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SUPPLEMENTARY INFORMATION FOR

Methodology for Quantifying Engineered Nanomaterial Release from Diverse Product Matrices under Outdoor Weathering Conditions and Implications for Life Cycle Assessment

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Nanocomposite Preparation

All nanocomposites used in this study were prepared with solution blending with nanoparticle loadings designated as a percent by mass (%w/w). Solution blending produces PNCs with a high degree of nanoparticle dispersion and excellent reproducibility and scalability on the lab scale. Solution blending requires, for both AgNPs and CNTs, that the NPs be first dispersed in an organic solvent. Upon formation of a stable dispersion, a polymer of choice was then added. Following a period of mixing, the NP-polymer suspension was then poured into Fisher aluminum weigh dishes (Cat. Number 08-732-105) and allowed to dry overnight. Prior to characterization and weathering, all nanocomposites are further dried for at least one additional night in a desiccator.

Nanomaterials

AgNPs were provided by Dune Sciences and CNTs were purchased from Carbon Solutions Inc., where they were synthesized by electric arc discharge over Ni/Y nanoparticle catalyst. Samples were used as received unless otherwise described. Comprehensive material characterization was conducted on the raw material and data, including TEM (as depicted in previous studies [1, 2]), XPS,ATR-FTIR, and SEM is included in the SI (Figures S1, S2, S6, S11, S12).

1.5% SWCNT-poly-ε-caprolactone (1.5%CNT-PCL)

Samples were prepared by first weighing out single-walled CNTs (SWCNTs, Mettler Toledo XS20) and adding them to a 50 mL Erlenmeyer flask filled with 21 mL of THF and 21 mL of chloroform. Ethyl cellulose (EC, 31.5 mg) was weighed out and also added to the flask. EC was added to act as a natural surfactant for the SWCNTs and facilitates uniform dispersion. This mass of EC does not significantly impact the chemical composition of the surface of the nanocomposites, as confirmed by both XPS and ATR-FTIR (data not shown) The SWCNT and solvent mixture are then capped with septa, clamped in place, partially submerged in a bath sonicator (70W, Branson 1800), and sonicated for three hours. Following sonication, 420 mg of PCL was added to this solution and sonicated for an additional hour. The final solution was then poured, in 6 mL portions, into 7 separate Fisherbrand Disposable Aluminum Dishes. The dishes were then covered, dried overnight and circular nanocomposite samples, referred to as coupons, were formed by evaporation.

1.5% SWCNT-polystyrene (1.5%CNT-PS)

1.5% CNT-PS samples were prepared by weighing and adding 12.6mg SWCNTs to a 50 mL Erlenmeyer flask filled with 42 mL of ortho-dichlorobenzene (O-DCB) and 0.42 mL of ethanol, added to quench sonopolymerization. This mixture was then sonicated (Branson 1800) into suspension for three hours. PS (840 mg) was then added to the flask and sonication continued for another three hours. The suspension was then poured, in 6 mL portions, into 7 separate Fisherbrand Disposable Aluminum Dishes. To ensure complete evaporation of O-DCB, the dishes were placed on a hot plate set for 100 ^{0}C. The dishes were then covered and allowed to dry overnight at 100^{0}C.

2% AgNP-polystyrene (2%AgNP-PS), 2% AgNP-poly (methyl methacrylate)(2%AgNP-PMMA), 0.04% AgNP-poly (methyl methacrylate)(0.04%AgNP-PMMA)

AgNP nanocomposites were prepared from an aqueous suspension of 20 nm AgNPs (Tween 20, NS20D_06062014B) provided by Dune Sciences, at an initial concentration of 1000 ppm; referred to hereafter as AgNP/H_2O. To disperse the NPs in a polymer matrix, an aliquot was first added to a 25 mL Erlenmeyer flask, placed in an oil bath, and gently stirred as it was heated at

70^0C for 20 hours. 2% AgNP samples required 8 mL of AgNP/H_2O and 0.04%AgNP samples required 160 µL of AgNP/H_2O. Following 20 hours of heating, all the water was removed and only the AgNPs remained. The particles are then re-suspended in 20 mL of chloroform (Figure S12). Following the addition of chloroform, the solution is stirred vigorously (1200 rpm) for 1 minute with a magnetic stir bar on a stir plate. At this time 400 mg of either polystyrene or poly (methyl methacrylate) were added. The flask was then capped and stirred for an additional 60 minutes at 1200 rpm. The suspension was then poured, in 6 mL portions, into aluminum weigh dishes, covered, and dried overnight at ambient temperature. To ensure stirring in chloroform resuspended most, if not all, of the original AgNPs present in the AgNP/H_2O. UV-Vis measurements taken of the as received suspension as well as the resuspended material showed that the characteristic SPR peak at 420 nm did not change significantly in profile or intensity before and after resuspension (SI 12).

Sample Characterization

X-ray photoelectron spectroscopy (XPS)

XPS was performed with a PHI 5400XPS, MgKα X-ray (1253.6eV) on PNC samples prior to weathering. Samples were sufficiently dry before analysis and bound to a metal sample stub using copper tape. Quantitative analysis of elemental regions of interest (C(1s), O(1s), and Ag(3d)), were collected on samples using a pass energy of 58.7eV, a step size of 0.125eV, and with 10 sweeps. Survey scans, that measure signal from all elements present, were performed as well to ensure samples were free of contamination. All data processing was carried out using CasaXPS. For each PNC type analyzed, spectra were collected on three samples from a given batch to assess uniformity in surface composition. The Ag-PNCs were produced in three batches, denoted by date of production (7-29-15, 8-4-15, and 8-11-15); three samples from each batch were analyzed with XPS, giving a total of 9 spectra for each Ag-PNC type. The average Ag composition on the surface of each PNC type (2%Ag-PS, 2%Ag-PMMA, 0.04%Ag-PS) was calculated from the mean average of concentrations measured for each of the 9 scans; the standard deviation was calculated from the 9 scans as well.

Scanning electron microscopy (SEM)

SEM imaging was conducted with a Jeol 6700F, FESEM. Ag NP and CNT nanocomposites samples were dried prior to imaging. All samples were bound to a conductive metal stub using copper tape and sputter-coated with platinum nanoparticles for 300 seconds, at a rate of 2nm/minute. This was done to minimize charging of the sample during imaging. Samples were imaged in two or three randomly selected locations across the surface to ensure uniformity of surface morphology. All images were processed using ImageJ.

Attenuated Total Internal Reflectance Fourier Transform IR (ATR-FTIR)

ATR-FTIR was performed with a Nicolet iS5 FT-IR Spectrometer, equipped with a diamond window; a sampling depth of 2 µm is reported by the manufacturer. Samples were dried prior to analysis and analyzed with resolution of 0.482cm^{-1}, with 32 scans collected; the background of the instrument was set to ambient atmosphere.

ICP-MS and Digestion – instrument and digestion procedure

Preweighed unweathered 2%Ag-PMMA and 2%Ag-PS were acid digested to determine original Ag content. Samples were transferred into a Teflon™ digestion vessel and 10 mL of ACS grade Nitric acid (67-70% HNO_3, Macron Fine Chemicals) was added to the vessel. The vessels were sealed and microwave digested (ramped to 200 C, held for 5 minutes)[3-5]. Following digestion, samples were quantitatively transferred (microwave containers were rinsed 3 times with MilliQ water, with each rinse volume contributed to the total volume) into 50 mL Falcon™

tubes and diluted to total volume of 50 mL using 18 MΩ ultrapure water (Millipore). Digestate was diluted 100x in ultrapure water prior to analysis by a quadrupole ICP-MS (NexION 300D series, Perkin Elmer). Total Ag was measured using mass 106.905 amu. Indium (114.116 amu) was used as an internal standard throughout the analysis. Perkin Elmer's Syngistix™ for ICP-MS software was used to collect data and calculate concentration.

Standard curves are established (R-squared values of >0.998) for both elements with six data points ranging from 0.1 to 30 µg/L using the SPEX CertiPrep standards (Metuchen, NJ).

A mixing t-piece was employed to introduce 10 ppb indium as an internal standard throughout the entire analyses as well as standard quality assurance and quality control measures. The internal standard is used to monitor and account for instrumental drift. Check standards and ultra-pure water blanks are analyzed approximately every fifteen samples. After about the 9th month of sampling NIST SRM 1640a for natural waters is included as a check as well. The standards are monitored for accuracy (within 10% variation from certified value) and blanks are used to ensure there is no sample carryover, as well as establish limits of detection for each analysis.

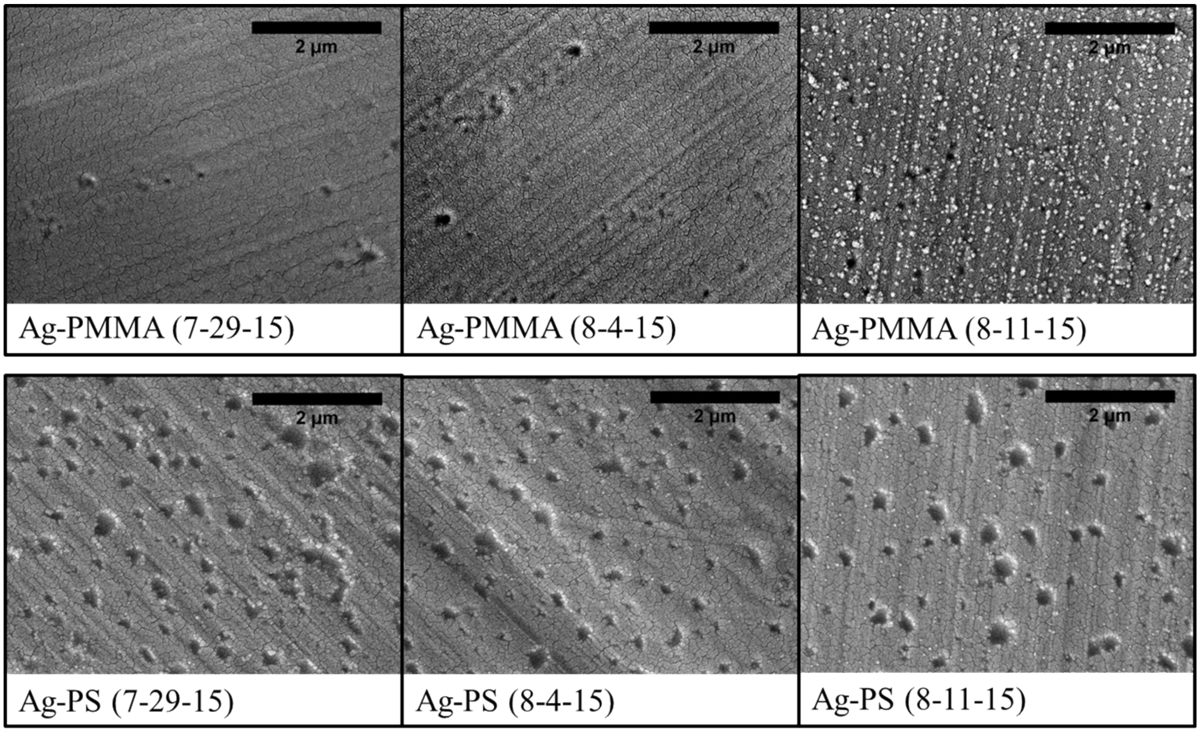
Each month, an instrumental limit of detection (LOD) is determined by quantifying the average intensity in at least three ultrapure water blank and adding 3σ (3 times the standard deviation). From each control blank, 5 mL are separated and used as matrix spikes. A standard solution of Ag and Y) is spiked into the blank to a concentration of 1ppb and analyzed to determine if the matrix is causing any interference. Recoveries of Ag and Y between 80-120% are considered acceptable.

Quantifying ENM release by ICP-MS

ICP-MS analysis is carried out on monthly release samples to determine total ENM release from products (here, Ag and SWCNT from PNCs). Yttrium (Y) is used to indicate SWCNT concentration due to the presence of Y nanoparticles in the SWCNT (~5 wt%) used in the PNCs. The Y nanoparticles are incorporated into SWCNTs during synthesis and have been previously used to quantify SWCNT particles.46-48 The acid rinse of the collection jars and acid digestion prior to ICP-MS results in AgNP dissolution and release of Y from CNTs. Since atmospheric dusts are also collected and can clog the ICP-MS introduction system, it is removed from the suspension by either settling (up to two days) or centrifugation prior to analysis. Ag and Y concentrations of each sample are analyzed using a Nexion300D ICP-MS (Perkin Elmer, Toronto, ON). Instrument settings are compiled in Table S1 and a detailed description of the analytical procedures are provided in the SI.

Data management

A coordinated data consolidation and management protocol/system is required given the volume and diversity of data collected. Every month data is collected from each location, including release values of 9 – 29 samples and the weather data collected from the weather station. A standardized spreadsheet is provided to each location that contains all sample names and corresponding columns to record the collected final volume. Upon completion of sampling, each location completes this file and sends, along with the weather station data (in .csv format) to the data center (Baltimore, MD) for processing. Following ICP-MS analysis, a single spreadsheet containing measured release values for all samples (all locations) is generated by the analytical center (Golden, CO) and sent to the data center for processing and compilation.



Ag-PMMA (7-29-15)
Ag-PMMA (8-4-15)
Ag-PMMA (8-11-15)
Ag-PS (7-29-15)
Ag-PS (8-4-15)
Ag-PS (8-11-15)

Figure S1: Representative SEM image of silver nanocomposites from each batch used in the study (Polystyrene – PS, Poly (methyl methacrylate) – PMMA). Silver nanoparticles appear as white dots in images collected and are approximately 20nm in diameter, when monodispersed.

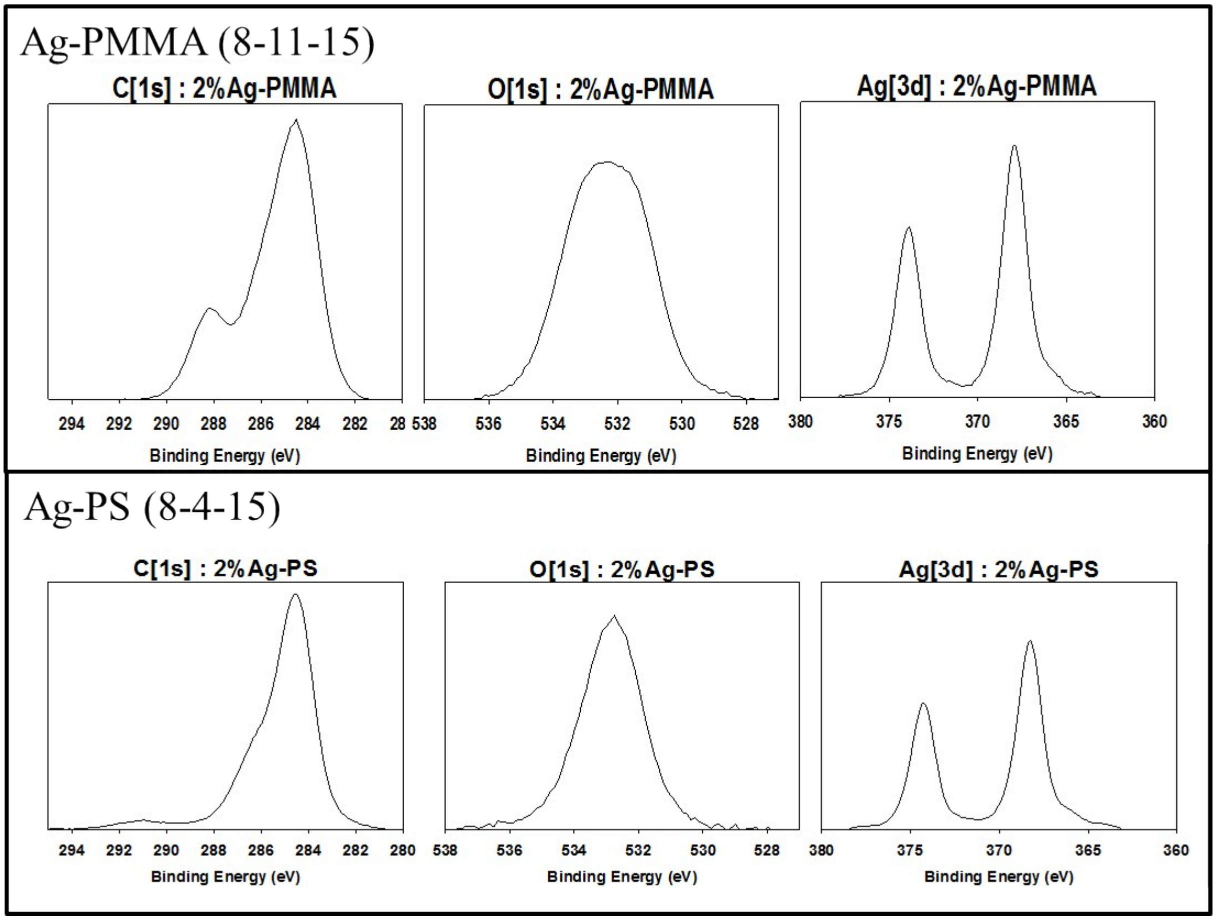


Figure S2: Representative XPS spectra collected of Ag-PNCs, used for determining surface composition , with batch denoted in parenthesis (note, XPS intensity are shown in arbitrary units).

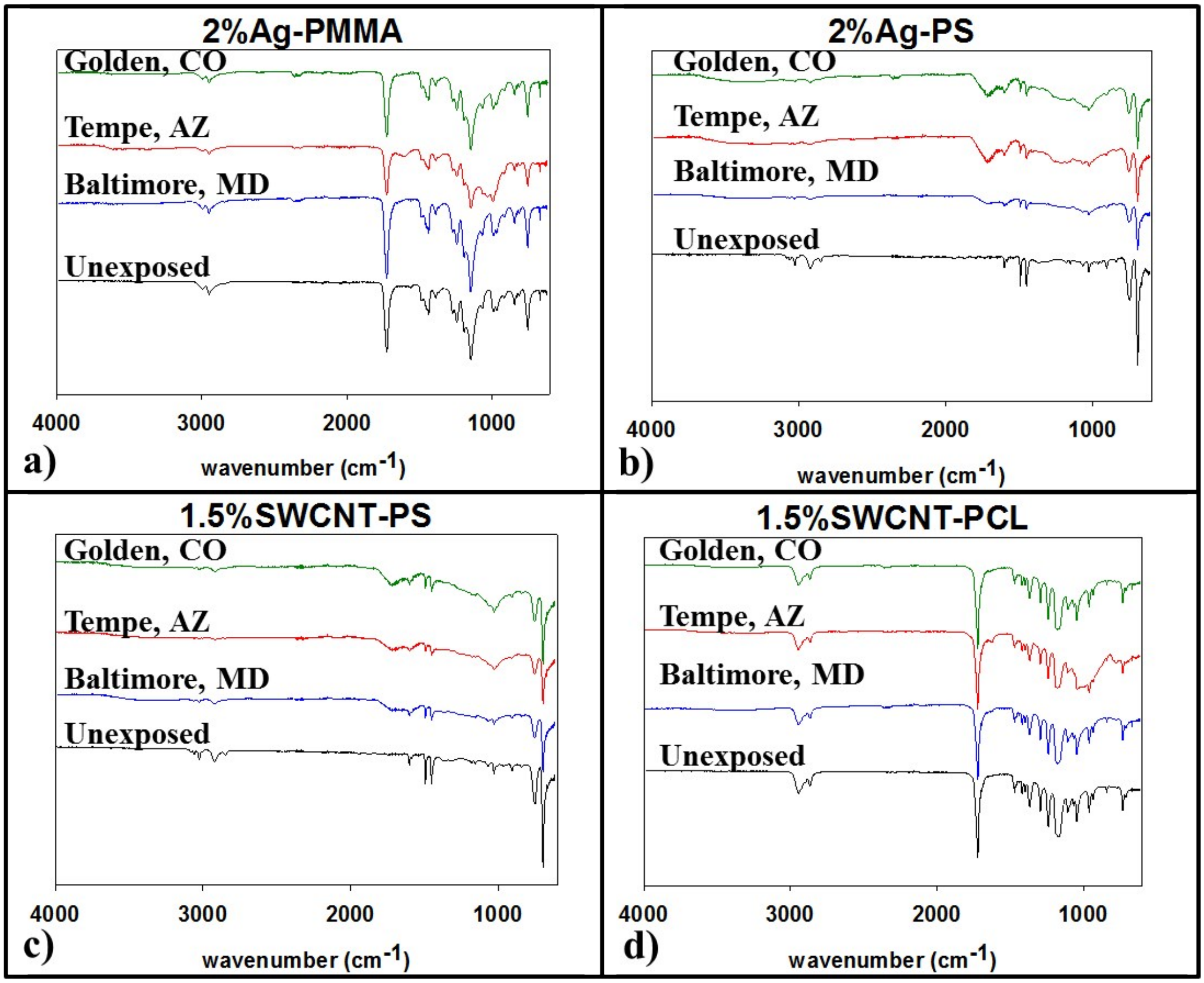
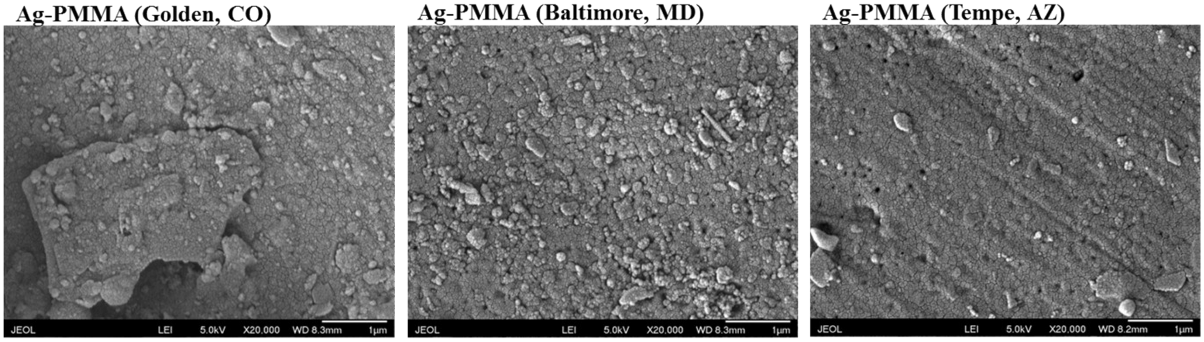


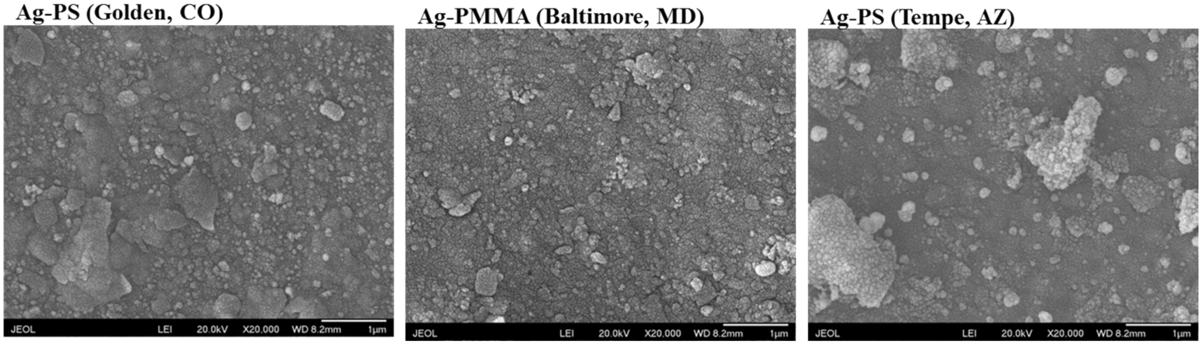
Figure S3: ATR-FTIR spectra of PNCs following weathering finds that the spectra collected of samples weathered at each location are consistent with each other, suggesting that samples weathered at each location experienced similar, shallow, depths of photodegradation.



Ag-PMMA (Golden, CO)

Ag-PMMA (Baltimore, MD)

Ag-PMMA (Tempe, AZ)



Ag-PS (Golden, CO)

Ag-PMMA (Baltimore, MD)

Ag-PS (Tempe, AZ)

Figure S4: SEM images of Ag-PNC samples following weathering reveals no Ag nanoparticles remain visible at the surface for either PNC type, at all three locations.

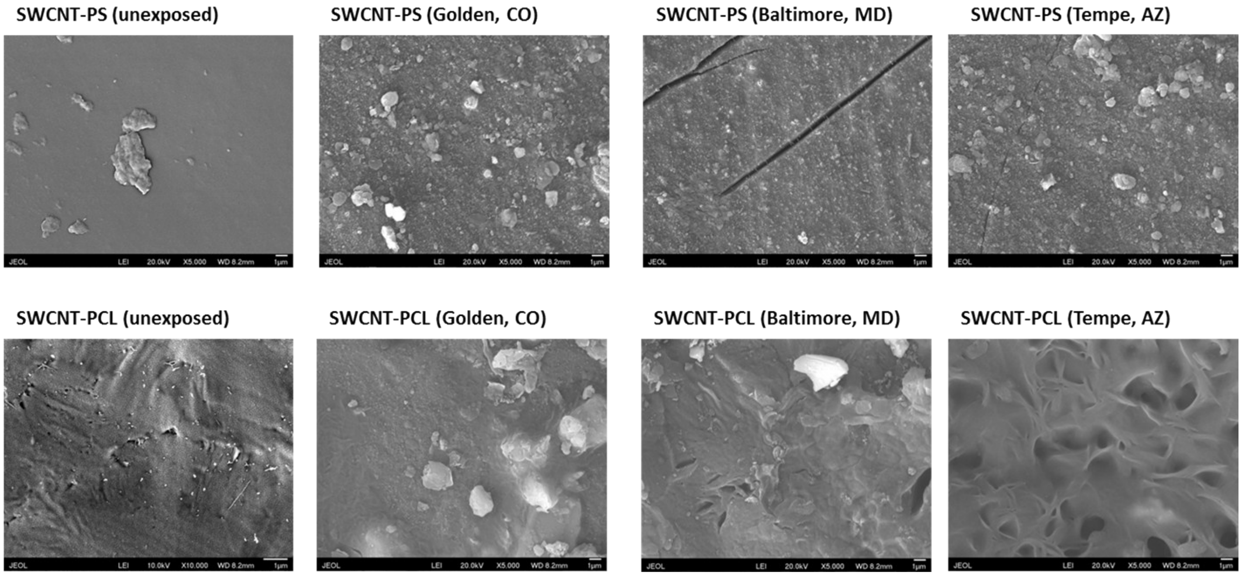
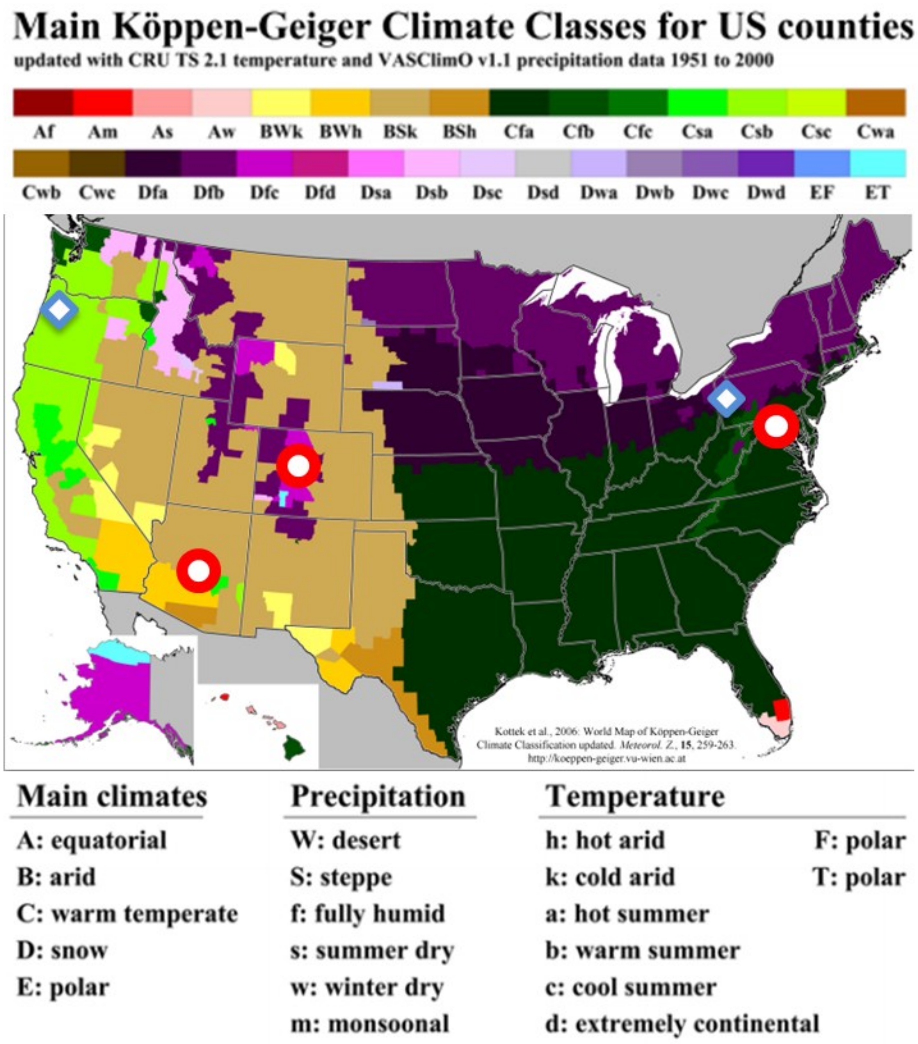
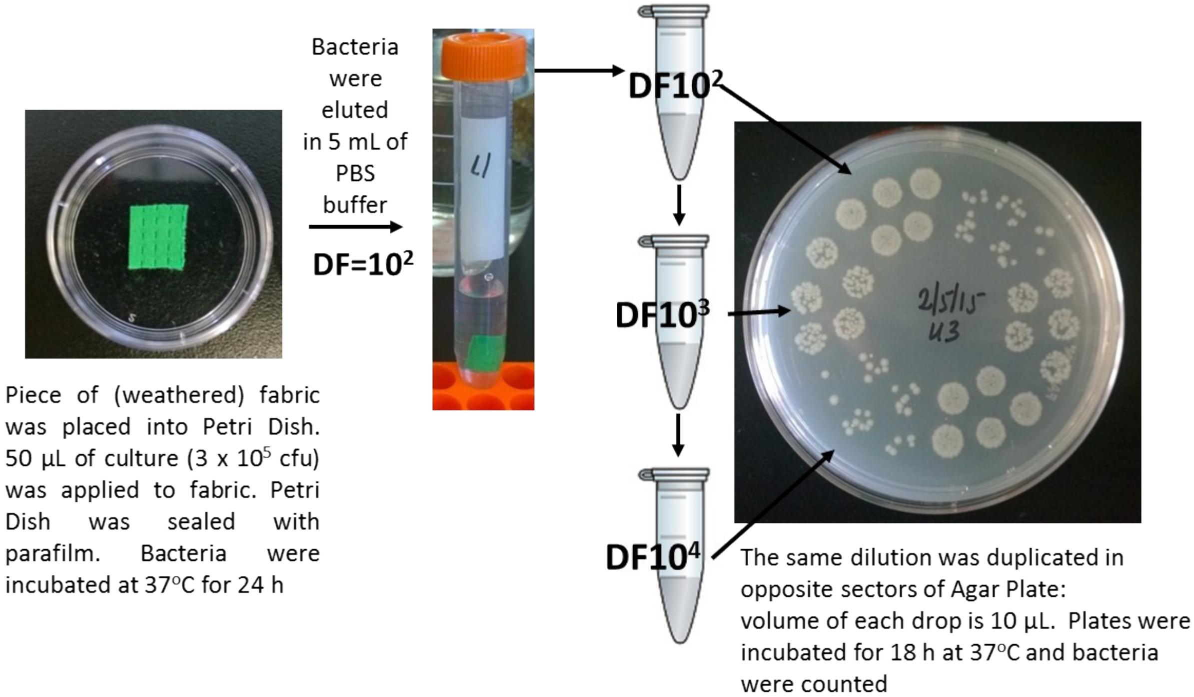

SWCNT-PS (unexposed)
SWCNT-PS (Golden, CO)
SWCNT-PS (Baltimore, MD)
SWCNT-PS (Tempe, AZ)
SWCNT-PCL (unexposed)
SWCNT-PCL (Golden, CO)
SWCNT-PCL (Baltimore, MD)
SWCNT-PCL (Tempe, AZ)

Figure S5: SEM imaging of SWCNT-PNC samples before and after weathering reveals no CNT accumulation at the surface of any PNC type or at any of the location.



Kottek et al., 2006: World Map of Köppen-Geiger Climate Classification updated. *Meteorol. Z.*, **15**, 259-263. http://koeppen-geiger.vu-wien.ac.at

Figure S6: Climate class map showing the experimental locations (phase 1 = red circles and phase 2 = blue diamonds) representing unique climate regions. Phase 2 are expansion locations to be included for future weathering studies.



Piece of (weathered) fabric was placed into Petri Dish. 50 µL of culture (3×10^5 cfu) was applied to fabric. Petri Dish was sealed with parafilm. Bacteria were incubated at 37°C for 24 h

The same dilution was duplicated in opposite sectors of Agar Plate: volume of each drop is 10 µL. Plates were incubated for 18 h at 37°C and bacteria were counted

Figure S7: Outline of experimental procedures used to determine efficacy of Ag textile.

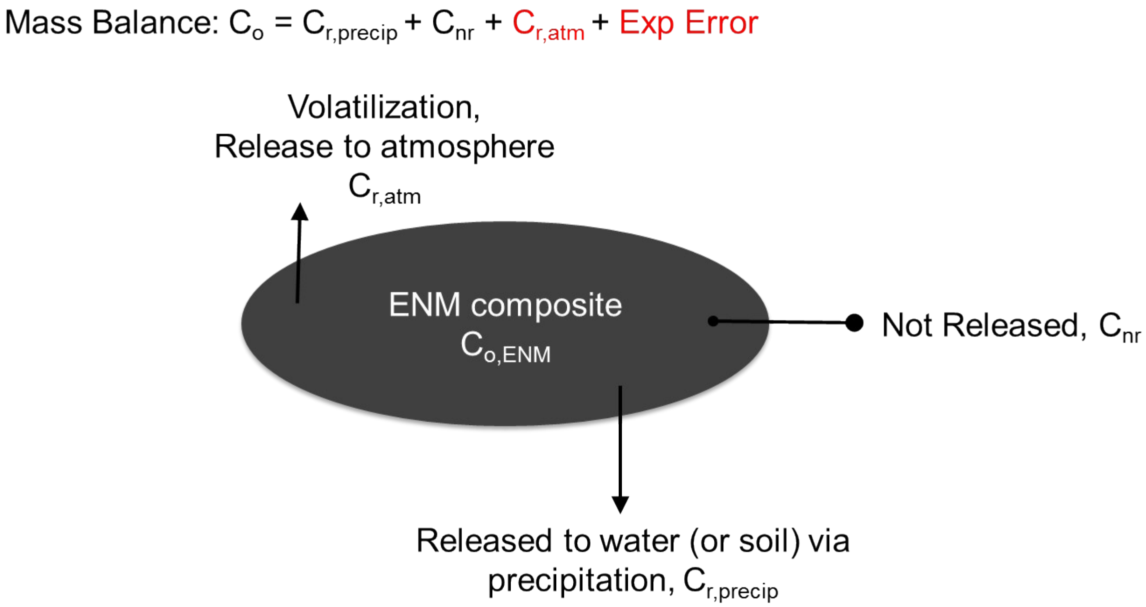


Figure S8: Schematic of the engineered nanomaterial (ENM) mass balance for the composites tested. The initial ENM concentration is determined for all samples ($C_{o,ENM}$) prior to commencing the weathering experiments, ENM release during weathering is captured monthly via precipitation collection and/or rinse of collection jar ($C_{r,precip}$), and ENM retained in the composite is determined from sacrificing samples and pre-determined time intervals (C_{nr}). One potential release pathway that is not captured in this method is volatilization or release to the atmosphere ($C_{r,atm}$). Finally, a certain level of experimental error is expected.

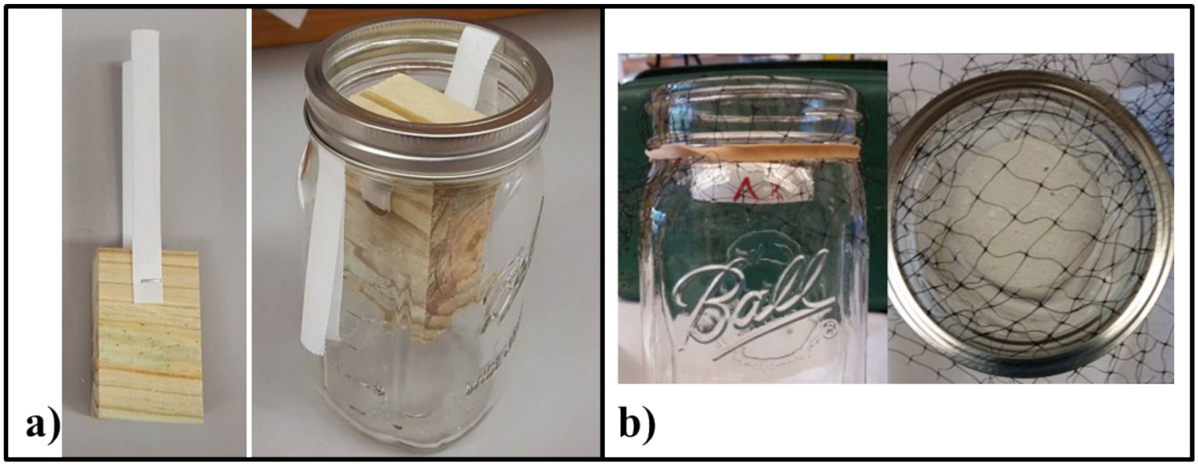


Figure S9: (a) Pressure treated lumber is used, as purchased, with the only alteration being cut down in size to fit within the collection jar and affixed to Teflon straps so it may hang freely and weather passively. (b) TX Active Cement puck provided by Lehigh Heidelberg Cement Group is held in place with thin nylon netting.

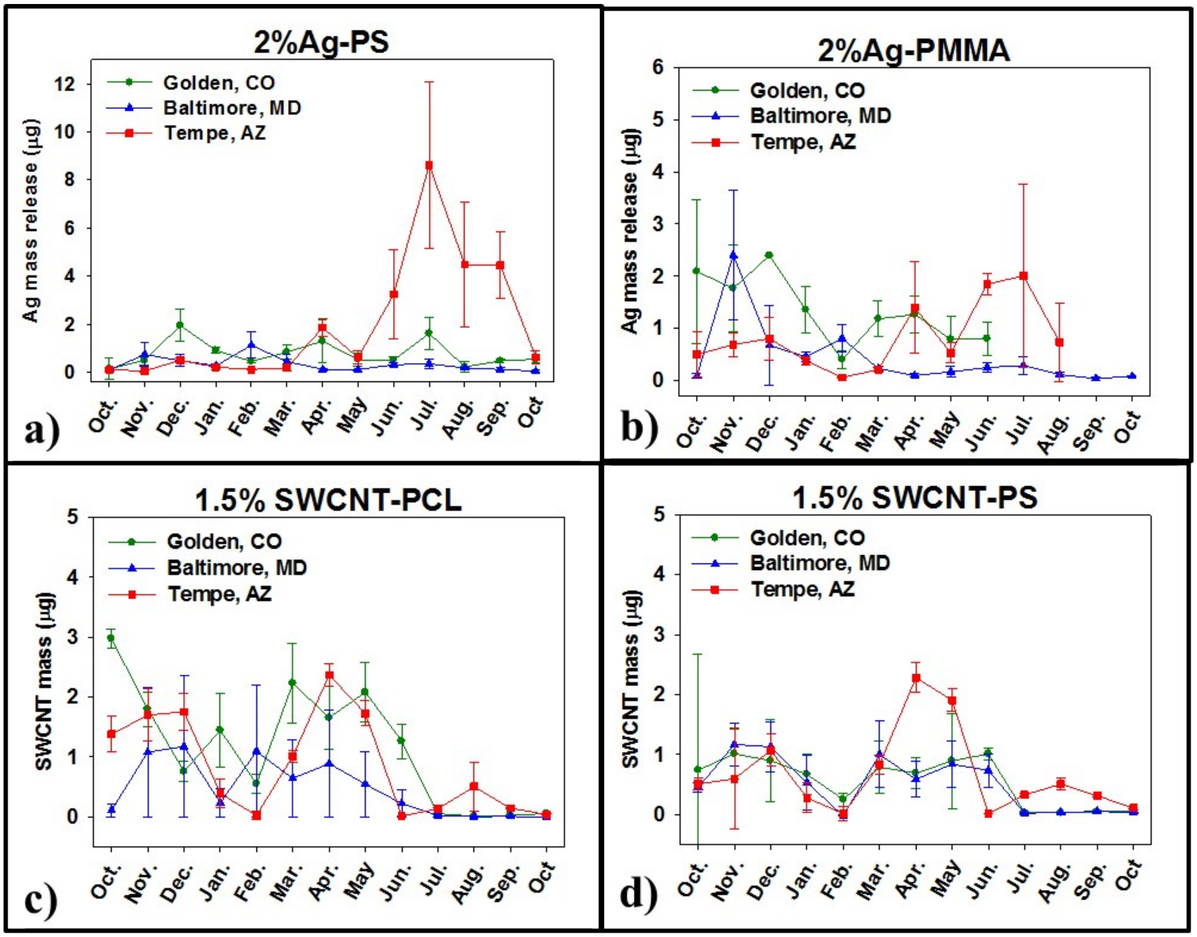


Figure S10: (a,b) Monthly Ag release mass measurements comparing Ag-PNCs located at all three sites. (c,d) Monthly SWCNT mass release measurements from SWCNT-PNCs located at all three sites. Error bars represent standard deviation of release mass measured from triplicate samples at each location. Release data demonstrates SWCNT and Ag release, however as it is shown in monthly increments, overall release trends are difficult to discern.

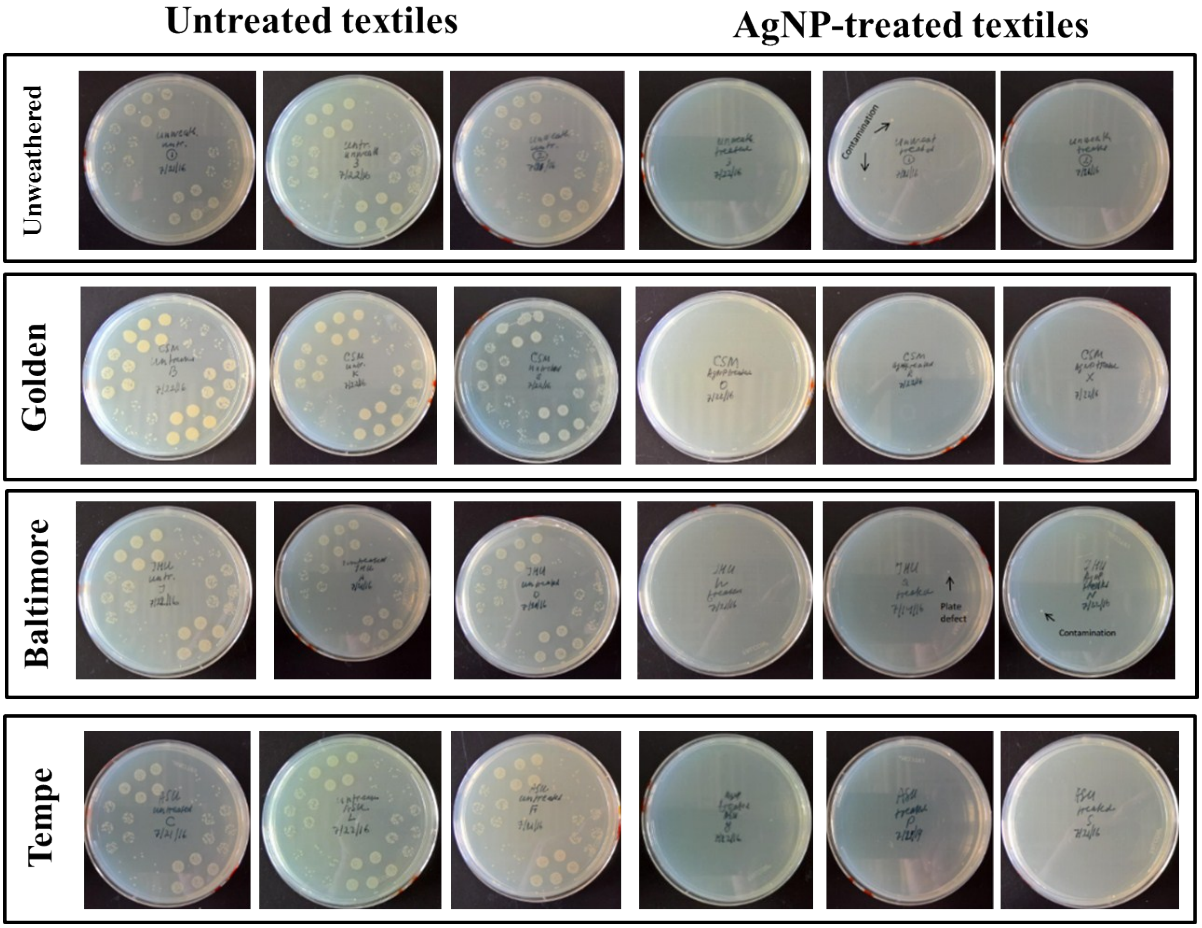


Figure S11: Pictures captured of triplicate antimicrobial efficacy test results, for each location. Images show that anti-microbial efficacy is maintained for all Ag treated textile samples in each location and that weathering has no impact on the antimicrobial efficacy of the untreated textile samples weathered in each location.

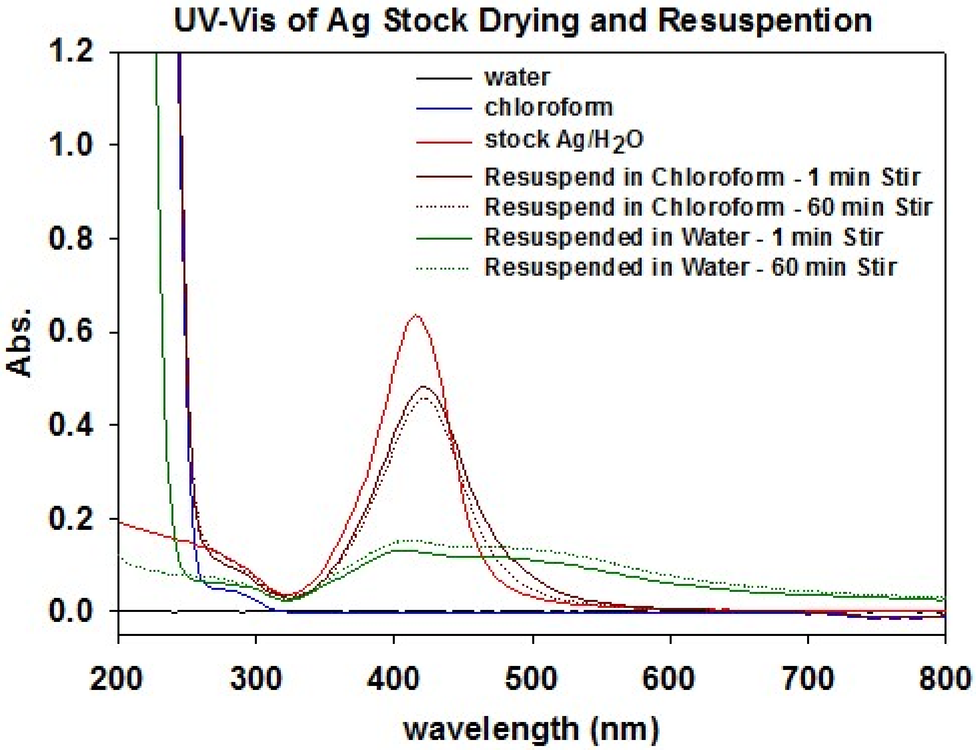


Figure S12: UV-Vis demonstrates effective resuspension of AgNPs in chloroform following drying of their as received aqueous suspension.

Parameter	Setting
Nebulizer Gas Flow	0.88-1.0 mL/min
Auxiliary Gas Flow	1.2 ml/min
Plasma Gas Flow	16 or 18 ml/min
ICP-RF Power	1600 V
Analog Stage Voltage	-1712
Pulse Stage Voltage	1250-1375
Deflector Voltage	-6.5 or -10
Cell Ent	-1.0 or -5.0
Cell Exit	-1.0 or -5.0
Cell Rod Offset	-15.0

Table S1. ICPMS Settings, shifts in setting occurred after some troubleshooting by Perkin Elmer technician and resulted in improved instrument performance.

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