

Measuring nanomaterial release during weathering of polymer nanocomposites & commercial products

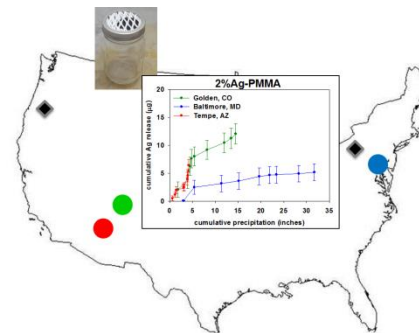
Howard Fairbrother

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Johns Hopkins University
Baltimore, MD, USA**



Overview

- **Part 1 - Release from polymer fragments**



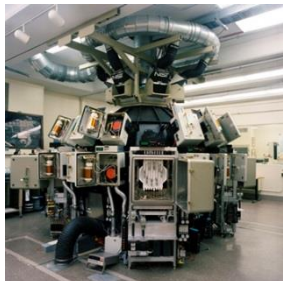
- **Part 2 - Release from commercial products**



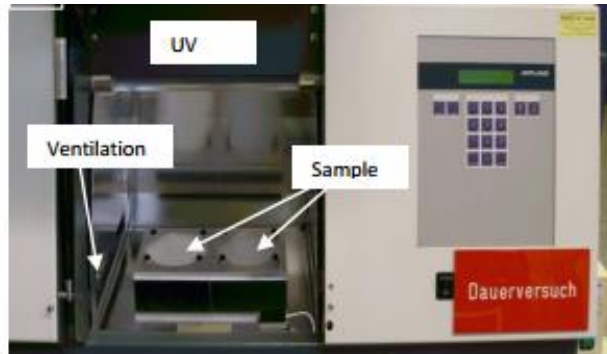
- **How do CNTs impact polymer photodegradation and identifying CNT release form**



Accelerated, simulated, & outdoor weathering approaches



Simulated
Photodegradation via High
Energy Radiant Exposure
(SPHERE)¹

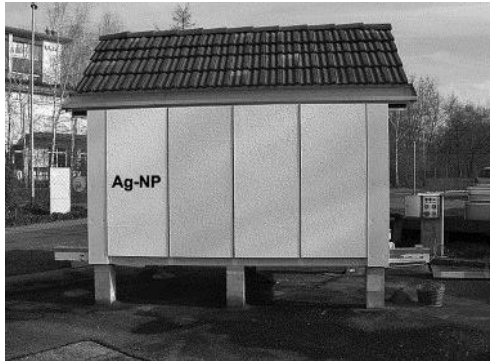


Suntest XLS+ (ISO 3892-2:2006)^{2,3}



FIG. 1 Suitably Mounted Specimens in a Frame

ASTM D1435 – Standard
Practice for Outdoor
Weathering of Plastics⁴



Model house for “façade
run off”^{5,6}

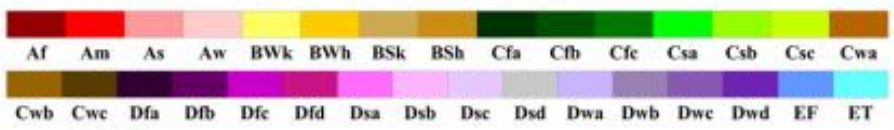
1) Chin, J.E., Ned, et al. Review of scientific instruments, 2004. 75(11): p. 8.
2) Petersen, E.J., et al. Carbon, 2014. 69: p. 194-205.
3) Hirth, S., et al. J Nanopart Res, 2013. 15.

4) Zaidi, L., et al. Polymer Degradation and Stability, 2010. 95(9): p. 1751-1758.
5) Kaegi, R., et al. Environmental Pollution, 2010. 158(9): p. 2900-2905. 3
6) Kaegi, R., et al., Environmental Pollution, 2008. 156(2): p. 233-239.

Outdoor Weathering Approach – completely natural

Main Köppen-Geiger Climate Classes for US counties

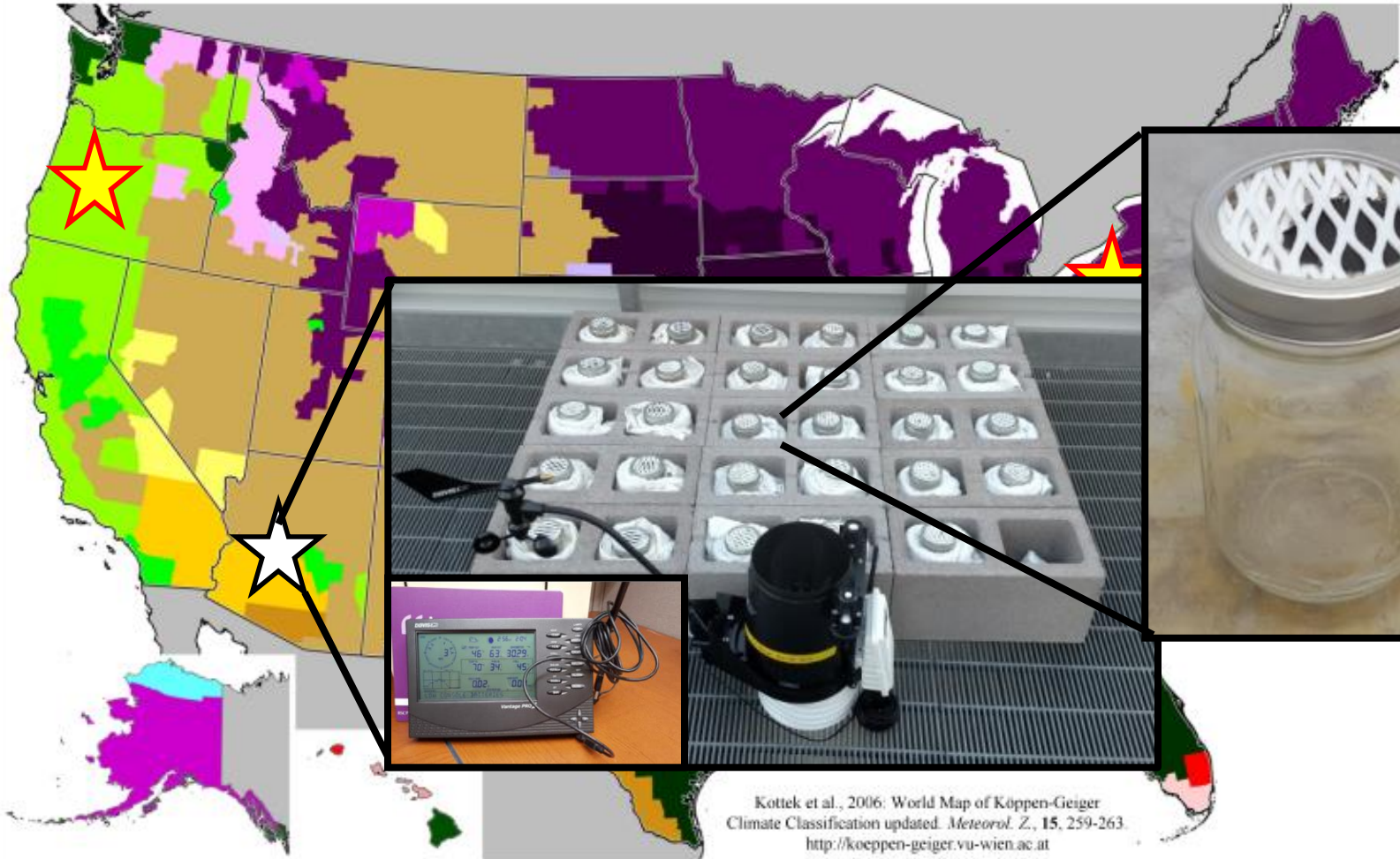
updated with CRU TS 2.1 temperature and VASCLimO v1.1 precipitation data 1951 to 2000



Main climates
 A: equatorial
 B: arid
 C: warm temperate
 D: snow
 E: polar

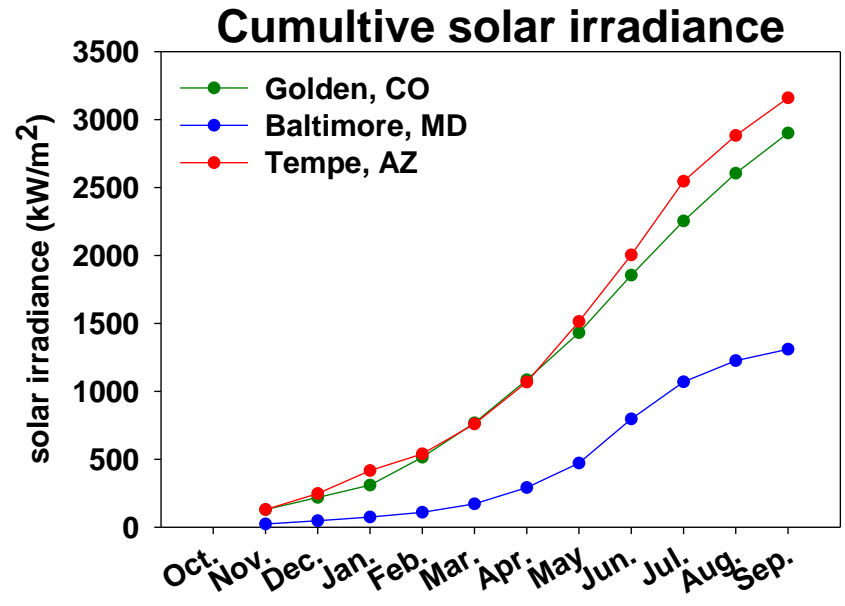
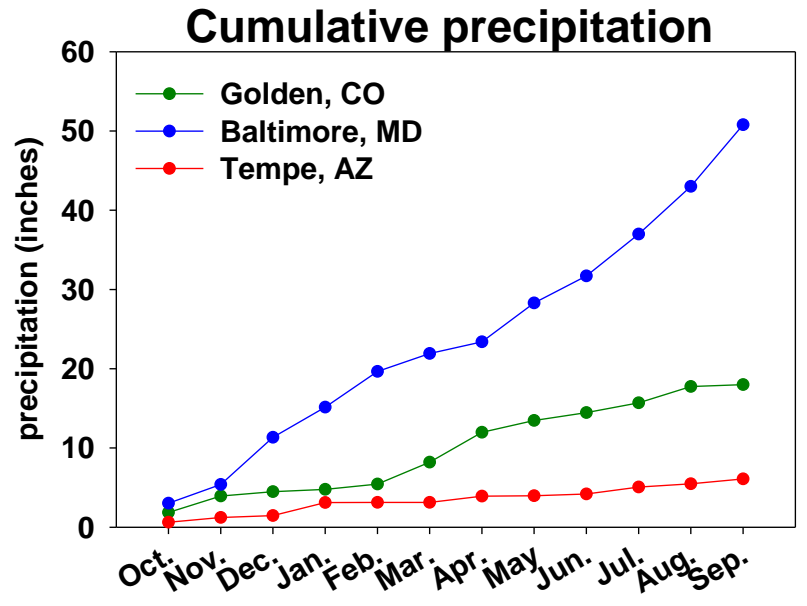
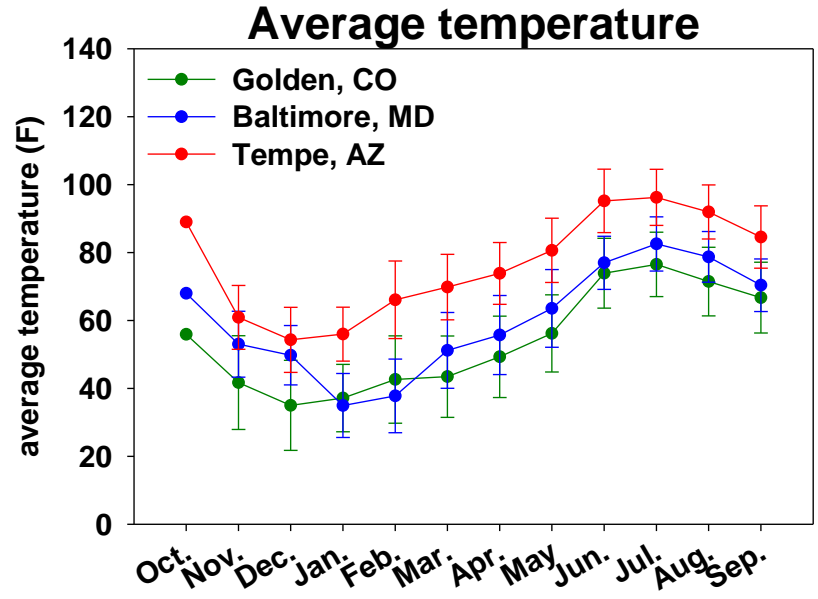
Precipitation
 W: desert
 S: steppe
 f: fully humid
 s: summer dry
 w: winter dry
 m: monsoonal

Temperature
 h: hot arid
 k: cold arid
 a: hot summer
 b: warm summer
 c: cool summer
 d: extremely continental
 F: polar
 T: polar

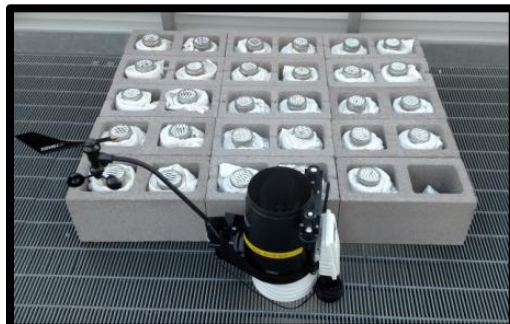


Kottek et al., 2006: World Map of Köppen-Geiger Climate Classification updated. *Meteorol. Z.*, 15, 259-263. <http://koepfen-geiger.vu-wien.ac.at>

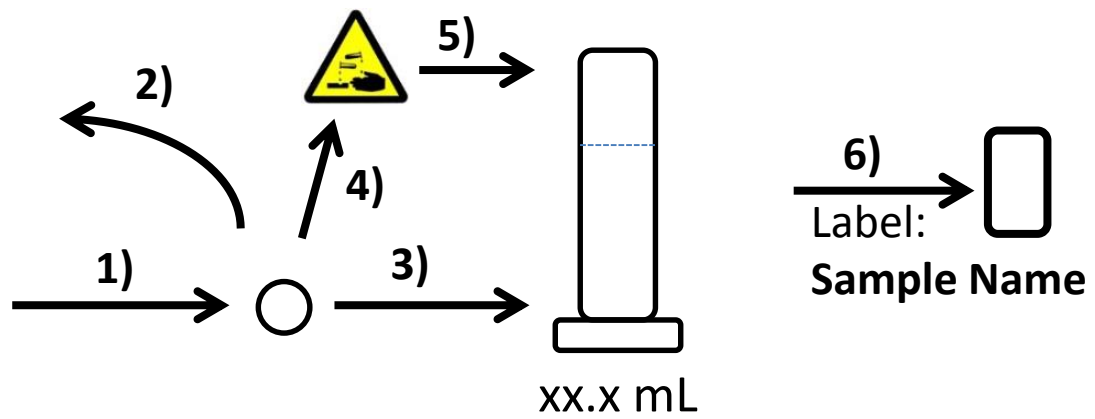
Results – Weather



Sampling Procedure



Sample retrieval and collection jar substitution

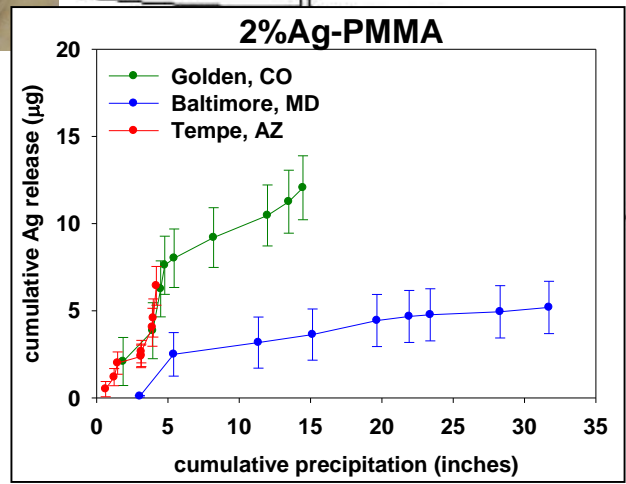
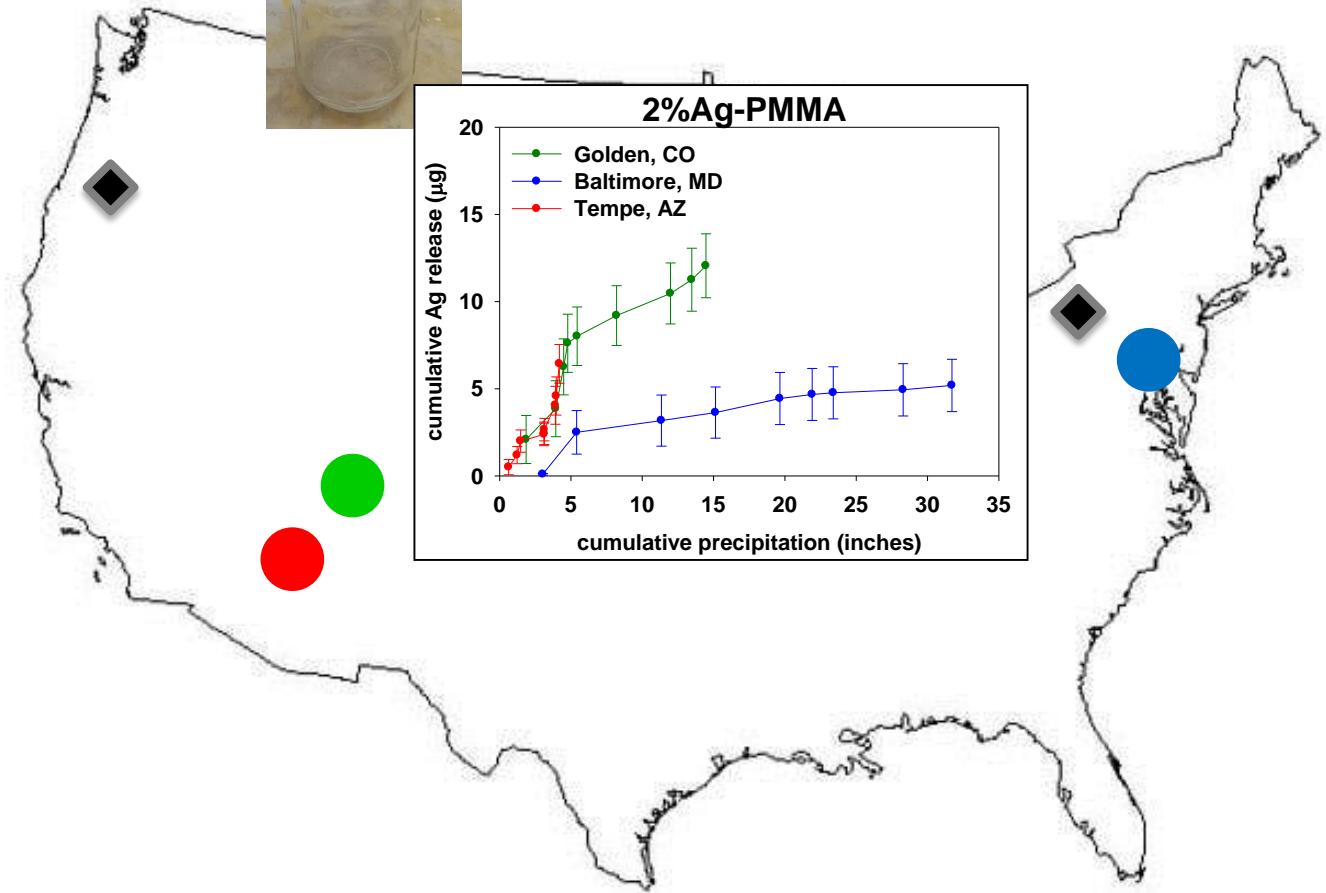


Rainwater collection and acid rinse

Seal for shipment

ICPMS used for detection due to specificity and sensitivity

Part 1 – Polymer Fragments



Samples for weathering



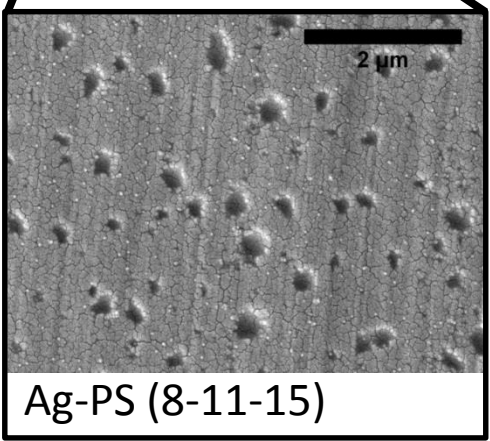
2% Ag-PS

2% Ag-PMMA

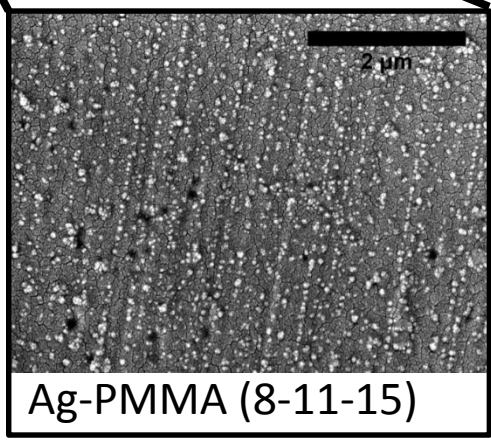
0.04% Ag-PS

1.5% SWCNT-PCL

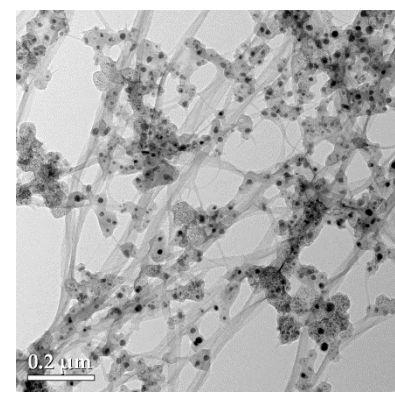
1.5% SWCNT-PS



Ag-PS (8-11-15)



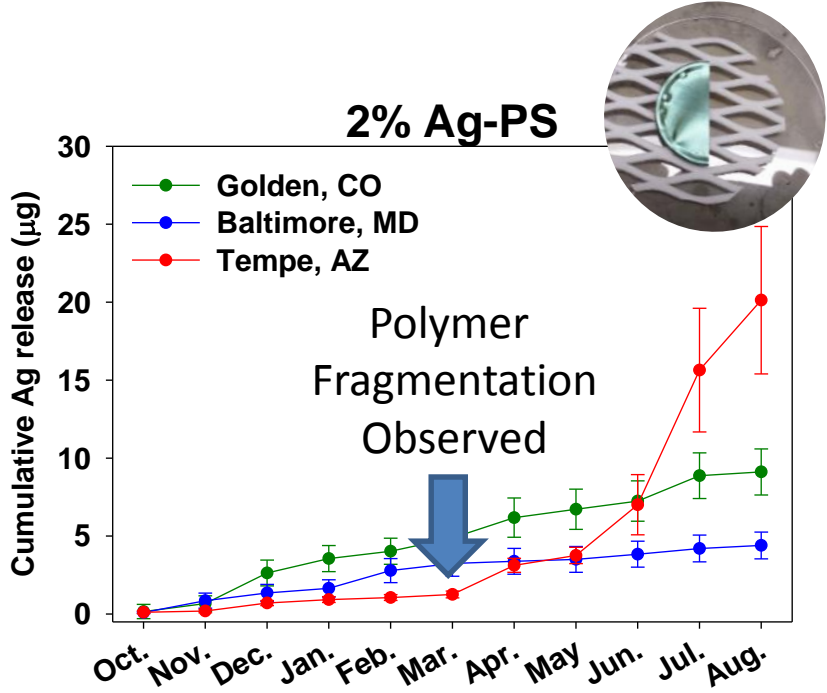
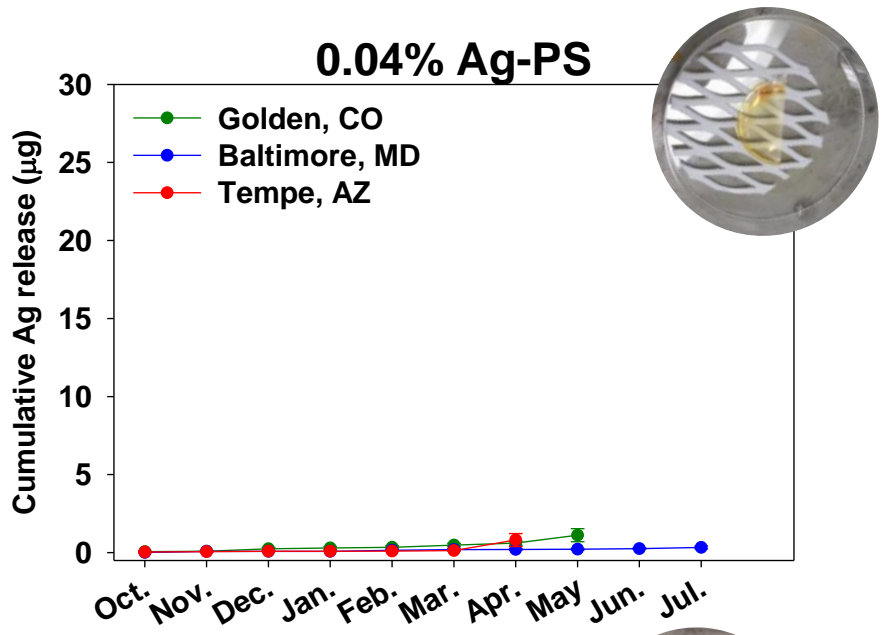
Ag-PMMA (8-11-15)



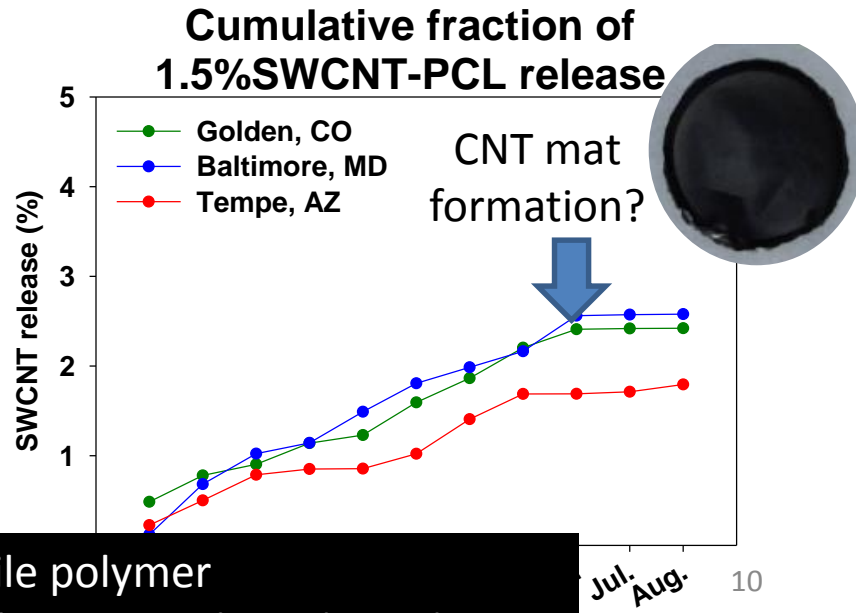
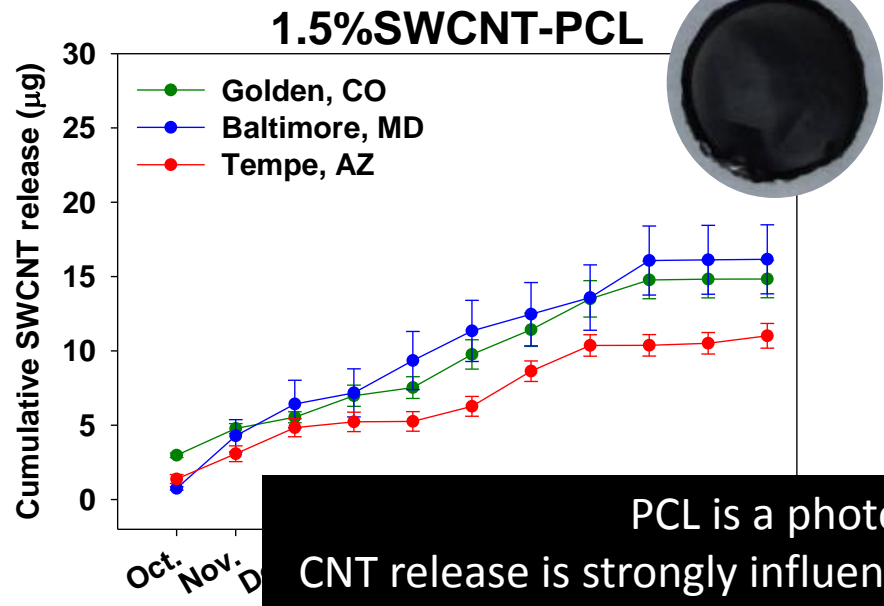
TEM of as received SWCNTs

	mass (mg)	stdev	SA of PNC (cm ²)	stdev	[Ag] from XPS	[Ag%] from ICP-MS
2% Ag-PS	54.02	5.19	8.09	0.59	5.07% (+/- 0.61)	1.32 (+/- 0.12)%
400ppm Ag-PS	46.51	3.56	6.99	0.7	0.06% (+/- 0.01)	
2%Ag - PMMA	73.1	4.41	8.9	0.63	3.72% (+/- 3.89)	1.62 (+/- 0.19) %
1.5%SWCNT-PCL	41.23	1.15	11.1	0.37		
1.5%SWCNT-PS	69.3	2.71	10.11	0.39		

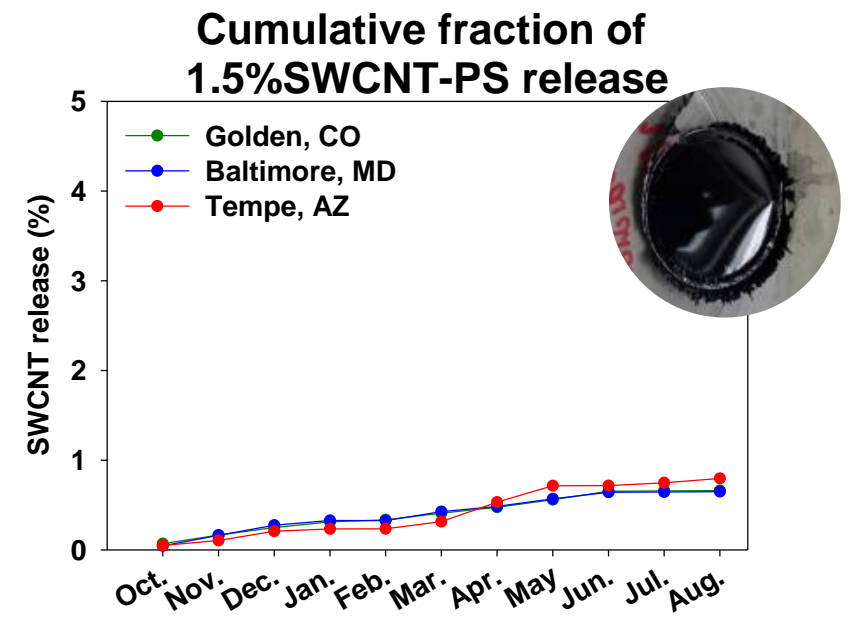
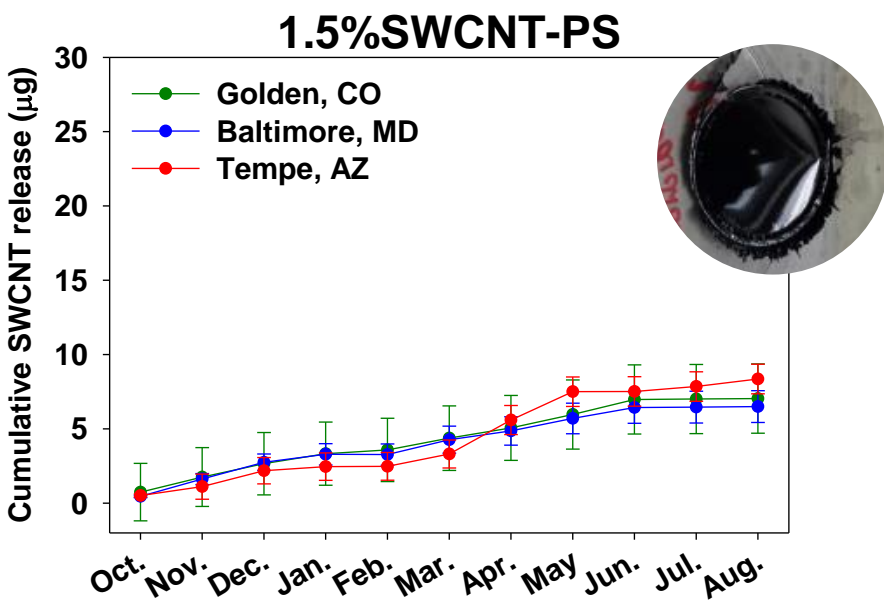
Results – Ag-PNCs Release



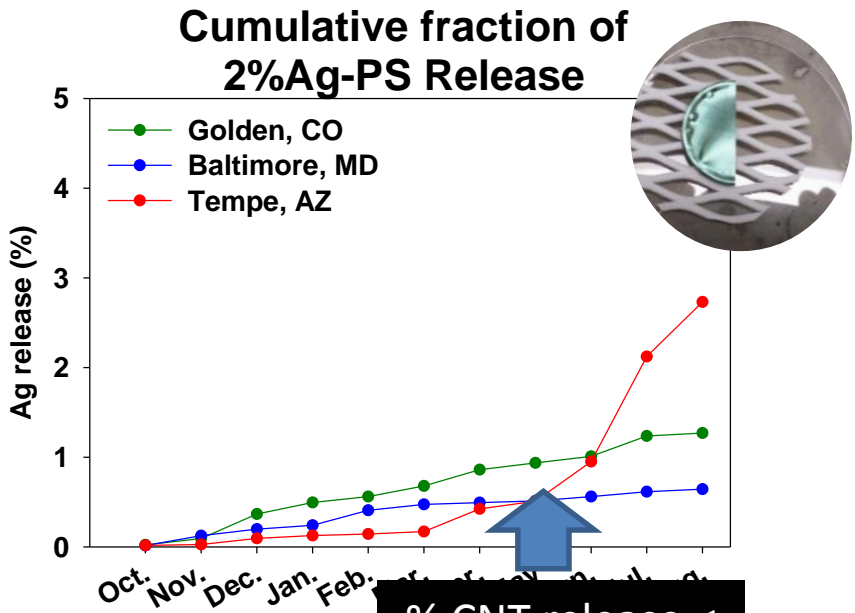
Results – SWCNT-PNCs Release



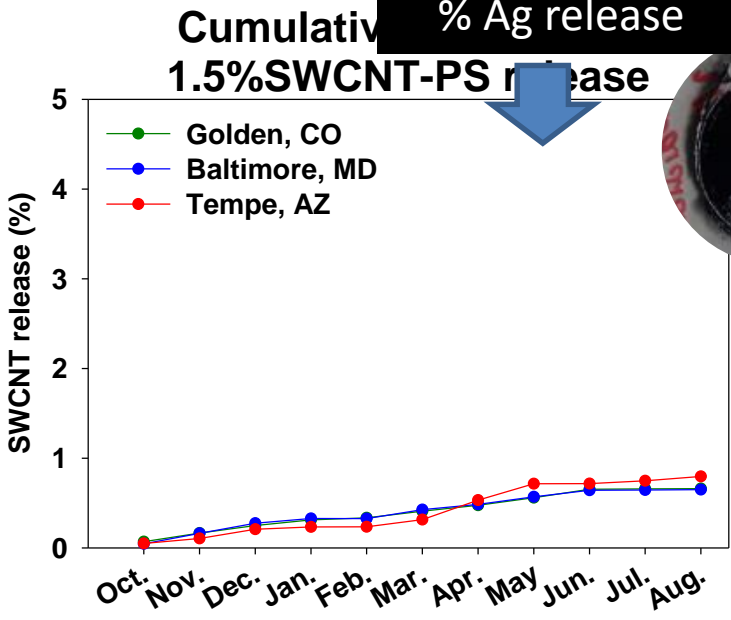
PCL is a photolabile polymer
 CNT release is strongly influenced by matrix photodegradation



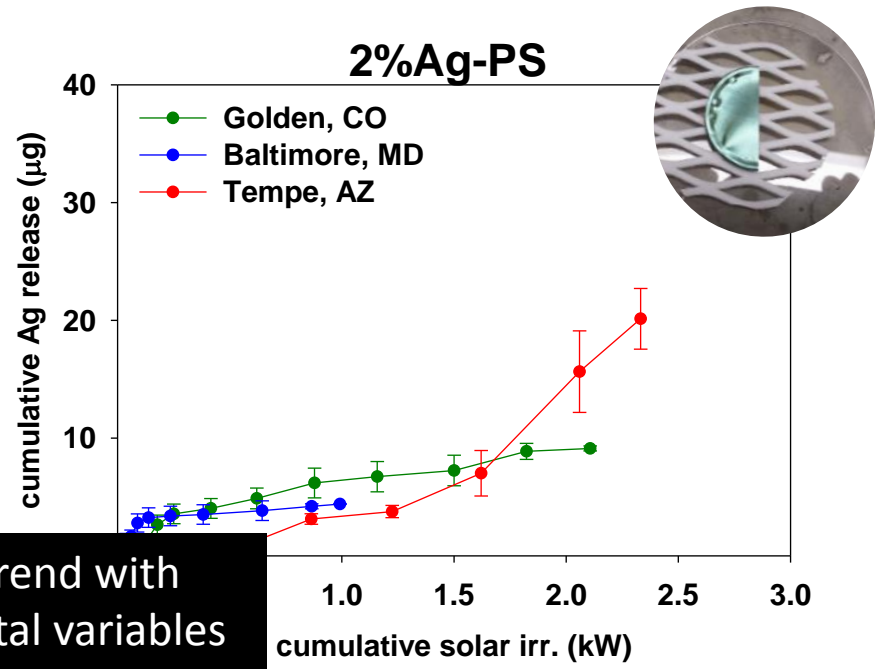
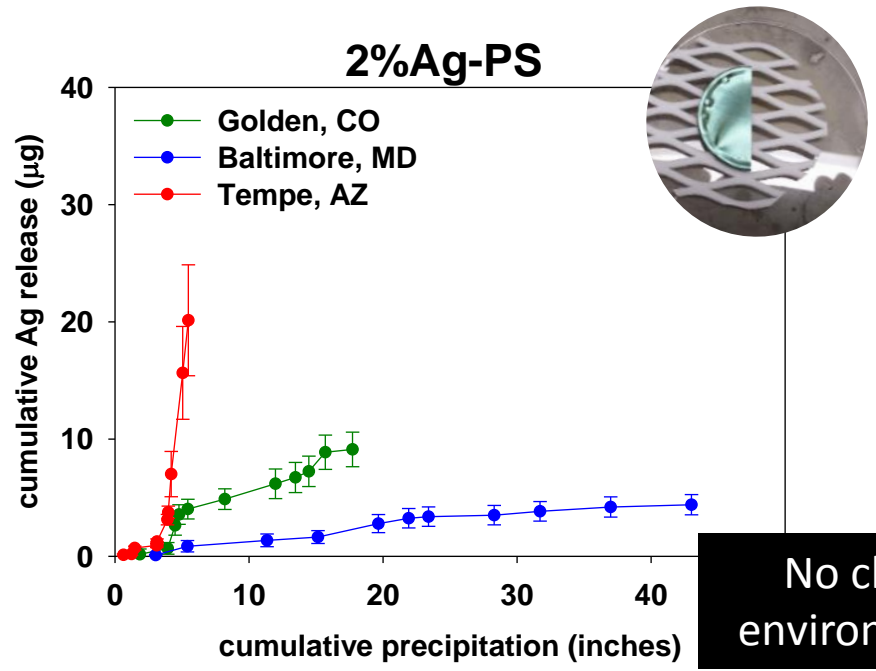
Results – Fractional Release from PNCs



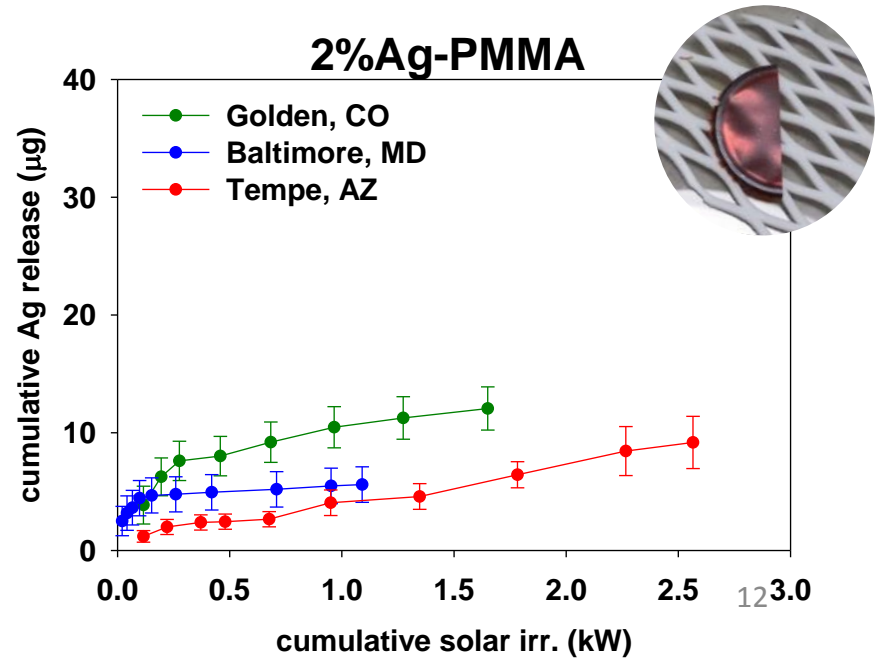
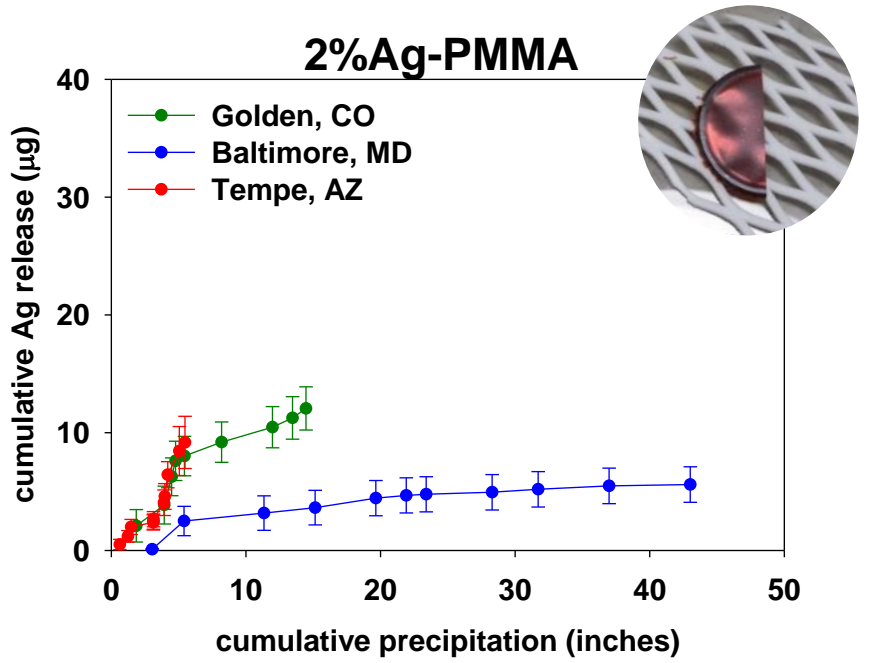
% CNT release < % Ag release



Results – Ag-PNC Release as a function of weather variables

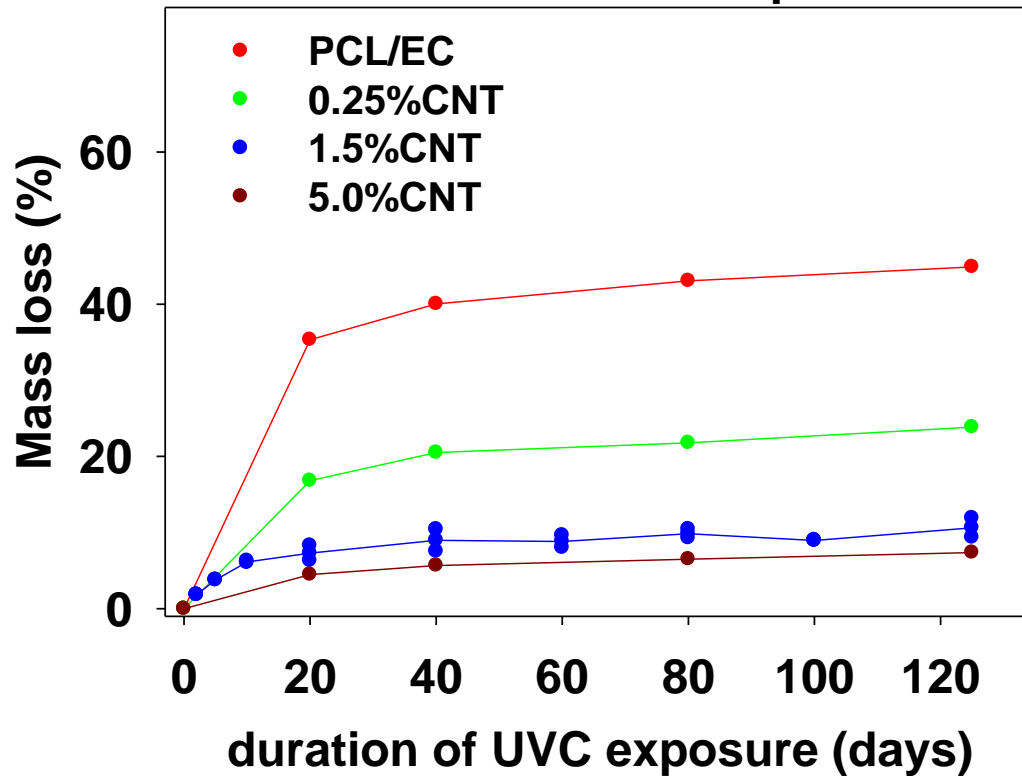


No clear trend with environmental variables

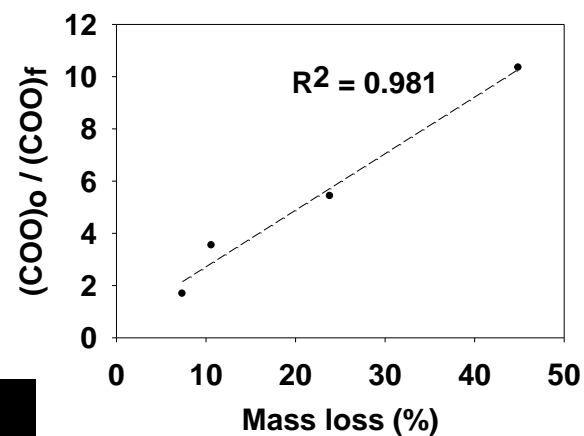
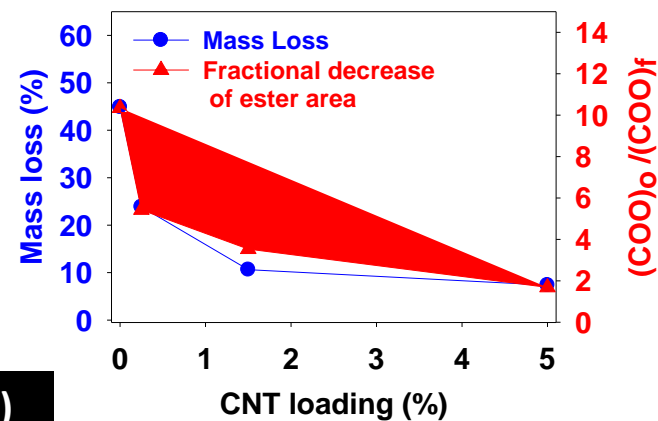
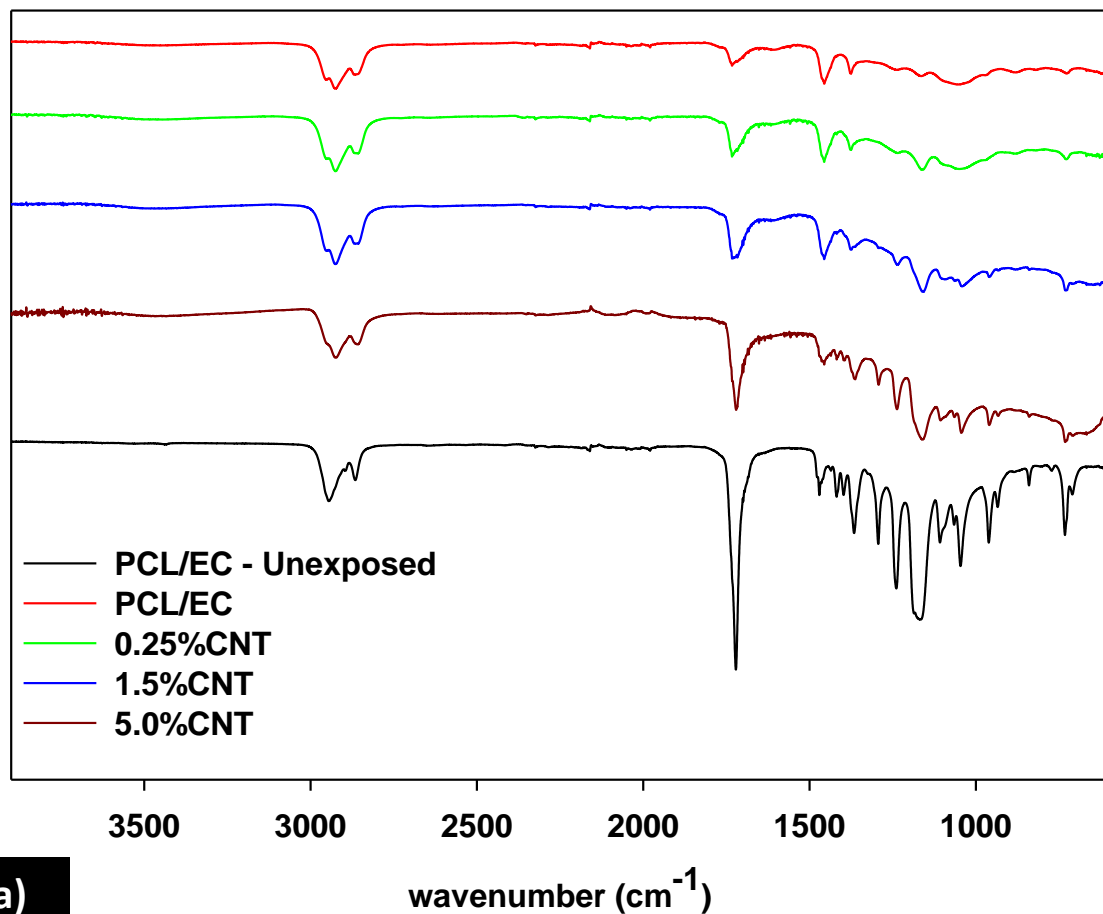


A slight sidebar: Influence of CNT Loading

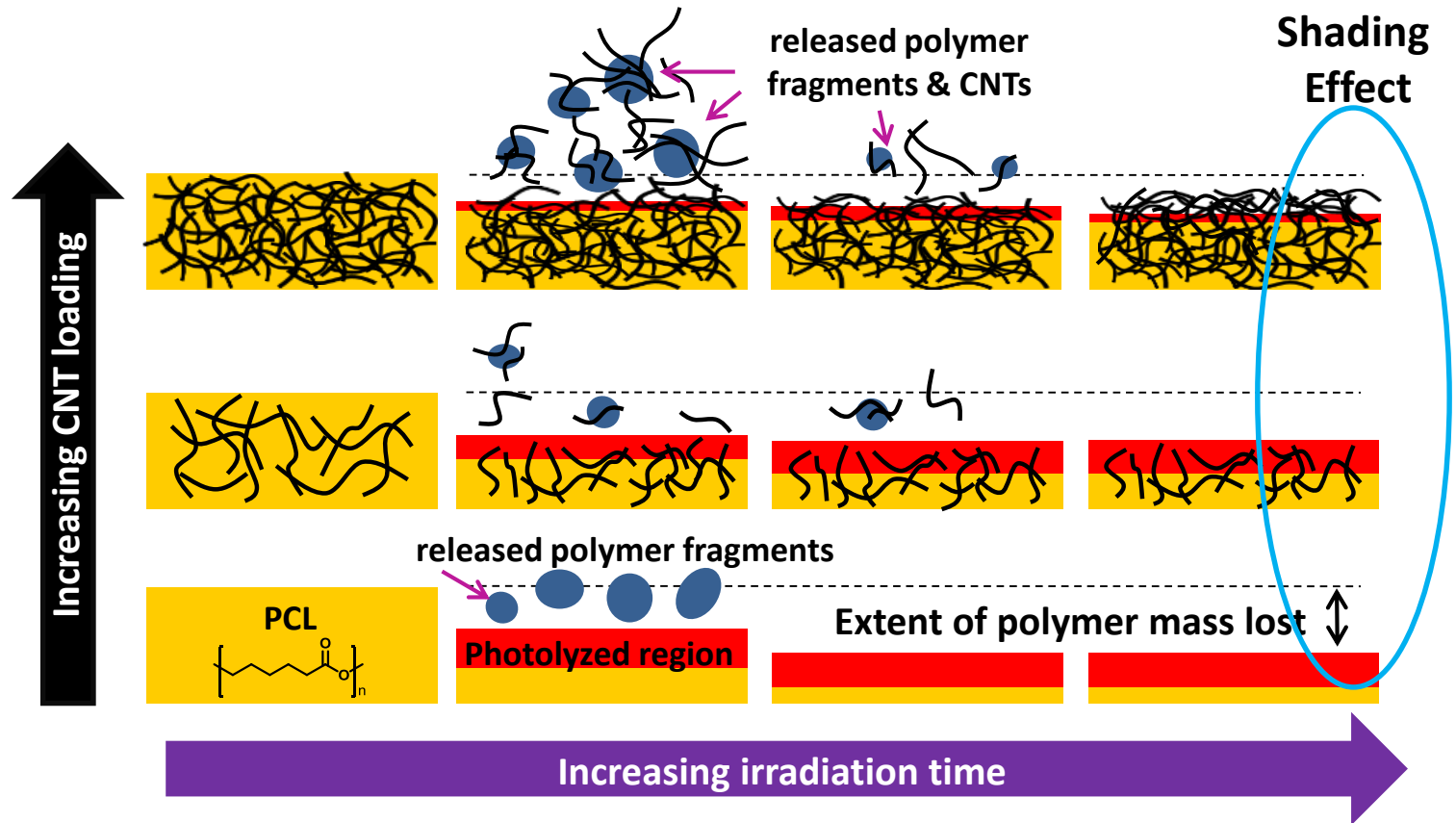
Mass loss of nanocomposites



Mass loss of SWCNT-PCL nanocomposites with varying SWCNT concentration (%w/w) following incremental periods of irradiation with 254nm light.



(a) ATR-FTIR analysis of the nanocomposites shows a reduction in ester (1720cm⁻¹) intensity following 125 days irradiation. (b) Following 125 days of exposure, the final mass loss and fractional decrease of ester band area track similarly with increased CNT loading. (c) mass loss increases linearly with the fractional decrease in ester band area



Representation of how the interface of polymer-CNT nanocomposites evolve as photodegradation proceeds, as a function of CNT loading.

CNT release will NOT scale linearly with loading

Part 2 - Release from commercial products

Pressure treated lumber



Contains:
CuNPs & purchased from
Home Depot

Blue pigment automotive paint

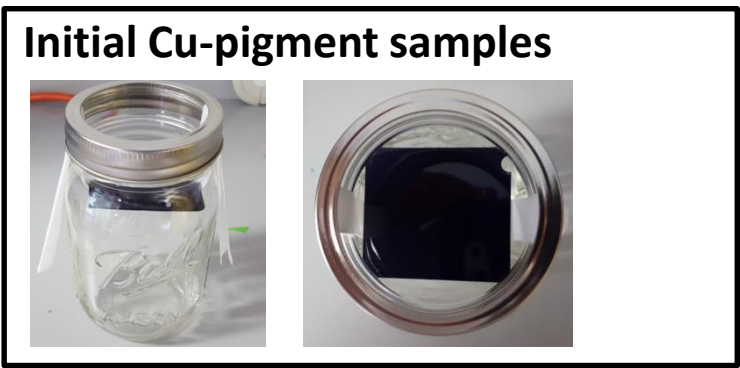


Contains:
CuNPs and provided by BASF



Wendel Wohleben

CuNP – pigment



July	Blank	Cu-Sample	Reference
Golden, CO	0.8 +/- 0.5 ug	0.9 +/- 0.5 ug	0.7 +/- 0.2 ug
Baltimore, MD	1.7 +/- 0.3 ug	2.7 +/- 1.5 ug	1.5 +/- 0.2 ug

August	Blank	Cu-sample	reference
Golden, CO	0.3 +/- 0.1	0.4 +/- 0.1	0.4 +/- 0.1
Baltimore, MD	1.4 +/- 0.4 ug	2.7 +/- 1.8 ug	4.3 +/- 1.8 ug

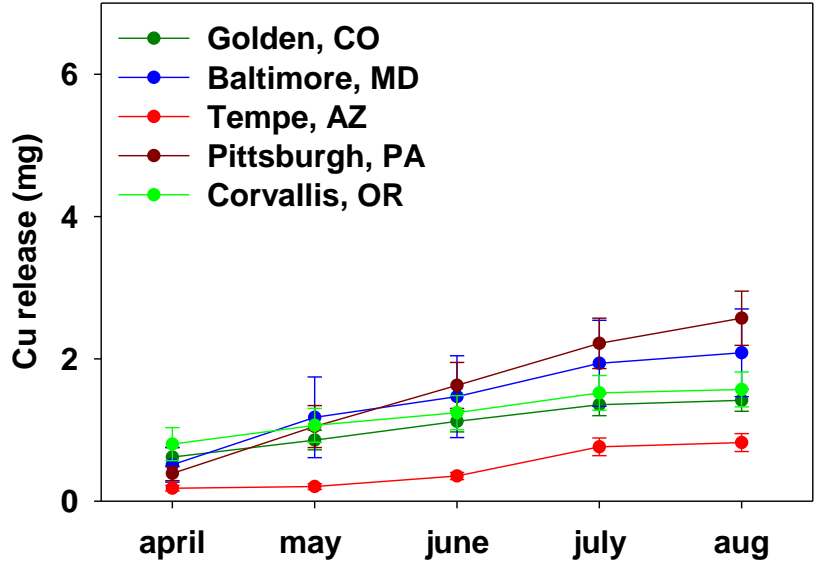


Background levels of Cu are much higher in Az

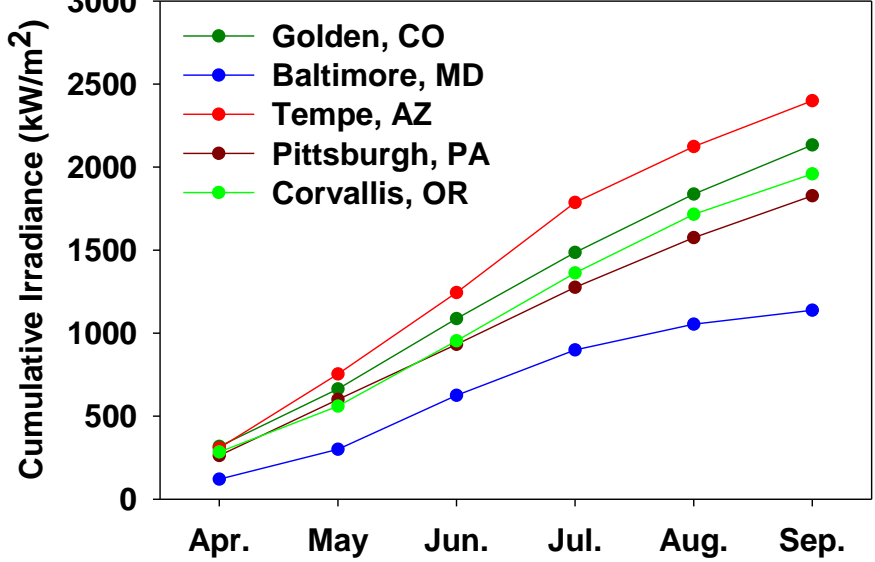
- Determining release of “naturally occurring NPs (e.g. Ti, Cu and Fe in some environments will be more challenging)

Release from Pressure treated lumber across the continental US

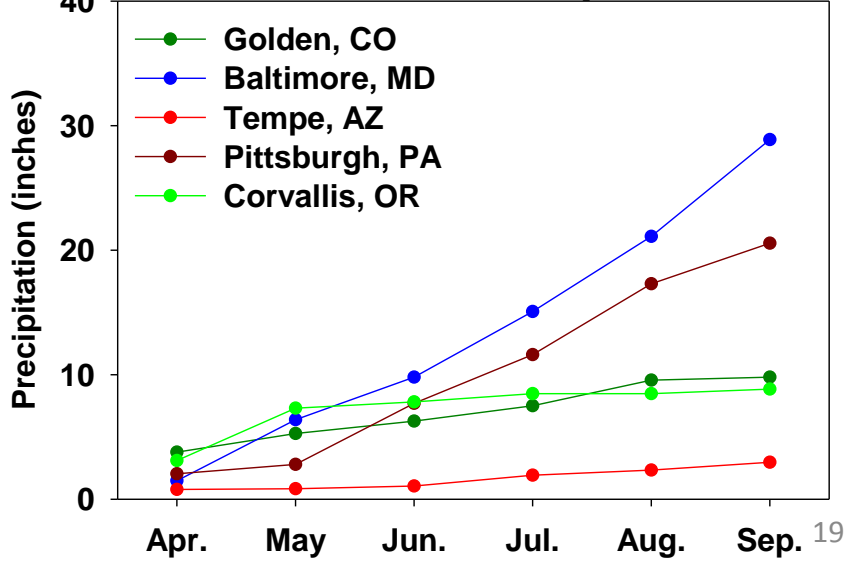
Cumulative Cu release



Cumulative Solar Irradiance

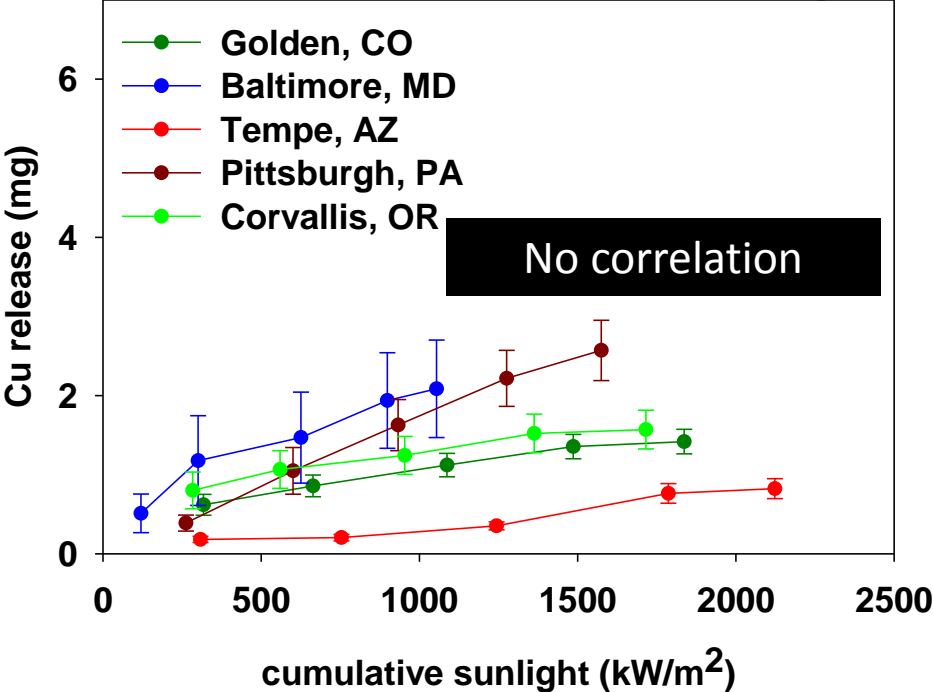


Cumulative Precipitation

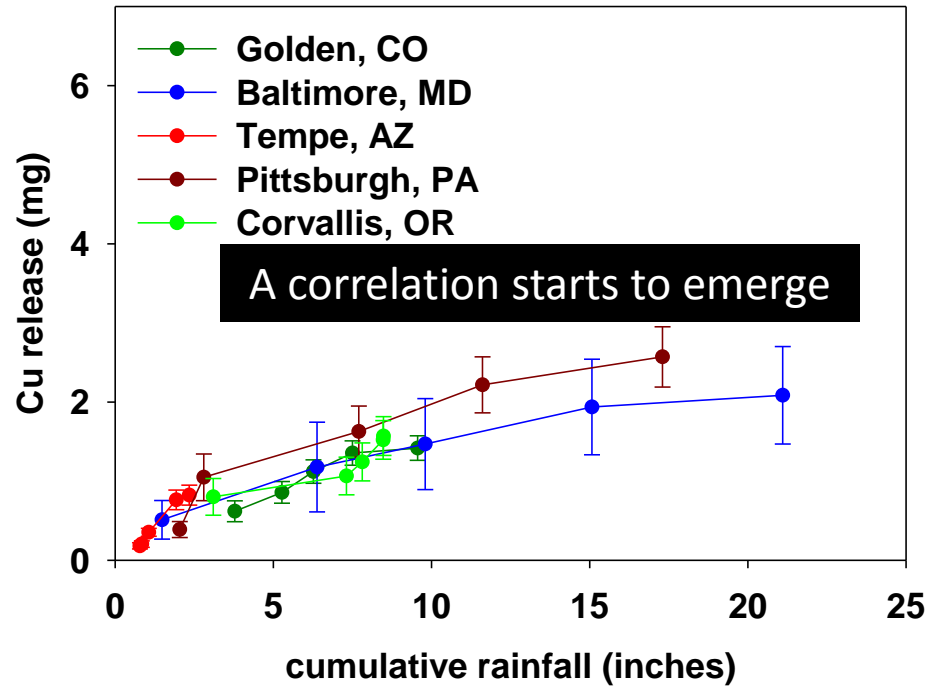


Release from Pressure treated lumber across the continental US – as a function of specific weather variables

Release as function of sunlight



Release as a function of rain



Acknowledgements



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CMU



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ASU



James Ranville
CSM



Yan Wang
U Pitt



Yuqiang Bi
ASU



Rob Reed
ASU & CSM



David Hannigan
ASU



Katie Challis
CSM



Ronald Lankone
JHU

