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Self-cleaning and de-pollution efficacies of photocatalytic architectural membranes

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Abstract

1 **Abstract**
2 Photocatalytic self-cleaning “cool” roofs and walls can maintain high albedos, saving building
3 cooling energy, reducing peak power demand, and mitigating the urban heat island effect.
4 Other environmental benefits result from their de-polluting properties. Specimens from two
5 different photocatalytic architectural membranes and a non-photocatalytic control were
6 exposed alongside vertically, facing west, for two years in three California sites, and retrieved
7 quarterly for testing. Photocatalytic materials showed excellent self-cleaning performance,
8 retaining albedos of 0.74 – 0.75. By contrast, the control material exhibited an albedo loss of up
9 to 0.10 units, with appreciable soiling observed by scanning electron microscopy. De-pollution
10 capacity was assessed by quantifying NO removal and NO_x deposition rates at 60 °C. Efficacy
11 varied with exposure location, weather conditions, and the nature of the photocatalytic
12 material. Seasonal effects were observed, with partial inhibition during the dry season and
13 reactivation during the rainy season.

14 **1 Introduction**

15 Highly reflective “cool” roofs and walls can save HVAC energy, reduce afternoon peak power
16 demand, and improve thermal comfort [1-8]. Environmental benefits include the mitigation of
17 the urban heat island effect by reducing outdoor air temperatures and smog formation [9-12],
18 and slowing global warming [13]. Another benefit of cool building envelope surfaces is
19 improving material durability by reducing damage induced by surface-temperature cycles [14].
20 However, those benefits can be significantly diminished over time as the albedo (solar
21 reflectance) of building envelopes is reduced due to soiling deposition and biological growth
22 [15-18]. For example, an evaluation of 586 roofing materials exposed in Miami (Florida) over a
23 3-year period showed that the mean albedo of aged products that had an initial albedo of 0.80
24 or higher, decreased to around 0.60 losing approximately 25% of the initial value. In the most
25 extreme cases, aged albedo could be as low as 0.25, corresponding to a loss of up to 70% of the
26 initial value [19].

27 Photocatalytic self-cleaning materials make building envelopes cooler by maintaining their
28 initially high albedo values over long periods of times. Several photocatalytic products are used
29 in construction, including cementitious coatings (such as mortar, plaster and stucco) [20-22],
30 limestone surface treatments [23], coated metal composite siding [24], architectural
31 membranes [25], and different roofing materials (e.g., tiles, shingles and precast panels) [26].
32 These represent a growing sector of the construction market. The global sales of photocatalytic
33 products increased from US\$740M in 2009 to US\$1.5 billion in 2014, and are predicted to reach
34 approximately US\$2.9 billion by 2020 [27]. For these reasons, a closer examination of
35 photocatalytic building envelope materials is warranted, to identify and quantifying benefits
36 and limitations.

37 The self-cleaning effect is due to the ultraviolet (UV) light catalyzed oxidation of deposited
38 soiling, in combination with its physical removal due to enhanced surface hydrophilicity
39 activated by sunlight [28, 29]. Self-cleaning activity has been documented primarily in
40 laboratory tests—e.g., by measuring the loss of deposited soot [30, 31] or bleaching of a dye
41 applied on the surface [32, 33] as a function of UV irradiation. Tracking the dye bleaching rate is

42 the basis for standardized methods that quantify the self-cleaning effect [34, 35].
43 Superhydrophilicity (very low water contact angle) has been observed in TiO₂-coated materials
44 under UV irradiation [36-38]. This property is used in ISO Standard 27448 to test the self-
45 cleaning performance of photocatalytic materials [39].

46 An environmental benefit that has been well documented in laboratory tests is the
47 photocatalytic elimination of atmospheric pollutants in contact with the catalyst surface,
48 including volatile organic compounds (VOCs) [40-42] and atmospheric nitrogen oxides (NO_x =
49 NO + NO₂) [43]. In the case of NO_x, photocatalytic oxidation enables a net removal of these
50 species from the atmosphere through their irreversible conversion to the non-volatile oxidation
51 byproducts nitrate (NO₃⁻) and HNO₃. The final stable oxidation byproducts can be washed off
52 the surface by rain or dew. Different test methods have been developed to evaluate the air
53 purification efficiency of photocatalytic materials by following NO_x elimination [44-46]. One of
54 the most commonly used is the ISO Standard 22197-1, which relies on quantifying nitric oxide
55 (NO) elimination under controlled air flow, temperature, humidity and illumination conditions
56 [47].

57 Both self-cleaning and de-polluting properties of photocatalytic construction materials have
58 been evaluated in a number of field demonstrations. The effective removal of NO_x from urban
59 air was demonstrated using a cement-based photocatalytic coating [22], a mineral-based paint
60 [48], and paving materials [49, 50]. However, other studies found a significantly weaker effect
61 [51, 52]. Photocatalytic performance can be affected by soiling deposition and loss of
62 photocatalyst due to abrasion and material weathering [53, 54]. Some studies report a
63 relatively low depletion of the photocatalyst, with at least 80% retention after a prolonged
64 exposure to the environment of up to two years [55, 56]. By contrast, materials in which the
65 photocatalyst was deposited as a coating without a strong attachment to the substrate yielded
66 higher catalyst depletion rates [54, 57].

67 This study investigated the performance of photocatalytic architectural membranes exposed
68 under real-world conditions. Architectural membranes are highly versatile materials used in
69 building envelopes as energy-efficient roofs, façades, canopies and skylights that provide

70 diffuse natural daylight to indoor environments. In addition to reducing their albedo, soiling
71 deposition onto translucent membranes can reduce the fraction of light transmitted through
72 the material [58, 59]. For that reason, photocatalytic TiO₂ coatings are promising, as they have
73 been shown to impart self-cleaning functionalities to fabrics [60]. Membranes based on
74 fluoropolymer materials, such as those reported here, have been shown to serve as substrates
75 for photoactive additives that imparted self-cleaning and anti-microbial activity [61-63]. The
76 main goal of this study was to quantify the performance of photocatalytic membrane
77 specimens that had been aged alongside a non-photocatalytic control material. Self-cleaning
78 properties were quantified in terms of albedo loss, and de-polluting properties were evaluated
79 by following NO removal rate and the NO_x deposition rate as a function of exposure time.
80 Specimens were exposed to the environment at three locations in California: Berkeley,
81 downtown Los Angeles, and Fresno over a two-year period.

82 83 **2 Methodology**

84 **2.1 Exposed materials**

85 The architectural membrane samples used in this study, manufactured under the Sheerfill®
86 brand name, were provided by Saint Gobain. Non-photocatalytic versions of this product, made
87 of polytetrafluoroethylene (PTFE)-coated fiberglass, have been in use for over 45 years as
88 roofing and façade membranes. TiO₂-coated photocatalytic membranes have been in the
89 market for about 10 years. The two different photocatalytic materials tested here were labeled
90 “P1” and “P2”, and corresponded to standard and alternative formulations of the Sheerfill II
91 EverClean product. General characteristics of these materials have been previously described
92 elsewhere [64]. Specimens of each of these samples were exposed alongside a matching
93 control sample “C1” (standard, non-catalytic Sheerfill II membrane). The C1 sample had the
94 same characteristics as P1 and P2, except for the photocatalytic functionality. Replicate 10 cm
95 by 10 cm specimens of each sample were prepared for exposure to the environment. These
96 samples were a subset of a larger “Cool Walls” study, which is reported elsewhere [7]. The

97 corresponding codes for the Cool Walls study were CW25 (sample P1), CW26 (sample P2) and
98 CW24 (sample C1, control). The as-received color of all samples was tan, which bleached to off-
99 white after several weeks of solar exposure. Per manufacturer's instructions, the initial albedo
100 of previously unexposed architectural membranes was measured on specimens that had been
101 pre-bleached in the laboratory by exposure to UV light in a laboratory weathering apparatus
102 (Model Q-UV, Q-Lab Corporation, Westlake, OH) for seven days. The pre-bleaching was
103 necessary to obtain samples representative of field installations. It simulates a process which
104 occurs under natural sunlight to turn the products from tan to white, as per the manufacturer's
105 documentation.

106 107 **2.2 Setup of exposure sites**

108 Photocatalytic and control specimens were exposed at three sites in California:

- 109 a) BK: a roof at the Lawrence Berkeley National Laboratory in Berkeley (San Francisco Bay
110 Area, 37.87° N, 122.27° W);
- 111 b) LA: a parking lot at the University of Southern California, in downtown Los Angeles
112 (34.05° N, 118.24° W); and
- 113 c) FR: a ground-level, uncovered concrete surface within a site belonging to an industry
114 partner in Fresno (Central Valley, 36.74° N, 119.79° W).

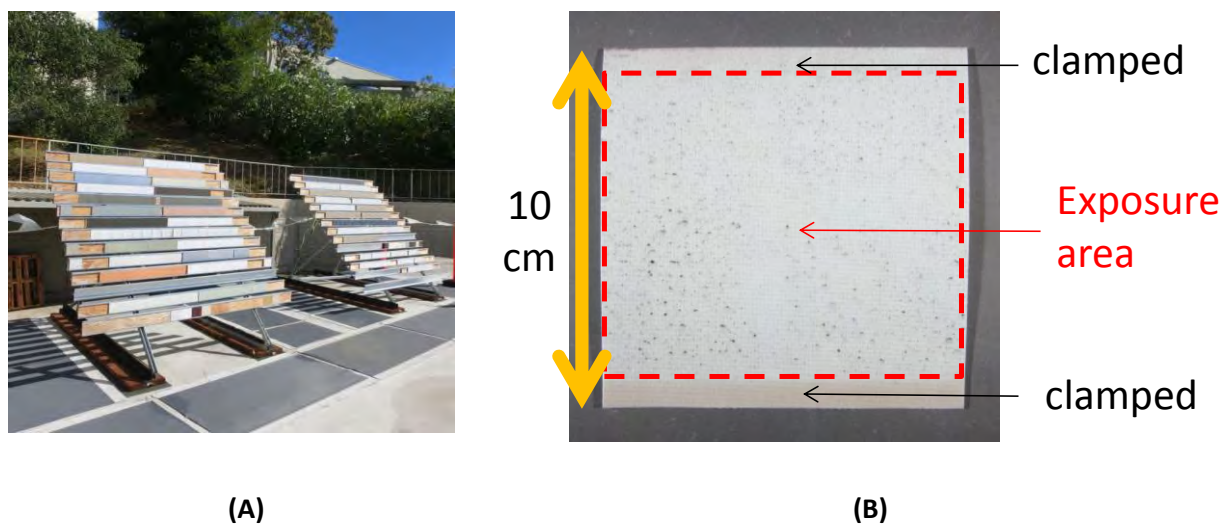
115 The Berkeley (BK) site was the cleanest, being far from highways and heavy traffic. On most
116 days, the exposure site received clean air directly from the Pacific Ocean. The Los Angeles (LA)
117 site was representative of pollution found at a large urban area. The Fresno (FR) site provided
118 exposure to air pollutants associated with agricultural activity, typical of the Central Valley.

119 Exposure racks were designed and built to hold a maximum of 280 specimens, arranged in 14
120 rows of 20 specimens each. The rows were horizontally staggered to prevent contamination
121 between vertically adjacent specimens. Racks were built in-situ at the three California sites
122 between March and April 2016, and specimens from different materials were installed

123 immediately after their construction, including those corresponding to the architectural
124 membrane samples P1, P2 and C1 [65]. Ten specimens of each sample were installed at each of
125 the three sites at the onset of the experiment. Specimens were mounted vertically, facing west.
126 Figure 1 illustrates the racks used to expose specimens, and a photo of an individual
127 architectural membrane specimen. Given the flexibility of this material, it was kept secured
128 against the wood backing by clamping on the top and bottom sections.

129

130



131 **Figure 1.** Images of (A) two of the three exposure racks used at the Berkeley site and (B) an
132 architectural fabric specimen. Specimens were secured against the wood backing by clamps on
133 the top and bottom sections.

134

135

136

137 Monthly rainfall and temperature data at each exposure site were obtained from nearby Global
138 Historical Climatology Network (GHCN) weather stations. The data sets were downloaded from
139 the National Oceanic and Atmospheric Administration [66]. The weather stations selected for
140 each site were:

141 a) USC00040693, in Berkeley, 3.2 km southeast of the Berkeley exposure site;

- 142 b) USW00093134, on the University of Southern California (USC) campus, 1.4 km west of
143 the Los Angeles exposure site; and
- 144 c) USW00093193, at the Fresno Yosemite International Airport, 9.9 km north of the Fresno
145 exposure site

146 Similarly, monthly air pollution data for Berkeley was obtained from the California Air
147 Resources Board [67], for Los Angeles from the South Coast Air Quality Management District
148 [68], and for Fresno from the US Environmental Protection Agency [69]. Each source was
149 selected based on their closer proximity to the corresponding site.

150

151 **2.3 Experimental procedures**

152 **2.3.1 Specimen retrieval, shipping, characterization, and storage**

153 Ten identical specimens from each of the products (P1, P2 and C1) were exposed side-by-side.
154 One specimen from each sample was retrieved quarterly from each site at approximately the
155 same time, following the schedule presented in Table S1 (Supporting Information). Specimens
156 were packed in individual glassine envelopes, and shipped to LBNL for laboratory analysis. The
157 samples were stored inside the same envelopes prior and after laboratory measurements.

158 There was no exposure to the environment after the specimens were retrieved from the racks.

159 Albedo was measured on all specimens with a solar spectrum reflectometer (Version 6, Devices
160 & Services, Dallas TX), using an air mass 1.5 global vertical (sun-facing) output added by the
161 manufacturer [70]. Measurement results were reported as the average \pm standard deviation of
162 multiple measurements. For the initial (unexposed) specimens, the reported standard deviation
163 corresponded to the standard deviation of three measurements performed at non-overlapping
164 locations on each specimen.

165 The image of each specimen was obtained with a digital camera (Canon PowerShot S90,
166 Melville, NY) using a setup that provided consistent lighting conditions. An 18% grey card was
167 used as the background.

168 The static water contact angle was measured on the surface of unexposed samples, and on
169 specimens that were exposed for two years on each site, with a Theta optical tensiometer
170 (Biolin Scientific, Gothenburg, Sweden) using the sessile drop method.

171 A Phenom XL scanning electron microscope (SEM, Thermo Fisher Scientific, Waltham MA) was
172 used to image the surface of samples after exposure and characterize the soiling deposition.
173 The microscope used a Back Scattered Detector (BSD) and an Energy Dispersive X-Ray
174 Spectroscopy (EDS) detector, with an acceleration voltage of 15 kV in both modes. Examination
175 of unexposed and exposed specimens allowed to evaluate the type of soiling matter deposited
176 on the samples during the exposure. In addition, SEM-EDS measurements were used to
177 evaluate the potential loss of Ti upon exposure to the environment, by comparing the Ti mass
178 fraction measured in unexposed and two-year exposed specimens.

179 **2.3.2 Measurement of the de-pollution performance**

180 The methodology used to evaluate the de-pollution performance was adapted from the
181 previously mentioned ISO Standard 22197-1 [47]. A flow of 3 L/min of laboratory air was pre-
182 treated with an activated carbon bed and a HEPA filter, and enriched with 1000 ppb nitric oxide
183 (NO) prior to entering the exposure chamber. The relative humidity (RH) was adjusted to 50%
184 by splitting the air flow, then circulating one of the flows through a water bubbler. Two mass
185 flow controllers were used to adjust the desired RH. In the exposure chamber, a specimen from
186 either sample P1, P2 or C1 was installed facing upwards in the center. A UV-A lamp with
187 maximum intensity at about 360 nm (Model TL-D, Actinic BL, Philips, Andover, MA) was used to
188 irradiate the specimen through a quartz window on the chamber's cover. The exposed surface
189 area for each specimen was 0.01 m². The distance between the window and the specimen was
190 5 mm. UV irradiance (320 - 400 nm; peak sensitivity at 360 nm) was measured using a digital
191 radiometer (Model UVX, UVP LLC, Upland, CA). It was highest at the center of the sample and
192 consistent over the exposed surface, with an average of 11.5 ± 1.5 W/m². The stability of the
193 lamp during the experimental period was verified by repeating irradiance measurements at
194 different times.

195 In previous work using the same setup, it was observed that raising the surface temperature
 196 from 25 °C to 60 °C increased the NO_x-removal efficacy of photocatalytic surfaces [26]. Here,
 197 the surface temperature was kept at 60 °C using an external circulating bath, to simulate
 198 conditions that are close to those found on building surfaces under the sun. Air exiting the
 199 chamber was split into two flows; one of them was directed to a chemiluminescence NO_x
 200 analyzer (Model 200A, Teledyne Technologies, Thousand Oaks, CA), which was calibrated at
 201 different times during the testing period. The other chamber air stream was used to measure
 202 air temperature and RH at the outlet prior to venting in a fume hood, using an in-line digital
 203 HHH6100 series T/RH sensor (Honeywell, Charlotte NC). NO and NO₂ concentrations at the
 204 reactor outlet, air temperature and RH in the chamber, and chamber (surface) temperature
 205 were measured at 0.2 Hz.

206 Tests carried out with each specimen comprised the following three segments:

- 207 a) pre-equilibration under a constant flow of NO-enriched air in the dark (about 1 h);
- 208 b) continuous UV irradiation under a constant flow of NO-enriched air (about 6 h), and
- 209 c) post-equilibration under a constant flow of NO-enriched air in the dark (about 1 h)

210 Figure S1 (Supporting Information) illustrates curves corresponding to typical NO and NO₂ traces.
 211 Removal rate of NO (r_{NO} , μmol h⁻¹) and formation rate of NO₂ (r_{NO_2} , μmol/h, from oxidation of
 212 NO) were calculated using the difference between the inlet and outlet concentrations of NO and
 213 NO₂, as follows:

214

$$r_{\text{NO}} = \frac{\int_0^{\tau} n_{\text{NO}_{\text{removed}}} dt}{\tau} = \frac{\int_0^{\tau} (c_{\text{NO}_i} - c_{\text{NO}_{\text{out}}}) dt}{\tau} \times \frac{Q}{V_n} \quad (1)$$

$$r_{\text{NO}_2} = \frac{\int_0^{\tau} n_{\text{NO}_2_{\text{formed}}} dt}{\tau} = \frac{\int_0^{\tau} (c_{\text{NO}_2_{\text{out}}} - c_{\text{NO}_2_i}) dt}{\tau} \times \frac{Q}{V_n} \quad (2)$$

215

216 where Q is the flow rate (L min^{-1}), τ is the irradiation duration (h), t is the time (h) and V_n is the
217 normalized gas volume for one mole of gas at standard pressure and room temperature (22.4 L).
218 The NO_x deposition rate was computed as the difference between NO removal and NO_2
219 formation rates per unit area, expressed in moles (R_{NO_x} , $\mu\text{mol h}^{-1} \text{m}^{-2}$). Assuming that nitrate and
220 NO_2 are the only NO oxidation byproducts, R_{NO_x} can be used to calculate the rate of nitrate
221 formation. This prediction corresponds to the maximum nitrate formation rate that can be
222 observed, and allows for an estimation of the maximum nitrate surface concentration, as
223 illustrated in Figure S1-B.

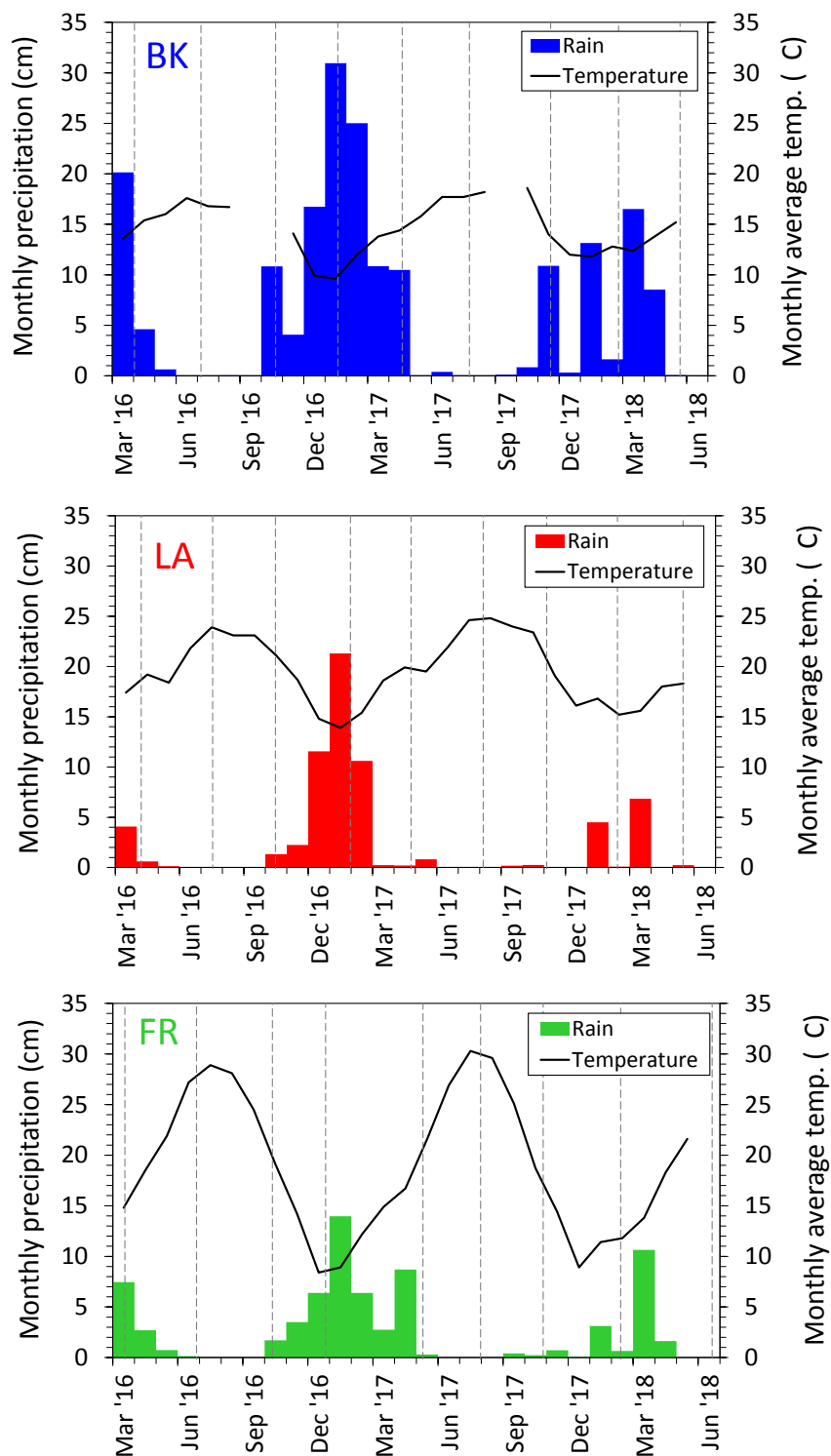
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225 **3 Results and discussion**

226 **3.1 Weather and air pollution measurements at each site**

227 Rain seasonal patterns at the three sites were similar, and are presented in Figure 2. Across the
228 three sites we observed a dry season from April to October, followed by rainy season through
229 the late fall, winter and beginning of spring. Additional descriptions of weather patterns at the
230 sites are included in the Supporting Information. We also provide air pollution results in Figure
231 S2.

232



233

234

235

Figure 2. Precipitation and temperature recorded at the Berkeley (BK), Los Angeles (LA), and Fresno (FR) sites. The vertical dotted lines correspond to the times at which specimens were retrieved.

236 **3.2 Physical chemical characterization of exposed materials**

237 **3.2.1 Contact angle measurements**

238 The water contact angle was measured on unexposed samples and on specimens retrieved
239 after two years of exposure. Figure 3 shows results for initial (pre-bleached) specimens, and for
240 those exposed for two years at each of the sites. The initial contact angle on control sample C1
241 (99 – 108°) was slightly smaller than those on photocatalytic samples P1 (108 – 123°) and P2
242 (107 – 114°). Initial contact angles of control and photocatalytic samples in our study were
243 significantly higher than those reported for photocatalytic limestone surfaces (40°) and their
244 corresponding uncoated controls (55°) as reported in a recent study [54]. This significant
245 difference in contact angle among different types of products may result from the more
246 hydrophobic nature of fluorinated polymeric matrices (including those from our study), as
247 compared with limestone.

248 The small difference in contact angle between control and photocatalytic materials observed in
249 our study may correspond to the presence of TiO₂ additives or changes in the surface
250 morphology in P1 and P2. The overall range of contact angle values measured for both control
251 and photocatalytic samples was consistent with those measured in TiO₂-coated polymer used in
252 cool roofing materials, which increased to 103° from 86° (uncoated polymer) upon coating with
253 TiO₂ [71]. However, not all TiO₂-modified polymers reported in the literature show the same
254 trend. On another study, addition of TiO₂ nanoparticles to a more hydrophobic polymer
255 building coating (initial water contact angle approximately 125°) decreased the contact angle of
256 unexposed specimens by 15-25° [23]. Such difference with the control material was retained
257 after one year of exposure in an urban environment.

258 In two of the three sites, the control sample C1 showed a significant reduction in contact angle
259 after two years of exposure, reaching an average of 81° in Berkeley, and an average of 85° in
260 Fresno. Such reduction in contact angle on the non-photocatalytic sample is consistent with
261 similar trends reported in the literature for limestone [54] and polymeric coatings [23]. These
262 may be associated with buildup of soiling materials, some of which may contribute to surface

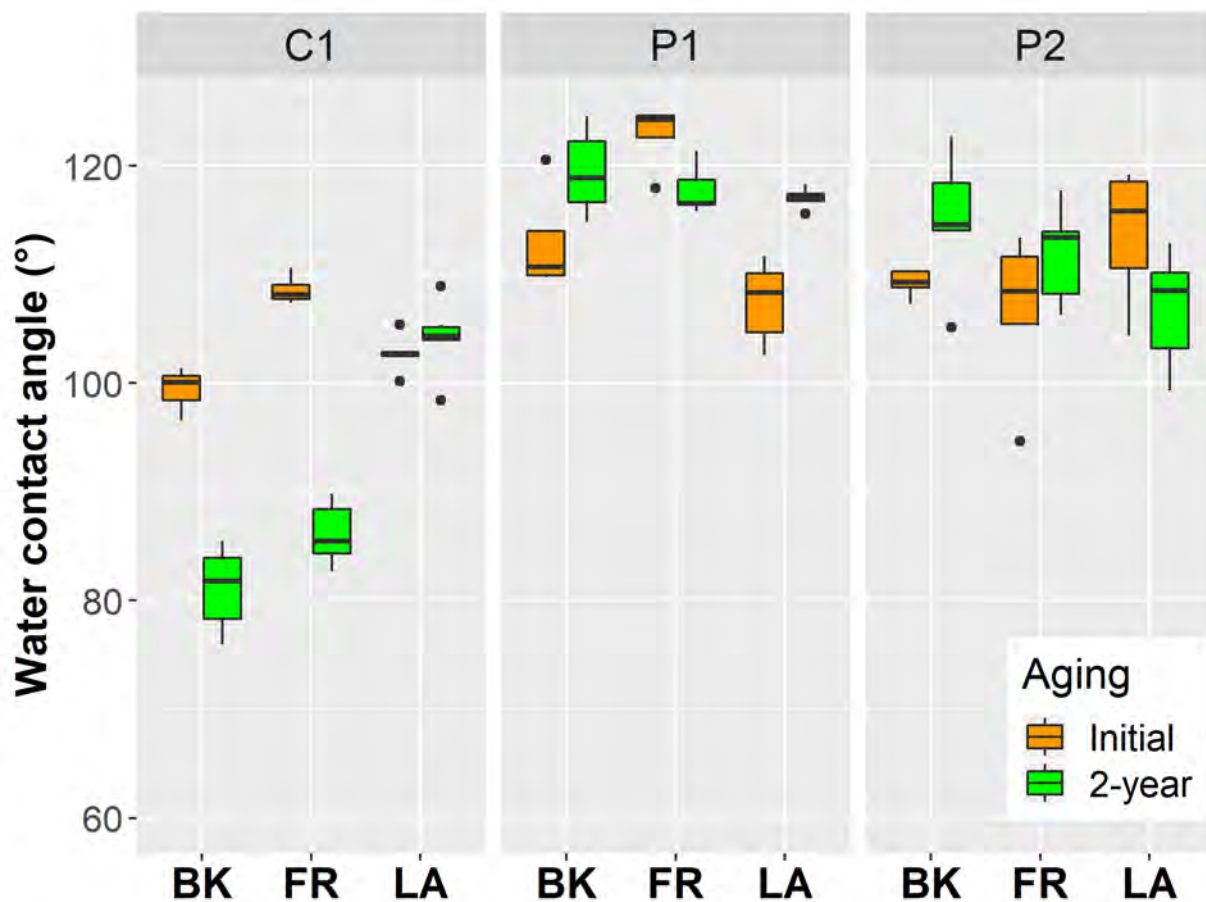
263 hydrophilicity (e.g., salts or organic acids). Contact angles measured in the P1 and P2 samples
264 did not show a significant change after two years of exposure. Those aged samples remained
265 within $\pm 6^\circ$, on average, with respect to the contact angle of unexposed (pre-bleached)
266 specimens. This result agrees with another report in the literature showing small changes in
267 surface hydrophilicity of photocatalytic building coatings subjected to accelerated climatic aging
268 [72]. By contrast, field aging of TiO₂-modified polymeric coatings showed a significant decrease
269 in contact angle values after one year of field exposure in an urban setting [23]. The small
270 contact angle changes observed in aged samples P1 and P2 on our study are consistent with the
271 limited accumulation of atmospheric deposition and soiling material on these photocatalytic
272 surfaces. These small changes in contact angle are consistent with the negligible changes
273 observed in albedo, as described below.

274 Some photocatalytic materials are known to become more hydrophilic under irradiation,
275 through photoinduced superhydrophilicity, with liquid water films facilitating the self-cleaning
276 effect by mechanical removal of particles and adsorbates from the surface [36-38]. However,
277 contact angle measurements in this study were performed in the absence of UV illumination,
278 and for that reason these tests did not explore the contribution of photoinduced hydrophilicity
279 to self-cleaning properties. The goal of these measurements, instead, was to assess changes in
280 hydrophilicity at the catalyst surface, primarily due to atmospheric deposition. Other possible
281 chemical changes could be attributed to material degradation, leading to the possible
282 photocatalyst loss over the exposure period, but SEM-EDS analysis of the surface prior and after
283 exposure showed that the content of TiO₂ was retained over the two-year field aging period (as
284 described in Section 3.2.2, below).

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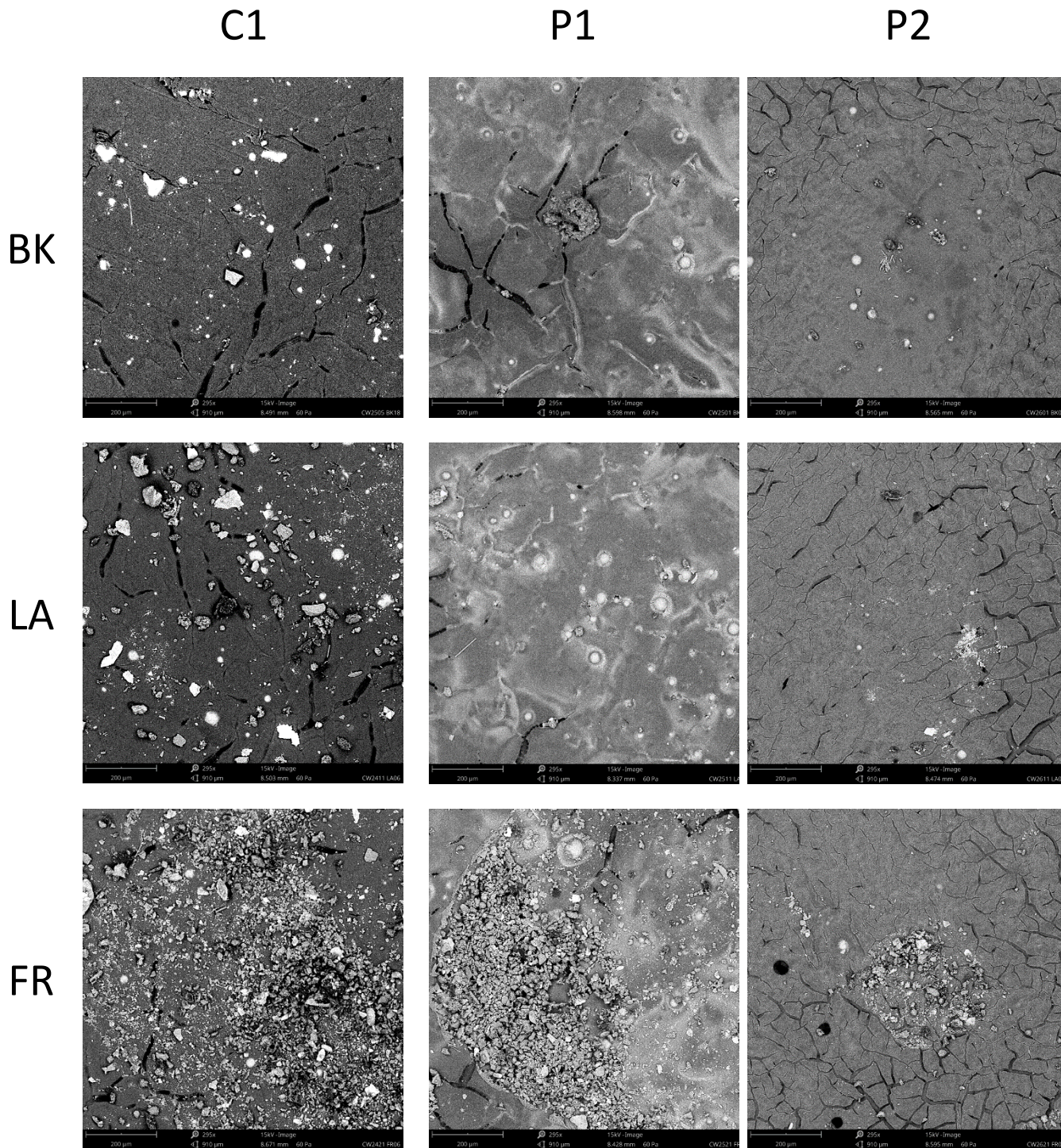
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290 **Figure 3.** Water contact angles measured before and after two years of natural exposure in three
291 California sites. The central line in each boxplot represents the median of six measurements, and the top
292 and bottom of the box the two central quartiles. Highest and lowest values in the distribution are shown
293 with whiskers, except for outliers falling beyond 1.5 times the interquartile range, IQR (black circles).

294 **3.2.2 Microscopic analysis**

295 The chemical nature and morphology of soiling particles was assessed by SEM-EDS. Analyses
296 included specimens from the three samples (C1, P1 and P2), exposed at the three locations
297 after six months of exposure. These corresponded to the highest level of soiling over the entire
298 study period. Microscope images of 1 mm by 1 mm regions on each specimen's surface are
299 shown in Figure 4. In each case, the images are a good representation of the whole sample. The
300 background in all images corresponds to the fluorinated polymer coating applied to the
301 fiberglass fibers of the architectural membrane, which in the case of P1 and P2 was
302 functionalized with photocatalytic TiO₂. Cracks shown on the polymer are not related to
303 exposure in the environment. These are features present in the unexposed material, as shown
304 in Figure S3 (Supporting Information).

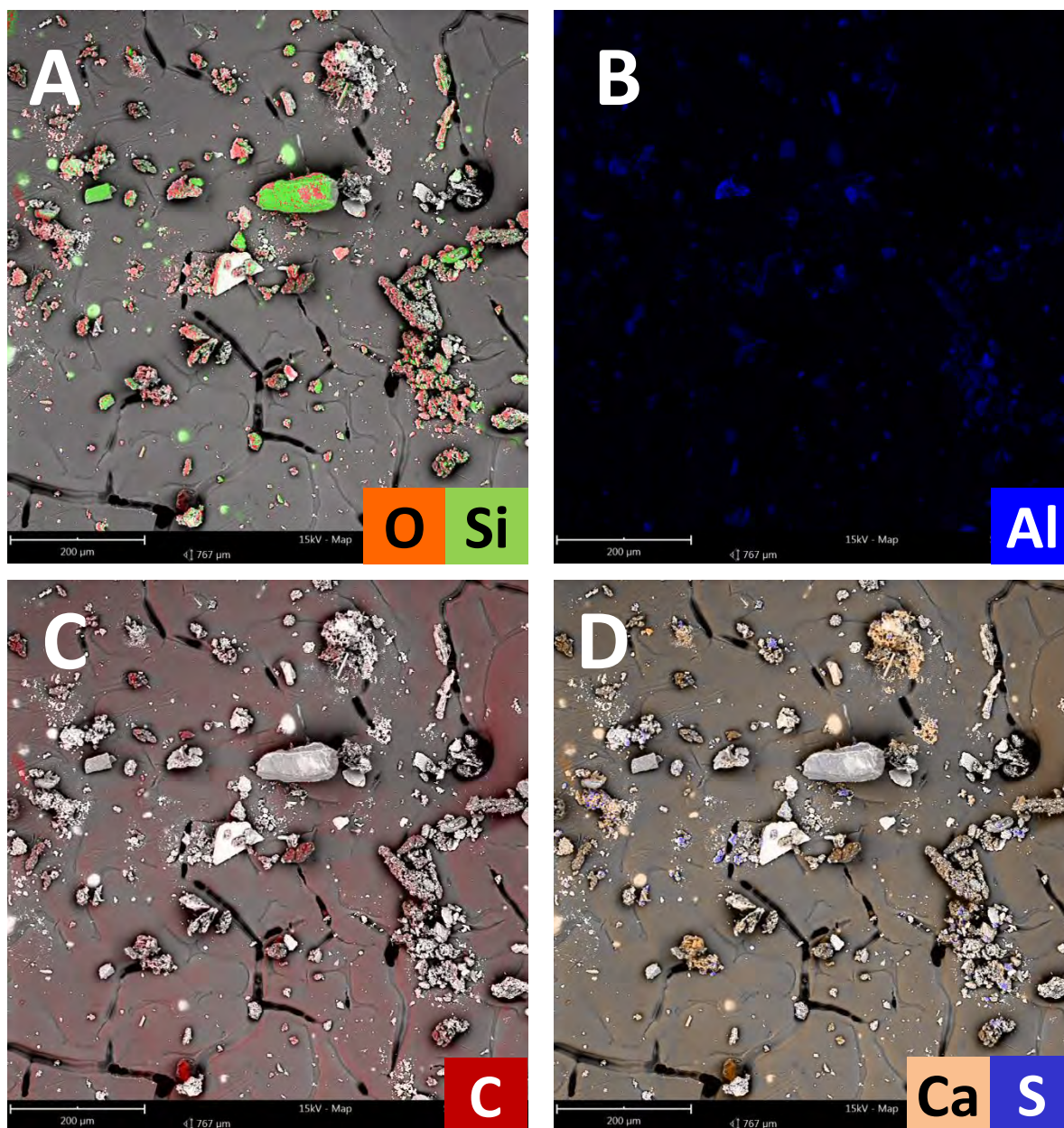
305 Particle deposition on specimens of control sample C1 was greater in Fresno than in Los
306 Angeles. By contrast, those exposed in Berkeley were the cleanest. In each of the exposure
307 sites, images of the two photocatalytic samples P1 and P2 showed less soiling than those of the
308 control sample C1. These results are consistent with visual inspection of the specimens and
309 with albedo measurements.



310 **Figure 4.** SEM images of C1 (control), P1 and P2 samples after six months of exposure at the Berkeley
311 (BK), Los Angeles (LA), and Fresno (FR) sites, showing soiling particles deposited on the surface. Image
312 magnification: 295x. Image size: 1 mm by 1mm.

313

314



315

316 **Figure 5.** SEM-EDS surface map of a C1 sample exposed in Los Angeles for six months. The soiling is
317 mostly composed of aluminosilicates, with particles containing (A) oxygen and silicon; (B) aluminum, (C)
318 carbon (soot); and (D) calcium and sulfur. Small amounts of phosphorus and nitrogen were also found in
319 some samples (not shown).

320 Analysis by SEM-EDS permitted a qualitative chemical characterization of soiling particles,
321 illustrated in Figure 5 for sample C1 after six months of exposure in Los Angeles. Additional
322 evidence is also presented as Supporting Information in Figure S4 (full SEM image) and Figure
323 S5 (surface map of soiling constituents). Elemental constituents of soiling particles included
324 oxygen, silicon, aluminum, carbon, calcium, sulfur, phosphorus and nitrogen. Larger particles
325 were primarily silica and alumino-silicates (Figure 5a and 5b). Carbon-containing particles were
326 often associated with calcium (Figure 5c and 5d). The carbon content is likely attributed to soot
327 particles. Sulfur was found in small aggregates (Figure 5d). Phosphorus and nitrogen (not shown
328 in Figure 5) were found occasionally in small quantities. This qualitative identification of several
329 elements confirmed the presence of common soiling constituents that had previously been
330 reported, including black carbon (soot), mineral dust (metal oxides, clays), inorganic salts
331 (containing Na^+ , Ca^{2+} , Cl^- and SO_4^{2-} as main ionic constituents) and organic matter [73]. This
332 analysis does not allow for a quantitative comparison between different locations, or between
333 photocatalytic and control materials, which showed presence of similar chemical species.

334 SEM-EDS analysis was also used to quantify Ti in unexposed and two-year exposed specimens,
335 to assess potential catalyst losses due to material weathering upon exposure to the
336 environment. It was observed that the amount of Ti remaining on the surface after 2 years in
337 the field was $95\% \pm 10\%$ for P1, and $112\% \pm 10\%$ for P2. These results suggest that there was no
338 significant catalyst loss during the two-year exposure period, consistent with findings from field
339 testing [56] and laboratory accelerated testing [55]. While those studies were carried out using
340 other photocatalytic construction (cementitious) materials, one common characteristic is that
341 TiO_2 additives were embedded in the material (rather than adsorbed as a coating), providing
342 greater durability.

343 **3.3 Evaluation of the self-cleaning effect**

344 **3.3.1 Visual inspection**

345 The self-cleaning effect was visible to the naked eye, as illustrated in Figure 6 for specimens
346 exposed in Fresno. Images from the other two sites show the same trends. Specimens of C1

347 were much more soiled than those of P1 and P2, leading to appreciable darkening and
348 formation of dust and particle clusters. This effect was more marked during the dry season and
349 was significantly reduced during the rainy season. The effect was also stronger in specimens
350 exposed in Los Angeles and Fresno, with respect to those aged in Berkeley.

351 **3.3.2 Albedo measurements**

352 Measurements of albedo as a function of exposure time confirmed that when the white control
353 sample C1 became dirtier, its albedo was reduced. Figure 7 compares, for each of the three
354 sites, the albedo recorded for the control sample C1 with that measured on the photocatalytic
355 samples P1 and P2. Both photocatalytic products showed a remarkable retention of the initial
356 albedo over the two-year study period in the three exposure sites, with minimal changes that
357 were in most cases of the same magnitude as the experimental error. For sample P1, the
358 average albedo comprising all specimens measured over two years was 0.745 ± 0.003 (BK),
359 0.741 ± 0.005 (LA) and 0.740 ± 0.006 (FR), compared with the initial measurement of $0.743 \pm$
360 0.001 . Similarly, for sample P2 it was 0.752 ± 0.006 (BK), 0.745 ± 0.007 (LA) and 0.746 ± 0.010
361 (FR), compared with the initial measurement of 0.747 ± 0.002 .

362 Results obtained for each site showed that specimens exposed in Los Angeles and Fresno were
363 more affected by soiling than those exposed in Berkeley. This is due to the presence of stronger
364 sources of atmospheric pollution in the proximity of the materials, as evidenced by higher $PM_{2.5}$
365 levels during the dry season at those sites. All three sites showed seasonal variations in the
366 albedo of the control specimen C1, falling during the dry season and rising during the rainy
367 season. The largest albedo difference (photocatalytic material minus control material) was 0.10,
368 and was observed in Los Angeles and Fresno during the summer of 2016. The gap between the
369 albedo of photocatalytic and control materials was reduced during the rainy season, due to the
370 cleaning of the control material by rain, which brought the albedo of the C1 specimens to
371 values closer to those from the P1 and P2 specimens.

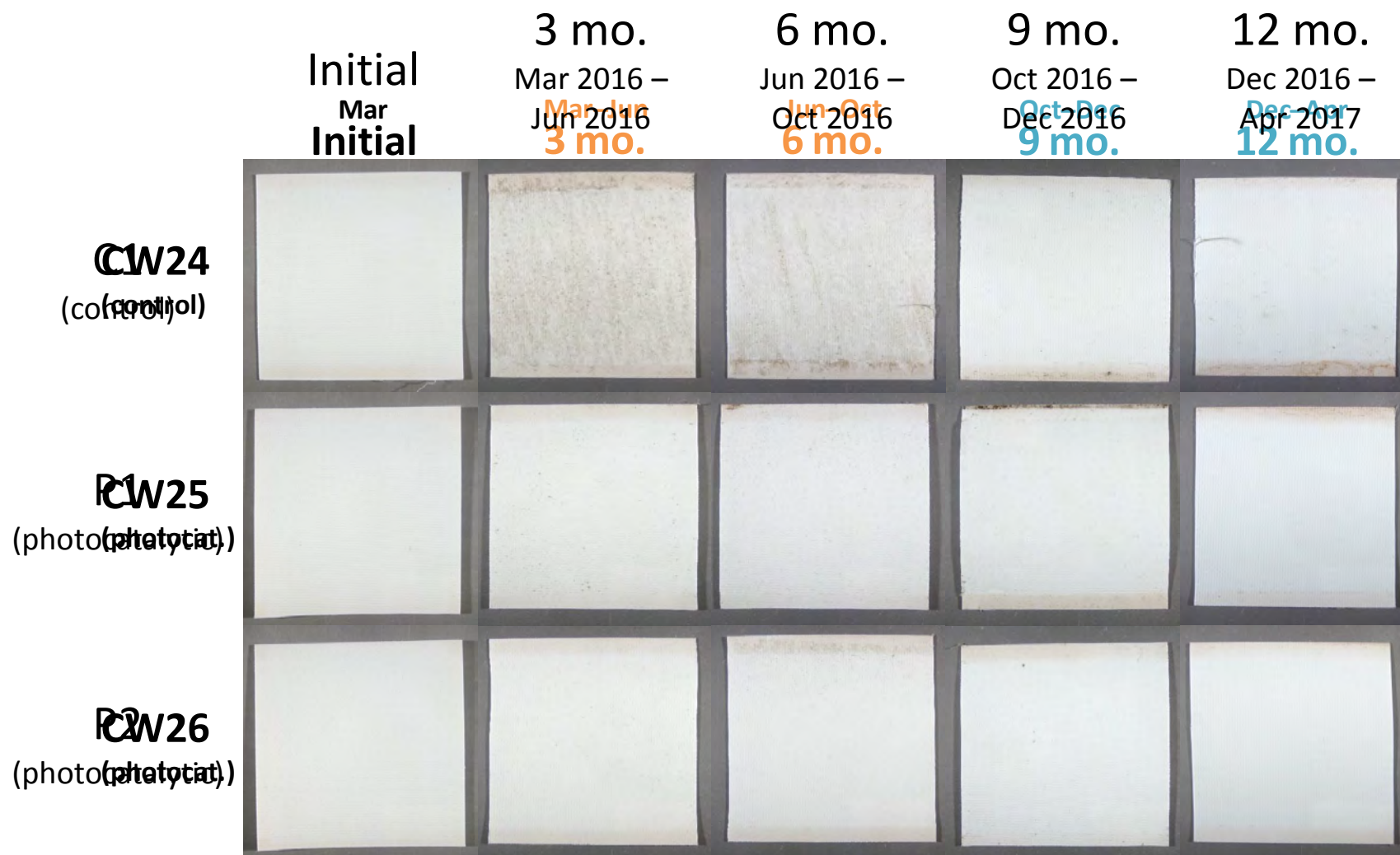


Figure 6. Images of specimens exposed at the Fresno site. Image size: 10 cm by 10 cm.

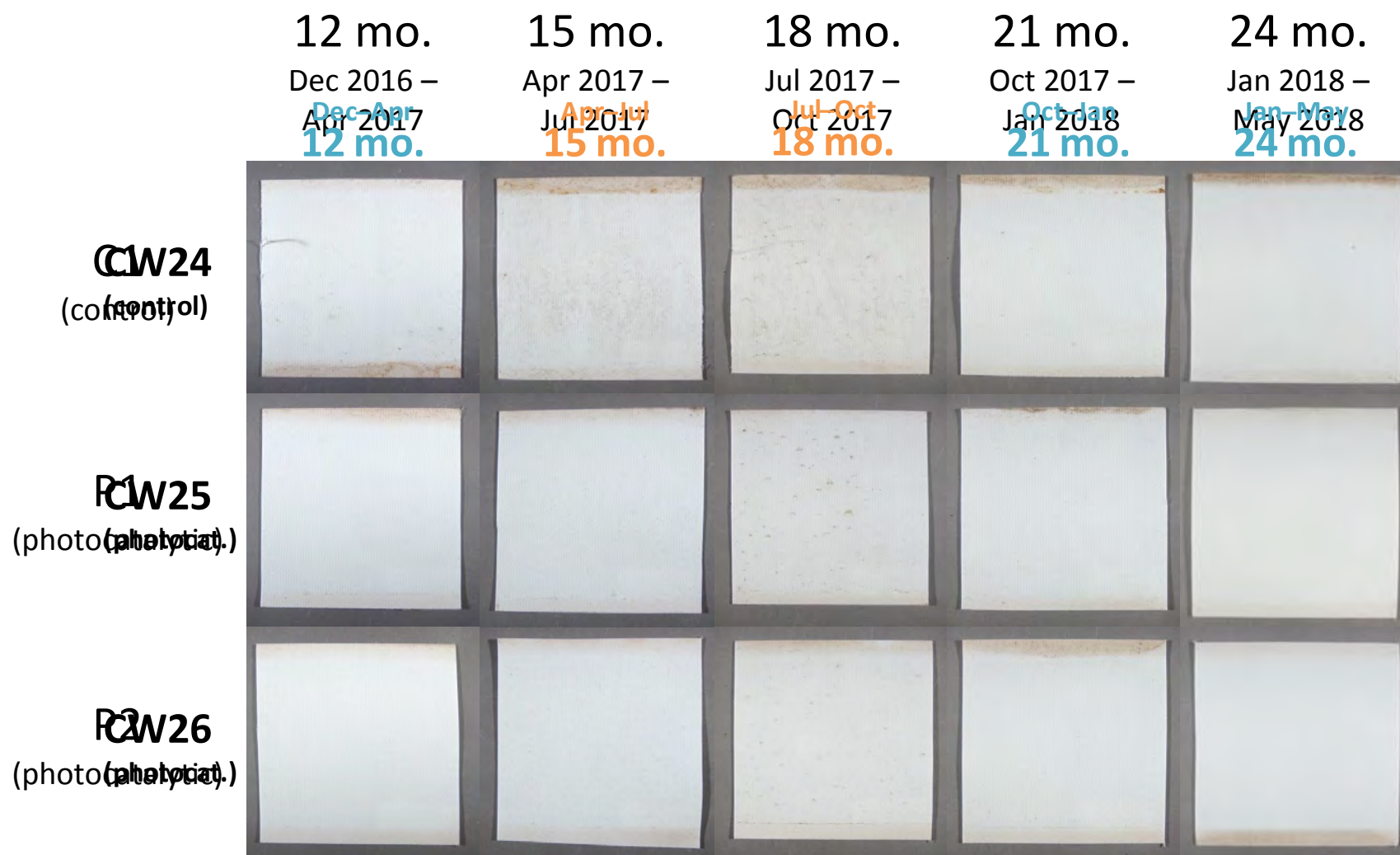
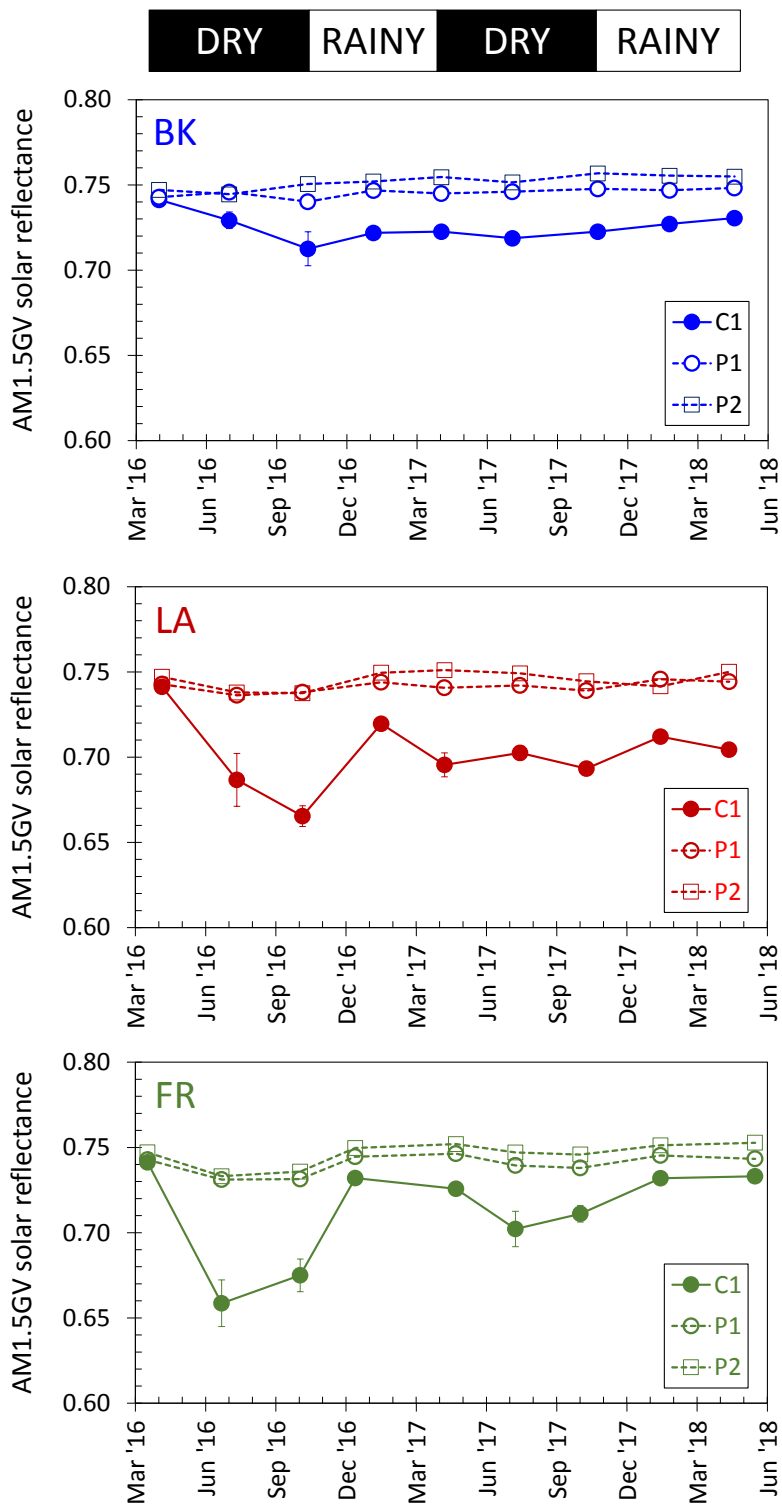


Figure 6. (Cont'd).



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Figure 7. Air mass 1.5 global vertical (sun-facing) solar reflectance (albedo) of architectural fabric C1 (control) vs. samples P1 and P2 (photocatalytic) measured in the Berkeley (BK), Los Angeles (LA), and Fresno (FR) sites.

368 **3.4 Evaluation of the de-pollution effect**

369 **3.4.1 NO and NO₂ concentration profiles**

370 Figure S1 (Supplemental Information) illustrates experimental results obtained in a typical
371 experiment carried out to evaluate the NO_x removal efficiency of the photocatalytic specimens
372 and the control material. On the x-axis, $t = 0$ corresponds to the time at which the UV lamp was
373 turned on. Before the UV lamp was turned on, the material reached equilibrium with the NO-
374 enriched atmosphere in the dark. When the control specimen C1 was used, no changes in NO
375 and NO₂ concentrations were observed under UV light, indicating that there was no reaction
376 taking place upon irradiation alone (Figure S1-A). However, when specimens from the materials
377 P1 and P2 were used, the NO and NO₂ curves showed features similar to those presented in
378 Figure S1-B. There was an initial sharp decline in NO concentrations, accompanied by an
379 increase in NO₂ concentrations. Subsequently, NO concentrations increased asymptotically
380 reaching a steady-state value after about 3 h of irradiation. During the same period, NO₂
381 concentrations declined reaching a plateau at the same time. After six hours of irradiation, the
382 UV lamp was turned off, and both NO and NO₂ concentrations rapidly recovered their initial
383 values (ca. 1000 ppb and 0 ppm, respectively). Measurements continued during approximately
384 1 h in the dark, to establish final equilibrium conditions.

385 **3.4.2 NO removal rates**

386 From the integration of the curves shown in Figure S1, the rate of NO elimination was
387 calculated using Eqs. (1) and (2). The NO removal rate is reported in Figure 8 for P1 and P2
388 specimens as a function of the exposure duration. The elimination of NO was the primary
389 photocatalytic process, which led to the formation of NO₂ and nitrate [74-77]. The P1 sample
390 showed a significantly higher NO elimination efficiency with respect to P2 in all three sites and
391 almost all weather conditions. Based on the results presented in Figure 8, the photocatalytic
392 activity of product P1 declined in all three sites during the dry season. This is likely due to
393 deposition and attachment of soiling agents onto the catalyst surface. Specimens exposed in
394 Berkeley and Fresno recovered their photocatalytic activity after a year of exposure, at the end

395 of the first rainy season. In Berkeley, the recovered activity exceeded the initial performance of
396 unexposed materials. This may have resulted from additional activation of the catalyst upon
397 environmental exposure over time. This activation could be caused by the removal of surface
398 coatings remaining from the manufacturing process, or by abrasion of the polymer matrix,
399 either of which could expose more catalyst particles. By contrast, the albedos of specimens
400 exposed in Los Angeles did not increase during the rainy season. This is likely due to less rain in
401 Los Angeles, and may also reflect the fact that the chemical nature of soiling in all three sites is
402 different. In the case of sample P2, NO removal rates were lower, but still showed some of the
403 same seasonal effects. For sample P2, specimens exposed in Fresno that were retrieved during
404 the dry season showed negative values of the NO removal rate, as NO concentrations
405 downstream of the test chamber were slightly higher than those measured upstream in the
406 challenge gas. This effect can be attributed to the possible presence of ammonium salts, and
407 possibly other reduced nitrogen contaminants, as part of the soiling mixture deposited on the
408 specimen surface. The photocatalytic oxidation of these species has been shown to produce
409 both NO and NO₂ [78].

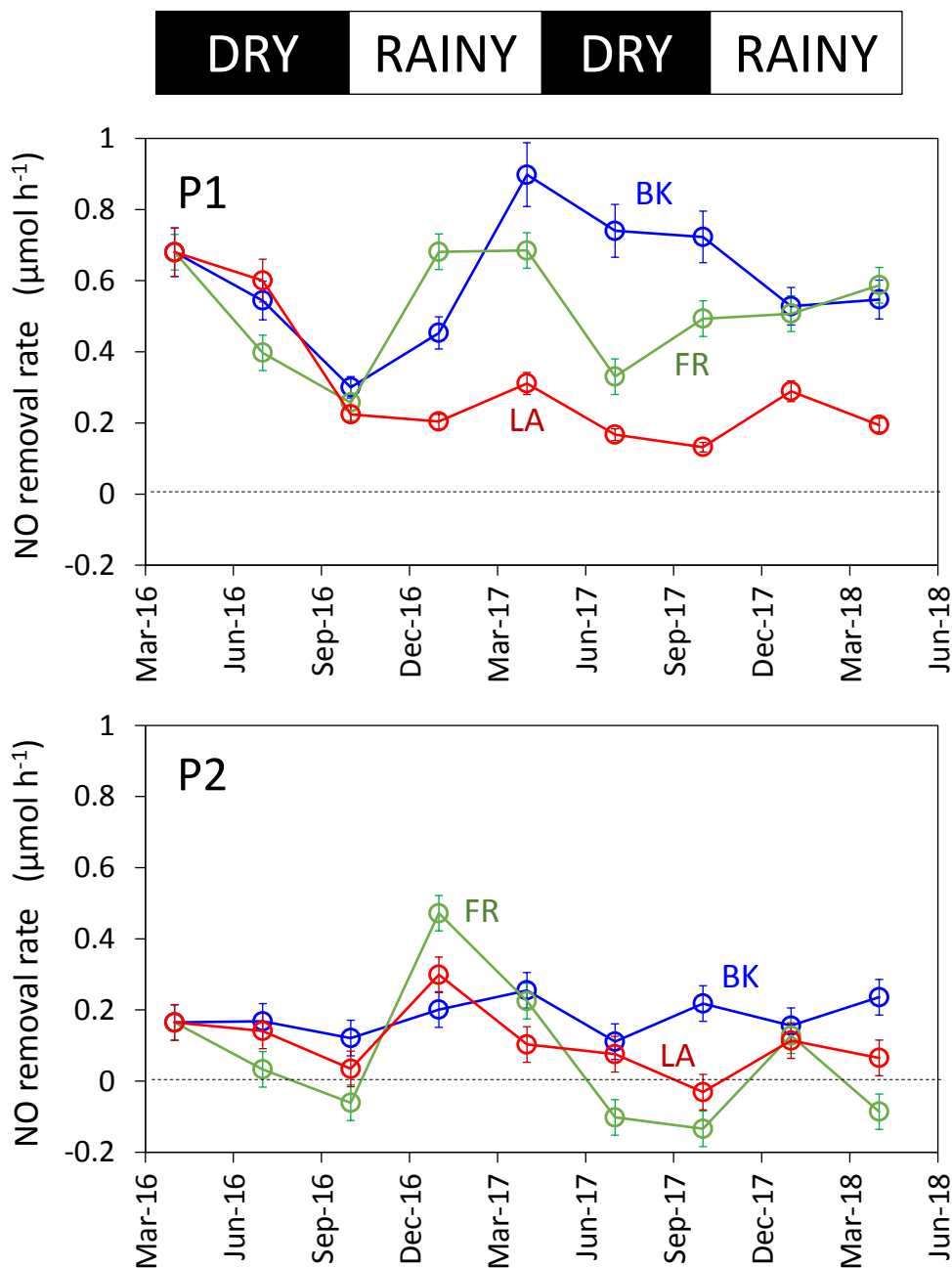
410 **3.4.3 NO_x deposition rates**

411 By subtracting the NO₂ formation rate from the NO removal rate, it was possible to determine
412 in each case the NO_x deposition rate, which is presented in Figure 9 for both photocatalytic
413 samples. Overall, the NO_x deposition rate was slower than the NO removal rate (primary
414 photocatalytic process), because a large fraction of NO was converted to NO₂, and did not
415 contribute to NO_x elimination. However, there was a net NO_x deposition rate in most
416 conditions. Similar to trends described above for NO removal, sample P1 was more effective in
417 the deposition of NO_x than sample P2. The P1 sample showed positive values for the NO_x
418 deposition rate for specimens exposed in all three sites over the entire exposure period, except
419 for one specimen in Fresno. In some cases, the NO_x deposition rate of aged materials was
420 higher than that determined for unexposed samples, owing to catalyst activation and soiling
421 removal as described above. The P2 sample showed negative NO_x deposition rates in Fresno
422 over the whole exposure period. In addition, a few specimens exposed in Los Angeles also had

423 negative values. As described above, these negative values represent higher downstream than
424 upstream concentrations, which can be attributed to the photocatalytic oxidation of nitrogen-
425 containing species in soiling material deposited on the specimens. This is particularly relevant
426 for ammonia aerosols, which are commonly found in rural environments with agricultural
427 activities such as the one surrounding the Fresno site [79].

428 While the photocatalytic materials were very effective in preventing albedo losses by removing
429 soiling agents that could be visualized with the naked eye and microscopy tools, it is likely that
430 some recalcitrant oxidation byproducts can remain attached to the catalyst and build up over
431 time during the dry season. Examples of those recalcitrant species are carboxylic and
432 polycarboxylic acids, which have a low vapor pressure and can attach to active sites, thus
433 partially inhibiting the catalysts ability to react with NO_x and other atmospheric species [80-82].
434 Similarly, inorganic species such as soluble salts formed as byproducts of the photocatalytic
435 process or present in atmospheric deposition could deactivate the catalyst [53, 54, 77]. This
436 effect can be reduced during the rainy season because, while those species are not volatile,
437 they are water soluble and can be dissolved and removed by liquid water present on the
438 surface.

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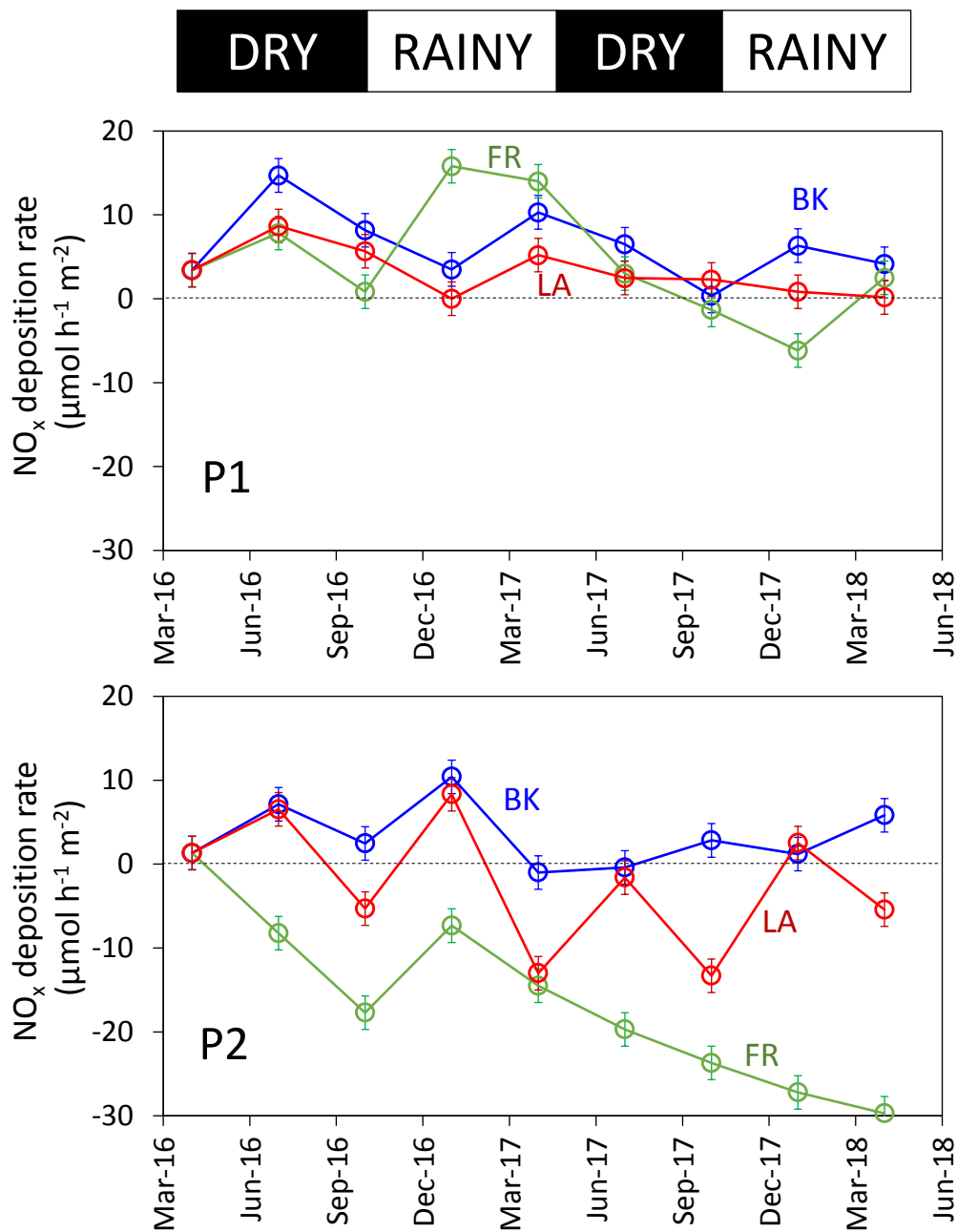
441

442 **Figure 8.** Laboratory-measured rates of NO removal by photocatalytic samples P1 and P2 exposed in
443 Berkeley (BK), Los Angeles (LA), and Fresno (FR). The control sample C1 did not catalyze the
444 elimination of NO.

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450 **Figure 9. Laboratory-determined** NO_x deposition rate over photocatalytic samples P1 and P2, exposed
 451 at the Berkeley (BK), Los Angeles (LA), and Fresno (FR) sites. The control sample C1 did not catalyze
 452 the elimination of NO_x.

453

454 **4 Conclusions**

455 This study illustrated the performance of advanced building materials under realistic conditions
456 over a long enough duration to assess initial changes and seasonal effects. The materials were
457 exposed in three different sites with different levels and chemical composition of atmospheric
458 pollution. Both photocatalytic products (P1 and P2) showed an excellent self-cleaning
459 performance in all three California sites and during all seasons. The photocatalyst additives can
460 successfully protect the surface from soiling buildup, preserving its original appearance and
461 energy benefits.

462 By contrast, the de-pollution effect showed a marked effect of both the exposure location and
463 weather. The de-pollution capacity of sample P1 was significantly higher than that of sample
464 P2, illustrating the critical role of product formulation in achieving the desired performance.
465 These results suggest that photocatalytic materials can achieve good self-cleaning results even
466 in cases in which they have limited capacity for atmospheric de-pollution. While NO removal
467 and a net NO_x deposition were observed in most cases, there were fluctuations that were
468 associated with the effects of atmospheric deposition (partial inhibition) and precipitation (re-
469 activation).

470 Future work should explore the effects of other climate and pollution conditions different from
471 those found in California, and durability of the photocatalyst performance over longer periods.
472 Other photocatalytic building materials should also be assessed under realistic exposure
473 conditions over long periods of time, such as those reported here.

474

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481

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