ cm}^{-3}$ , std. dev.: 0.2 to 8  
277  $\text{cm}^{-3}$ ), a continuous evolution can be observed in these two parameters in case of the  
278 nanocoated samples.

279 Coming back to the nature of the EAPNC variation with time, as observed in figure 4 (b), an  
280 analytic model had been presented by Shandilya et al. <sup>46</sup> which approximates such a variation  
281 in terms of 4 phases for the present nanocoating and one other commercial one: Tipe<sup>®</sup> E502,  
282 TitanPE Technologies, Inc. (see figure 5). When an uncoated reference sample is abraded

283 (figure 4 (a)), the EAPNC reaches a maximum limit swiftly (represented by segment **EF** in  
284 figure 5(a); named as *phase I*) and then remains constant until the end of the abrasion  
285 (represented by segment **FI** in figure 5(a); named as *phase IV*). However, the EAPNC, in case  
286 of a nanocoated sample (figure 4 (b)), passes through two intermediate phases (represented by  
287 segments **FG** & **GH** in figure 5(b); named as *phases II* and *III* resp.) before becoming  
288 constant at the end i.e. *phase IV*. Obviously, for an uncoated surface, the phases II and III are  
289 absent in the evolution of the EAPNC.

290 If physically interpreted, the *phase I* is contributed by the evolution of the contact surface  
291 conditions between the abradant and the nanocoated sample surface when the abrasion starts.  
292 During this phase, an ascending EAPNC is observed. In *phase II*, the EAPNC is constant and  
293 the abrasion of the nanocoated sample surface takes place under a stable state. The  
294 nanocoating is getting removed gradually or slowly through its abrasion wear. The duration of  
295 this phase also signifies the apparent nanocoating life. By the end of *phase II*, the surface  
296 nanocoating layer is no more stable and just the nanocoating-brick interface is left. With the  
297 advent of *phase III*, the brick surface starts to get exposed gradually and by the end of this  
298 phase, it is completely exposed. Therefore, the EAPNC, during *phase IV*, arrives at the same  
299 level as that of an uncoated reference sample and remains constant afterwards.

300 Three quantities:

301 (i) **Emission Transition Pace (ETP)** i.e.  $(\Delta C/\Delta t)_I$ ;

302 (ii) **Stable Emission Level (SEL)** i.e.  $(\#C)_{II}$ ;

303 (iii) **Stable Emission Duration (SED)** i.e.  $T_{II}$

304 can also be identified from figure 5 (a) and (b) and are discussed in the following. These are  
305 the important indicators for assessing the nanocoating useful life and EAPNC. In figure 6 (a)  
306 and (b), they are plotted as a function of the weathering duration. In figure 6 (a), we see that  
307 the **ETP** (defined as the rate of change of the EAPNC) increases with weathering duration for

308 weathered nanocoated samples whereas for the uncoated reference, it remains constant.  
309 Moreover, *ETP* values for non-weathered, 2 and 4 months weathered nanocoated samples lie  
310 beneath the uncoated reference sample. But for 6 and 7 months weathered nanocoated  
311 samples, they lie above. On the basis of figure 2 and 4, we have already hypothesized a  
312 change in the nanocoating removal mechanism during the transition of the weathering  
313 duration from 4 to 6 months. Therefore, one may conclude that if the *ETP* value of the  
314 EAPNC, from a nanocoated sample, lies beneath the one corresponding to its uncoated  
315 reference substrate, the nanocoating removal mechanism is dominated by the abrasion wear.  
316 If opposite, the uprooting of the nanocoating is more dominant. Under given abrasion  
317 conditions, if *ETP* does not increase with the weathering duration (as observed in case of the  
318 uncoated reference), it implies no change in the abrasion conditions, regardless of the  
319 weathering duration. But if it increases (as observed in case of the weathered nanocoated  
320 samples), it implies the change in the abrasion conditions. In the present case, such a change  
321 is imparted by the deterioration of the nanocoating, as shown, qualitatively, in figure 2. The  
322 second quantity, *SED*, is a direct indicator of the nanocoating life - higher the *SED*, higher is  
323 the nanocoating life time. It appears to decrease with the weathering duration (figure 6 (b)).  
324 When  $SED = 0$ , it means that the nanocoating disappears as soon as its abrasion starts.  
325 Quantitatively, it allows extrapolating the effect of the shorter weathering durations to that of  
326 the longer ones without prolonging the weathering test in reality. In figure 6 (b), if the *SED*  
327 average values, from first 2 months of weathering, are extrapolated, we observe that *SED*  
328 reduces to 0 in 11 months. The extrapolation of the extreme limits (i.e. through maximum  
329 value of *SED* for 0 months and minimum value of *SED* for 2 months) can be used to calculate  
330 the minimum useful life of the nanocoating under present weathering conditions. If it is done  
331 in the present case, we observe that *SED* reduces to 0 in 6 months- this is exactly what we  
332 observe in the figure 6 (b). Moreover, the average value of *SED* is decreasing from 320 s to

333 110 s (i.e. a reduction factor of ~3) in mere first 4 months of weathering. The EAPNC during  
334 SED is equal to *SEL*. In figure 6 (b), it appears to increase with the weathering duration.  
335 Since SED= 0 for 6 and 7 months of weathering, therefore, SEL value for these durations  
336 cannot be calculated.

337 If summarized, we can say that under the present experimental conditions, a step-wise and  
338 complete surface deterioration of the nanocoated samples was observed as a function of the  
339 duration of a weathering by UV, temperature and water. This surface deterioration led directly  
340 to an increase of the emitted aerosol particles number concentration (measured within the  
341 volume of the sampling hood) and the TiO<sub>2</sub> content of the aerosolized wear particles. A  
342 considerable presence of free TiO<sub>2</sub> nanoparticles was observed in the case of the 7 months  
343 weathered nanocoated samples. This was a fundamental change observed in the chemical  
344 composition of the aerosol particles, as for short weathering durations, TiO<sub>2</sub> nanoparticles  
345 were always found to be embedded inside the released coarse wear particles with a polymeric  
346 matrix. This increase might still continue for longer weathering durations. With a high  
347 specific surface area, these free nanoparticles aerosols now accentuate a potential risk in terms  
348 of nano- toxicity. In case of leaching, no such effects were observed during 7 months of  
349 weathering. However, fears still remain on how and in what concentrations the leaching of  
350 TiO<sub>2</sub> might occur during prolonged weathering durations. This study also proposed an outline  
351 to understand the phenomenon of aerosolization and the indicators, like *Emission Transition*  
352 *Pace*, *Stable Emission Level* and *Stable Emission Duration*, for its monitoring. They were  
353 found to be significant to quantitatively predict the emitted aerosol particles number  
354 concentration and nanocoating useful life by the means of linear extrapolation from shorter  
355 weathering durations. It is possible to extend this study to a broad spectrum of nanocoatings,  
356 with the prospect of seeking their optimal formulations on the basis of nano risk i.e. emissions  
357 control.

358

### 359 **Acknowledgements**

360 This work has been carried out in the framework of the Labex SERENADE (ANR-11-LABX-  
361 0064) and the A\*MIDEX project (ANR-11-IDEX-0001-02), funded by the French  
362 Government program, Investissements d'Avenir, and managed by the French National  
363 Research Agency (ANR). The authors would like to thank the French Ministry of  
364 Environment (DRC 33 and program 190) and ANSES (Nano-data project 2012/2/154, APR  
365 ANSES 2012) for financing the work. We are equally grateful to Olivier Aguerre-Chariol,  
366 Patrice Delalain, Pauline Molina and Farid Ait-Ben-Ahmad for their cooperation and advice  
367 during the experiments.

368

### 369 **Supporting Information Available**

370 More details on the materials used during the study can be found in the supporting  
371 information. This information is available free of charge via the Internet at  
372 <http://pubs.acs.org/>.

373

### 374 **Acknowledgements**

- 375 [1] Torgal, F.P.; Jalali, S. Eco-efficient construction and building materials. *Constr. Build.*  
376 *Mater.* **2011**, *25*, 582-590.
- 377 [2] Stamate, M.; Lazar, G. Application of titanium dioxide photocatalysis to create self-  
378 cleaning materials. *Romanian Technical Sciences Academy MOCM* **2007**, *13-3*, 280-285.
- 379 [3] Vorbau, M.; Hillemann, L.; Stintz, M. Method for the characterization of the abrasion  
380 induced nanoparticle release into air from surface coatings. *Aerosol Sci* **2009**, *40*, 209-  
381 217.



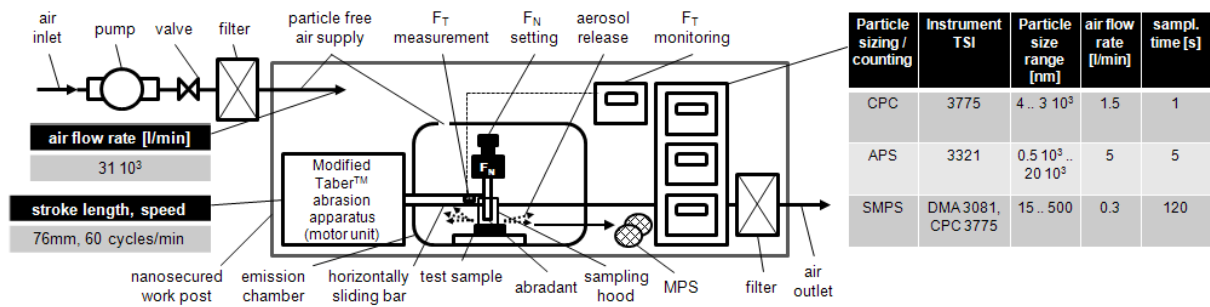
- 382 [4] Shandilya, N.; Le Bihan, O.; Morgeneyer, M. A review on the study of the generation of  
383 (nano-) particles aerosols during the mechanical sollicitation of materials. *J Nanomater*  
384 **2014**, Art. ID 289108.
- 385 [5] Le Bihan, O.; Shandilya, N.; Gheerardyn, L.; Guillon, O.; Dore, E.; Morgeneyer, M..  
386 Investigation of the Release of Particles from a Nanocoated Product. *Advances in*  
387 *Nanoparticles* **2013**, 2, 39-44.
- 388 [6] Göhler, D.; Nogowski, A.; Fiala, P.; Stintz, M. Nanoparticle release from nanocomposites  
389 due to mechanical treatment at two stages of the life-cycle. *J Phys Conf Ser* **2013** 429  
390 (2013) 012045; DOI: 10.1088/1742-6596/429/1/012045.
- 391 [7] Allen, N.S.; Edge, M.; Corrales, T.; Childs, A.; Liauw, C.M.; Catalina, F.; Peinado, C.;  
392 Minihan, A.; Aldcroft, D. Ageing and stabilisation of filled polymers: an overview.  
393 *Polym Degrad Stabil* **1998**, 61, 183-199.
- 394 [8] Allen, N.S.; Edge, M.; Ortega, A.; Sandoval, G.; Liauw, C.M.; Verran, J.; Stratton, J.;  
395 McIntyre, R.B. Degradation and stabilisation of polymers and coatings: nano versus  
396 pigmentary titania particles. *Polym Degrad Stabil* **2004**, 85, 927-946.
- 397 [9] Hsu, L.Y.; Chein, H.M. Evaluation of nanoparticle emission for TiO<sub>2</sub> nanopowder  
398 coating materials. *J Nanopart Res* **2007**, 9, 157-163.
- 399 [10] Al-Kattan, A.; Wichser, A.; Vonbank, R.; Brunner, S.; Ulrich, A.; Zuind, S.; Nowack, B.  
400 Release of TiO<sub>2</sub> from paints containing pigment-TiO<sub>2</sub> or nano-TiO<sub>2</sub> by weathering. *Env*  
401 *Sci Process Impact* **2013**, 15, 2186-2193.
- 402 [11] Kaegi, R.; Ulrich, A.; Sinnet, B.; Vonbank, R.; Wichser, A.; Zuleeg, S.; Simmler, H.;  
403 Brunner, S.; Vonmont, H.; Burkhardt, M.; Boller, M. Synthetic TiO<sub>2</sub> nanoparticle  
404 emission from exterior facades into the aquatic environment. *Environ Pollut* **2008**, 156,  
405 233-239.

- 406 [12]Hirth, S.; Cena, L.; Cox, G.; Tomovic, Z.; Peters, T.; Wohlleben, W. Scenarios and  
407 methods that induce protruding or released CNTs after degradation of nanocomposite  
408 materials. *J Nanopart Res* **2013**, 15, 1504-1518.
- 409 [13]Wohlleben, W.; Brill, S.; Meier, M. W.; Mertler, M.; Cox, G.; Hirth, S.; von Vacano, B.;  
410 Strauss, V.; Treumann, S.; Wiench, K.; Ma-Hock, L.; Landsiedel, R. On the lifecycle of  
411 nanocomposites: comparing released fragments and their in vivo hazards from three  
412 release mechanisms and four nanocomposites. *Small* **2011**, 7, 2384-2395.
- 413 [14]Al-Kattan, A.; Wichser, A.; Zuin, S.; Arroyo, Y.; Golanski, L.; Ulrich, A.; Nowack, B.  
414 Behavior of TiO<sub>2</sub> released from nano-TiO<sub>2</sub>-containing paint and comparison to pristine  
415 nano-TiO<sub>2</sub>. *Environmental Science & Technology* **2014**, 48, 6710-6718.
- 416 [15]Gondikas, A. P.; von der Kammer, F.; Reed, R. B.; Wagner, S.; Ranville, J. F.; Hofmann,  
417 T. Release of TiO<sub>2</sub> nanoparticles from sunscreens into surface waters: a one-year survey  
418 at the old danube recreational lake. *Environmental Science & Technology* **2014**, 48, 5415-  
419 5422.
- 420 [16]von Goetz, N.; Lorenz, C.; Windler, L.; Nowack, B.; Heuberger, M.; Hungerbuhler, K.  
421 Migration of Ag- and TiO<sub>2</sub>- (nano)particles from textiles into artificial sweat under  
422 physical stress: experiments and exposure modeling. *Environmental Science &*  
423 *Technology* **2013**, 47, 9979-9987.
- 424 [17]Windler, L.; Lorenz, C.; von Goetz, N.; Hungerbuhler, K.; Amberg, M.; Heuberger, M.;  
425 Nowack, B. Release of titanium dioxide from textiles during washing. *Environmental*  
426 *Science & Technology* **2012**, 46, 8181-8188.
- 427 [18]Zhang, W.; Crittenden, J.; Li, K. G.; Chen, Y. S.; Attachment efficiency of nanoparticle  
428 aggregation in aqueous dispersions: modeling and experimental validation.  
429 *Environmental Science & Technology* **2012**, 46, 7054-7062.

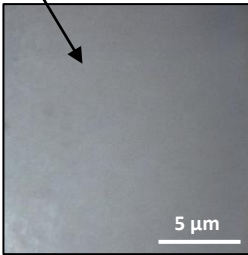
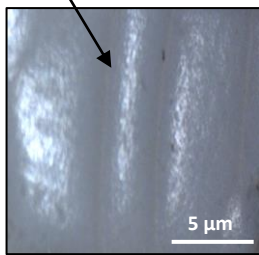
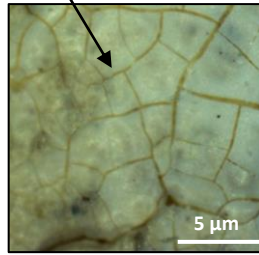
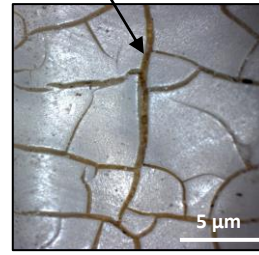
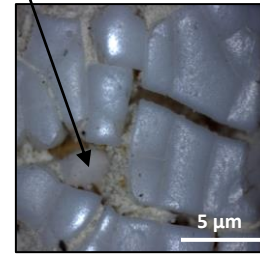


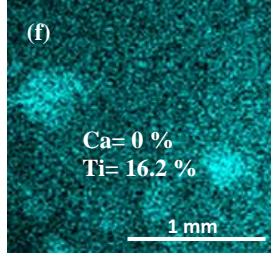
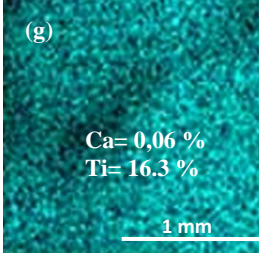
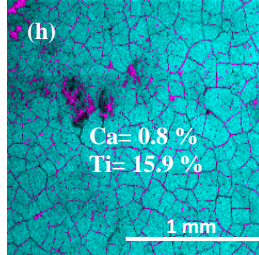
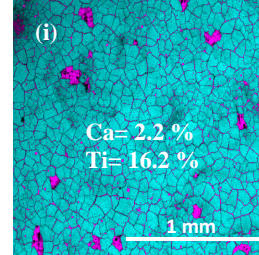
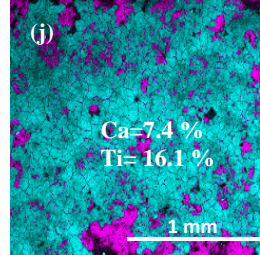
- 430 [19]Stefano, Z.; Marco, G.; Arlen, F.; Luan, G. Leaching of nanoparticles from experimental  
431 water-borne paints under laboratory test conditions. *Journal of Nanoparticle Research*  
432 **2013**, 16, 2185.
- 433 [20]Petkovic, J.; Zegura, B.; Stevanovic, M.; Drnovsek, N.; Uskokovic, D.; Novak, S. DNA  
434 damage and alterations in expression of DNA damage responsive genes induced by TiO<sub>2</sub>  
435 nanoparticles in human hepatoma HepG2 cells. *Nanotoxicology* **2011**, 5, 341-353.
- 436 [21]Unnithan, J.; Rehman, M.U.; Ahmad, F.J.; Samim, M. Aqueous Synthesis and  
437 Concentration-Dependent dermal toxicity of TiO<sub>2</sub> nanoparticles in wistar rats. *Biol Trace*  
438 *Elem Res* **2011**, 143, 1682-1694.
- 439 [22]Warheit, D.B.; Brock, W.J.; Lee, K.P.; Webb, T.R.; Reed, K.L. Comparative pulmonary  
440 toxicity inhalation and instillation studies with different TiO<sub>2</sub> particle formulations.  
441 *Toxicol Sci* **2005**, 88, 514-524.
- 442 [23]Yamashita, K.; Yoshioka, Y.; Higashisaka, K.; Mimura, K.; Morishita, Y.; Nozaki, M.;  
443 Yoshida, T.; Ogura, T.; Nabeshi, H.; Nagano, K.; Abe, Y.; Kamada, H.; Monobe, Y.;  
444 Imazawa, T.; Aoshima, H.; Shishido, K.; Kawai, Y.; Mayumi, T.; Tsunoda, S.; Itoh, N.;  
445 Yoshikawa, T.; Yanagihara, I.; Saito, S.; Tsutsumi, Y. Silica and titanium dioxide  
446 nanoparticles cause pregnancy complications in mice. *Nat Nanotechnol* **2011**, 6, 321-328.
- 447 [24]Barnard, A.S. One-to-one comparison of sunscreen efficacy, aesthetics and potential  
448 nanotoxicity. *Nat Nanotechnol* **2010**, 5, 271-274.
- 449 [25]Auffan, M.; Rose, J.; Bottero, J.Y.; Lowry, G. V.; Jolivet, J.P.; Wiesner, M. R. Towards a  
450 definition of inorganic nanoparticles from an environmental, health and safety  
451 perspective. *Nat Nanotechnol* **2009**, 4, 634-641.
- 452 [26]AFNOR. Paints and varnishes – Methods of exposure to laboratory light sources – Part 1:  
453 General guidance, ISO 16474-1, **2012**.

- 454 [27] Morgeneuyer, M.; Shandilya, N.; Chen, Y.M.; Le Bihan, O. Use of a modified Taber  
455 abrasion apparatus for investigating the complete stress state during abrasion and in-  
456 process wear particle aerosol generation. *Chem Eng Res Des*, DOI:  
457 <http://dx.doi.org/10.1016/j.cherd.2014.04.029>
- 458 [28] ASTM. International. Standard Test method for the abrasion of organic coatings by the  
459 Taber Abradant, ASTM D4060, **2007**.
- 460 [29] ASTM. International. Standard Test Methods for Dry Abrasion Mar Resistance of High  
461 Gloss Coatings, ASTM D6037, **1996**.
- 462 [30] ASTM. International, Standard Test Method for Resistance of Transparent Plastics to  
463 Surface Abrasion, ASTM D1044, **2008**.
- 464 [31] Golanski, L.; Guiot, A.; Pras, M.; Malarde, M.; Tardif, F. Release-ability of nano fillers  
465 from different nanomaterials (toward the acceptability of nanoproduit). *J Nanopart Res*  
466 **2012**, 14, 962-970.
- 467 [32] Hassan, M.M.; Dylla, H.; Mohammad, L.N.; Rupnow, T. Evaluation of the durability of  
468 titanium dioxide photocatalyst coating for concrete pavement. *Constr Build Mater* **2010**,  
469 24, 1456-1461.
- 470 [33] Morgeneuyer, M.; Le Bihan, O.; Ustache, A.; Aguerre Chariol, O. Experimental study of  
471 the aerosolization of fine alumina particles from bulk by a vortex shaker. *Powder Technol*  
472 **2013**, 246, 583-589.
- 473 [34] Le Bihan, O.; Morgeneuyer, M.; Shandilya, N.; Aguerre Chariol, O.; Bressot, C. In  
474 *Handbook of Nanosafety- Measurement, Exposure and Toxicology*; Vogel, U.,  
475 Savolainen, K., Wu, Q., Van Tongeren, M., Brouwer, D., Berges M., Eds.; Academic  
476 Press: San Diego **2014**; Ch. 7

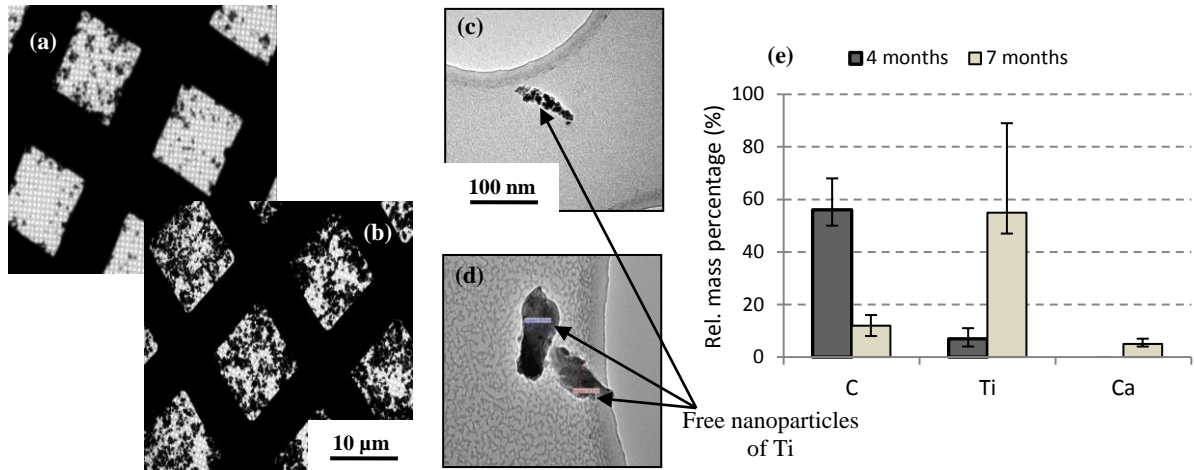
- 477 [35] Göhler, D.; Stintz, M.; Hillemann, L.; Vorbau, M. Characterization of Nanoparticle  
478 Release from Surface Coatings by the Simulation of a Sanding Process. *Ann Occup Hyg*  
479 **2010**, 54, 615-624.
- 480 [36] R'mili, B.; Le Bihan, O.; Dutouquet, C.; Aguerre Charriol, O.; Frejafon, E. Sampling by  
481 TEM Grid Filtration. *Aerosol Sci Tech* **2013**, 47, 767-775.
- 482 [37] Shandilya, N.; Le Bihan, O.; Morgeneyer, M., Effect of the normal load on the release of  
483 aerosol wear particles during abrasion. *Tribol Lett* **2014**, 55, 227-234.
- 484 [38] Brockmann, J.E. In *Aerosol Measurement- Principles, Techniques and Applications*;  
485 Kulkarni, P., Baron, P.A., Willeke, K., Eds.; John Wiley & Sons: New Jersey **2011**, Ch.  
486 6.
- 487 [39] White, L.R. Capillary rise in powders. *J Colloid Interf Sci* **1982**, 90, 536-538.
- 488 [40] Murray, M. Cracking in coatings from colloidal dispersions: An industrial perspective.  
489 Proceedings Rideal Lecture, London, 20 April **2009**.
- 490 [41] Dufresne, E.R.; Corwin, E.I.; Greenblatt, N.A.; Ashmore, J.; Wang, D.Y.; Dinsmore,  
491 A.D.; Cheng, J.X.; Xie, X.S.; Hutchinson, J.W.; Weitz, D.A. Flow and Fracture in Drying  
492 Nanoparticle Suspensions. *Phys Rev Lett* **2003**, 91, 224501-1 - 224501-4.
- 493 [42] Tirumkudulu, M.S.; Russel, W.B. Cracking in Drying Latex Films. *Langmuir* **2005**, 21,  
494 4938-4948.
- 495 [43] Hare, C.H. The Degradation of Coatings by Ultraviolet Light and Electromagnetic  
496 Radiation. *Protective Coatings and Linings* **1992**.
- 497 [44] Shandilya, N.; Le Bihan, O.; Bressot, C.; Morgeneyer, M. Evaluation of the particle  
498 aerosolization from n-TiO<sub>2</sub> photocatalytic nanocoatings under abrasion. *J Nanomater*  
499 **2014**, Art. ID 185080.



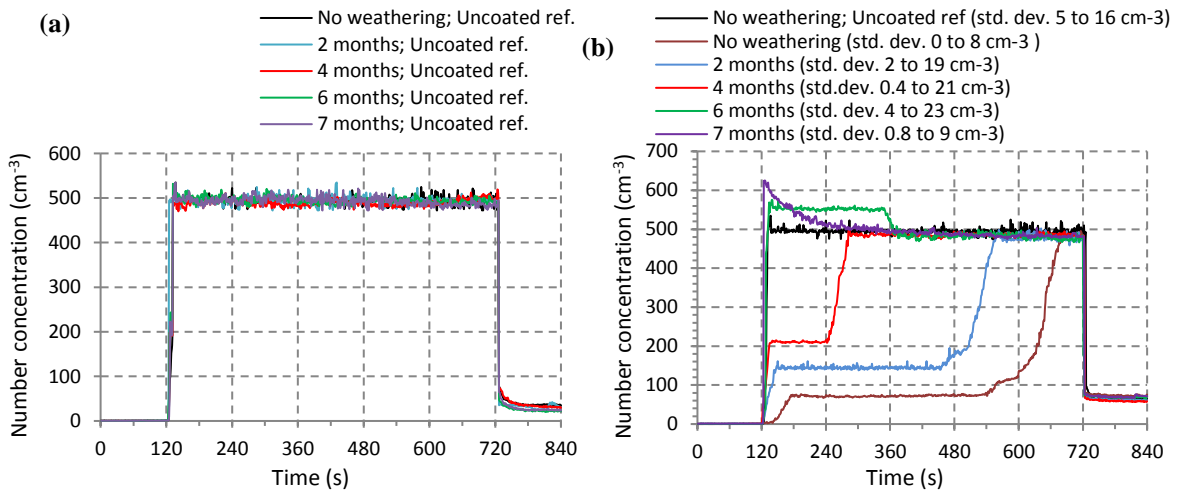
**Figure 1.** Experimental set-up

	No weathering	2 months of weathering	4 months of weathering	6 months of weathering	7 months of weathering
Optical Microscopy of the nanocoated test samples	(a) Continuous and intact form of the nanocoating 	(b) Ridge and valley formation on the nanocoated surface 	(c) Cracking of the nanocoated surface 	(d) Crack broadening 	(e) Lump formation 
Spatial distribution mapping of Ca and Ti over nanocoated test samples  Ca  Ti 	(f) Ca= 0 % Ti= 16.2 %  Nanocoating deposited all over the surface	(g) Ca= 0,06 % Ti= 16.3 %  No effect; Exposed surface = 0.1 mm <sup>2</sup>	(h) Ca= 0.8 % Ti= 15.9 %  Brick exposure through cracks; Exposed surface = 0.53 mm <sup>2</sup>	(i) Ca= 2.2 % Ti= 16.2 %  Exposed surface = 1.19 mm <sup>2</sup>	(j) Ca=7.4 % Ti= 16.1 %  Exposed surface = 2.83 mm <sup>2</sup>

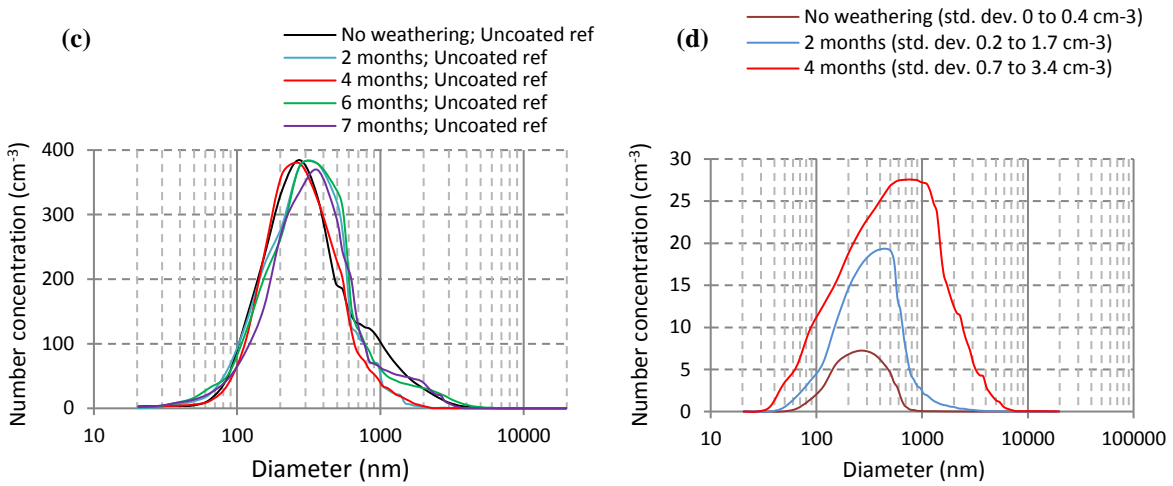
**Figure 2.** Microscopic analysis of the nanocoated sample



**Figure 3.** TEM image of the aerosol particles emitted from the abrasion of (a) 4 months (b) 7 months weathered nanocoated samples (c), (d) Free nanoparticles emitted from the abrasion of 7 months weathered nanocoated samples (e) Chemical analysis of the aerosol particles emitted from the abrasion of 4 and 7 months weathered nanocoated samples

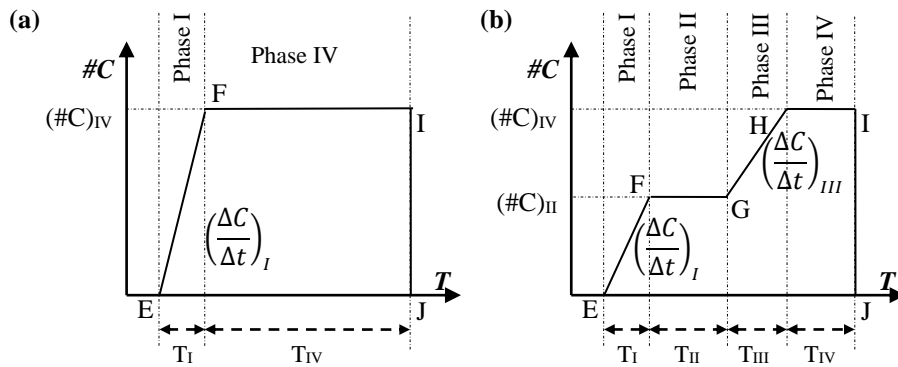




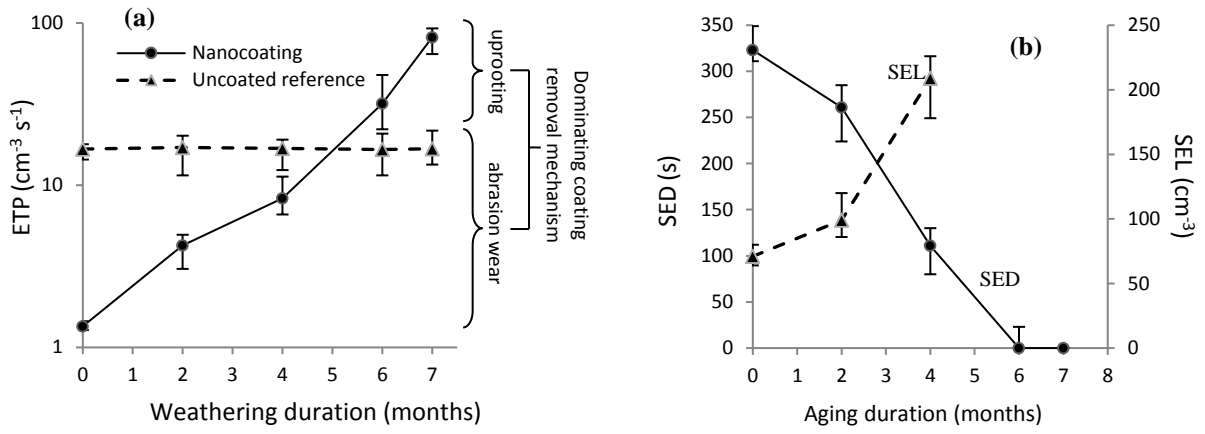


**Figure 4.** EAPNC during the abrasion of weathered (a) uncoated reference sample (b) nanocoated samples

PSD of the emitted aerosol particles during the abrasion of weathered (c) uncoated reference sample ( $t= 120$  s to 720 s) (d) nanocoated samples (corresponding to the phase during which the concentration is constant for the first time in figure 4 (b))



**Figure 5.** Variation of aerosol particle number concentration generated from (a) uncoated and (b) nanocoated surface samples



**Figure 6.** Variation of (a) ETP (b) SED and SEL with the weathering duration