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

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Abstract

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

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

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

The self-cleaning effect is due to the ultraviolet (UV) light catalyzed oxidation of deposited soiling, in combination with its physical removal due to enhanced surface hydrophilicity activated by sunlight [28, 29]. Self-cleaning activity has been documented primarily in laboratory tests—e.g., by measuring the loss of deposited soot [30, 31] or bleaching of a dye applied on the surface [32, 33] as a function of UV irradiation. Tracking the dye bleaching rate is
the basis for standardized methods that quantify the self-cleaning effect [34, 35].

Superhydrophilicity (very low water contact angle) has been observed in TiO$_2$-coated materials under UV irradiation [36-38]. This property is used in ISO Standard 27448 to test the self-cleaning performance of photocatalytic materials [39].

An environmental benefit that has been well documented in laboratory tests is the photocatalytic elimination of atmospheric pollutants in contact with the catalyst surface, including volatile organic compounds (VOCs) [40-42] and atmospheric nitrogen oxides (NO$_x$ = NO + NO$_2$) [43]. In the case of NO$_x$, photocatalytic oxidation enables a net removal of these species from the atmosphere through their irreversible conversion to the non-volatile oxidation byproducts nitrate (NO$_3^-$) and HNO$_3$. The final stable oxidation byproducts can be washed off the surface by rain or dew. Different test methods have been developed to evaluate the air purification efficiency of photocatalytic materials by following NO$_x$ elimination [44-46]. One of the most commonly used is the ISO Standard 22197-1, which relies on quantifying nitric oxide (NO) elimination under controlled air flow, temperature, humidity and illumination conditions [47].

Both self-cleaning and de-polluting properties of photocatalytic construction materials have been evaluated in a number of field demonstrations. The effective removal of NO$_x$ from urban air was demonstrated using a cement-based photocatalytic coating [22], a mineral-based paint [48], and paving materials [49, 50]. However, other studies found a significantly weaker effect [51, 52]. Photocatalytic performance can be affected by soiling deposition and loss of photocatalyst due to abrasion and material weathering [53, 54]. Some studies report a relatively low depletion of the photocatalyst, with at least 80% retention after a prolonged exposure to the environment of up to two years [55, 56]. By contrast, materials in which the photocatalyst was deposited as a coating without a strong attachment to the substrate yielded higher catalyst depletion rates [54, 57].

This study investigated the performance of photocatalytic architectural membranes exposed under real-world conditions. Architectural membranes are highly versatile materials used in building envelopes as energy-efficient roofs, façades, canopies and skylights that provide
diffuse natural daylight to indoor environments. In addition to reducing their albedo, soiling deposition onto translucent membranes can reduce the fraction of light transmitted through the material [58, 59]. For that reason, photocatalytic TiO$_2$ coatings are promising, as they have been shown to impart self-cleaning functionalities to fabrics [60]. Membranes based on fluoropolymer materials, such as those reported here, have been shown to serve as substrates for photoactive additives that imparted self-cleaning and anti-microbial activity [61-63]. The main goal of this study was to quantify the performance of photocatalytic membrane specimens that had been aged alongside a non-photocatalytic control material. Self-cleaning properties were quantified in terms of albedo loss, and de-polluting properties were evaluated by following NO removal rate and the NO$_x$ deposition rate as a function of exposure time. Specimens were exposed to the environment at three locations in California: Berkeley, downtown Los Angeles, and Fresno over a two-year period.

2 Methodology

2.1 Exposed materials

The architectural membrane samples used in this study, manufactured under the Sheerfill® brand name, were provided by Saint Gobain. Non-photocatalytic versions of this product, made of polytetrafluoroethylene (PTFE)-coated fiberglass, have been in use for over 45 years as roofing and façade membranes. TiO$_2$-coated photocatalytic membranes have been in the market for about 10 years. The two different photocatalytic materials tested here were labeled “P1” and “P2”, and corresponded to standard and alternative formulations of the Sheerfill II EverClean product. General characteristics of these materials have been previously described elsewhere [64]. Specimens of each of these samples were exposed alongside a matching control sample “C1” (standard, non-catalytic Sheerfill II membrane). The C1 sample had the same characteristics as P1 and P2, except for the photocatalytic functionality. Replicate 10 cm by 10 cm specimens of each sample were prepared for exposure to the environment. These samples were a subset of a larger “Cool Walls” study, which is reported elsewhere [7]. The
corresponding codes for the Cool Walls study were CW25 (sample P1), CW26 (sample P2) and CW24 (sample C1, control). The as-received color of all samples was tan, which bleached to off-white after several weeks of solar exposure. Per manufacturer’s instructions, the initial albedo of previously unexposed architectural membranes was measured on specimens that had been pre-bleached in the laboratory by exposure to UV light in a laboratory weathering apparatus (Model Q-UV, Q-Lab Corporation, Westlake, OH) for seven days. The pre-bleaching was necessary to obtain samples representative of field installations. It simulates a process which occurs under natural sunlight to turn the products from tan to white, as per the manufacturer’s documentation.

2.2 Setup of exposure sites

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

a) BK: a roof at the Lawrence Berkeley National Laboratory in Berkeley (San Francisco Bay Area, 37.87° N, 122.27° W);

b) LA: a parking lot at the University of Southern California, in downtown Los Angeles (34.05° N, 118.24° W); and

c) FR: a ground-level, uncovered concrete surface within a site belonging to an industry partner in Fresno (Central Valley, 36.74° N, 119.79° W).

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

Exposure racks were designed and built to hold a maximum of 280 specimens, arranged in 14 rows of 20 specimens each. The rows were horizontally staggered to prevent contamination between vertically adjacent specimens. Racks were built in-situ at the three California sites between March and April 2016, and specimens from different materials were installed
immediately after their construction, including those corresponding to the architectural membrane samples P1, P2 and C1 [65]. Ten specimens of each sample were installed at each of the three sites at the onset of the experiment. Specimens were mounted vertically, facing west. Figure 1 illustrates the racks used to expose specimens, and a photo of an individual architectural membrane specimen. Given the flexibility of this material, it was kept secured against the wood backing by clamping on the top and bottom sections.

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

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

a) USC00040693, in Berkeley, 3.2 km southeast of the Berkeley exposure site;
b) USW00093134, on the University of Southern California (USC) campus, 1.4 km west of the Los Angeles exposure site; and

c) USW00093193, at the Fresno Yosemite International Airport, 9.9 km north of the Fresno exposure site

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

2.3 Experimental procedures

2.3.1 Specimen retrieval, shipping, characterization, and storage

Ten identical specimens from each of the products (P1, P2 and C1) were exposed side-by-side. One specimen from each sample was retrieved quarterly from each site at approximately the same time, following the schedule presented in Table S1 (Supporting Information). Specimens were packed in individual glassine envelopes, and shipped to LBNL for laboratory analysis. The samples were stored inside the same envelopes prior and after laboratory measurements. There was no exposure to the environment after the specimens were retrieved from the racks.

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

The image of each specimen was obtained with a digital camera (Canon PowerShot S90, Melville, NY) using a setup that provided consistent lighting conditions. An 18% grey card was used as the background.
The static water contact angle was measured on the surface of unexposed samples, and on specimens that were exposed for two years on each site, with a Theta optical tensiometer (Biolin Scientific, Gothenburg, Sweden) using the sessile drop method.

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

### 2.3.2 Measurement of the de-pollution performance

The methodology used to evaluate the de-pollution performance was adapted from the previously mentioned ISO Standard 22197-1 [47]. A flow of 3 L/min of laboratory air was pretreated with an activated carbon bed and a HEPA filter, and enriched with 1000 ppb nitric oxide (NO) prior to entering the exposure chamber. The relative humidity (RH) was adjusted to 50% by splitting the air flow, then circulating one of the flows through a water bubbler. Two mass flow controllers were used to adjust the desired RH. In the exposure chamber, a specimen from either sample P1, P2 or C1 was installed facing upwards in the center. A UV-A lamp with maximum intensity at about 360 nm (Model TL-D, Actinic BL, Philips, Andover, MA) was used to irradiate the specimen through a quartz window on the chamber’s cover. The exposed surface area for each specimen was 0.01 m². The distance between the window and the specimen was 5 mm. UV irradiance (320 - 400 nm; peak sensitivity at 360 nm) was measured using a digital radiometer (Model UVX, UVP LLC, Upland, CA). It was highest at the center of the sample and consistent over the exposed surface, with an average of 11.5 ± 1.5 W/m². The stability of the lamp during the experimental period was verified by repeating irradiance measurements at different times.
In previous work using the same setup, it was observed that raising the surface temperature from 25 °C to 60 °C increased the NO\textsubscript{x}-removal efficacy of photocatalytic surfaces [26]. Here, the surface temperature was kept at 60 °C using an external circulating bath, to simulate conditions that are close to those found on building surfaces under the sun. Air exiting the chamber was split into two flows; one of them was directed to a chemiluminescence NO\textsubscript{x} analyzer (Model 200A, Teledyne Technologies, Thousand Oaks, CA), which was calibrated at different times during the testing period. The other chamber air stream was used to measure air temperature and RH at the outlet prior to venting in a fume hood, using an in-line digital HIH6100 series T/RH sensor (Honeywell, Charlotte NC). NO and NO\textsubscript{2} concentrations at the reactor outlet, air temperature and RH in the chamber, and chamber (surface) temperature were measured at 0.2 Hz.

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

a) pre-equilibration under a constant flow of NO-enriched air in the dark (about 1 h);

b) continuous UV irradiation under a constant flow of NO-enriched air (about 6 h), and

c) post-equilibration under a constant flow of NO-enriched air in the dark (about 1 h)

Figure S1 (Supporting Information) illustrates curves corresponding to typical NO and NO\textsubscript{2} traces. Removal rate of NO ($r_{NO, \mu mol \cdot h^{-1}}$) and formation rate of NO\textsubscript{2} ($r_{NO_2, \mu mol/h}$, from oxidation of NO) were calculated using the difference between the inlet and outlet concentrations of NO and NO\textsubscript{2}, as follows:

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

$$r_{NO_2} = \frac{\int_0^\tau n_{NO_2} \text{formed} \, dt}{\tau} = \frac{\int_0^\tau (c_{NO_2_{out}} - c_{NO_{2i}}) \, dt}{\tau} \times \frac{Q}{V_n}$$ (2)
where \( Q \) is the flow rate (L min\(^{-1} \)), \( \tau \) is the irradiation duration (h), \( t \) is the time (h) and \( V_n \) is the normalized gas volume for one mole of gas at standard pressure and room temperature (22.4 L).

The \( \text{NO}_x \) deposition rate was computed as the difference between NO removal and \( \text{NO}_2 \) formation rates per unit area, expressed in moles (\( R_{\text{NO}_x} \), \( \mu \text{mol h}^{-1} \text{m}^{-2} \)). Assuming that nitrate and \( \text{NO}_2 \) are the only NO oxidation byproducts, \( R_{\text{NO}_x} \) can be used to calculate the rate of nitrate formation. This prediction corresponds to the maximum nitrate formation rate that can be observed, and allows for an estimation of the maximum nitrate surface concentration, as illustrated in Figure S1-B.

3 Results and discussion

3.1 Weather and air pollution measurements at each site

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

3.2.1 Contact angle measurements

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

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

In two of the three sites, the control sample C1 showed a significant reduction in contact angle after two years of exposure, reaching an average of 81° in Berkeley, and an average of 85° in Fresno. Such reduction in contact angle on the non-photocatalytic sample is consistent with similar trends reported in the literature for limestone [54] and polymeric coatings [23]. These may be associated with buildup of soiling materials, some of which may contribute to surface
hydrophilicity (e.g., salts or organic acids). Contact angles measured in the P1 and P2 samples did not show a significant change after two years of exposure. Those aged samples remained within ±6°, on average, with respect to the contact angle of unexposed (pre-bleached) specimens. This result agrees with another report in the literature showing small changes in surface hydrophilicity of photocatalytic building coatings subjected to accelerated climatic aging [72]. By contrast, field aging of TiO$_2$-modified polymeric coatings showed a significant decrease in contact angle values after one year of field exposure in an urban setting [23]. The small contact angle changes observed in aged samples P1 and P2 on our study are consistent with the limited accumulation of atmospheric deposition and soiling material on these photocatalytic surfaces. These small changes in contact angle are consistent with the negligible changes observed in albedo, as described below.

Some photocatalytic materials are known to become more hydrophilic under irradiation, through photoinduced superhydrophilicity, with liquid water films facilitating the self-cleaning effect by mechanical removal of particles and adsorbates from the surface [36-38]. However, contact angle measurements in this study were performed in the absence of UV illumination, and for that reason these tests did not explore the contribution of photoinduced hydrophilicity to self-cleaning properties. The goal of these measurements, instead, was to assess changes in hydrophilicity at the catalyst surface, primarily due to atmospheric deposition. Other possible chemical changes could be attributed to material degradation, leading to the possible photocatalyst loss over the exposure period, but SEM-EDS analysis of the surface prior and after exposure showed that the content of TiO$_2$ was retained over the two-year field aging period (as described in Section 3.2.2, below).
Figure 3. Water contact angles measured before and after two years of natural exposure in three California sites. The central line in each boxplot represents the median of six measurements, and the top and bottom of the box the two central quartiles. Highest and lowest values in the distribution are shown with whiskers, except for outliers falling beyond 1.5 times the interquartile range, IQR (black circles).
3.2.2 Microscopic analysis

The chemical nature and morphology of soiling particles was assessed by SEM-EDS. Analyses included specimens from the three samples (C1, P1 and P2), exposed at the three locations after six months of exposure. These corresponded to the highest level of soiling over the entire study period. Microscope images of 1 mm by 1 mm regions on each specimen’s surface are shown in Figure 4. In each case, the images are a good representation of the whole sample. The background in all images corresponds to the fluorinated polymer coating applied to the fiberglass fibers of the architectural membrane, which in the case of P1 and P2 was functionalized with photocatalytic TiO$_2$. Cracks shown on the polymer are not related to exposure in the environment. These are features present in the unexposed material, as shown in Figure S3 (Supporting Information).

Particle deposition on specimens of control sample C1 was greater in Fresno than in Los Angeles. By contrast, those exposed in Berkeley were the cleanest. In each of the exposure sites, images of the two photocatalytic samples P1 and P2 showed less soiling than those of the control sample C1. These results are consistent with visual inspection of the specimens and with albedo measurements.
Figure 4. SEM images of C1 (control), P1 and P2 samples after six months of exposure at the Berkeley (BK), Los Angeles (LA), and Fresno (FR) sites, showing soiling particles deposited on the surface. Image magnification: 295x. Image size: 1 mm by 1mm.
Figure 5. SEM-EDS surface map of a C1 sample exposed in Los Angeles for six months. The soiling is mostly composed of alumino-silicates, with particles containing (A) oxygen and silicon; (B) aluminum, (C) carbon (soot); and (D) calcium and sulfur. Small amounts of phosphorus and nitrogen were also found in some samples (not shown).
Analysis by SEM-EDS permitted a qualitative chemical characterization of soiling particles, illustrated in Figure 5 for sample C1 after six months of exposure in Los Angeles. Additional evidence is also presented as Supporting Information in Figure S4 (full SEM image) and Figure S5 (surface map of soiling constituents). Elemental constituents of soiling particles included oxygen, silicon, aluminum, carbon, calcium, sulfur, phosphorus and nitrogen. Larger particles were primarily silica and alumino-silicates (Figure 5a and 5b). Carbon-containing particles were often associated with calcium (Figure 5c and 5d). The carbon content is likely attributed to soot particles. Sulfur was found in small aggregates (Figure 5d). Phosphorus and nitrogen (not shown in Figure 5) were found occasionally in small quantities. This qualitative identification of several elements confirmed the presence of common soiling constituents that had previously been reported, including black carbon (soot), mineral dust (metal oxides, clays), inorganic salts (containing Na\(^+\), Ca\(^{2+}\), Cl\(^-\) and SO\(_4^{2-}\)) as main ionic constituents) and organic matter \[73\]. This analysis does not allow for a quantitative comparison between different locations, or between photocatalytic and control materials, which showed presence of similar chemical species.

SEM-EDS analysis was also used to quantify Ti in unexposed and two-year exposed specimens, to assess potential catalyst losses due to material weathering upon exposure to the environment. It was observed that the amount of Ti remaining on the surface after 2 years in the field was 95% ± 10% for P1, and 112% ± 10% for P2. These results suggest that there was no significant catalyst loss during the two-year exposure period, consistent with findings from field testing \[56\] and laboratory accelerated testing \[55\]. While those studies were carried out using other photocatalytic construction (cementitious) materials, one common characteristic is that TiO\(_2\) additives were embedded in the material (rather than adsorbed as a coating), providing greater durability.

### 3.3 Evaluation of the self-cleaning effect

#### 3.3.1 Visual inspection

The self-cleaning effect was visible to the naked eye, as illustrated in Figure 6 for specimens exposed in Fresno. Images from the other two sites show the same trends. Specimens of C1
were much more soiled than those of P1 and P2, leading to appreciable darkening and formation of dust and particle clusters. This effect was more marked during the dry season and was significantly reduced during the rainy season. The effect was also stronger in specimens exposed in Los Angeles and Fresno, with respect to those aged in Berkeley.

### 3.3.2 Albedo measurements

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

Results obtained for each site showed that specimens exposed in Los Angeles and Fresno were more affected by soiling than those exposed in Berkeley. This is due to the presence of stronger sources of atmospheric pollution in the proximity of the materials, as evidenced by higher PM$_{2.5}$ levels during the dry season at those sites. All three sites showed seasonal variations in the albedo of the control specimen C1, falling during the dry season and rising during the rainy season. The largest albedo difference (photocatalytic material minus control material) was 0.10, and was observed in Los Angeles and Fresno during the summer of 2016. The gap between the albedo of photocatalytic and control materials was reduced during the rainy season, due to the cleaning of the control material by rain, which brought the albedo of the C1 specimens to 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).
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.
3.4 Evaluation of the de-pollution effect

3.4.1 NO and NO\textsubscript{2} concentration profiles

Figure S1 (Supplemental Information) illustrates experimental results obtained in a typical experiment carried out to evaluate the NO\textsubscript{x} removal efficiency of the photocatalytic specimens and the control material. On the x-axis, \( t = 0 \) corresponds to the time at which the UV lamp was turned on. Before the UV lamp was turned on, the material reached equilibrium with the NO-enriched atmosphere in the dark. When the control specimen C1 was used, no changes in NO and NO\textsubscript{2} concentrations were observed under UV light, indicating that there was no reaction taking place upon irradiation alone (Figure S1-A). However, when specimens from the materials P1 and P2 were used, the NO and NO\textsubscript{2} curves showed features similar to those presented in Figure S1-B. There was an initial sharp decline in NO concentrations, accompanied by an increase in NO\textsubscript{2} concentrations. Subsequently, NO concentrations increased asymptotically reaching a steady-state value after about 3 h of irradiation. During the same period, NO\textsubscript{2} concentrations declined reaching a plateau at the same time. After six hours of irradiation, the UV lamp was turned off, and both NO and NO\textsubscript{2} concentrations rapidly recovered their initial values (ca. 1000 ppb and 0 ppm, respectively). Measurements continued during approximately 1 h in the dark, to establish final equilibrium conditions.

3.4.2 NO removal rates

From the integration of the curves shown in Figure S1, the rate of NO elimination was calculated using Eqs. (1) and (2). The NO removal rate is reported in Figure 8 for P1 and P2 specimens as a function of the exposure duration. The elimination of NO was the primary photocatalytic process, which led to the formation of NO\textsubscript{2} and nitrate \([74-77]\). The P1 sample showed a significantly higher NO elimination efficiency with respect to P2 in all three sites and almost all weather conditions. Based on the results presented in Figure 8, the photocatalytic activity of product P1 declined in all three sites during the dry season. This is likely due to deposition and attachment of soiling agents onto the catalyst surface. Specimens exposed in Berkeley and Fresno recovered their photocatalytic activity after a year of exposure, at the end
of the first rainy season. In Berkeley, the recovered activity exceeded the initial performance of unexposed materials. This may have resulted from additional activation of the catalyst upon environmental exposure over time. This activation could be caused by the removal of surface coatings remaining from the manufacturing process, or by abrasion of the polymer matrix, either of which could expose more catalyst particles. By contrast, the albedos of specimens exposed in Los Angeles did not increase during the rainy season. This is likely due to less rain in Los Angeles, and may also reflect the fact that the chemical nature of soiling in all three sites is different. In the case of sample P2, NO removal rates were lower, but still showed some of the same seasonal effects. For sample P2, specimens exposed in Fresno that were retrieved during the dry season showed negative values of the NO removal rate, as NO concentrations downstream of the test chamber were slightly higher than those measured upstream in the challenge gas. This effect can be attributed to the possible presence of ammonium salts, and possibly other reduced nitrogen contaminants, as part of the soiling mixture deposited on the specimen surface. The photocatalytic oxidation of these species has been shown to produce both NO and NO\(_2\) [78].

### 3.4.3 NO\(_x\) deposition rates

By subtracting the NO\(_2\) formation rate from the NO removal rate, it was possible to determine in each case the NO\(_x\) deposition rate, which is presented in Figure 9 for both photocatalytic samples. Overall, the NO\(_x\) deposition rate was slower than the NO removal rate (primary photocatalytic process), because a large fraction of NO was converted to NO\(_2\), and did not contribute to NO\(_x\) elimination. However, there was a net NO\(_x\) deposition rate in most conditions. Similar to trends described above for NO removal, sample P1 was more effective in the deposition of NO\(_x\) than sample P2. The P1 sample showed positive values for the NO\(_x\) deposition rate for specimens exposed in all three sites over the entire exposure period, except for one specimen in Fresno. In some cases, the NO\(_x\) deposition rate of aged materials was higher than that determined for unexposed samples, owing to catalyst activation and soiling removal as described above. The P2 sample showed negative NO\(_x\) deposition rates in Fresno over the whole exposure period. In addition, a few specimens exposed in Los Angeles also had
negative values. As described above, these negative values represent higher downstream than upstream concentrations, which can be attributed to the photocatalytic oxidation of nitrogen-containing species in soiling material deposited on the specimens. This is particularly relevant for ammonia aerosols, which are commonly found in rural environments with agricultural activities such as the one surrounding the Fresno site [79].

While the photocatalytic materials were very effective in preventing albedo losses by removing soiling agents that could be visualized with the naked eye and microscopy tools, it is likely that some recalcitrant oxidation byproducts can remain attached to the catalyst and build up over time during the dry season. Examples of those recalcitrant species are carboxylic and polycarboxylic acids, which have a low vapor pressure and can attach to active sites, thus partially inhibiting the catalysts ability to react with NOx and other atmospheric species [80-82].

Similarly, inorganic species such as soluble salts formed as byproducts of the photocatalytic process or present in atmospheric deposition could deactivate the catalyst [53, 54, 77]. This effect can be reduced during the rainy season because, while those species are not volatile, they are water soluble and can be dissolved and removed by liquid water present on the surface.
Figure 8. Laboratory-measured rates of NO removal by photocatalytic samples P1 and P2 exposed in Berkeley (BK), Los Angeles (LA), and Fresno (FR). The control sample C1 did not catalyze the elimination of NO.
Figure 9. Laboratory-determined NO\textsubscript{x} deposition rate over photocatalytic samples P1 and P2, exposed at the Berkeley (BK), Los Angeles (LA), and Fresno (FR) sites. The control sample C1 did not catalyze the elimination of NO\textsubscript{x}. 
4 Conclusions

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

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

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

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