Nano-waste: Potential Environmental Health and Safety (EHS) Implications during Thermal Decomposition of Nano-Enabled Products (NEPs)

Dilpreet Singh, Georgios Sotiriou, Christa Watson, Wendel Wohlleben, Philip Demokritou

Sixth Sustainable Nanotechnology Organization Conference

Los Angeles, CA

November 7, 2017

HARVARD T.H. CHAN SCHOOL OF PUBLIC HEALTH

CENTER FOR NANOTECHNOLOGY AND NANOTOXICOLOGY

http://hsph.harvard.edu/nano

Presentation Outline

- Introduction – Lifecycle Perspective Risk Assessment of NEPs
- Knowledge Gaps for End of Life: Thermal Decomposition Scenario
- Research Strategy:
  - Development of a novel “<u>Integrated Exposure Generation System</u>” to assess thermal decomposition and associated EHS implications of NEPs
  - Results for industrially-relevant NEPs
  - Conclusions, Outlook and Significance

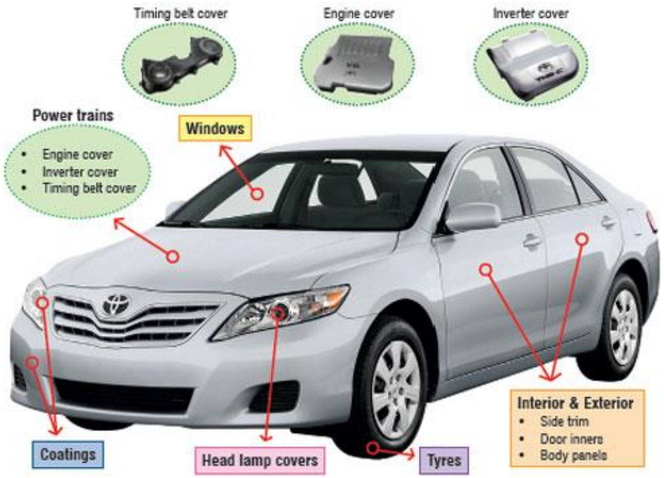
"The nano the better": The new motto of many industries

- **Engineered nanomaterials (ENMs, < 100 nm)** are increasingly being incorporated into a variety of consumer products **(called nano-enabled products, NEPs)**

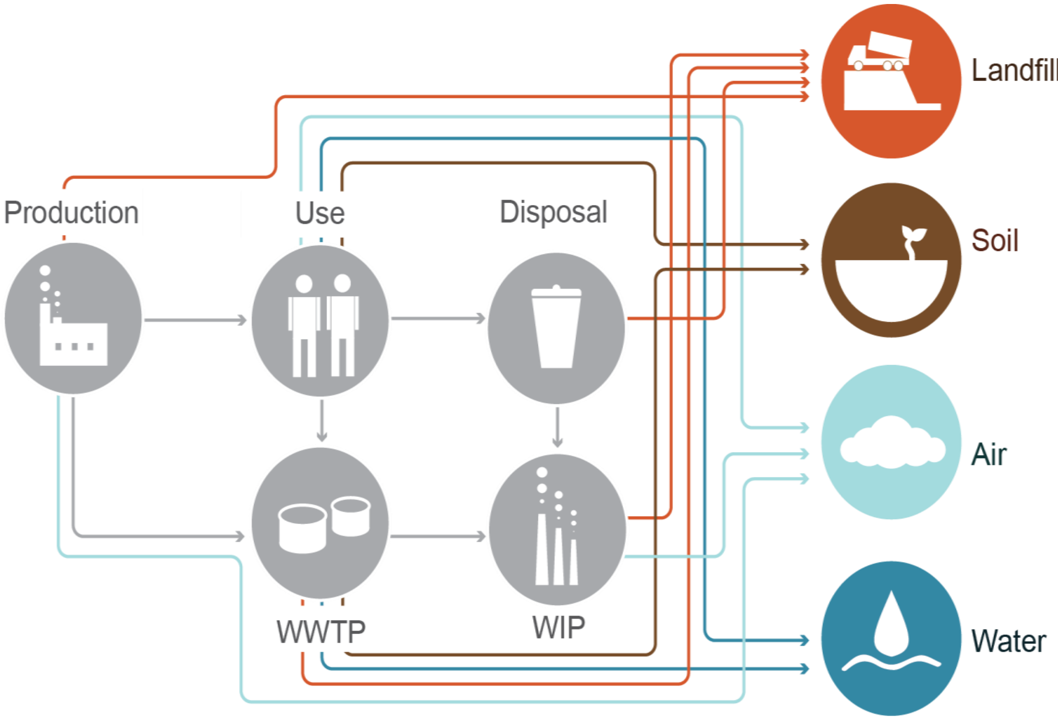
- **Examples** include cosmetics, paints, coatings, building materials, automobiles, printer toners, thermoplastics, and so on…

- ENMs impart **superior properties** like mechanical strength, thermal stability, optoelectronics, antibacterial resistance, etc. making them desirable in high performance products

- Global value of NEPs, ENMs and nano-intermediates projected to reach **US $4.4 trillion** by 2018 ***(Lux Research 2014)***



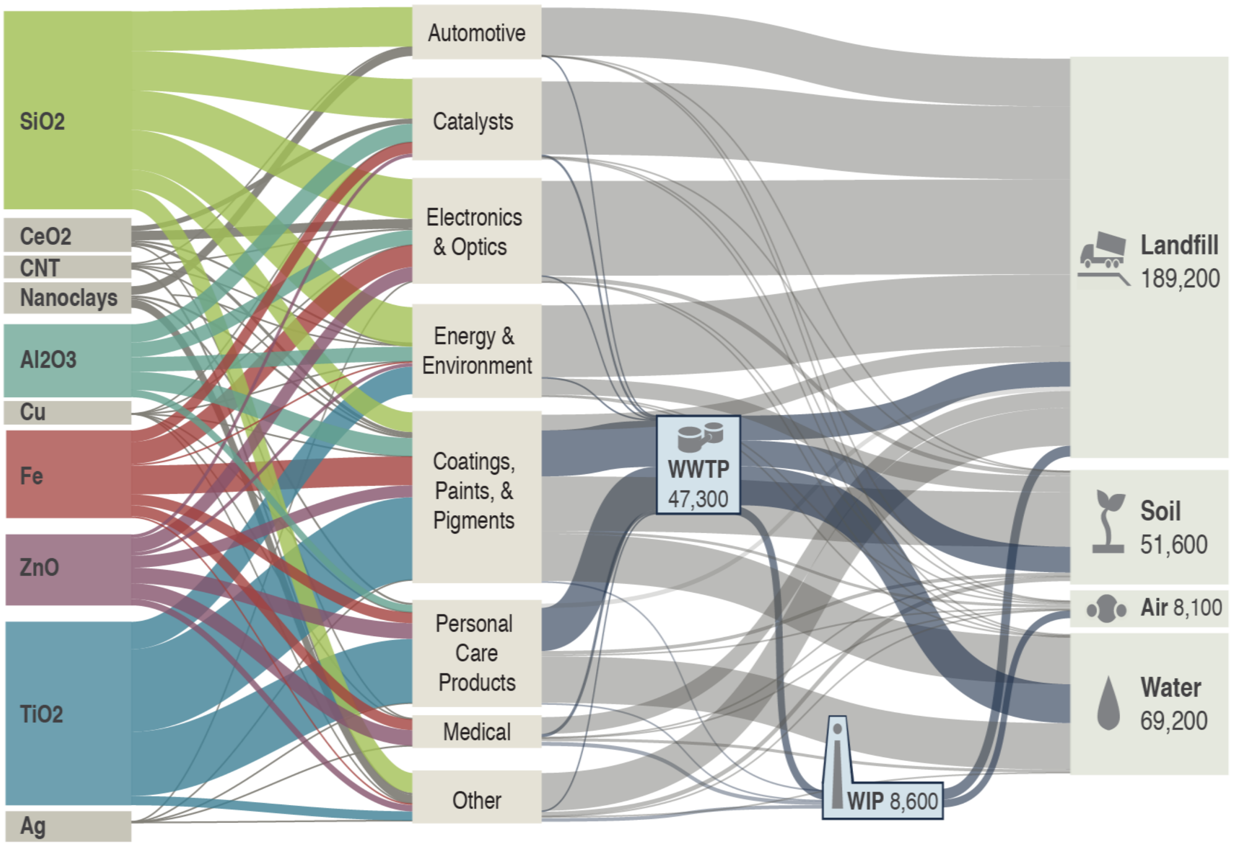
Life-cycle considerations of ENMs across value chain and life cycle



Keller and Lazareva, ES&TL, 2014

- ENM properties change in both value-chain, and across life cycle of NEPs
- Limited data on ENM release across LC of NEPs
- Fragmentary exposure data for both environmental media and human populations

Nano-waste crisis: ENMs from major applications across life cycle



(all flows in metric tons/yr, 2010 estimates from Future Markets, Inc.)

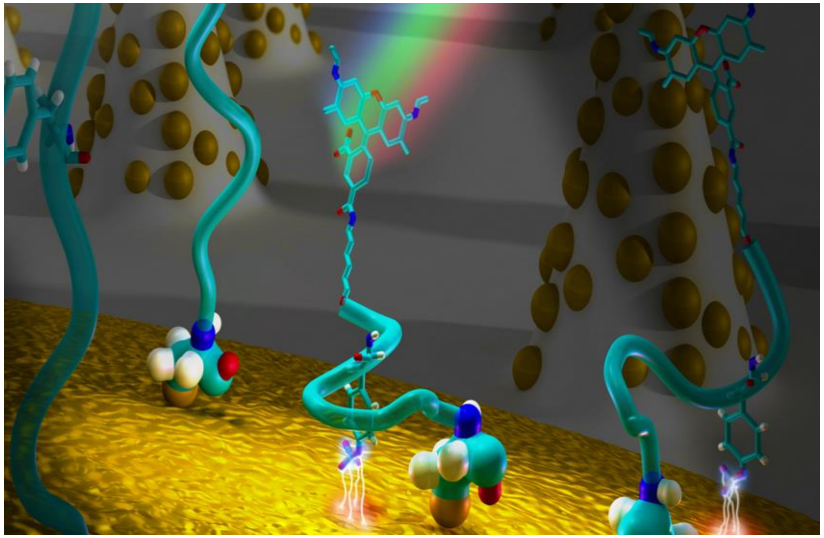
Keller and Lazareva, ES&TL, 2014

- 60-80 % of ENMs end up in landfills
- 190,000 m. tons/yr of ENMs in landfills
- 20,000 m. tons/yr in WIP
- Two applications contribute the most in releases in environmental media:
  - Personal care products
  - Coatings, paints and pigments

How is Nano Risk being assessed?

- ENMs have unique properties as compared to their macroscale counterparts

- Mounting evidence shows that some ENMs may elicit adverse biological and environmental effects



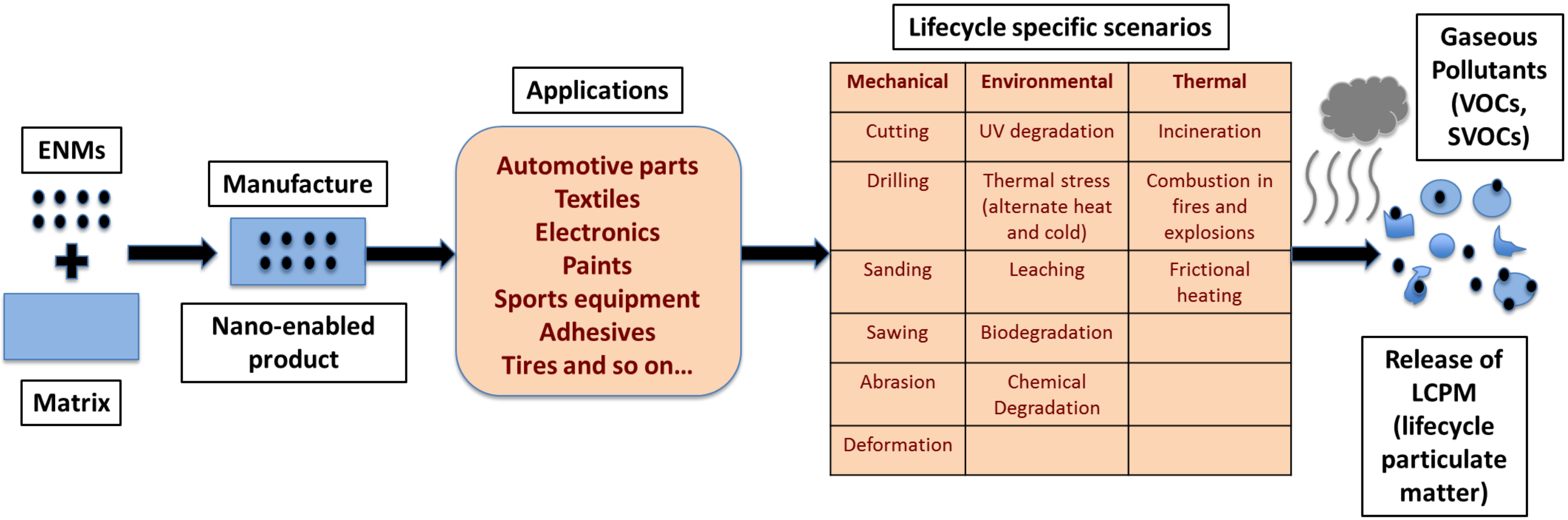
Source: http://nanobionics.mntl.illinois.edu/LNBL/

- **HOWEVER,** the current ***"modus operandi"*** in nano risk assessment focuses only on the hazards of pristine ENMs, which is not appropriate to address risks associated with NEPs across their lifecycle

- Nano risk assessment must include exposure data across the lifecycle (from **Manufacture → Consumer Use → End-of-Life**) and toxicology of associated nano-releases, since **RISK** = **EXPOSURE** x **HAZARD**

Lifecycle Particulate Matter (LCPM) Releases from NEPs

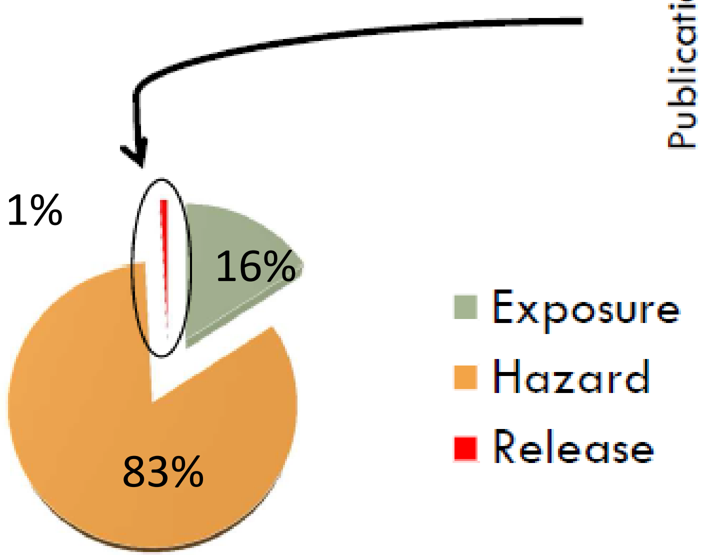
Releases from NEPs will be Application- and Lifecycle Scenario- specific

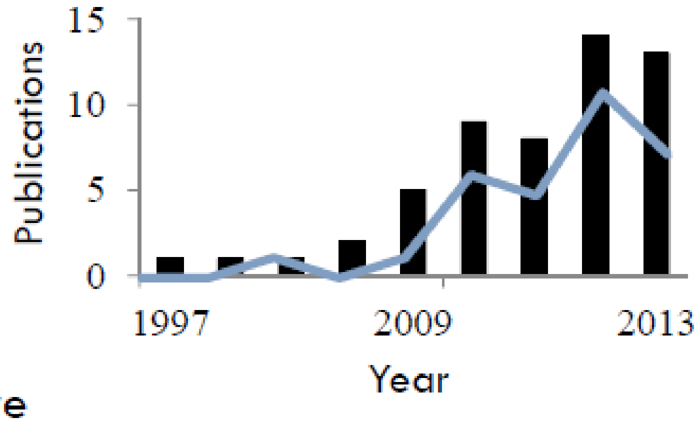


Mechanical	Environmental	Thermal
Cutting	UV degradation	Incineration
Drilling	Thermal stress (alternate heat and cold)	Combustion in fires and explosions
Sanding	Leaching	Frictional heating
Sawing	Biodegradation	
Abrasion	Chemical Degradation	
Deformation		

- Released LCPM expected to have **different physicochemical, morphological and toxicological properties** than the pristine ENMs
- Released LCPM may or may not contain the ENMs originally incorporated in the matrix
- LCPM release may be accompanied by release of **gaseous co-pollutants** such as semi/volatile organic compounds (e.g., PAHs)
- Overall LCPM + gaseous release and their physicochemical and toxicological properties **may be different** for a NEP compared to a product without ENMs

Limited but emerging research on LCPM release for families of NEPs





Froggett et al, Part Fibre Toxicol 2014, 11:17

*~**54** studies focused on inducing, detecting & characterizing release from solid nanocomposites*

Major drawback: Lack of standardized, reproducible LC specific nanorelease methodologies

Prior TD Studies and their Limitations

- Very few studies
- Prior studies: On either ***pristine nanomaterials*** or ***surrogate wastes spiked with "free" ENMs***
  - Walser et al. (2012) investigated fate of raw CeO_2 nanoparticles in an incinerator and found that they do not escape into the atmosphere but would likely end up in the solid waste residues
  - Vejerano et al. (2014) studied the fate of ENMs spiked to paper/plastic wastes during incineration and found that very small amounts of ENMs partition to the aerosol phase; most of them partition to bottom ash
- Most studies focus only on characterization of size and concentration of the released aerosol
  - Bouillard et al. (2013) studied incineration of CNT-polymer composites and found that a large fraction of released PM was in the nano-regime (<100 nm) and contained some released CNTs
- In toto, there is lack of a detailed and systematic investigation of potential factors (combustion conditions, NEP properties) governing TD behavior of families of NEPs

Knowledge Gaps related to TD of NEPs

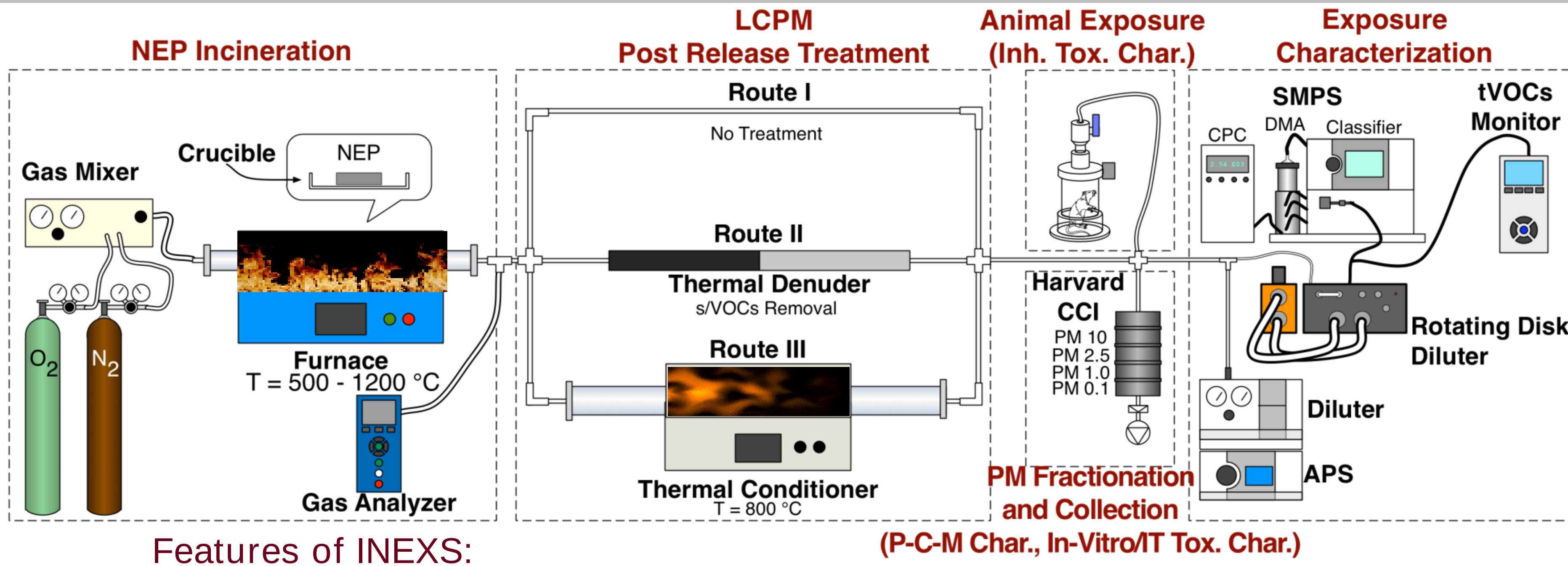
There is lack of a STANDARDIZED, REPRODUCIBLE & VERSATILE methodology to investigate the thermal decomposition (TD) behavior of families of NEPs and its associated EHS implications

- SPECIFICALLY, following **Knowledge Gaps** remain:
  - *Is there* engineered nanomaterial release *during TD of NEPs?*
  - *How does* nanofiller impact the physicochemical and morphological (P-C-M) properties *of byproducts?*
  - *What is the* role of NEP matrix *in nanofiller release and P-C-M properties of byproducts?*
  - *How does* nanofiller presence affect the toxicological profile *of byproducts?*
  - *What is the* fate and transport of byproducts *in various natural environments?*

Research Strategy

TASK 1	Development Integrated Exposure Generation System for the EHS Characterization of Incinerated NEPs	
TASK 2	Detailed Physicochemical and Morphological Characterization of Byproducts (Released Aerosol **AND** Residual Ash) of Industry Relevant NEPs	
TASK 3	Assessment of EHS Implications of Byproducts (Released Aerosol **AND** Residual Ash)	
	in-vitro and in-vivo Toxicological Characterization	Fate and Transport of Residual Ash in Environment
TASK 4	Safer-by-design Nano-Enabled Products	

Development of Integrated Exposure Generation Platform (INEXS)



Features of INEXS:

- Digitally controlled temperature (up to 1200 ^{0}C) and ramp rate
- Controlled combustion conditions (O_2 : N_2 ratio)
- Real-time monitoring of aerosol size and concentration, gaseous composition and total VOC concentration
- Suitable for both P-C-M and toxicological characterization of released lifecycle particulate matter (LCPM)

- Sampling of size fractionated LCPM ($PM_{0.1}$, $PM_{0.1-2.5}$, $PM_{>2.5}$) using the Harvard Compact Cascade Impactor (CCI) **(Demokritou et al., Journal of Aerosol Science, 2004)**
- Provision to treat the released aerosol through different routes: Route 1 (no treatment), Route 2 (thermal denuder to selectively remove SVOCs), and Route 3 (thermal conditioner for additional heat treatment for a minimum residence time to simulate commercial incineration facilities)

Sotiriou et al, Environmental Science: Nano (2015).

INEXS Setup in Lab

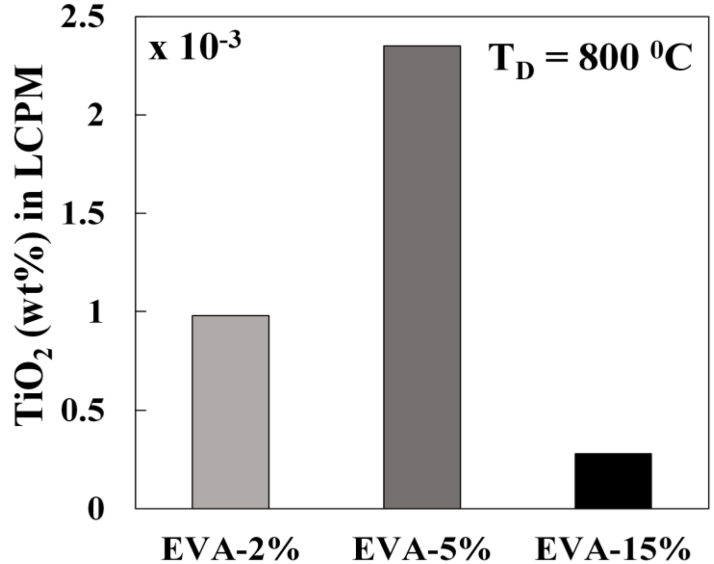
Industrially-relevant NEPs (Thermoplastics)

Matrix	Nanofiller	Nanofiller Loading (wt%)	Applications
Polyurethane (PU)	-	-	Automotive, buildings, textiles
	Carbon black (CB)	0.1%	
	Carbon nanotubes (CNT)	0.1%	
Polyethylene (PE)	-	-	Packaging, buildings, construction
	Fe_2O_3	1%, 5%	
	Organic dye	2%	
Polycarbonate (PC)	-	-	Automotive, electronics
	CNT	3%	
Polypropylene (PP)	-	-	Packaging, electronics
	CNT	3%	
Ethylene vinyl acetate (EVA)	-	-	Packaging, biomedical devices
	TiO_2	2%, 5%, 15%	

Sotiriou et al, J. Haz. Mat. (2016); Singh et al, Env. Sci.: Nano (2016)

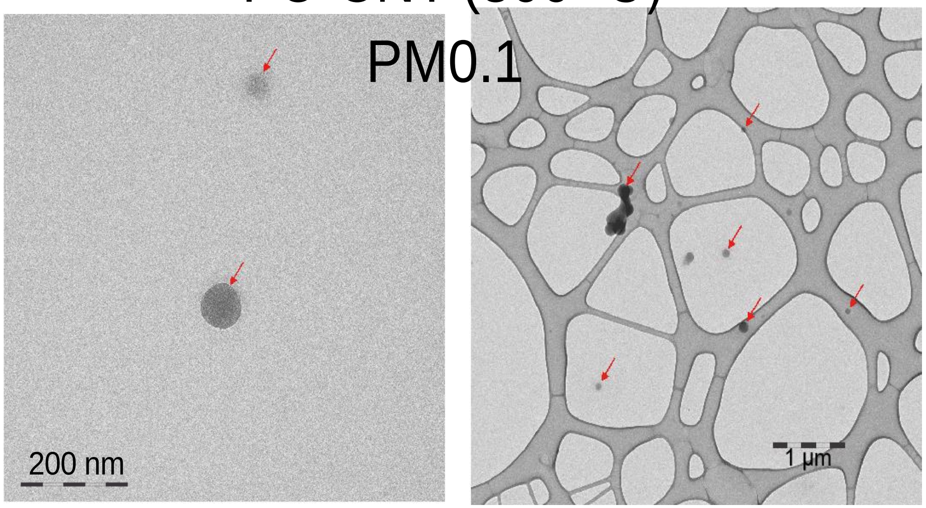
Results *(1/10)*: Is there nanofiller release in the air?

- **Yes**, there is a **detectable release** of nanofiller, especially for **inorganic nanofillers** such as **Fe_2O_3** (PE matrix) and **TiO_2** (EVA matrix)
  - *Fe: 0.026 wt% in $PM_{0.1}$ for T_D = 800 ^{0}C [ICP-MS]*
  - *TiO_2: <0.0024 wt% in $PM_{0.1}$ for T_D = 800 ^{0}C [ICP-MS]*
  - *There is a "Nanofiller Loading Effect" on the nanofiller concentration in released aerosol*
- However, **no release in the air** is observed for **carbonaceous nanofillers** such as carbon nanotubes (CNTs), irrespective of polymer matrix (PU, PP, PC)



PU-CNT (800 ˚C)

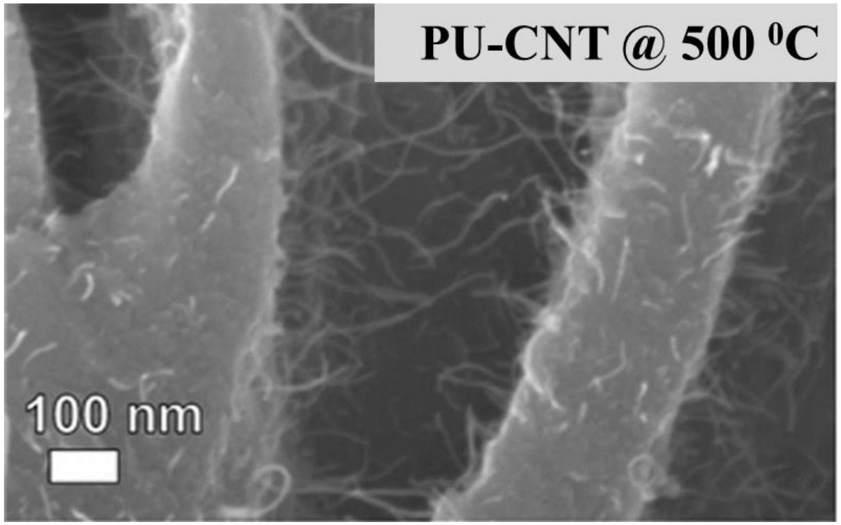
PM0.1

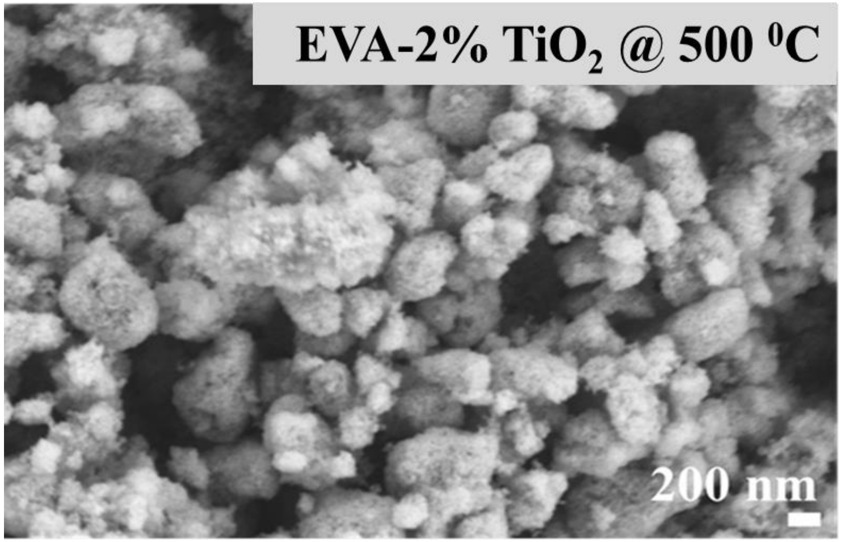


Singh et al, Environmental Science: Nano (2016)

Results *(2/10)*: Is nanofiller present in the residual ash?

- **Yes, most of the nanofiller is found in the residual ash** after thermal decomposition of NEP
- **Carbonaceous nanofillers (e.g., CNTs)** are found in residual ash only at the lower decomposition temperature of 500 ^{0}C; but they are fully combusted at 800 ^{0}C
  - *CNTs are homogenously dispersed throughout the degraded PU matrix and protrude from the surface*
- **Inorganic nanofillers (e.g., TiO_2, Fe_2O_3)** are present in residual ash at both low and high decomposition temperatures.
  - *TiO_2 is present as loose nanoparticles while the EVA matrix is completely combusted*
- Nanofiller concentration in residual ash is **significantly enriched** as compared to its original concentration in the NEP
  - **Potential** *for further release of nanofiller from degraded polymer matrix of residual ash under natural weathering conditions in landfills*

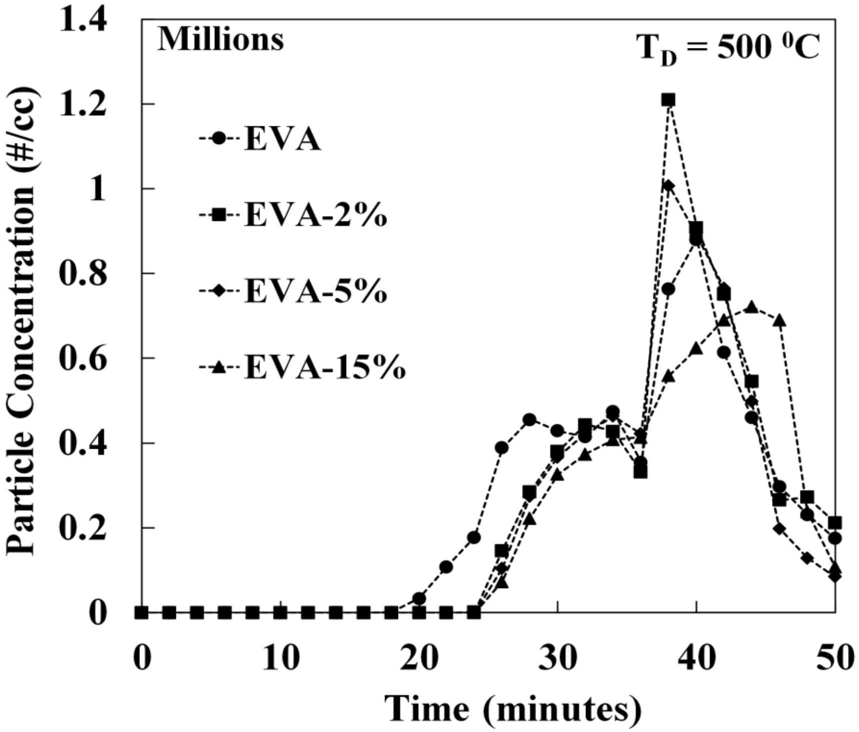


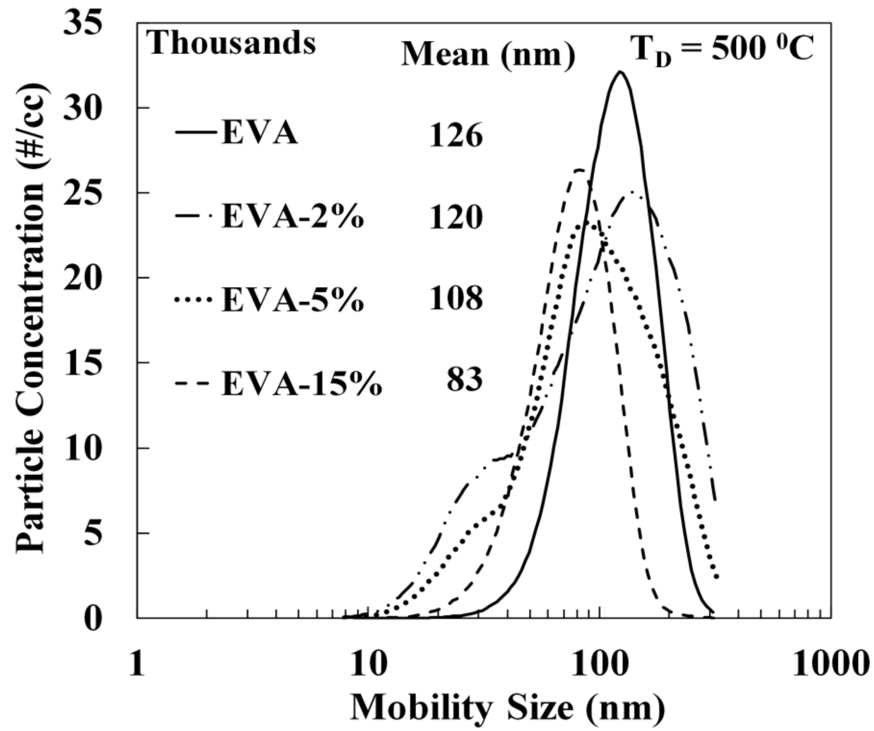


Singh et al, Environmental Science: Nano (2016)

Results *(3/10)*: Does nanofiller affect released aerosol size/concentration?

Real-time LCPM characterization: EVA vs. EVA-TiO_2





- **Yes,** nanofiller presence affects both released aerosol concentration and size distribution
- A "Nanofiller Loading Effect" is also observed on both released aerosol concentration and size
  - *Both concentration and size tend to **decrease** with increasing nanofiller loading*
  - *Possibly due to combustibility changes with nanofiller loading*

Results *(4/10)*: Does nanofiller or polymer matrix determine LCPM EC/OC chemistry?

Elemental/Organic Carbon (EC/OC) Analysis of $PM_{0.1}$

NEP	Released Aerosol			
	500ºC		800ºC	
	EC (%)	OC (%)	EC (%)	OC (%)
PU	0.9	99.1	0.8	99.2
PU-CNT	0.7	99.3	0.9	99.1
PU-CB	0.6	99.4	0.7	99.3
PE	0.4	99.6	0.3	99.7
PE-5% Fe_2O_3	0.3	99.7	0.3	99.7
PE-2% org. dye	0.3	99.7	0.3	99.7
EVA	0.3	99.7	0.4	99.6
EVA-2% TiO_2	0.3	99.7	0.3	99.7
EVA-5% TiO_2	0.3	99.7	0.3	99.7
EVA-15% TiO_2	0.4	99.6	0.2	99.8

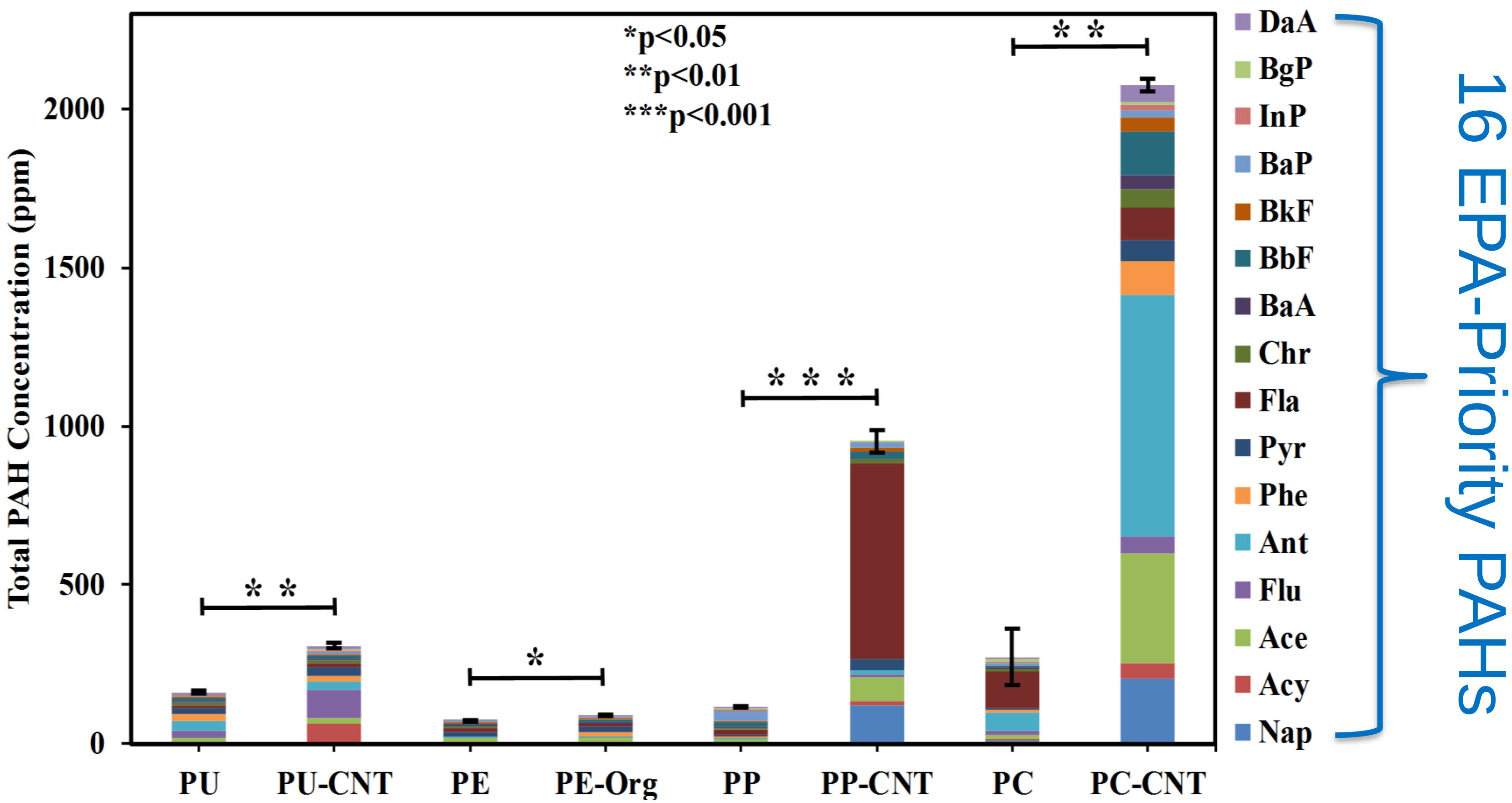
- Overall EC-OC chemistry of LCPM appears to be **governed by the "Host Polymer Matrix"**, rather than the nanofiller.
  - *LCPM contains >99 wt% of organic carbon (OC) irrespective of nanofiller or loading or final decomposition temperature.*

More Questions??

- How about the organic species in the released LCPM?

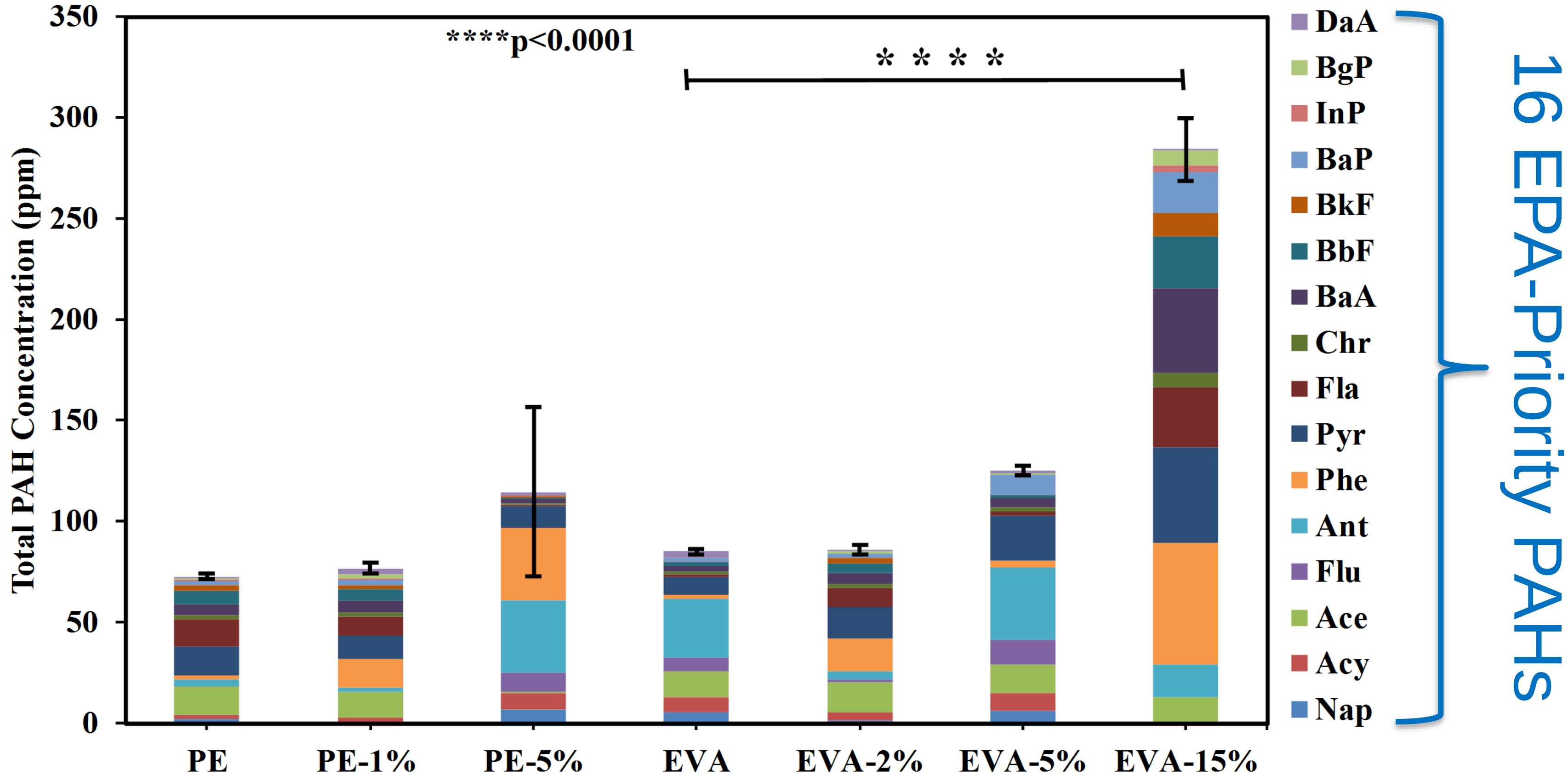
- Can certain released ENMs and gaseous co-pollutants synergistically modify p-c-m properties of OC and enhance toxicological profile of released LCPM?

Results (5/10): How does nanofiller presence affect LCPM PAH content?



- The **presence of nanofiller** enhances the **Total PAH content** of LCPM
  - *Enhancement for PC-CNT was highest, nearly 8 times that of PC*

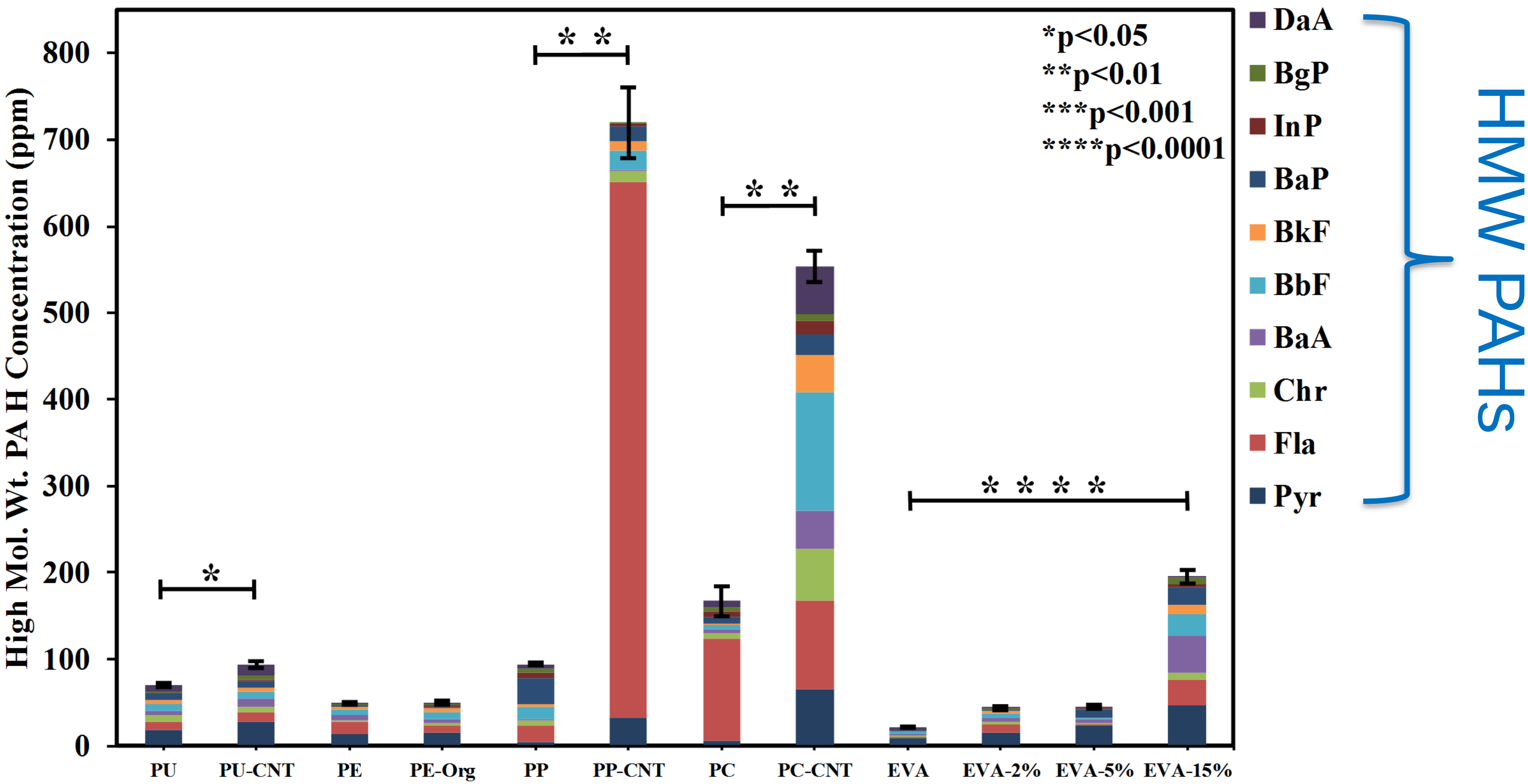
Results (6/10): How does nanofiller loading affect LCPM PAH content?



- **Increase in nanofiller loading** <u>enhances</u> the **Total PAH content** of LCPM for PE-Fe2O3 and EVA-TiO2
- Probably attributed to the catalytic activity of released metal oxide ENMs

Singh et al, Environmental Science & Technology (2017)

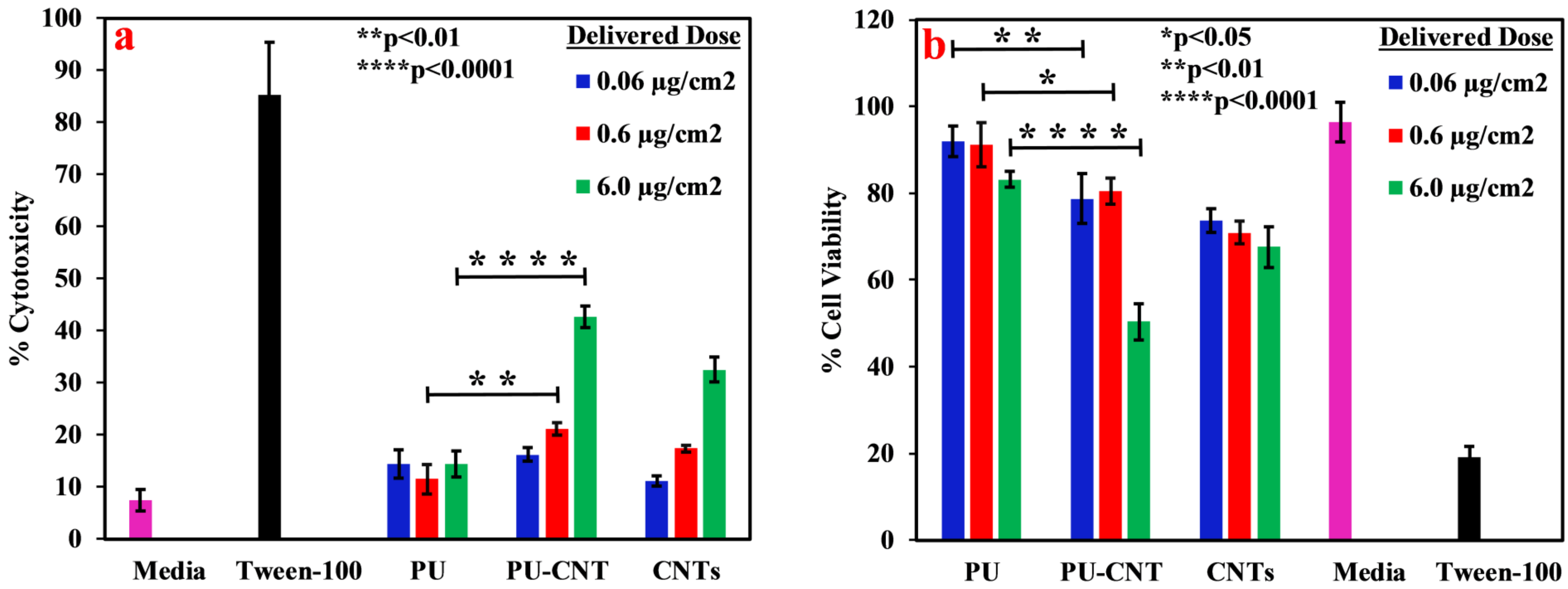
Results *(7/10)*: Does nanofiller affect LCPM PAH speciation?



The presence of nanofiller enhances concentration of the Higher Molecular Weight (HMW, mol. wt. > 178.2) PAHs that are considerably more toxic/carcinogenic than the LMW PAHs ---> does this translate to increased toxicity of LCPM in presence of nanofiller?

Results (8/10): Does nanofiller affect toxicological profile of released LCPM?

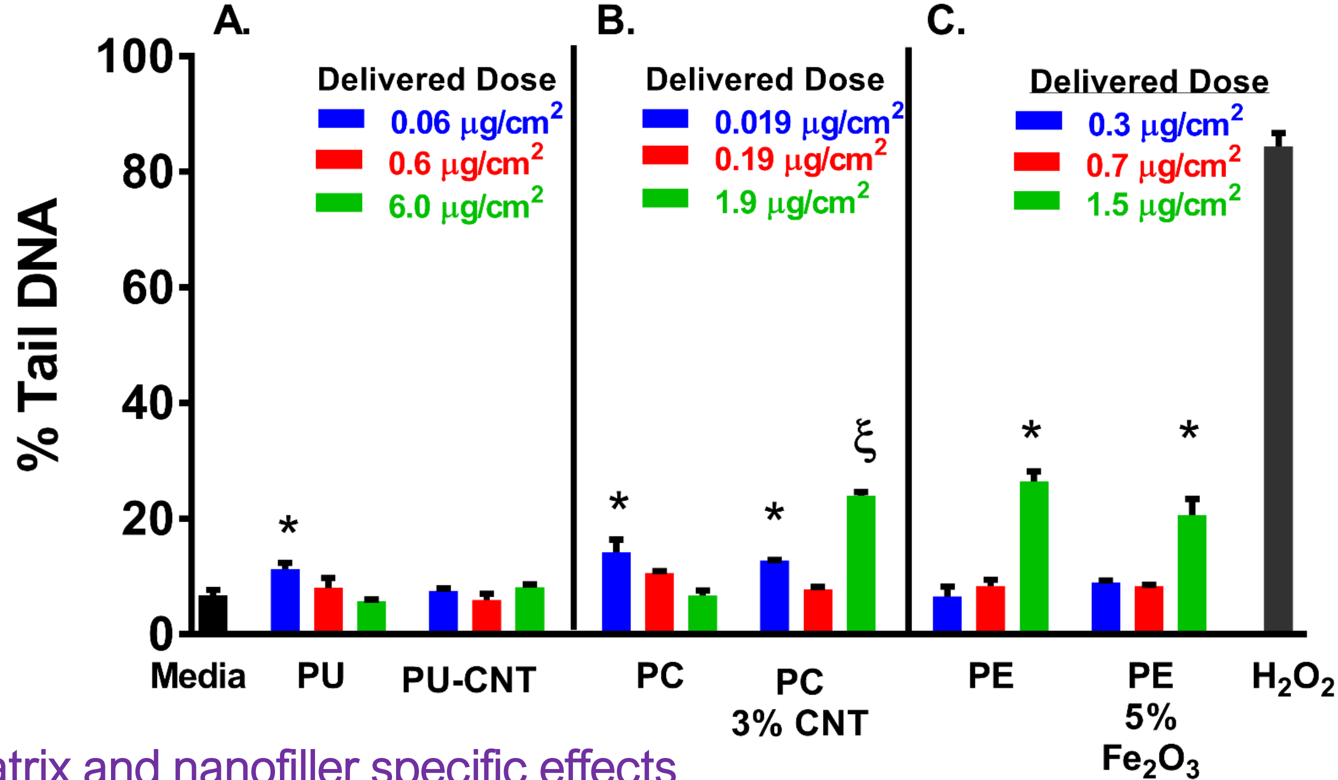
In-Vitro Toxicological Assessment of released LCPM ($PM_{0.1}$) against human small airway epithelial cells: Case Study of PU vs. PU-CNT



- **<u>Yes</u>**, there is a "Nanofiller-specific Effect" on the toxicity of released LCPM
- The $PM_{0.1}$ LCPM from PU-CNT exhibits <u>significantly higher cytotoxicity</u> as compared to pure PU
- The $PM_{0.1}$ LCPM from PU-CNT exhibits <u>significantly lower cell viability</u> as compared to pure PU

Results *(10/10)*: Can released LCPM induce DNA damage?

CometChip Platform for Assessment of Genotoxic Potential: Case Study of PU vs. PU-CNT, PC vs. PC-CNT and PE vs. PE-Fe_2O_3



- <u>Yes</u>, matrix and nanofiller specific effects
- LCPM from PC-CNT induces <u>more single stranded DNA breaks</u> compared to the pure PC
- No significant nanofiller effect on DNA damage was observed for PU vs. PU-CNT and PE vs. PE-Fe_2O_3

Watson-Wright et al, NanoImpact (2017)

Conclusions/Outlook

Conclusions:

- We developed an Integrated Exposure Generation System (INEXS) for a systematic investigation of the thermal decomposition of a wide variety of thermoplastics and associated EHS implications.
- There is nanofiller release in the air, and seems more likely for metal/metal oxide ENMs than carbonaceous nanofillers.
- Bulk of the nanofiller is retained in the residual ash as loosely held nanoparticles and therefore raises concerns about its release, fate and transport in the environment.
- Released LCPM chemistry is determined by the polymer matrix on the macro-scale (EC/OC), but the nanofiller plays an important role in the speciation distribution of organic compounds such as PAHs.
  - **Nanofiller enhances total PAH content as well HMW (more toxic) PAHs in the LCPM due to catalytic effects of released LCPM**
- There is a nanofiller-specific effect on the toxicity and risks of released LCPM particles, most probably attributed to the nanofiller-mediated change in PAH profile of LCPM
  - **LCPM from NEPs shows higher cytotoxicity and DNA damage in-vitro as compared to polymer without nanofiller for thermoplastics containing catalytic nanometals**

Future work

- We aim to investigate thermal degradation and associated EHS implications of industrially-relevant nano-enabled building materials such as Nano-enabled Paints/Coatings under a variety of TD scenarios including the incomplete combustion scenario relevant for indoor building fires.
- We will study the Fate and Transport of Residual Ash under various natural environments (soil, aquifers, streams, etc.)

Significance/Impact of Results

- Research addresses critical EHS issues pertaining to the thermal degradation of NEPs in a commercial incinerator and during uncontrolled fire scenarios

- Linking specific toxicological and EHS effects arising from thermal decomposition of NEPs to NEP properties and combustion conditions can help industry to
  - **Come up with safer-by-design formulations for nano-coatings**
  - **Design more effective exposure control strategies for professionals such as incineration facility workers and firemen**
  - **Design specialized disposal methods for incinerated residues containing ENMs, e.g., effective barrier liners for landfills**

- Regulators can use the realistic exposure and toxicological data to regulate and manage risks at end-of-life of NEPs without relying on toxicological data of pristine nanomaterials

List of Publications

Environmental Science Nano
ROYAL SOCIETY OF CHEMISTRY
PAPER
View Article Online
View Journal
CrossMark
Cite this: DOI: 10.1039/c4en00210e

An integrated methodology for the assessment of environmental health implications during thermal decomposition of nano-enabled products†

Georgios A. Sotiriou,[a] Dilpreet Singh,[a] Fang Zhang,[a] Wendel Wohlleben,[ab] Marie-Cecile G. Chalbot,[c] Ilias G. Kavouras[c] and Philip Demokritou*[a]

Environmental Science & Technology
Article
pubs.acs.org/est

Nanofiller Presence Enhances Polycyclic Aromatic Hydrocarbon (PAH) Profile on Nanoparticles Released during Thermal Decomposition of Nano-enabled Thermoplastics: Potential Environmental Health Implications

Dilpreet Singh,[†] Laura Arabella Schifman,[‡,§] Christa Watson-Wright,[†] Georgios A. Sotiriou,[†,∥] Vinka Oyanedel-Craver,[‡] Wendel Wohlleben,[⊥] and Philip Demokritou*[,†]

ELSEVIER
Contents lists available at ScienceDirect
Journal of Hazardous Materials
journal homepage: www.elsevier.com/locate/jhazmat
CrossMark

Thermal decomposition of nano-enabled thermoplastics: Possible environmental health and safety implications

Georgios A. Sotiriou[a], Dilpreet Singh[a], Fang Zhang[a], Marie-Cecile G. Chalbot[b], Eleanor Spielman-Sun[c], Lutz Hoering[d], Ilias G. Kavouras[b], Gregory V. Lowry[c], Wendel Wohlleben[a,d], Philip Demokritou[a,*]

ELSEVIER
Contents lists available at ScienceDirect
NanoImpact
journal homepage: www.journals.elsevier.com/nanoimpact
Research Paper
CrossMark

Toxicological implications of released particulate matter during thermal decomposition of nano-enabled thermoplastics

Christa Watson-Wright, Dilpreet Singh, Philip Demokritou *

Environmental Science Nano
ROYAL SOCIETY OF CHEMISTRY
PAPER
CrossMark
Cite this: *Environ. Sci.: Nano*, 2016, 3, 1293

End-of-life thermal decomposition of nano-enabled polymers: effect of nanofiller loading and polymer matrix on by-products†

Dilpreet Singh,[a] Georgios A. Sotiriou,‡[a] Fang Zhang,§[a] Joey Mead,[b] Dhimiter Bello,[b] Wendel Wohlleben[c] and Philip Demokritou*[a]

OXFORD
SOT Society of Toxicology
www.toxsci.oxfordjournals.org
TOXICOLOGICAL SCIENCES, 146(2), 2015, 321–333
doi: 10.1093/toxsci/kfv095
Advance Access Publication Date: May 20, 2015
Research Article

Linking Exposures of Particles Released From Nano-Enabled Products to Toxicology: An Integrated Methodology for Particle Sampling, Extraction, Dispersion, and Dosing

Anoop K. Pal*[,1], Christa Y. Watson*[,1], Sandra V. Pirela*, Dilpreet Singh*, Marie-Cecile G. Chalbot[†], Ilias Kavouras[†], and Philip Demokritou*[,2]

Acknowledgements

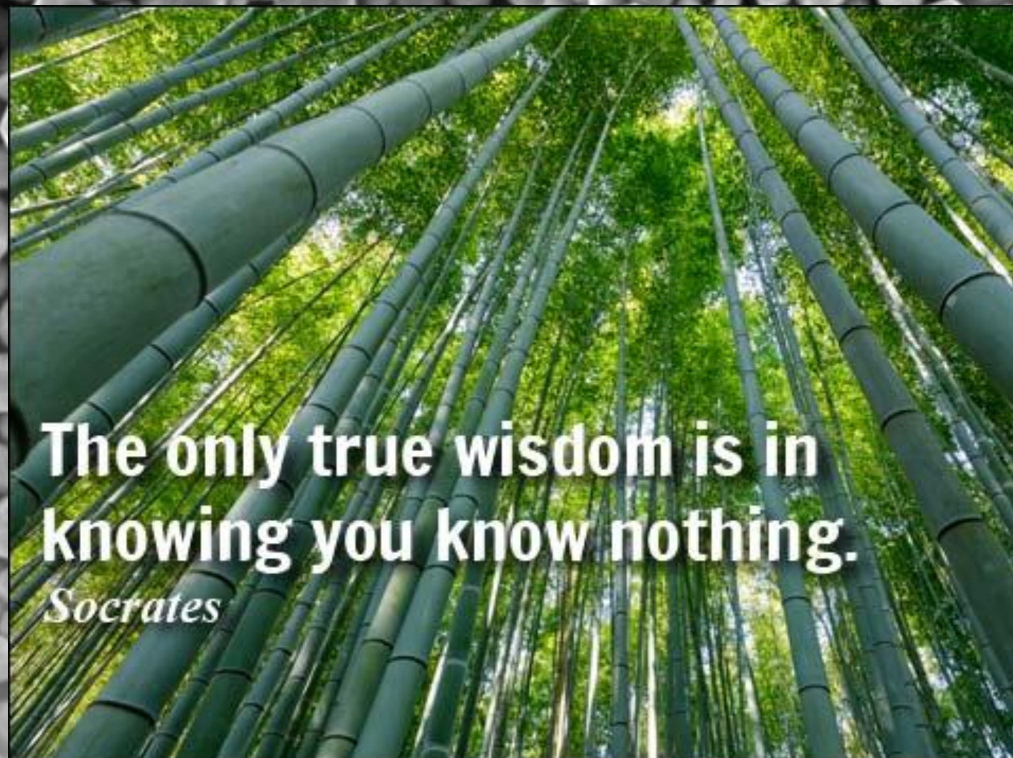
- Advisor: Prof. Philip Demokritou
- NSF (grant no. 1436450 and 1235806)
- BASF AG
- MARINA Consortium
- Sustainable Nanotechnology Organization (SNO)

NSF

BASF
The Chemical Company

MARINA
MANAGING RISKS OF NANOMATERIALS
SEVENTH FRAMEWORK PROGRAMME

Thank you for your attention!



Questions?

Dilpreet.Singh@mail.harvard.edu