Non-linear release dynamics for a CeO₂ nanomaterial embedded in a protective wood stain, due to matrix photo-degradation

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5

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18 HIGHLIGHTS.

19 • Release of Ce due to matrix photo-degradation

20 • 2 distinct phases of release

21 • The release of 1 wt.% of the initial Ce mass appears as a realistic scenario for outdoor exposure of
22 ca. 3.5 years

23 • The presence of CeO₂ nanoparticles in the acrylic stain modifies the behavior of the matrix toward
24 weathering.

25 ABSTRACT.

26 The release of CeO₂-bearing residues during the weathering of an acrylic stain enriched with CeO₂
27 nanomaterial designed for wood protection (Nanobyk brand additive) was studied under two different
28 scenarios: (i) a standard 12-weeks weathering protocol in climate chamber, that combined condensation,
29 water spraying and UV-visible irradiation and (ii) an alternative accelerated 2-weeks leaching batch
30 assay relying on the same weathering factors (water and UV), but with a higher intensity of radiation
31 and immersion phases. Similar Ce released amounts were evidenced for both scenarios following two
32 phases: one related to the removal of loosely bound material with a relatively limited release, and the
33 other resulting from the degradation of the stain, where major release occurred. A non-linear evolution
34 of the release with the UV dose was evidenced for the second phase. No stabilization of Ce emissions
35 was reached at the end of the experiments. The two weathering tests led to different estimates of long-
36 term Ce releases, and different degradations of the stain. Finally, the photo-degradations of the
37 nanocomposite, the pure acrylic stains and the Nanobyk additive were compared. The incorporation of
38 Nanobyk into the acrylic matrix significantly modified the response of the acrylic stain to weathering.

39

40

41 KEYWORDS. Aging of nanomaterials, engineered nanomaterials (ENM) release, photo-degradation,
42 polymer nanocomposites, acrylic stain.

43 CAPSULE.

44 The weathering of a nano-CeO₂-enriched acrylic stain caused a multi-regime non-linear Ce release,
45 accompanied by mutually dependent aging of both the matrix and the CeO₂-nanomaterial.

46

47 MANUSCRIPT TEXT.

48 **Introduction**

49 The necessity to better estimate and characterize the release of engineered nanomaterials (ENMs) from
50 products has been pointed out repeatedly these past years (Caballero-Guzman and Nowack, 2016;
51 Mackevica and Foss Hansen, 2016; Reijnders, 2009; Som et al., 2010). Real exposure assessments are
52 indeed still hampered by the difficulty to detect and quantify ENMs in complex natural environments
53 (Szakal et al., 2014). While models have been developed to compensate the lack of direct
54 measurements, they often have to rely on oversimplifications and extrapolations in order to estimate the
55 exposure resulting from ENMs release (Caballero-Guzman and Nowack, 2016), which lowers their
56 reliability. A more accurate determination of ENMs flows at all stages of the products lifecycle is then
57 required.

58 The use phase is particularly challenging, as uncontrolled releases of ENMs can result from consumer
59 handling or aging of the products. Such releases cannot be easily determined in the everyday life. Then
60 the simulation of relevant aging scenarios under controlled conditions at the lab-scale appears as a good
61 option.

62 The release of ENM during the use phase will depend on the nanoproduct category. For instance, the
63 release from liquid suspensions is inherent to use and will be around 100%, while the release from solid
64 nanocomposites is more difficult to predict. Solid nanocomposites are materials constituted with a solid

65 matrix and ENMs that can be either deposited at the solid surface or incorporated in the bulk as filling
66 agents (nanofiller). The release of ENM from a solid nanocomposite can proceed from the leaching of
67 ENMs by a liquid, via desorption from the surface, dissolution, or diffusion inside the matrix (Bossa et
68 al., 2017; Duncan and Pillai, 2015). But it can also arise from the degradation of the solid matrix itself,
69 caused by a mechanical action (Bressot et al., 2017) or (photo)chemical reactions (Duncan, 2015).

70 Products with an outdoor application will be especially exposed to photo-degradations due to
71 weathering processes. The weathering of solid nanocomposites has been the focus of several studies
72 since the release of TiO₂ nanoparticles from facades was evidenced for the first time by Kaegi *et al.*
73 (Kaegi et al., 2008). Outdoor weathering setups with rain collectors were developed and allowed
74 measuring the release of silver nanoparticles from an acrylic white paint (Kaegi et al., 2010) or from
75 wood protective stains (Künniger et al., 2014) under natural conditions. However, such realistic
76 scenarios required long-term exposures and many other groups preferred short-term lab-scale artificial
77 weathering, that are pre-validated to correlate with material degradation CEN standards (Podgorski et
78 al., 2003). In the past decade, short-term artificial weathering has been performed on paint (Wang and
79 Nowack, 2018), stains (Shandilya et al., 2015), cement (Bossa et al., 2017; Wohlleben et al., 2011) and
80 plastic nanocomposites (Fernández-Rosas et al., 2016; Neubauer et al., 2017; Nguyen et al., 2010;
81 Wohlleben et al., 2017), either using homemade setups (Al-Kattan et al., 2013; Bernard et al., 2011;
82 Olabarrieta et al., 2012; Pellegrin et al., 2009) or commercial climate chambers (Fiorentino et al., 2015;
83 Hirth et al., 2013; Vilar et al., 2013; Zuin et al., 2013). Although a variety of weathering protocols have
84 been tested, they most often included the exposure of the material to an artificial light source, simulating
85 the full solar spectra (Busquets-Fité et al., 2013; Wohlleben et al., 2013), or restricted to its UV-part
86 (Al-Kattan et al., 2013; Chin et al., 2004; Fiorentino et al., 2015). It was often combined with an
87 exposure to water such as controlled relative humidity (Nguyen et al., 2010), periodic condensation
88 (Fiorentino et al., 2015) or water spraying phases (Fernández-Rosas et al., 2016), representative for
89 humidity, dew or rain, respectively. Depending on the groups, different methods were applied for
90 release assessment. Some focused on quantifying the spontaneous release of ENMs during the

91 weathering assays, using collectors to gather particles detached by gravity (Nguyen et al., 2011), or run-
92 off waters from spraying (Al-Kattan et al., 2015; Busquets-Fité et al., 2013). However, this involved
93 large volumes of water (up to 5000L (Al-Kattan et al., 2013)). As an alternative, some authors
94 implemented external release assessment, with (Hirth et al., 2013; Hsu and Chein, 2007) or without
95 additional mechanical stress (Zuin et al., 2013) (e.g. shaking, sonication, abrasion). Although these
96 different approaches were found successful, the diversity of protocols and setups made difficult the
97 comparison between studies, the understanding of the mechanisms and laws governing ENMs release.

98 Recently, efforts were made towards harmonization of the experimental protocols, in the framework
99 of large pilot interlaboratory studies (Wohlleben et al., 2017, 2014). They converged towards
100 weathering procedures in climate chambers with or without periodic water spraying, and external
101 release assessment. This harmonized protocol yielded contrasted results, depending on the nature on the
102 material: UV-resistant polymers such as polyethylene led to minimal release, while epoxy resins
103 experienced strong degradations under UV, entailing an accumulation of the ENMs at the surface, and
104 eventually their release. A comparative study on a wide range of nanocomposites estimated that release
105 rates from different matrices were spreading across 5 orders of magnitude while the impact of the
106 nanofiller itself on the release rate was limited to one order of magnitude (Wohlleben and Neubauer,
107 2016). It was then proposed that matrix degradability determined to a large extent the response of a
108 nanocomposite to weathering and the ENMs release behavior.

109 In this study, we focused on a single polymer matrix and analyzed the impact of the addition of a
110 nanomaterial to its weathering. We used an acrylic stain that offers a good resistance to UV (Chiantore
111 et al., 2000; Forsthuber et al., 2013) and is commonly employed for wood protection. It was enriched
112 with a CeO₂ nanomaterial, which acts as a UV-absorber and brings an additional protection to the stain.
113 We studied the weathering of this nanocomposite to answer two questions: i) is there a potential for
114 release of the nanomaterial upon aging of a UV-resistant matrix ? ii) is the weathering of the acrylic
115 matrix modified in presence of the CeO₂ nanomaterial? In addition, we characterized a parameter rarely
116 addressed in details i.e. the evolution of the release rate with the UV irradiation. Two artificial

weathering procedures were applied: a standard 12-weeks weathering protocol in a climate chamber, that combined condensation, water spraying and UV-visible irradiation, close to the harmonized protocol mentioned above; and an alternative accelerated 2-weeks batch assay applying the same weathering factors (water and UV), but with a higher intensity of radiation. In both experiments, the nanocomposite was weathered along with the reference stain without CeO₂ addition, in order to evaluate the impact of the nanomaterial on the aging. Surface degradations were monitored as an indicator for weathering. The release of Ce (as dissolved and/or particulate fraction) was quantified with short time steps (e.g. 24h to 72h), to analyze the release dynamics during weathering and relate it to the degradations of the stain surface. Finally the physico-chemical transformation of the nanomaterial within the stain with weathering duration was characterized to give an insight into aging mechanisms.

Material and methods

Materials

An acrylic stain commercialized by Castorama under one of its brand (Lasure Intérieur- Extérieur casto') was chosen for this study. It was deposited in three layers, on larch substrates, freshly sanded with 180 grain paper, observing 2-hours drying between successive layers and 24h final drying.

Two groups of samples were prepared. In the first group (called n-CeO₂), the stain was enriched with citrate-coated CeO₂ nanoparticles, to improve UV filtering. For this, a commercial suspension (Nanobyk-3810) was added to the stain at 7wt.%, and this mix was applied to the upper face (*i.e.* exposed face) of the substrate sample (Figure 1). The characterization and aging of Nanobyk additive was done previously (Auffan et al., 2014). Lateral and lower faces were coated with the stain alone to protect the wood substrate during weathering.

In parallel, a second group of samples (called ACR) was painted on all faces with the Ce-free stain. It was used as a reference to evaluate the impact of ENM addition on the aging of the stain.

For the weathering experiments in the climate chamber (Suntest samples), larch blocks of 27 x 27 x 13 mm were cut. They were weighed before and immediately after the application of each layer of stain. Taking into account a 18% CeO₂ content for Nanobyk additive (Tella et al., 2014), the amount of CeO₂ deposited on each sample (upper face) was calculated, and is reported in Table 1.

For batch experiments, the stain deposit was made on a larger piece of wood (600 x 35 x 11 mm), cut afterwards into 35 x 35 x 11 mm blocks. Lateral faces were covered with Ce-free stain after cutting. This method resulted in a less accurate determination of CeO₂ content, as final samples could not be weighed individually. CeO₂ surface concentration and stain density were then assessed based on the assumption that batch samples exhibited the same final CeO₂ content (wt.%) as Suntest samples.

Table 1. Exposed surface, dry stain mass and density, mean CeO₂ mass deposited on samples, and resulting CeO₂ content (wt.%) and surface concentration. Standard deviation is reported in parenthesis. On batch samples, no data was available regarding the final mass of the stain. An equivalent CeO₂ final content (wt.%) to Suntest samples was assumed and CeO₂ surface concentration, stain density and stain mass after drying were calculated based on this assumption (in italics).

	Suntest		Batch	
	n-CeO ₂	ACR	n-CeO ₂	ACR
Exposed surface (mm ²)	729	729	1225	1225
Stain mass after drying (mg)	38 (18)	48 (36)	<i>40 (20)</i>	<i>27 (22)</i>
Stain density (g.m ⁻²)	52 (24)	70 (47)	<i>33 (17)</i>	<i>22 (18)</i>
Deposited CeO ₂ (mg)	1.5 (0.2)	-	1.8 (0.3)	-
Final CeO ₂ content (wt.%)	4.5 (1.5)	-	<i>4.5 (1.5)</i>	-
CeO₂ surface concentration (mg.m⁻²)	2089 (273)	-	1481 (289)	-

Artificial weathering

Two artificial weathering procedures, based on a succession of dry irradiation and immersion or water spraying phases, were tested. The two sets of experiments were both built on a cycle of 7 days applying the same weathering factors but they were not designed to be compared in term of Ce release and stain degradation. The first one was performed in a climate chamber Suntest XLS+ (Atlas

Material testing Solutions, Germany) for 12 weeks. It combined dry UV irradiation phases with water spraying events to simulate as much as possible a long-term “realistic” scenario. The weathering program was inspired from a standardized protocol (NF EN 927-6, 2006) specific to wood stains, but it was adapted to quantify in details Ce releases and release rates with the UV irradiation and to differentiate Ce release as dissolved Ce from particulate Ce.

A second simplified and accelerated protocol was developed for a 2-weeks batch experiment (batch test). It was designed to provide complementary information on the light effect by comparing release from illuminated samples and non-illuminated samples (dark samples). The purpose of this protocol was to determine whether the release behavior of a solid nanocomposite could be estimated with a short-term experiment.

Weathering in the climate chamber Suntest XLS+:

As described in standard NF EN 927-6, the weathering program was based on weekly cycles repeated for 12 weeks. The weekly weathering cycle started with a 24h condensation, performed in a homemade setup outside the climate chamber (Figure S1, Supplementary Content). Then, ACR and n-CeO₂ samples were introduced inside the Suntest XLS+ and alternatively exposed to Xe lamp and Milli-Q water spraying for the rest of the week. Adaptations to the standard protocol were made, in order to quantify Ce releases and monitor their evolution during weathering. First of all, the volume of water sprayed was strongly reduced, by lowering the spraying frequency from 30 minutes every 180 minutes (NF EN 927-6), to four 20 minutes events, distributed over the week as described by Figure 1a. The water flowing at the surface of samples during spraying phases was collected in order to evaluate Ce releases induced by weathering. To do so, groups of 6 samples, representing a total exposed surface of 4374 mm², were placed inside 800mL glass beakers. Raised and slanted PTFE holders were used, to avoid immersion and water stagnation at the sample surface. A total of five beakers (3 with n-CeO₂ and 2 with ACR) holding 6 samples were fitted inside the climate chamber, arranged on a rotating plate (PL SPP 2 with PMMA plate Ø 300mm, MG Industries, France) to ensure

homogenous spraying on all the samples (Figure 1c). Each beaker was weighed before and after each “rain” event to determine the exact volume of water received by the samples. In average $145 \text{ mL} \pm 42 \text{ mL}$ water were collected in one beaker during the 20 minutes spraying, which corresponded to a mean L/S ratio (rain volume/exposed stain mass) around 500 - 600 for each rain event. The cumulative L/S ratio at the end of the experiment was between 24000 and 30000 (depending on the beaker). Water sampling from these lixiviates was carried out 3 times a week as indicated by the asterisks in Figure 1a for ICP-MS analysis. More details on the water sampling protocol can be found in Supplementary content.

During irradiation phases, the intensity of radiation was set to $65 \text{ J.m}^{-2}.\text{s}^{-1}$ (300nm-400nm) at chamber floor, resulting in an effective UV intensity of $91 \text{ J.m}^{-2}.\text{s}^{-1}$ at the elevated position of samples. Complementary with UV dose, irradiance in the 300 nm – 800nm range was measured once a week with an external radiometer MacSolar (SOLARC, Germany) and was found to be around $500 \text{ J.m}^{-2}.\text{s}^{-1}$ at the sample surface. The chamber temperature was around 30°C (max 36.6°C) during dry irradiation phases and 21°C (max 30.5°C) during water spraying, while black body temperature (BST panel) was measured respectively at 52°C (max 64.4°) and 21°C (max 32.9°C). An additional measurement of the temperature at sample surface during an irradiation phase indicated a value of *ca* 36°C .

At the end of each weekly cycle, one n-CeO₂ and one ACR sample were withdrawn from the experiment and replaced by fresh samples. The degradation of the stain could then be followed week after week. After 12 weeks, 1000 mm precipitations and a UV dose of 513 MJ.m^{-2} (2826 MJ.m^{-2} in the 300 nm – 800 nm range) were accumulated by the oldest samples. In France, such precipitations and irradiance are usually reached in 8-12 months depending on the area (INES Education, n.d.; “Météo France - Météo et Climat,” n.d.)

Batch weathering:

In this test, a higher intensity of radiation (i.e. radiant exposure in the 300-800 nm range) was used and full immersion of the sample was substituted to water spraying in order to accelerate weathering.

Immersion was also selected because it could be implemented more easily. The detailed experimental protocols are described below.

Batch weathering was based on a weekly cycle as during the Suntest experiments. It alternated dry irradiation phases with 5 immersions, distributed over the week as shown in Figure 2. During immersions, stained samples (ACR and n-CeO₂ samples, n=3 for each condition) of 35 x 35 x 11 mm, with an exposed surface of 1225 mm², were placed in separate polypropylene (PP) beakers and submerged for 1.5h in 150mL Milli-Q water. One beaker without sample was also set up for blank. Constant magnetic stirring ensured a good homogenization of the leachate. pH and conductivity were measured before and after each immersion. At the end of immersion, a 20mL-aliquot was extracted for ICP-MS analysis. It was compensated with an equivalent volume of Milli-Q water to maintain a constant L/S ratio (immersion volume/stain mass) of 3750 during the whole experiment. Between two immersions, samples were withdrawn from the PP beakers and exposed to a 400W HPI-T Plus Metal Halide lamp (Philips, France, see Figure S2 for emission spectra). Beakers with leachate were covered and maintained in the dark to avoid leachate evolution until the next immersion. The distance of the sample to the lamp was adjusted to reach a high intensity of radiation. Mean irradiance at sample surface was measured at 105 J.m⁻².s⁻¹ for UV range (290nm-390nm) and 1300 J.m⁻².s⁻¹ for the 300nm-800 nm range, with a PCE-UV34 radiometer (PCE Ibérica S.L., Spain.) and MacSolar radiometer, respectively.

The experiment was reproduced for 2 consecutive weeks resulting in a UV dose of 97 MJ.m⁻² (1367 MJ.m⁻² in the 300 nm-800 nm range) at the end of the assay. Sample temperature alternated between 44°C during irradiation phase and 27°C during immersions.

The same weathering experiment of 2 weekly cycles was also performed in the dark (immersion step without irradiation) to investigate the influence of light on the degradation of the stain and nanomaterials release. The experimental setup and the weekly weathering cycle are detailed in Figure 2.

Quantification of Ce release

Ce concentration in lixiviates of both experiments was analyzed by ICP-MS (Nexion 300, Perkin Elmer, France) after acidification at 2,5% HNO₃ (Ultrapure NORMATON 67%) following Ce isotope (¹⁴⁰Ce). In the Suntest experiments, 20mL of sub-sample were filtrated at 10kDa (using Amicon 8050 unit with cellulose membrane) before acidification in order to determine dissolved fraction of Ce in the lixiviates.

Alteration of the nanocomposite due to weathering

The degradation of the stains was estimated based on the detection of defects. Three phenomena defined in standard NF EN 927-6 were monitored: blistering, flaking and cracking. Blistering is defined as a lifting of the stain from the underlying surface, which appears as bubbles or blisters in the paint, usually caused by heat, moisture or a combination of both. It can eventually lead to peeling of the stain if not corrected. Cracking indicates splitting of the paint film through at least one coat, leading to failure of the paint. In its early stages, the problem appears as hairline cracks; in its later stages, flaking, i.e. a peeling of the paint from the underlying surface in the form of flake, can occur.

The observation of defects was made by optical microscopy at magnification x5 and x10, on a Leica DM RXP microscope. ISO standards 4628-1(2003) (ISO 4628-1, 2003), 4628-2(2003) (ISO 4628-2, 2003), 4628-4(2003) (ISO 4628-4, 2003) and 4628-5(2003) (ISO 4628-5, 2003) were used as references to rate defect size and density. Grades for defects density and size are detailed in supporting information (tables S4 and S5).

Moreover, the oxidation state of Ce inside the stain was characterized before and after weathering, as an indicator for the alteration of CeO₂ nanomaterial. To this end, a thin laminate of the exposed face of Suntest samples was cut and analyzed by X-ray Absorption Near-Edge Spectroscopy (XANES) at the Ce-L₃ edge (5723 eV). Acquisition was made in the fluorescence mode (Canberra Ge-solid-state detector) on the CRG-FAME BM30B beamline at the ESRF (Grenoble, France). The beam size was 100µm x 300µm. Ce^{III}-oxalate and the commercial additive Nanobyk-3810, which contained only

Ce^{IV}O₂ nanoparticles as determined previously (Auffan et al., 2014), were used as Ce^{III} and Ce^{IV} reference compounds, respectively. Each spectrum was at least the sum of two scans. XANES data were processed using an IFEFFIT software package (Ravel and Newville, 2005). Linear Combination Fits were performed in order to determine the relative Ce^{III} and Ce^{IV} contents.

Results

Dynamics of Ce release

Ce releases measured after water spraying events in the Suntest and immersions of batch experiments are reported in Figure 3a and Figure 4a. Data were plotted as a function of the UV dose. A table giving the equivalence between weathering time in weeks, UV dose and irradiation in the 300 nm – 800 nm range for both experiments is presented in Table S3.

For the Suntest experiments, Ce was detected in all lixiviates obtained from n-CeO₂ samples, while it was below the ICP-MS detection limit (DL < 0.1 ng.g⁻¹) for the majority of ACR samples. Occasional levels above DL probably result from a contamination and cannot be considered as representative for a release of Ce from the stain matrix.

Besides the strong initial release ($327 \pm 28 \mu\text{g.m}^{-2}$), the measured Ce releases varied from a few $\mu\text{g.m}^{-2}$ to $\sim 200 \mu\text{g.m}^{-2}$. This corresponded to Ce concentrations between 0.1 and 5 $\mu\text{g.L}^{-1}$ in “rain” waters. In Figure 3a, strong fluctuations are observed between consecutive time points. They are due to the modulations of the weekly weathering cycle in Suntest experiments, that imposed different irradiation times (22h, 44h or 72h) or number of water spraying events (1 or 2) between two sampling events (Figure 1a). In order to reduce this variation and better observe the general trend, Ce releases of Suntest experiment were integrated over the weekly cycle (Figure 3b). Two different regimes of emissions can be distinguished. During the four first weeks of weathering (total UV irradiation $\leq 155 \text{ MJ.m}^{-2}$) Ce releases are erratic with a rather decreasing trend. After 5 weeks, weekly emissions start increasing.

287 Their magnitude increases with cumulative UV irradiation, and no stabilization is reached at the end of
288 the experiment (12 weeks, 513 MJ.m⁻²).

289 The chemical analysis of the Suntest samples filtrated at 10kDa (Figure 3b, light blue) shows that Ce
290 is released in the form of both particulate and dissolved species. The calculated Dissolved/Total Ce ratio
291 varies strongly during the four first weeks of experiments, but after 155 MJ.m⁻² (4 weeks), it oscillates
292 between 0.3 and 0.5 with a mean value of 0.4. CeO₂ nanoparticles in the additive initially consist in pure
293 Ce^{IV} (cerianite CeO₂) (Auffan et al., 2014) and are considered to be poorly soluble in aquatic media
294 (Söhnel and Garside, 1992) . The presence of dissolved Ce in the lixiviates indicates an alteration of the
295 nanomaterial and implies the reduction of Ce^{IV} to Ce^{III} (more soluble at pH 6).

296 For batch experiment (Figure 4a), a release of 75-250 µg.m⁻² of Ce was detected directly after
297 immersion 1 regardless of the irradiation regime (dark or light). Cerium release did not exceed
298 background levels from 32 MJ.m⁻² to 46 MJ.m⁻² (immersion 4), then increased for n-CeO₂ samples
299 exposed to light, while they remained below the DL for samples kept in the dark. The first measurable
300 releases at 46 MJ.m⁻² were around 0.08 mg.m⁻² of Ce, then kept increasing to reach 1.3 ± 0.4 mg.m⁻² of
301 Ce at 97 MJ.m⁻². This trend was disturbed only by a strong release event at 77 MJ.m⁻² (2.9 ± 1.8 mg.m⁻²
302 of Ce, immersion 1, week 2), which is probably the result of the longer irradiation period of 72h at the
303 beginning of the new cycle. Combined with the absence of Ce release from dark samples after
304 immersion 1, this shows a clear correlation between exposure to sunlight and Ce emissions. Once again,
305 no stabilization in Ce release was observed at the end of the experiment, which is consistent with the
306 trend measured for the Suntest experiments at higher cumulated UV doses.

307 The two aging scenarios express a very similar behavior, with two distinct phases for Ce release. The
308 initial phase (phase I) showed an overall decreasing trend with time and no clear dependency on light. In
309 the second phase (phase II) emissions increased with weathering and are light-dependent. No plateau in
310 Ce release was observed at the end of both assays.

311 Ce releases cumulated over the duration of the experiments were plotted in Figure 3c and Figure 4b.
312 They confirmed the similar trends observed for both experiments. At the end of the aging experiments,

the total Ce release reached $2.8 \pm 0.3 \text{ mg.m}^{-2}$ for the Suntest and $6.0 \pm 2.4 \text{ mg.m}^{-2}$ for the batch assay. In both cases, this represented less than 1wt.% of the initial Ce mass ($\sim 0.16\text{wt.}\%$ for Suntest samples, $\sim 0.5\text{wt.}\%$ for batch samples). A strong initial release was measured during the first rain event of the Suntest experiments ($327 \pm 28 \text{ }\mu\text{g.m}^{-2}$ of Ce) accounting for 12% of total Ce emissions. The initial release was much lower in batch test, ($< 0.1 \text{ }\mu\text{g}$ of Ce) accounting for only 1.3% of the total Ce emissions. For the two tests, most of the Ce release took place in the second part of the experiment (phase II), representing 73% and 98% of Ce emissions, for the Suntest protocol (after 155 MJ.m^{-2}) and batch experiment (after 46 MJ.m^{-2}), respectively.

In order to get an insight on Ce release for longer weathering durations, release curves obtained in the two experiments were fitted by a second order polynomial law. Fitting parameters are reported in Table 2. Fits were extrapolated to assess the irradiation necessary to reach the release of 1%, 10% or 100% of the initial Ce mass in our specific experimental conditions (i.e. for a given type and thickness of stain). For the Suntest protocol, 1wt.% of the initial Ce amount is predicted to be released after 1250 MJ.m^{-2} , 10% after 3800 MJ.m^{-2} and 100% after 11800 kWh.m^{-2} . According to the Solar Radiation Data (“SoDa - Web Services,” n.d.), the annual UV dose corresponding to the area of Marseille in France is around 350 MJ.m^{-2} . Based on this data, the release of 1% of the initial Ce mass corresponds to 3.5 years of aging of the stain. However, the release of 10wt.% or 100wt.% of the Ce present in the stain would require 10 and 33 years, respectively. The fit of batch data leads to very different values, with 1% of total Ce mass being released after 130 MJ.m^{-2} , 10% after 355 MJ.m^{-2} and 100% after 1070 MJ.m^{-2} . These values correspond to outdoor exposures of 4 months, 1 year and 3 years in the south of France.

333

334 **Table 2.** Parameters of the polynomial fit of release curves. $y = m_0 + m_1 \cdot x + m_2 \cdot x^2$.

Experiment	m_0	m_1	m_2	R^2
Suntest	0.8171	- 0.0024	1×10^{-5}	0.997
Batch	- 0.158	- 0.0479	1.1×10^{-3}	0.995

335

336

337 Figure 5 shows the evolution of defect density and size for ACR and n-CeO₂ stains observed for the two
338 aging scenarios. Before weathering, the samples were generally free of defects. Isolated flakes were
339 present on a few samples but cracking and blistering were not observed. The samples that were
340 weathered in the dark did not develop any defect (not shown). On the contrary, defects appeared at the
341 surface of samples that were exposed to light (Figure S4). The batch aging protocol induced blistering
342 for both Ce-enriched or Ce-free stain, but no cracking nor flaking was observed (Figure 5c and d).
343 Similar blisters sizes and densities were measured for ACR and n-CeO₂ samples, with a growing
344 magnitude as aging proceeded. For ACR samples weathered in Suntest XLS+, defects mainly took the
345 shape of flakes and cracks (Figure 5a). Blistering was rarely observed. Defects appeared at a very early
346 stage of the experiments. However their density remained rather low (mainly grade 1, as defined in ISO
347 4628-2, 4628-4 and 4628-5) and their size ranked mostly S1 (*i.e.* = only visible under magnification
348 x10) or S2 (*i.e.* = incipiently visible with normal and corrected vision) on some occasions (indicated by
349 a star symbol). Neither defect density nor size showed a significant evolution with the UV dose,
350 confirming the good resistance of this material to weathering.

351 A totally different pattern emerged for n-CeO₂ samples. Their surface remained rather free of defects
352 during the four first weeks of experiment, showing a good initial resistance to weathering. Nevertheless,
353 after 155 MJ.m⁻² (dotted line in Figure 5b), defects started multiplying. As ACR samples, n-CeO₂
354 samples displayed cracks under microscopic magnification (x10) but their density reached higher
355 grades. Flaking was absent from the nanocomposite surface after weathering, but contrary to the
356 reference material, dense and large blisters became visible. No significant variations in defect sizes were
357 observed with aging, but the density was clearly higher after 4 weeks weathering (155 MJ.m⁻²),
358 correlated with the change in Ce release regime (Figure 3b).

359 Cracks are the defects most frequently reported for acrylic stains weathered under both artificial (Aloui,
360 2006; Irmouli et al., 2012; Kielmann and Mai, 2016; Olsson et al., 2014; Popescu and Simionescu,
361 2013) and natural conditions (De Windt et al., 2014; Olsson et al., 2014). They can sometimes lead to

362 flaking, but blistering is usually not expected. This scenario matches well the observations made on
363 ACR samples of our Suntest experiment but deviates from what was observed for the rest of samples.
364 During batch testing, blistering was developed in a similar way for Ce-enriched or Ce-free stain. This
365 effect could then find an origin in the experimental protocol itself, where repeated immersions could
366 favor water penetration and entrapment at the wood/stain interface. After Suntest weathering (and
367 periodic condensation phases), n-CeO₂ samples showed a significant blistering, which was absent from
368 the surface of ACR samples (Ce-free stain);

369 In addition to wood stain degradation, the oxidation state of Ce inside the stain was monitored as an
370 indicator for the alteration of the CeO₂ nanomaterial. XANES spectra of the Nanobyk additive and the
371 non-weathered n-CeO₂ sample are given in Figure 6. They exhibit two peaks (double white line) at ~
372 5728 eV and ~ 5735 eV, corresponding respectively to the final states 2p4f¹5d¹L and 2p4f⁰5d² of Ce^{IV}
373 (Dexpert et al., 1987; Finkelstein et al., 1992) . Both match perfectly showing that CeO₂ nanoparticles
374 were not altered by their incorporation into the stain and its deposition onto a wood substrate. After 12
375 weeks of weathering following the Suntest protocol (513 MJ. m⁻² UV dose), the double white line
376 characteristic of Ce^{IV} states is still visible on the XANES spectra. However a third peak appeared at
377 ~5724 eV that is the absorption energy of the Ce^{III} reference compound. Cerium^{III} oxalate is also plotted
378 in Figure 6 and presents a single white line, corresponding to the 2p_{3/2} / 4f¹5d electronic transition
379 (Takahashi et al., 2002), at ~5724 eV. Consequently, we assume that part of the Ce initially present in
380 the stain as Ce^{IV} was then reduced to Ce^{III} during weathering. Linear Combination Fits (LCF) were
381 performed on the derivatives of XANES spectra to determine the relative Ce^{IV} and Ce^{III} contents. The
382 results are reported in Table 3 for three different locations on the sample. On average, a Ce^{III} content of
383 38% ± 4% was found.

384

385 **Table 3.** Results of the Linear Combination Fits (LCF) performed on the derivatives of XANES spectra measured at three
386 different spots of an n-CeO₂ sample weathered for 12 weeks in Suntest XLS+ (513 MJ.m⁻²). The error on the calculated Ce^{IV}
387 and Ce^{III} content is ± 10%

n-CeO ₂ 12 weeks	Ce ^{IV}	Ce ^{III}	R	chi ²
Spot 1	73%	42%	0.012981	0.03407
Spot 2	79%	33%	0.010084	0.02433
Spot 3	75%	38%	0.015139	0.03815

388

389

390 Discussion

391 *Release of Ce*

392 The release of Ce from an acrylic matrix enriched with a CeO₂ nanomaterial (Nanobyk additive) was
393 evidenced with our two weathering protocols. Far from being a negligible phenomenon, Ce emissions
394 from 2 to 200 µg.m⁻² were measured for each rain event from the beginning of the Suntest experiment.
395 After 46 MJ.m⁻², Ce release ranging from 0.08 to 2.9 mg.m⁻² was also systematically observed during
396 the immersions of the batch test. The residual release detected for samples maintained in the dark in
397 batch experiment indicates that the exposure to UV (and visible) irradiation is the driving force of the
398 release. Water certainly acts as a vector removing degradation debris from the sample surface, but did
399 not induce weathering in the absence of UV. Combined to UV, it very likely contributed to accentuate
400 the weathering via hydrolytic reactions, as suggested by Wohlleben et al. in the case of polyamide
401 (Wohlleben et al., 2014). Cumulated over the experiment, Ce release caused by water spraying events
402 during Suntest testing reached *ca.* 3 mg.m⁻². Recently, harmonized weathering protocols have been
403 proposed, using external release measurements (Wohlleben et al., 2017) that would exclude such
404 spontaneous release from their assessment, resulting in an inaccurate determination of the released
405 mass.

406

407 *Dynamics of Ce release*

408 The evolution of release as a function of the UV irradiation was thoroughly analyzed in our two
409 weathering scenarios. They revealed dynamic release processes that could similarly be divided in two
410 distinct phases and presented common features in both experiments. The first phase (phase I) showed a
411 decreasing trend with time, similarly to what was described by other authors for paints (Al-Kattan et al.,
412 2013; Kaegi et al., 2010). As no clear dependency on light exposure was found, the release mechanism
413 is certainly a wash off of loosely bound material from the surface. Unlike in the above-cited studies, in
414 this experiment, the initial phase was followed by a second one, where Ce emissions increased for
415 irradiated samples and kept growing until the end of the tests. The exposure to UV-visible radiation and
416 the dose received by the samples appeared as key parameters in that phase. In particular, phase II
417 showed a significant accentuation of Ce release with increasing exposure to UV radiation. We postulate
418 then, that release was a consequence of the photo-degradation of the stain, as already witnessed for
419 epoxy (Nguyen et al., 2011) or polyamide (Fernández-Rosas et al., 2016). In both experiments, it was
420 found that the release measured in the second phase accounted for more than 70% of the total Ce release
421 (73% in Suntest and 98% in batch test). Therefore the release due to photo-degradation largely
422 predominates over the release of loose material in this study. No stabilization of Ce release was reached
423 at the end of our experiments. Increased Ce emissions are expected, if weathering proceeds on the same
424 trend, but they could also accentuate and accelerate if matrix aging gets worse. Indeed, previous work
425 already showed that strong damages occurred on commercial photocatalytic stains after 7 months lab
426 weathering, with a direct impact on the amount and the form of TiO₂ nanoparticles released during
427 abrasion processes (Shandilya et al., 2015). Prolonged laboratory tests or higher radiant exposures are
428 necessary to determine the long-term release behavior.

429 It is interesting to highlight that the release rates determined in phase II did not follow a linear trend,
430 and were fitted instead by a 2nd order function. Until now, release studies often provided as result a
431 single value of release rate. This is appropriate when release observes a constant or linear trend, as
432 reported for nano-SiO₂ in acrylic paints (Al-Kattan et al., 2015) or epoxy (Nguyen et al., 2010).
433 However, a recent review (Koivisto et al., 2017) pointed out that release may not always be linearly

proportional to the UV dose. The authors introduced a relation to describe the release due to UV radiation as follow:

$$R = a \times D^b$$

Where R is the release rate in mg.m^{-2} , D the UV irradiation energy in MJ.m^{-2} , and a and b are fitting parameters. A b factor around 1, implying linearity between the release rate and UV dose, was determined on four occasions for release data found in the literature, but values of $b \neq 1$ were predominant. Our results support a non-linear release function in the case of the n-CeO₂ nanocomposite, but could not be fitted satisfactorily by a power law. This may be due to the fact that the release function proposed by Koivisto *et al.* is analogous to the Schwarzschild's law, and describes photo responses resulting from irradiation (Martin et al., 2003). In our experiments an additional factor of degradation was present in the form of water, which may cause a divergence from the power law. Besides, we identified two distinct regimens of Ce release, similarly to what was observed for Si release from 5 wt. % nano-SiO₂ epoxy composite (Sung et al., 2015) and polyurethane nanocomposite (Jacobs et al., 2016).

It suggests that different processes may be at stake in ENM release and emphasizes the need for investigating the dynamics of release more carefully.

Long-term release estimates

Surprisingly, despite very different weathering conditions, our experimental aging protocols displayed a very good agreement in their overall release tendencies (i.e. stain degradation and Ce release). However, significant deviations appeared with a more quantitative analysis Extrapolation of the data indeed led to totally different estimates of the UV doses necessary to reach 1wt.%, 10wt.% or 100wt.% release of the Ce initially present in the material. In the Suntest experiment, the release of 1% of the initial Ce mass appeared as a realistic scenario for an outdoor exposure of *ca.*3.5 years. The release of 10% of the initial Ce puts the aging well beyond the typical recommended 5 year lifetime of an outdoor wood stain, and the 100% release of Ce would even take 33 years. On the other hand the extrapolation of batch data (i.e.

460 implying repeated full immersion of the samples) concluded that 1% release should be achieved after a
461 few months, 10% short after 1 year and 100% after about 3 years. All these durations lied within the
462 lifetime of the stain (ca. 5 years) and a 100% release could then be expected based on this experiment.

463

464 *Stain degradation due to weathering*

465 In addition to release quantification, the alteration of the stain caused by weathering was
466 characterized, based on the occurrence of defects (blisters, flakes or cracks) at the sample surface. It
467 unveiled another divergence between the two weathering protocols, in the defects produced on the
468 stains. Blistering was predominant on both ACR and n-CeO₂ samples of the batch testing, while it was
469 rarely observed under natural circumstances. This suggested that the applied weathering conditions may
470 be unrealistic and questioned the reliability of the release assessment in that case. On the contrary, the
471 weathering of ACR stains in the Suntest XLS+, showing slight cracking and flaking, was consistent
472 with what is usually observed under natural conditions (De Windt et al., 2014; Olsson et al., 2014). This
473 confirmed both the good resistance of acrylic stains to weathering and the realistic character of the
474 Suntest experiment.

475 Contrary to ACR samples, the n-CeO₂ samples weathered with the Suntest protocol showed a
476 densification of their defects after 155 MJ.m⁻². It coincided with the increase of Ce release, reinforcing
477 the hypothesis that Ce emissions of phase II resulted from a degradation of the stain. It also suggested
478 that there is a relationship between defect formation and release. A high density of defects was observed
479 on the Suntest samples and the release rate at 110 MJ.m⁻² was around 0.7 mg.m⁻². For the batch samples,
480 the density and size of surface defects remained lower, but they displayed an almost ten times higher
481 release rate at 97 MJ.m⁻² : 6 mg.m⁻². Therefore we conclude that Ce release was not a direct
482 consequence of the formation of cracks or blisters. We rather think that these are two outcomes of the
483 same degradation phenomenon. If the correlation between the formation of defects and release can be
484 confirmed on other systems, defects could however serve as an indicator for release in the future.

485 The higher cracking density measured for n-CeO₂ samples with respect to the pure acrylic stain, may
486 result from a stiffening of the film, due to dense Ce. The n-CeO₂ samples also developed blisters that
487 were not observed on the ACR samples (CeO₂-free stain). This suggests that the incorporation of CeO₂
488 nanoparticles to the acrylic matrix modified its response to weathering.

489

490 *Aging of CeO₂ nanomaterial inside the stain*

491 Finally the presence of dissolved Ce was evidenced in lixiviates. X-ray absorption spectroscopy proved
492 that the reductive dissolution of the CeO₂ nanomaterial started in the stain, leading to the release of
493 dissolved Ce^{III} in the lixiviates. The initial CeO₂ nanoparticles experienced a transformation during the
494 weathering of the nanocomposite, resulting in the release of a material significantly different from the
495 pristine CeO₂ nanoparticles. In the past years, literature reviews established that ENM release from a
496 solid nanocomposite often took the form of nanomaterial embedded in matrix fragments (Froggett et al.,
497 2014) behaving differently than the pristine ENM (Al-Kattan et al., 2014). Here, we bring new elements
498 suggesting that even if free ENMs were released, they may have experienced transformations during the
499 weathering process, affecting their fate, their transport, their interactions with organisms and thus
500 modify their behavior in the environment compared to pristine material. Strikingly, the aging of the
501 Nanobyk additive in water under UV radiation brought into light an alteration of the CeO₂ nanoparticles
502 (Auffan et al., 2014). However it consisted in a reorganization of Ce atoms at the nanoparticle surface
503 and in that case, no reduction of Ce^{IV} to Ce^{III} was detected. In this study, a different response to aging
504 was observed for the Nanobyk additive incorporated to the acrylic stain. On the other hand the acrylic
505 stain also displayed a different weathering behavior with or without embedded nanomaterial. This
506 advocates for the need of studying nanocomposites as novel materials, with potentially different
507 responses than their separate compounds.

508 **Conclusions**

509 The dynamics of Ce release from a CeO₂-acrylic nanocomposite designed for wood protection was
510 investigated under short- and middle-term assays. It revealed two different regimes of release, as well as
511 a non-linear relationship between the release rate and UV irradiation, highlighting that release
512 phenomena cannot always be properly described by a single release rate value. Efforts should then be
513 made to better characterize the dynamics of release from nanocomposites and help to improve the
514 accuracy of ENM flow models (Wang and Nowack, 2018).

515 In this work, two weathering scenarios (a realistic middle-term experiment in climate chamber and a
516 simplified short-term batch test), specifically designed to monitor the evolution of the release rates with
517 time and UV doses were tested. They displayed a good agreement regarding the occurrence of dual
518 release regimes. In absence of a release plateau during the experiments, polynomial fits of the release
519 curves were used to provide estimates of long-term release. The similarity in general release trends
520 between the two tests showed here some limits, as they led to very different estimates of Ce releases.
521 Indeed, calculations indicate that after 3.5 years, 100 wt.% of the initial Ce will be released based on the
522 batch experiment vs 1 wt.% in the Suntest experiment).

523 The two protocols also produced different surface defects on the stains. In particular the defects
524 observed on batch samples were pointed out as unrealistic, while the Suntest protocol mimicked natural
525 weathering more faithfully. This supports the reliability of the release rates determined with this
526 procedure and makes it a good candidate for standardized tests. The good agreement of batch
527 experiment on the overall release tendency, suggests that it could rather serve as a screening test, to
528 evaluate the release behavior of a nanocomposite. Systematic testing on a range of materials is
529 necessary before such a use could be validated.

530 Based on the Suntest experiment the release of 1% of the initial Ce mass during the lifetime of the
531 stain appears as realistic. However longer experiments are needed to confirm this estimate. An
532 intensification of the matrix degradations could indeed induce the loss of the acrylic polymer structure,
533 resulting in a third phase of release.

Finally, the incorporation of CeO₂ nanoparticles into the acrylic matrix has been shown to modify the response of the stain to weathering while the CeO₂ nanomaterial experienced a transformation that was not expected based on previous weathering experiments. The weathering of a nanocomposite cannot be decomposed as the weathering of two isolated parts. Synergistic effects can arise between the matrix and its nanomaterial, making the study of the weathering of nanocomposites necessary.

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747 FIGURES.

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Figure 1. Experimental setup and procedure for weathering in climate chamber. **a** Weekly weathering cycle. Gray areas correspond to dry irradiation (UV-vis) phases while 20 minutes spraying events (MilliQ-water) appear in light blue. Water sampling is notified by an asterisk whenever the case. **b** Experimental setup inside Suntest XLS+ (right). Irradiation under Xe lamp and water spraying phases were applied alternatively. n-CeO₂ wood samples were coated with stain enriched with CeO₂ additive on their exposed face (= upper face), and Ce-free stain on the remaining faces, as illustrated by the left scheme. ACR samples were coated with Ce-free acrylic stain on all 6 faces.

Figure 2. Experimental setup for batch weathering composed of successive dry irradiation and immersion phases. Left: Dry irradiation phases. Right: immersion phases. The weekly weathering cycle is described by the timeline. Gray areas correspond to dry irradiation phases while immersions (1.5h) appear in light blue. The same cycle was carried out in parallel under light exposure (irradiation + immersion) and in the dark (immersions only) for ACR and n-CeO₂ samples (n=3 for each condition). The setups for dry irradiation phases and immersion phases are illustrated in gray and blue frames respectively.

Figure 3. Ce releases taking place during water spraying of Suntest experiment. **a** Ce release measured between two sampling events (not cumulated). Negative releases were isolated from the series as they represent artifacts of measurement due to the sampling method. **b** Ce releases integrated over the weekly cycles of Suntest experiment. Dissolved Ce determined on samples filtrated at 10kDa is represented in light blue. The dotted line marks a change in release regime after 4 weeks weathering (155 MJ.m^{-2} UV dose). **c** Cumulative release of total and dissolved Ce calculated for Suntest experiment. Ce background measured on ACR samples was included in the error bars. Ce releases of phase II were fitted by a polynomial law of the second order (in red). Fit parameters are given in Table 2.

Figure 4. Ce releases taking place immersions of batch experiment. The data was averaged over three replicates. Standard deviation is represented in error bars. **a** Ce release measured for n-CeO₂ samples maintained in the dark (grey) or exposed to light (blue), during each immersion. A mean Ce background of 0.04 mg.m⁻² was estimated based on Ce level in the blank beaker (no sample) and is indicated by the red horizontal line on the graph. **b** Cumulative Ce releases calculated for batch experiment, for n-CeO₂ samples maintained in the dark (grey) and exposed to light (blue). Ce releases of phase II were fitted by a polynomial law of the second order (in red). Fit parameters are given in Table 2.

Figure 5. Assessment of stain degradation according to blistering, flaking and cracking criteria. **a** Defect density observed on ACR samples of Suntest experiment as a function of the UV dose. Crack size ranked S1 (only visible with magnification x10 – marked Cracks 2) for all non-zero values. For flaking most samples displayed an S1 except for the 4 points marked with a star where larger defects could be observed (marked Flakes 1) (S2, incipiently visible with normal and corrected vision). **b** Defect density observed on n-CeO₂ samples of Suntest experiment as a function of the UV dose. For blistering, most samples displayed an S3 ranking (clearly visible with normal corrected vision) (marked Blister 3), except for points indicated by a star (S2). The crack size was S1 on all samples (marked Cracks 4). **c, d** Evolution of defect density and size for **c** ACR and **d** n-CeO₂ samples exposed to light in batch experiment. The blister size was S3 (marked Blister 5 and Blister 6). No defects were observed on samples that were maintained in the dark. On **b** and **d** the dotted lines mark the onset of phase II determined from release curves. Numbers (1-6) refer to defects (cracks, flake, and blister) observed by optical microscopy (magnifications x5 and x10) and shown as example.

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Figure 6. XANES spectra measured at the Ce L3-edge on an n-CeO₂ sample, before and after 12 weeks weathering under Suntest protocol (513 MJ.m⁻² UV dose). The spectra obtained on the initial and weathered nanocomposite (n-CeO₂ before aging and n-CeO₂ 12 weeks, respectively) are compared to those of a Ce^{III} reference (Ce^{III}-oxalate) and Nanobyk additive, serving here as Ce^{IV} reference. For the 12 weeks weathered n-CeO₂ sample, Linear Combination Fits based on Ce^{III} and Ce^{IV} reference spectra were computed (dotted line). The corresponding Ce^{III} and Ce^{IV} relative contents are reported in Table 3.

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a. ACR - Suntest

b. n-CeO₂ - Suntest

c. n-ACR - Batch

d. n-CeO₂ - Batch

1 Supporting Information for:

2 Non-linear release dynamics for a CeO₂ nanomaterial embedded in a
3 protective wood stain, due to matrix photo-degradation

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Figure S1. Homemade setup used for condensation phases in Suntest weathering (outside climate chamber). Ultrapure water is boiled in a flask. Vapor is directed towards a double-wall reactor where it is chilled and condenses at the surface of wood samples.

Sampling and physico-chemical characterization of “rain” waters in Suntest experiment.

40mL-aliquots of the water collected in beakers were taken after rain events #1 and #4 (Figure 1a) for further analyses. The beakers were then re-introduced in Suntest XLS+ with the remaining water volume. Whenever necessary, controlled amounts of Milli-Q water were added to the beakers to compensate for evaporation and prevent drying out. After spraying event #3 the whole water volume was collected and empty beakers were returned to the climate chamber for the longest 72h irradiation phase. pH and conductivity of all the aliquots were measured immediately after sampling. Redox potential was also measured once a week, on aliquots taken after rain event #3. Short sonication (15s) was applied before, but no stirring was maintained during the measurement of physico-chemical parameters.

Figure S2. Emission spectra of Philips HPI-T Plus Metal Halide lamp. Downloaded from <http://www.lighting.philips.fr/>.

Table S3. Equivalence between weathering time in weeks, UV dose and radiant exposure in the 300nm - 800nm range for Suntest and batch experiments.

Weathering time (weeks)	Suntest experiment		Batch experiment	
	UV dose (MJ.m ⁻²)	Radiant exposure 300nm-800nm (MJ.m ⁻²)	UV dose (MJ.m ⁻²)	Radiant exposure 300nm-800nm (MJ.m ⁻²)
1	40	218	53	707
2	66	360	97	1367
3	111	607		
4	155	856		
5	199	1102		
6	245	1353		
7	290	1606		
8	335	1844		
9	379	2089		
10	424	2335		
11	469	2580		
12	513	2826		

36 **Table S4.** Defect density

Grade	Defect density
0	No defects, i.e undetected
1	Very little, i.e defects are rarely observed and are not significant
2	Few defects, i.e a small but significant amount of defects is observed
3	Moderate number of defects
4	Considerable number of defects
5	Dense concentration of defects

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38 **Table S5.** Defect size

Grade	Defect size
0	Not visible at magnification x10
1	Only visible with optical magnification up to x10
2	Incipiently visible with normal or corrected vision
3	Clearly visible with normal or corrected vision (up to 0.5mm)
4	From 0.5mm to 5mm
5	Above 5 mm

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