RULES AND RATES OF RELEASE FROM NANO-ENABLED PRODUCTS:
CORRELATING PROCESS, PRODUCT MATRIX AND NANOMATERIAL

Wendel Wohlleben (BASF SE)

with original data from Richard G. Zepp (US EPA, NERL, Athens GA, USA); E. Sahle-Demessie (US EPA, NRMRL, Cincinnati OH, USA); Socorro Vázquez-Campos (LEITAT, Terrassa (Barcelona) Spain), Janet Carter (OSHA), Christopher Kingston (National Research Council Canada, Ottawa Canada); Richard Canady (Neutral Science L3C); Brad Acrey; Chia-Ying Chen (both US EPA, NERL, Athens GA, USA).

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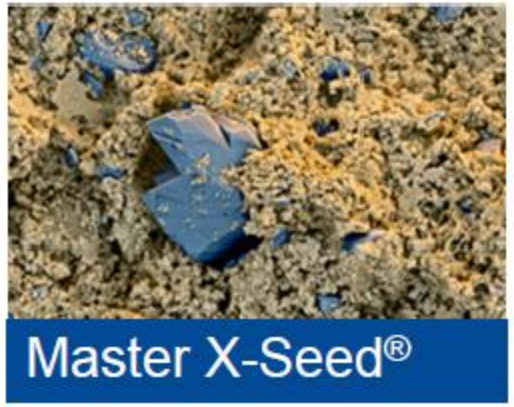
Examples of nano-enabled products

Co-continous inorg-org scratch-resistent coating

CSH seed crystals as cement accelerator



ENM-slurry polishes wafers by CMP

Organic aerogel insulation

Surface-passivated inductive metals

Ultrafiltration by designed porosity

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Chem Soc Rev (2015)

CrossMark

Cite this: DOI: 10.1039/c4cs00362d

Industrial applications of nanoparticles

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1. Highlights from reviews:
   state of release science
2. Release protocol reproducibility
3. Rates and rules of release
4. Complex scenarios

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“Release assessment regards the detachment of a fragment from a larger whole, such as a consumer product during use, and includes the release mechanism, form of the released entity, release scenario, probability of release, and lifecycle simulation, if relevant.”

As a rule, the “form of the released entity” is not identical to the pristine ENM.

Release symposium proceedings online

Including the NanoRelease State of the Science Report.

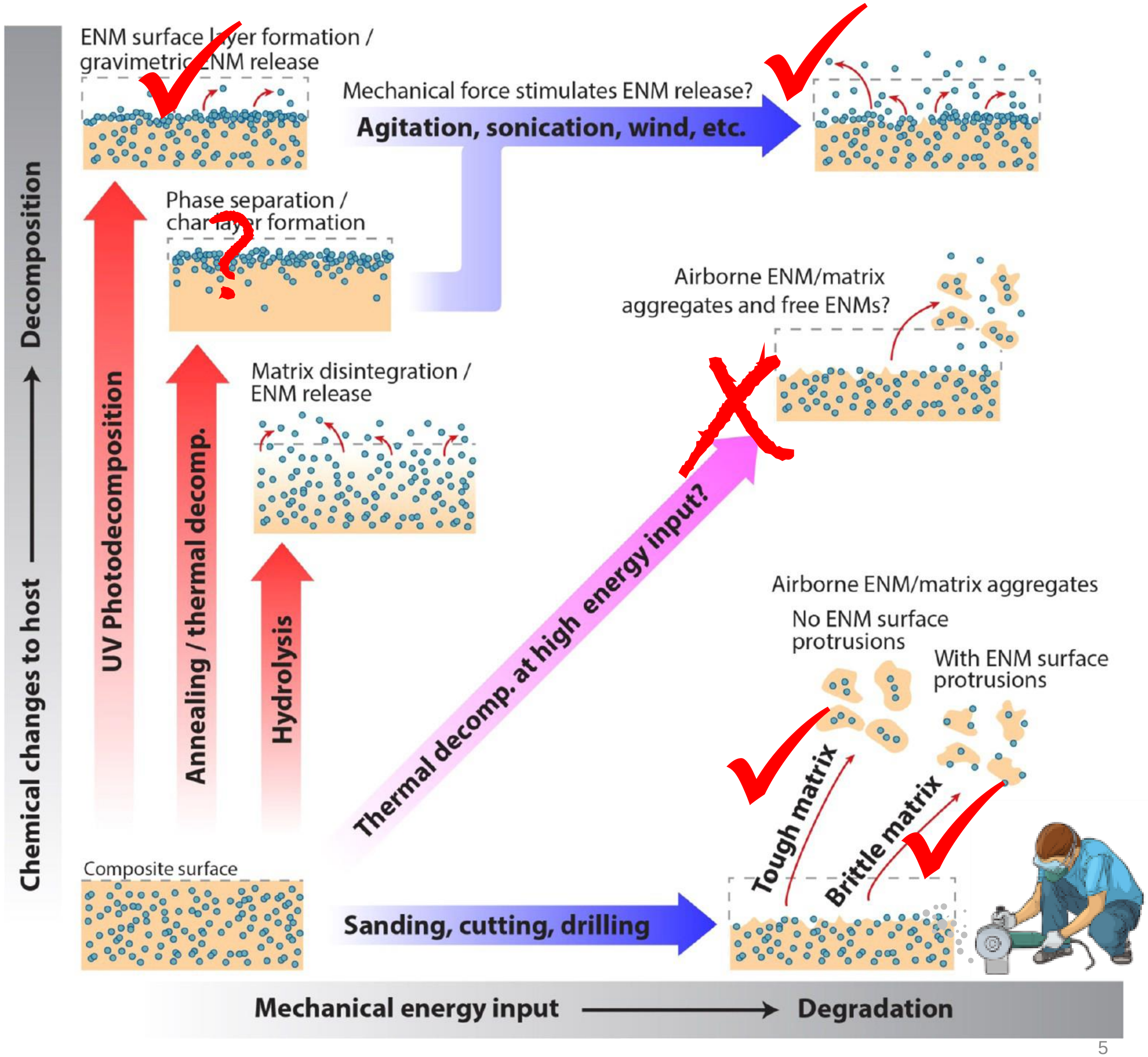
S Harper, W Wohlleben, M Doa, B Nowack, S Clancy, R Canady, A Maynard

J. Physics Conf. Ser. **617** (2015) 012026 (*open access*)

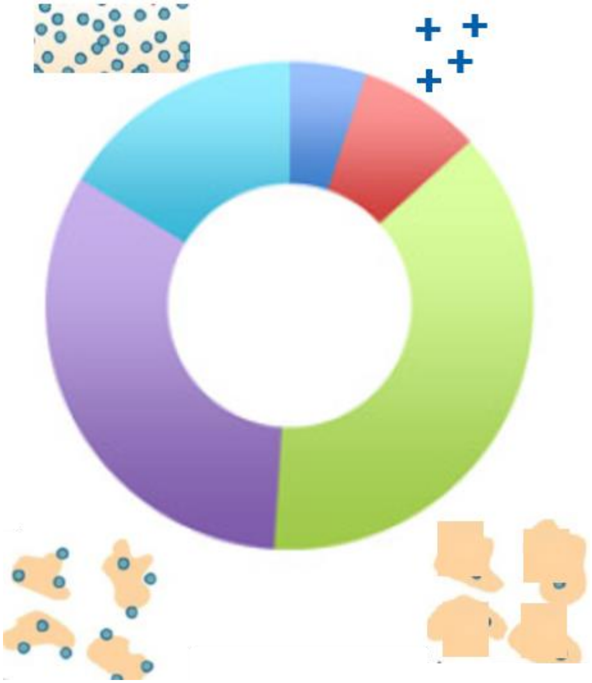
Release

Versions of this scheme for fibers:
Hirth et al (**2013**)
J. Nanoparticle Res. 15:1504.
Harper et al (**2015**) NanoRelease
J. Physics Conf. Ser. 617 012026

This scheme:
Duncan et al. (US-FDA)
ACS Applied Materials & Interfaces (**2014**) 7: 20-39.

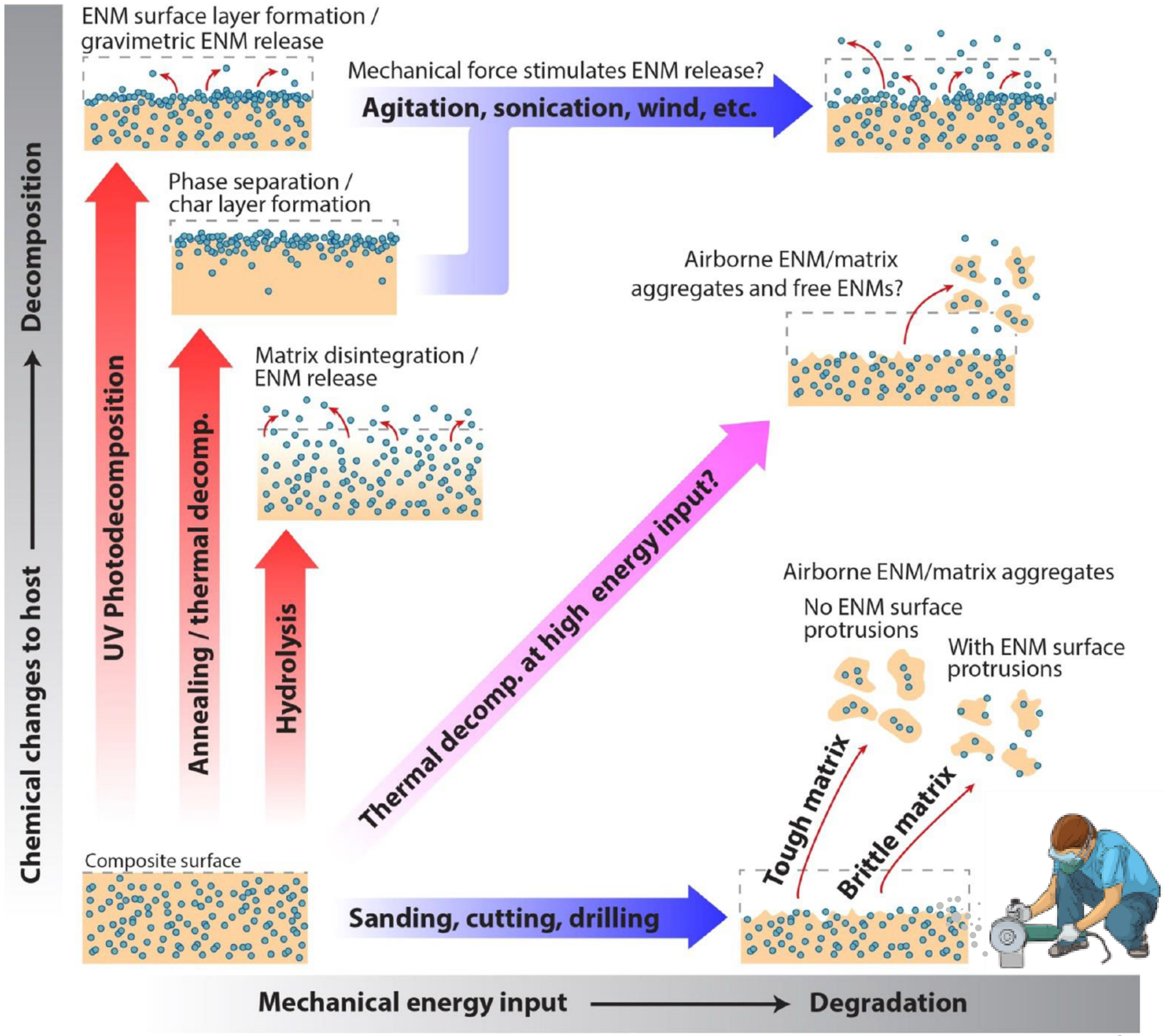


Transformation Release



NanoRelease **2014**
Stephan Froggett et al.
Part. Fiber Toxicol 11:15

US-FDA **2014**
Timothy V. Duncan et al.
ACS Applied Materials & Interfaces **7**: 20-39.



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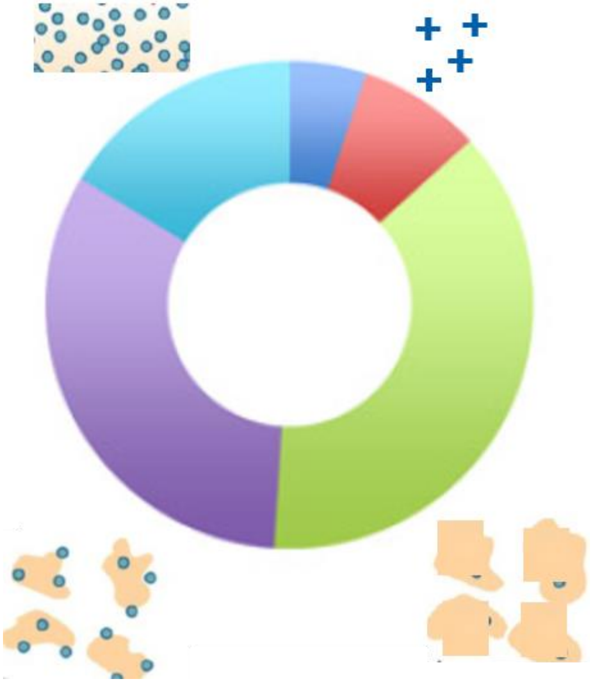
Transformation ↔ Release Processes



NanoRelease **2014**
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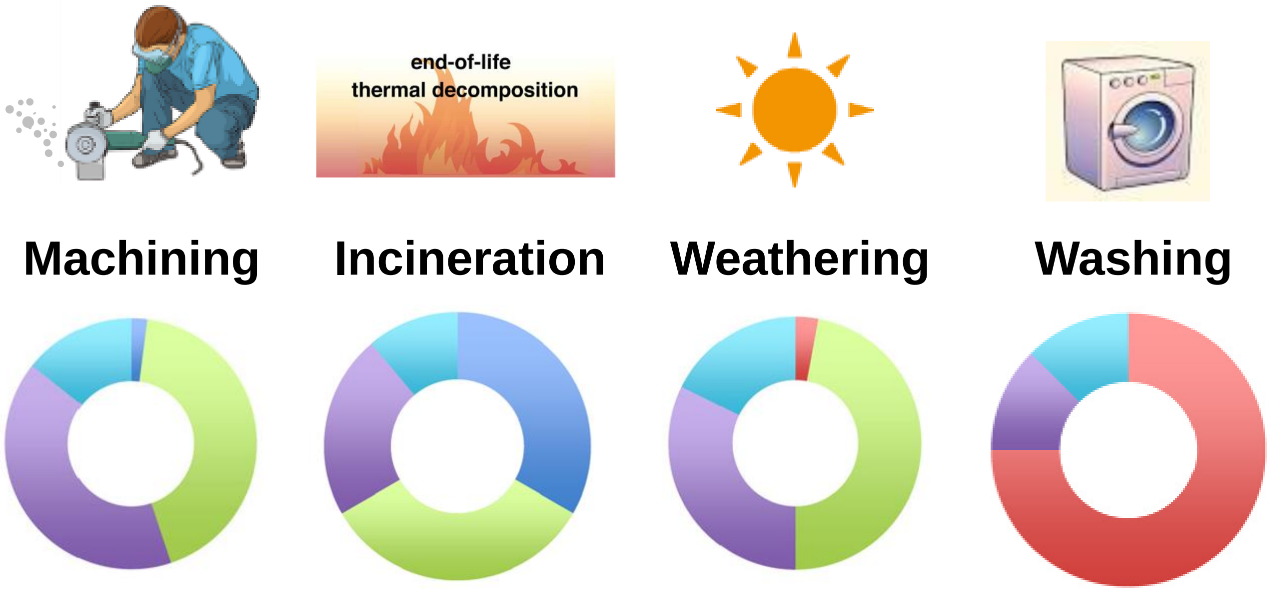


Form of release (54 studies combined)

Compare transformation / release review by D. Mitrano et al., Environ. Int. 77 (**2015**) 132–147

Release Rates & Metrics ⟲ Release Processes

320 different scenarios on NEPs: textiles, thermosets, thermoplastics, coated surfaces, sprays, and other articles including cement, ceramics, dental fillings and laser printer toners.

- **Mechanical treatment: ca. 10^5 to 3×10^{10} particles/s.**
  - (after weathering: up to 2.7×10^6 particles/s).

- **Artificial weathering: ca. 10^1 to 10^5 mg/m^2** fragments containing ENM (at UV ca.150 MJ/m^2)
  - including ca. 10^{-4} to 10^3 mg/m^2 ENM, (for comparison: **10^{-3} to 10^2 particles/s**)
  - alternative release metric: **10^{-1} to 10^3 mg/MJ**
- **Pump sprays: 1.1×10^8 particles/g.** Propellant sprays: 8.6×10^9 particles/g.

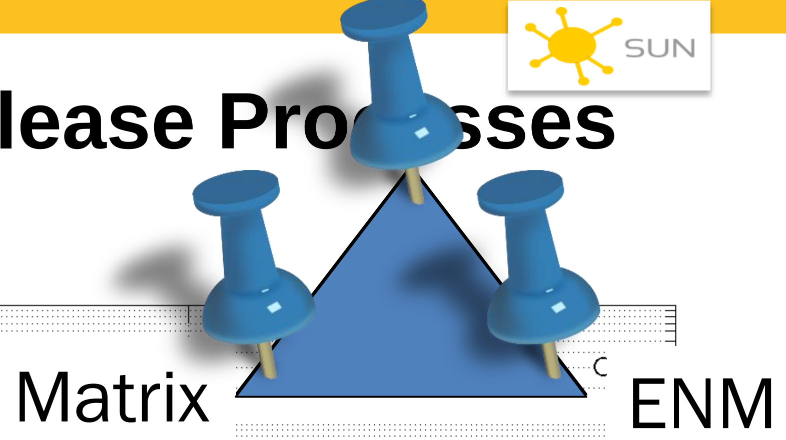
- First **wash** and rinse of textiles: **0.5 to 35 % of initial** Ag // 0.01 to 3.4 % of initial Ti.

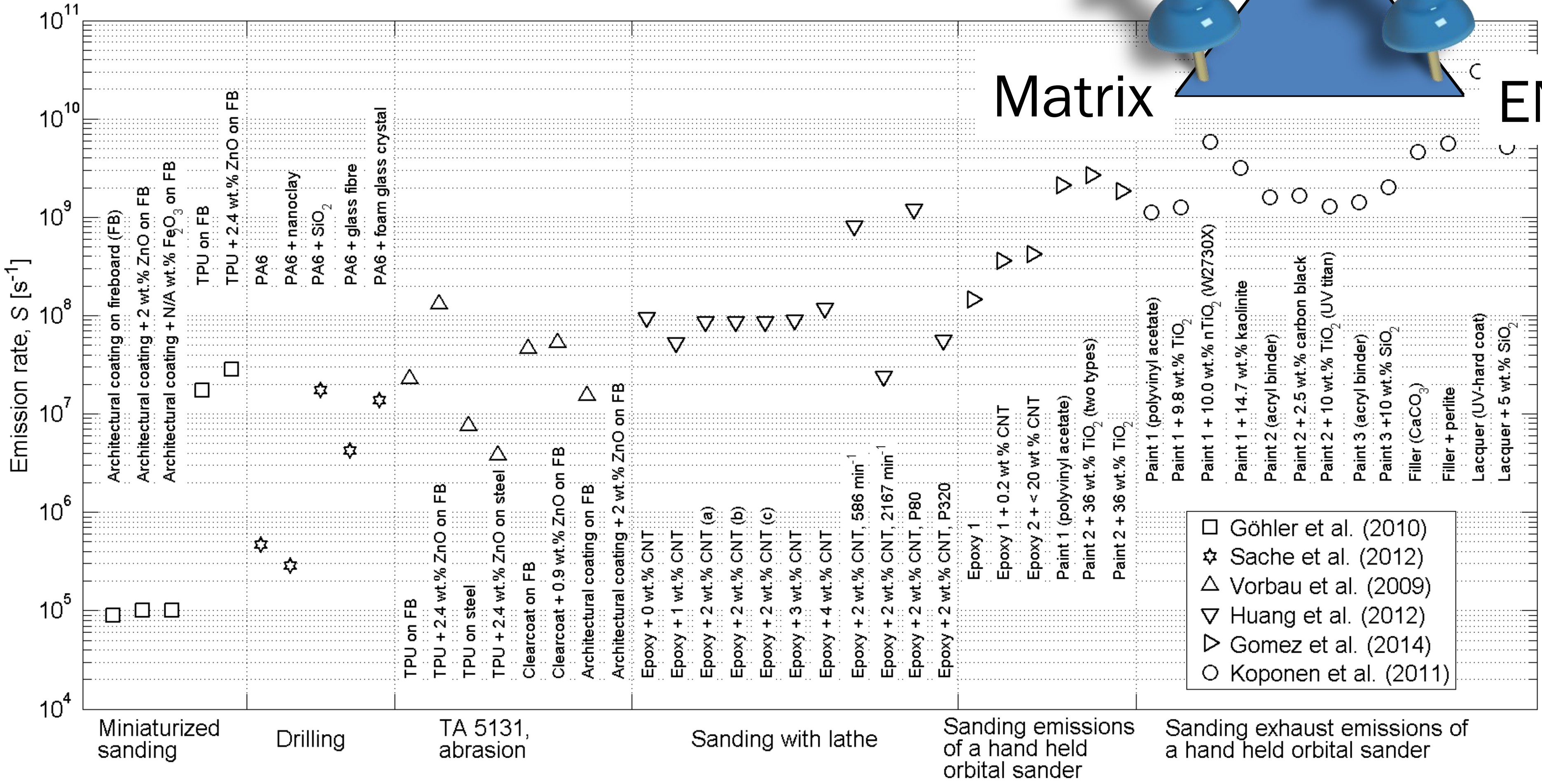
The characteristics of the released particles varied from consisting of pure NM to fully matrix-embedded NM depending on the products and processes.

Quantitative material releases from products and articles containing manufactured nanomaterials: A critical review
Antti Joonas Koivisto, Alexander Christian Østerskov Jensen, Kirsten Inga Kling, Asger Nørgaard, Anna Brinch, Frans Christensen, Keld Alstrup Jensen (NRCWE + COWI), submitted (**2016**)

Release Rates

Release Processes





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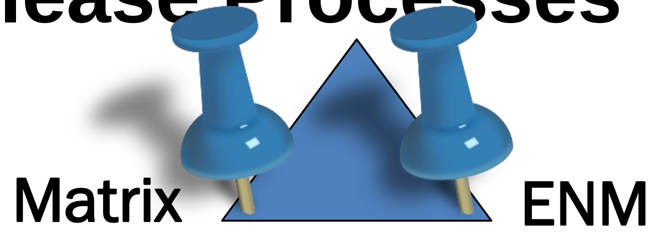
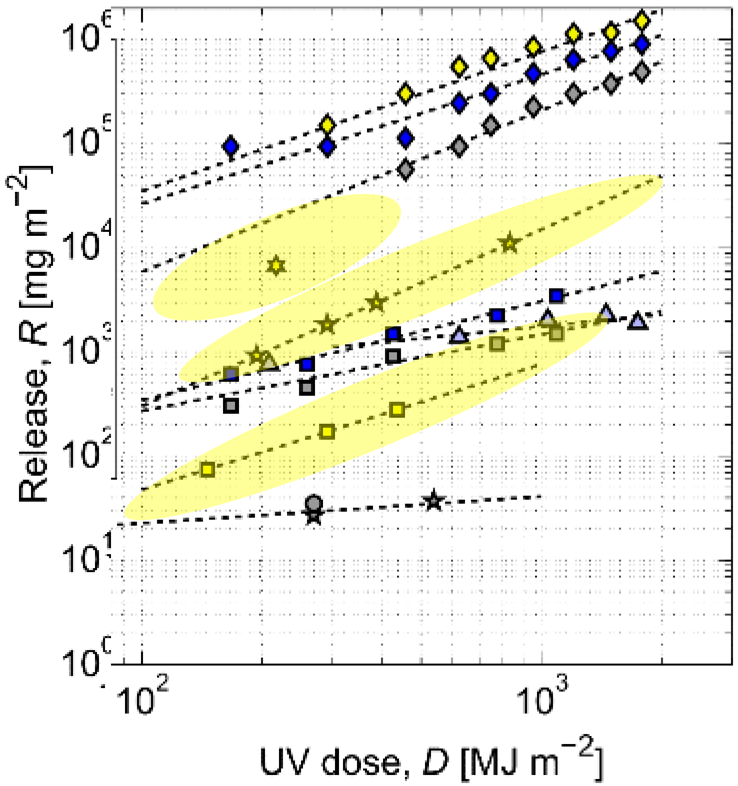
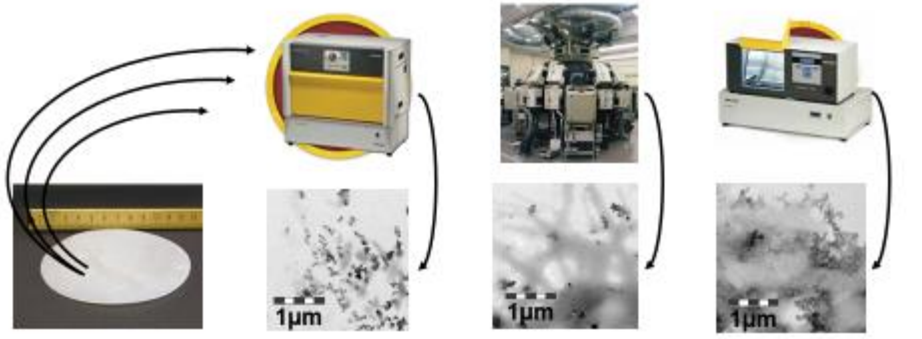
Release Rates ⟵ Release Processes







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0.5 mg/MJ	4 mg/MJ	31 mg/MJ

A pilot interlaboratory comparison ...Environ Chem (**2014**) 11:402
→ **aging+sampling process** is more critical than analysis

Quantitative material releases from products and articles containing manufactured nanomaterials: A critical review
Antti Joonas Koivisto, Alexander Christian Østerskov Jensen, Kirsten Inga Kling, Asger Nørgaard, Anna Brinch, Frans Christensen, Keld Alstrup Jensen (NRCWE + COWI), submitted (**2016**)

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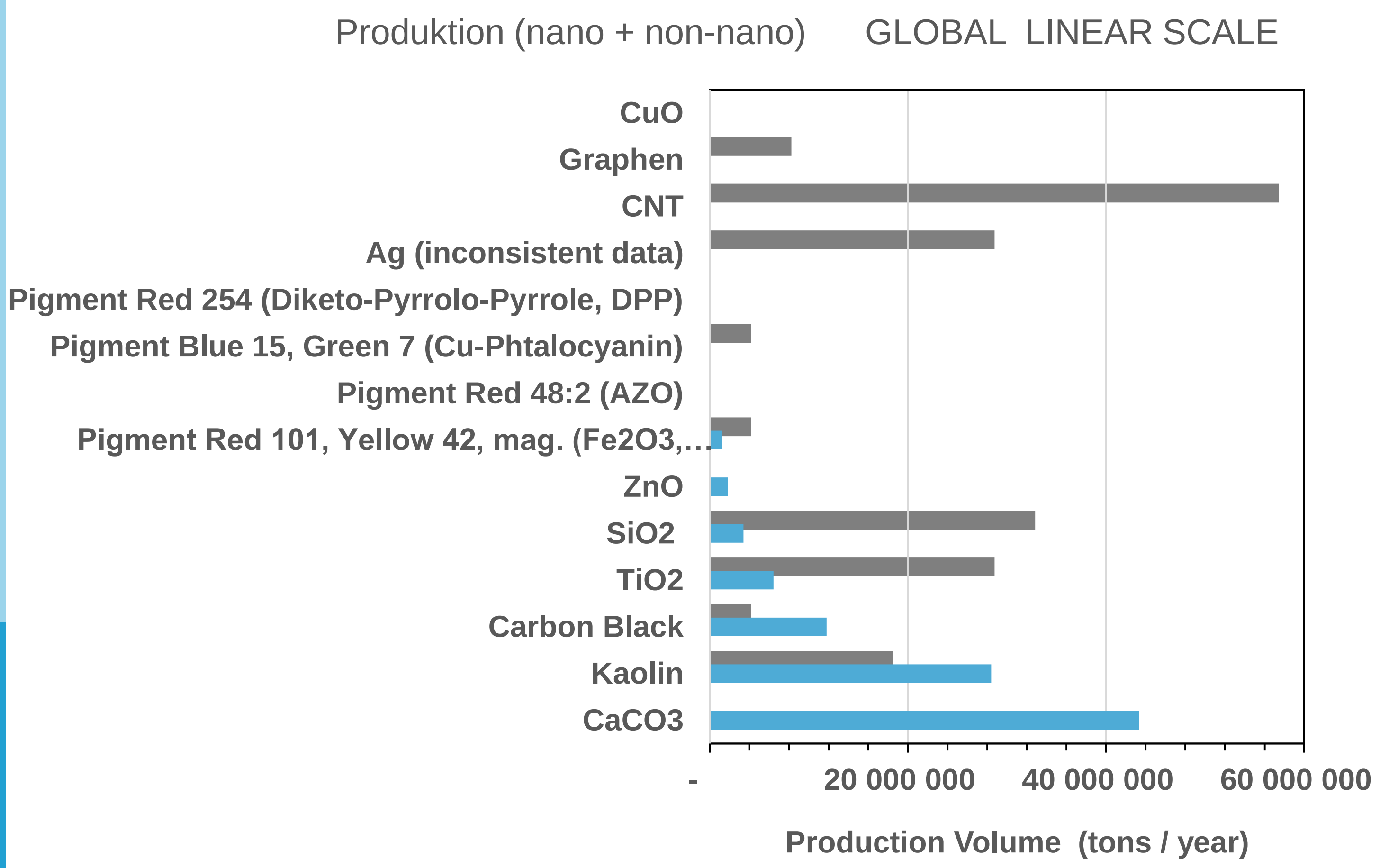
Scratching at the tip of the iceberg?

Release nanomaterials compared to production volumes



Relative share of ENM in release studies from Stephan Froggett et al. (**2014**) Part. Fiber Toxicol 11:15

As alternative approach with same conclusion, compare: Ministère de l'Environnement, de l'Énergie et de la Mer (**2015**) Éléments issus des déclarations des substances à l'état nanoparticulaire

This substance-specific market data from IHS Chemical Economics Handbook (various reports, **2014 - 2015**); supplemented with: Freedonia, *World Kaolin* (**2012**). FutureMarkets, *Zinc Oxide* (**2012**) Lux Research, CNT, graphene (**2015**)

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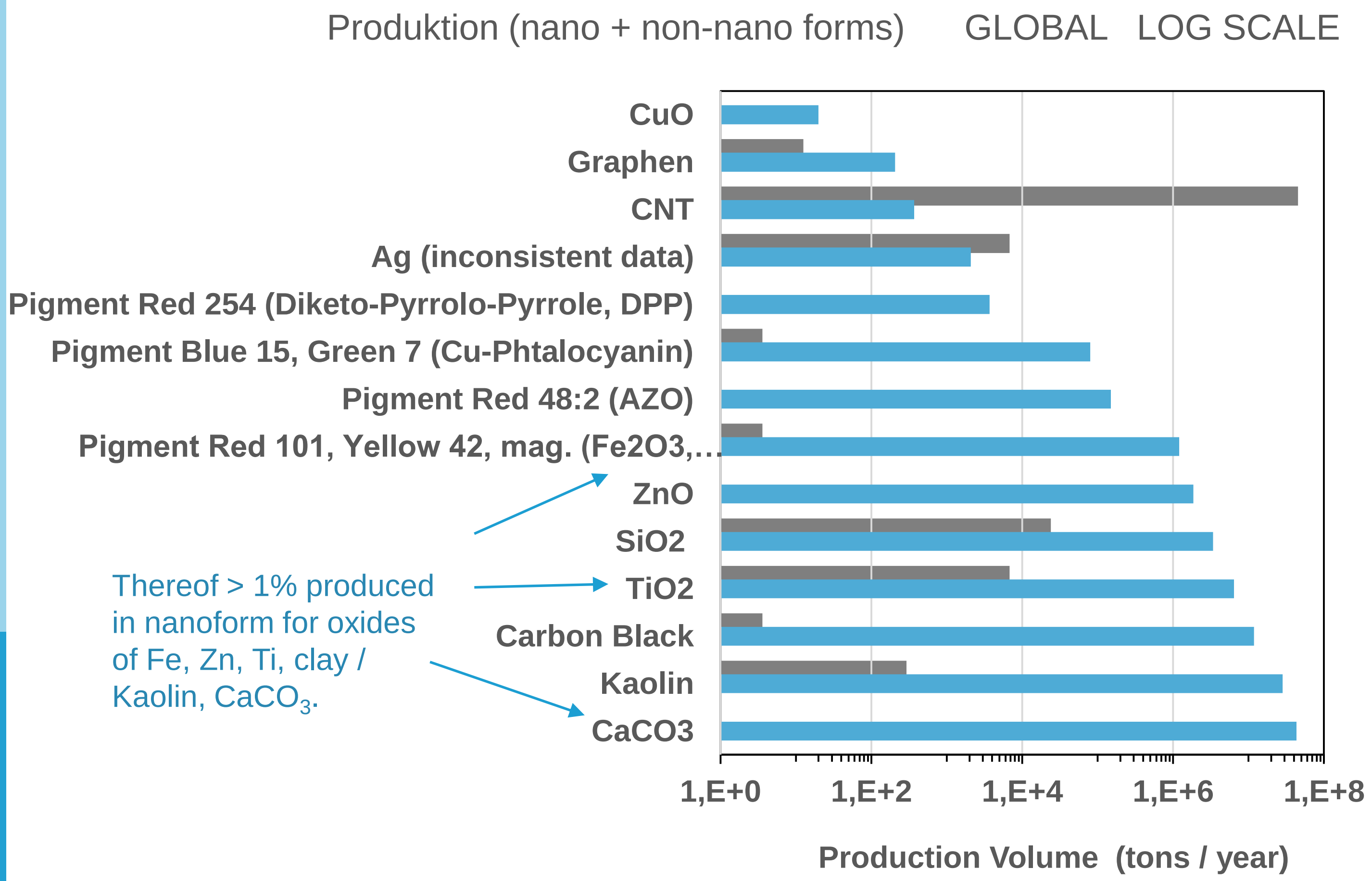
Scratching at the tip of the iceberg?

Release nanomaterials compared to production volumes



Thereof > 1% produced in nanoform for oxides of Fe, Zn, Ti, clay / Kaolin, $CaCO_3$.

Relative share of ENM in release studies from Stephan Froggett et al. (**2014**) Part. Fiber Toxicol 11:15

Substance-specific market reports from IHS Chemical Economics Handbook (various reports, 2014 - 2015); supplemented with: Freedonia, *World Kaolin* (2012). FutureMarkets, *Zinc Oxide* (2012) Lux Research, CNT, graphene (2015)

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Interim summary on „release“ state of science

Knowledge is based on a relatively narrow range of ENM and matrices, which is not fully representative for all materials in EU regulatory focus.

Reproducability is good intra-lab but limited inter-lab.
→ Extract mechanism of matrix and ENM modulations only from same-lab studies.

We need:

- Inter-laboratory standardization of metrology to characterize and quantify released entities
- Systematic comparison of release phenomena to extract rules on process, matrices, ENM.
- Diversification beyond Ag, CNT, SiO_2, TiO_2 to assess release from the high production volume materials in scope of the EC regulatory nanodefinition.
- Exploration of combined stresses and secondary fragmentation.
- Exploration of fate, uptake, effects of released entities on humans and the environment

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Reproducibility of release protocols

1. Aging of neat matrix vs. NEP	(ISO available)
2. Sampling of release	(sophisticated)
3. Analysis of fragments / leachates	(ISO available)

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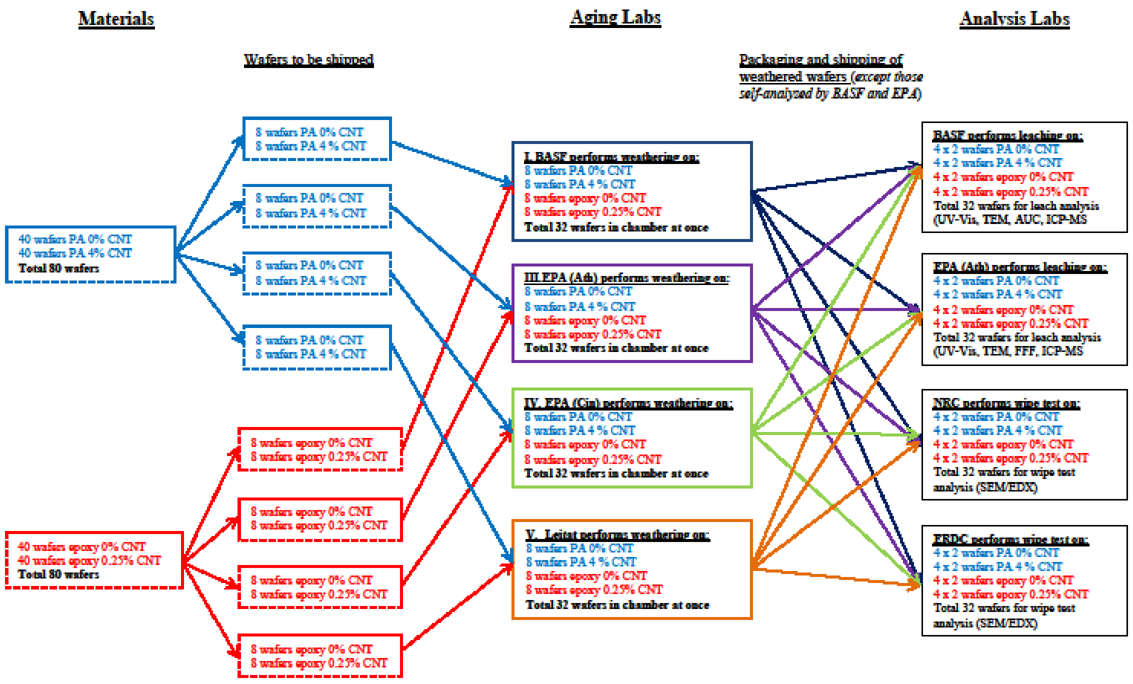
NanoRelease

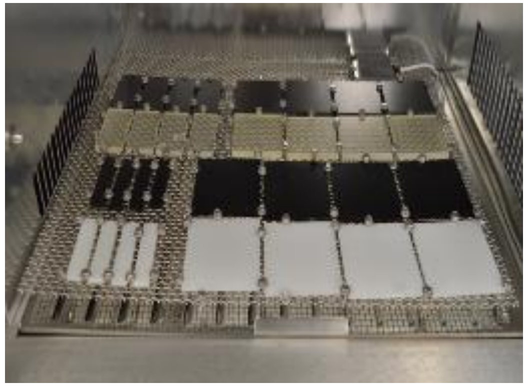
United States Environmental Protection Agency

Interlab comparison on weathering release

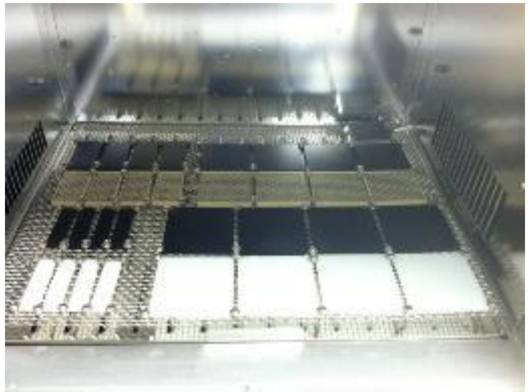
160 specimen PA and epoxy, w/ and w/o mwCNT



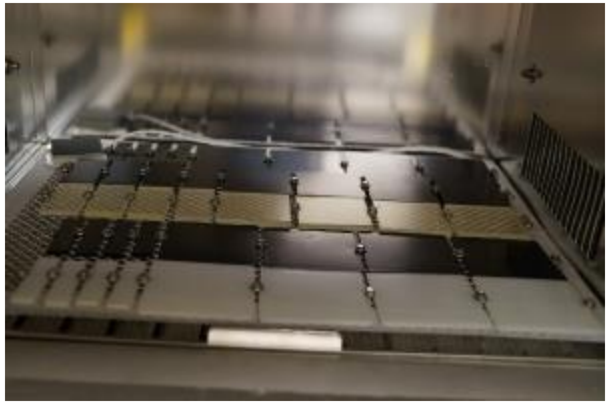
Aging in 2 US, 2 EU labs (ISO 4892)



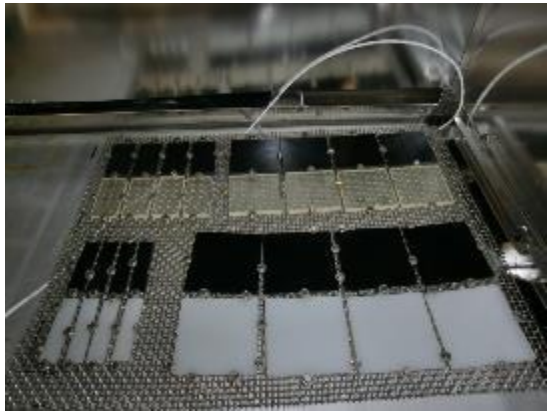
BASF – Ludwigshafen, Germany



EPA – Athens GA, USA



EPA – Cincinnati OH USA



LEITAT – Barcelona, SPAIN

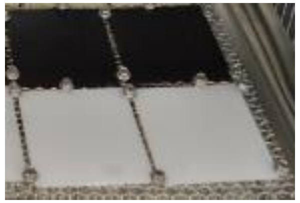
Wendel Wohlleben[1], Christopher Kingston[2], Janet Carter[3], E. Sahle-Demessie[4], Socorro Vázquez-Campos[5], Brad Acrey[6], Chia-Ying Chen[6], Ernest Walton[7], Heiko Egenolf[1], Philipp Müller[1], Richard Zepp[6] *

Carbon (**2016**), accepted

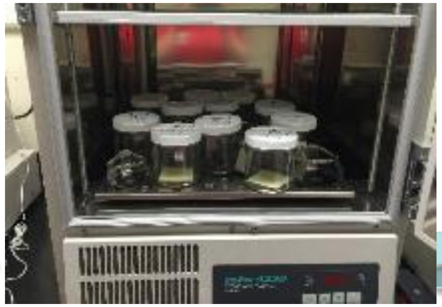
Interlab comparison on weathering release

160 specimen PA and epoxy, w/ and w/o mwCNT

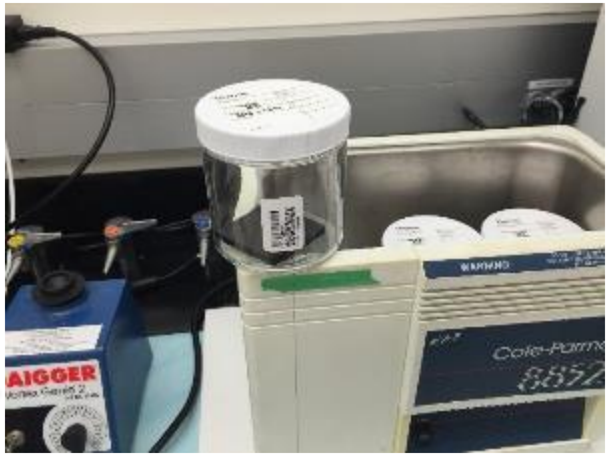
Sampling + analysis in 1 US, 1 EU lab



Each sample in 10.0 mL leaching fluid (EPA Method 1311)



Enclosed platform shaker, 24h



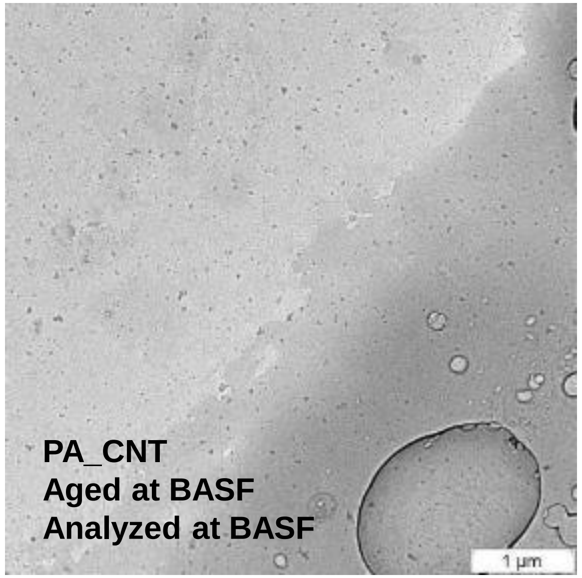
immersion bath sonication, 1h

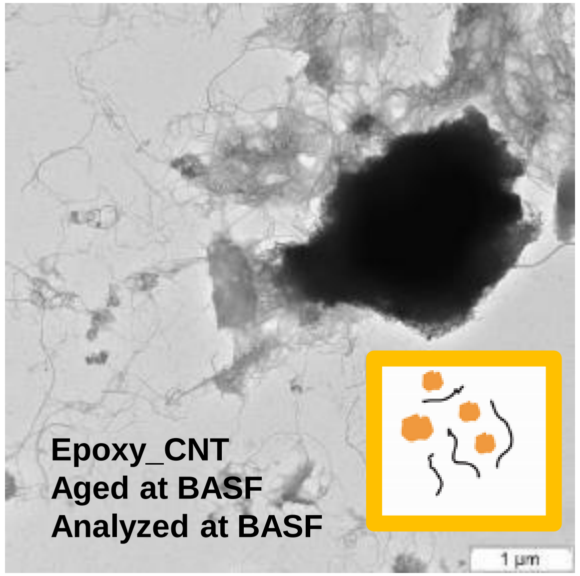
For each 4-mL aliquot apply the following analyses:

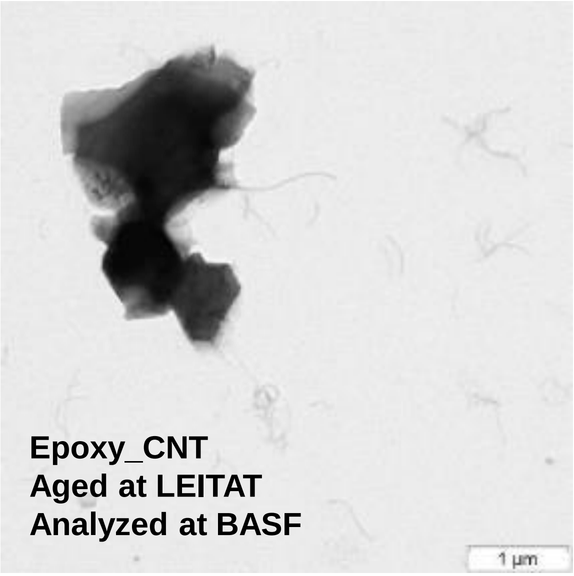
- ➔ **TEM** “characterize which structures are observed”
  - ➔ washing or dilution, sonicate, place drop on TEM grid, evaporate water.
- ➔ **ICP-MS** “tracer elements of ENM”, here Co
  - ➔ with acid digestion of any released fragments
- ➔ **UVVis** “absorption/scattering of leaching fluid”
- ➔ **Absorbance Ultracentrifugation (AUC) or Field Flow Fractionation (FFF)** “characteristic size of free ENM” / “absorption in size range 5-100nm”
  - ➔ de-agglomeration by addition of SDS to 10g/L, batch sonication 1h.

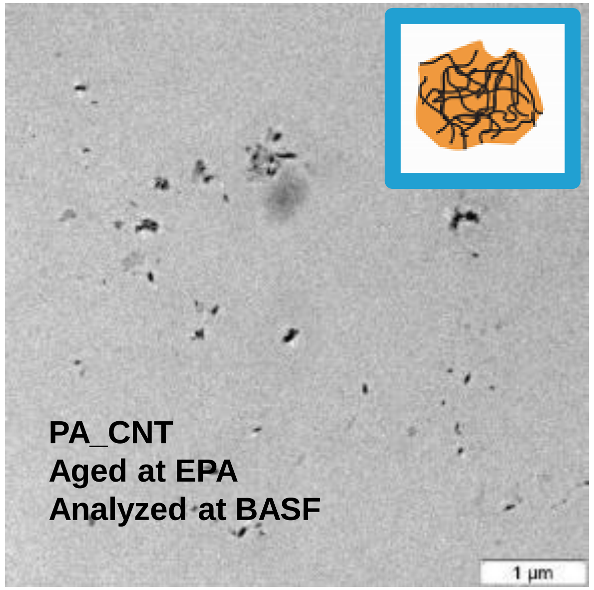
NanoRelease

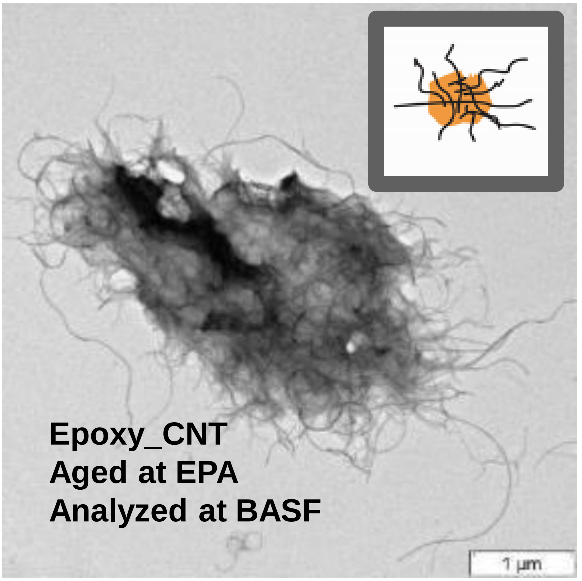
Interlaboratory comparison: exemplary TEM scans

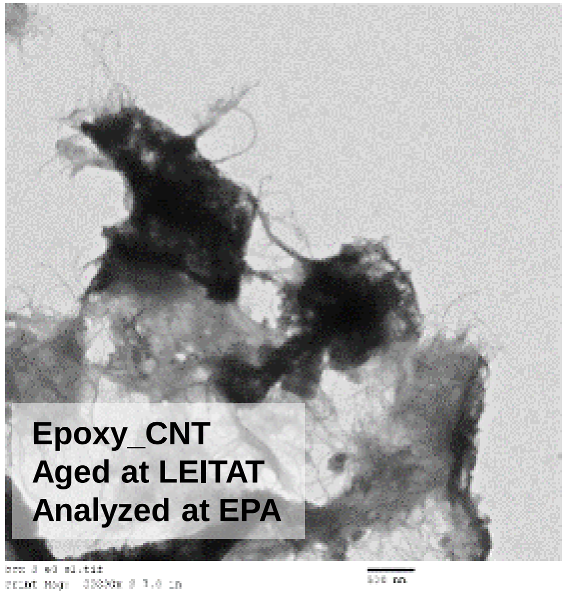












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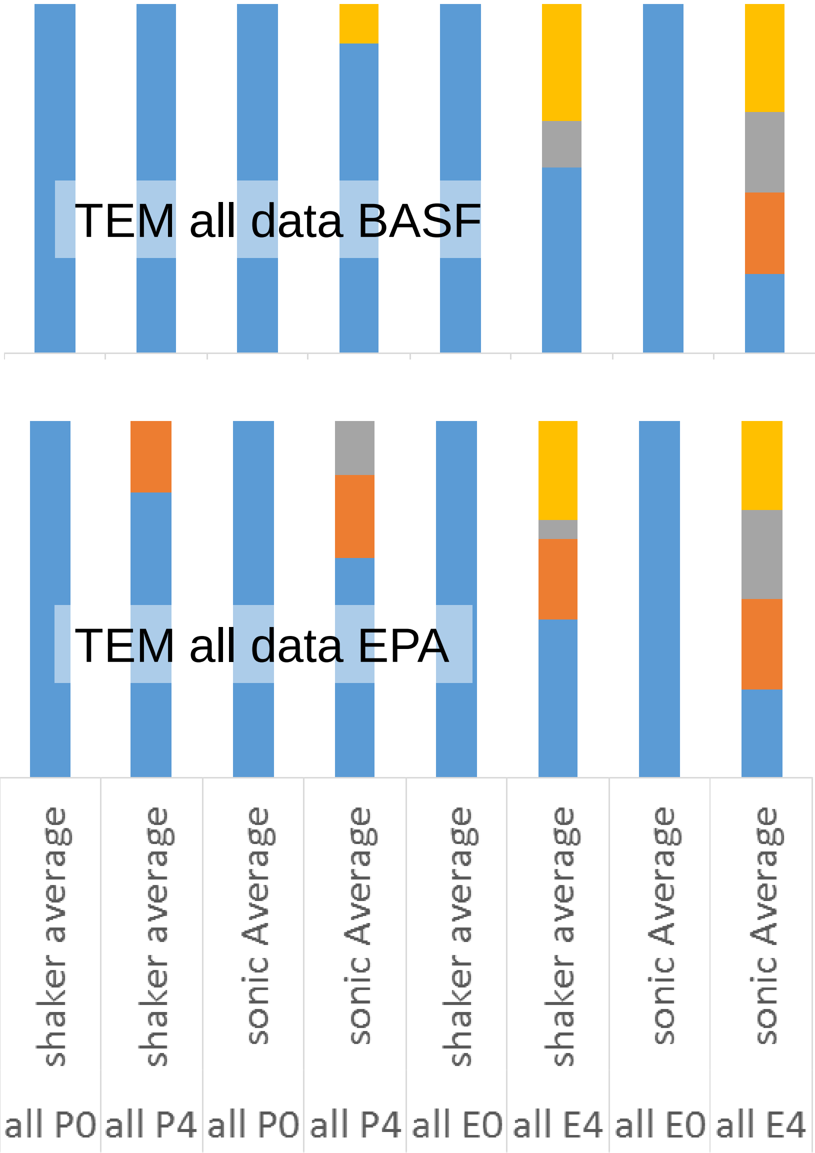
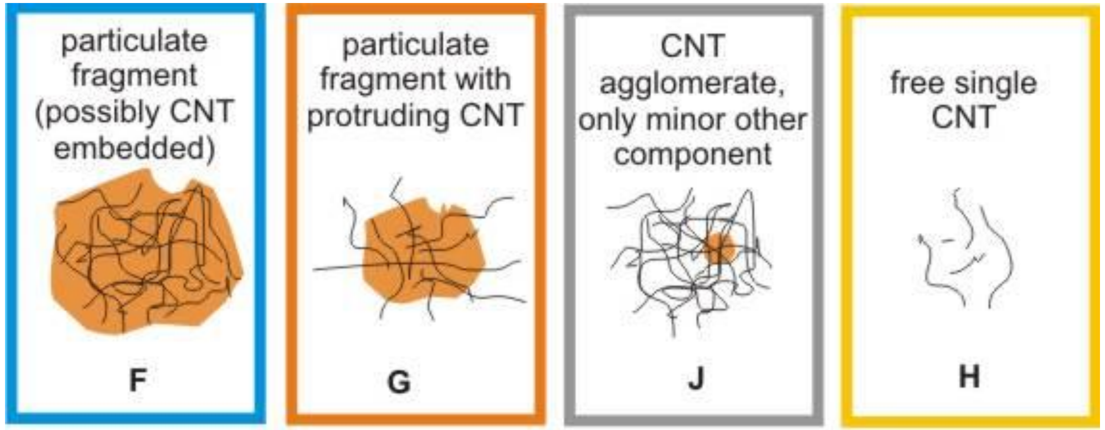
Form of release, TEM statistics from interlab comparison



More than 400 TEM images were evaluated manually. Fibrillar structures were identified as MWCNTs, if all three rules were in line with the MWCNT positive control:

- observed hollow core
- matching diameter between 5nm and 20nm
- matching length (not longer than 2µm).

Excellent reproducibility.
Minor subjectivity in categories F vs. G



F - H as in the release systematics by Harper et al. 2015

Wohlleben, Kingston, Zepp et al., Carbon (**2016**), accepted

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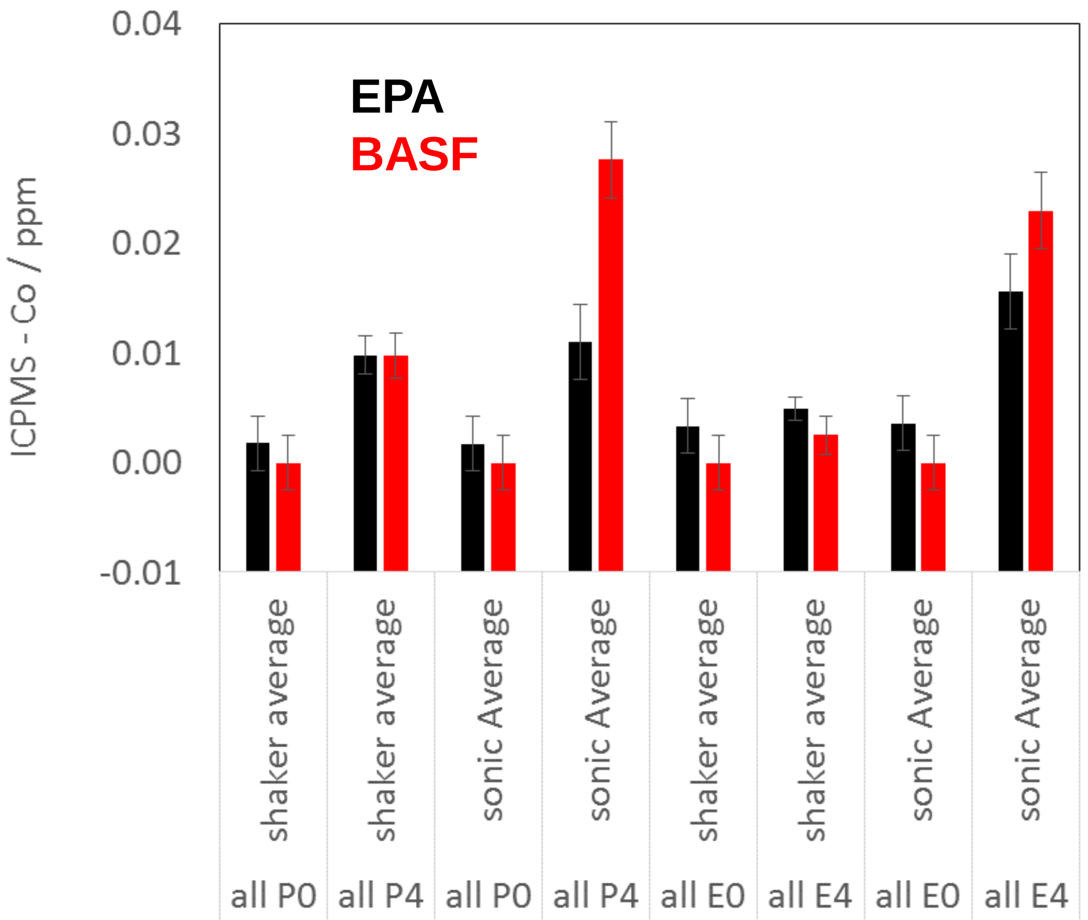
Rate of Release:
ICP-MS statistics: quantitative agreement

NanoRelease



- N=8 statistics, aged at four different labs; no outliers removed.
  - Discrepancy at P4 sonic-sampling is due to EPA ICPMS w/o digestion.
- Note 16-fold lower content of mwCNT in epoxy vs. PA; hence ICPMS is consistent with UVVis and AUC: much higher release rate from epoxy than from PA **matrix**.
- Opposite sign of modulation by ENM:

  CNT-PA **<** PA but CNT-epoxy **>** epoxy.

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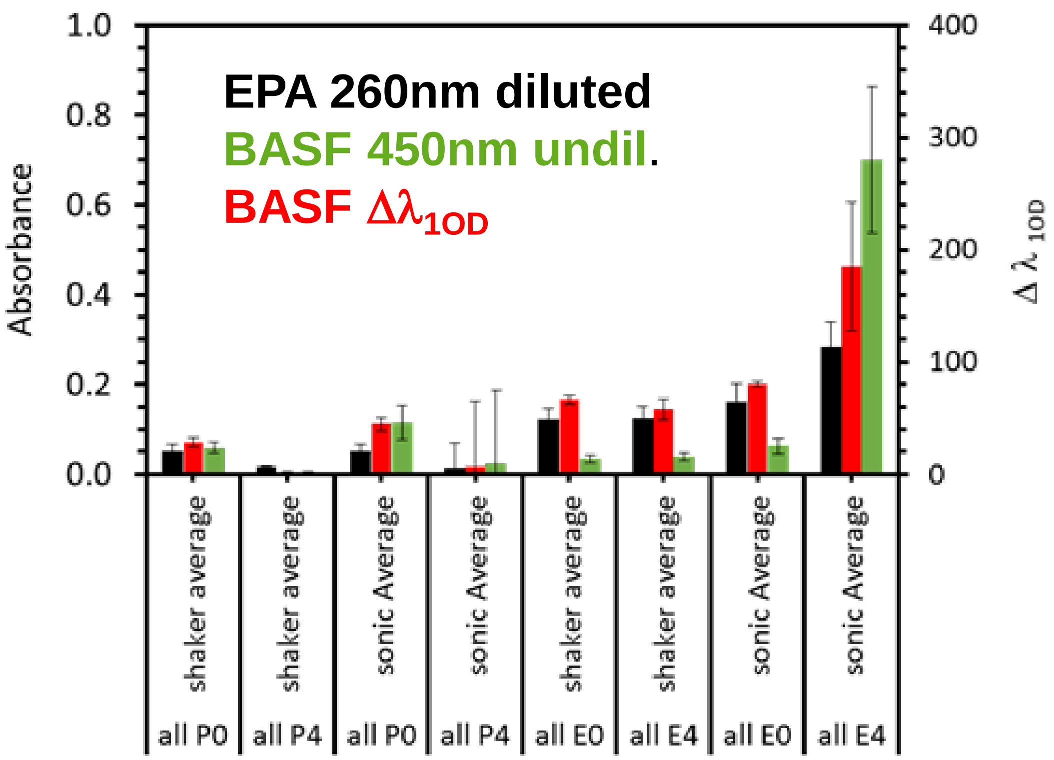
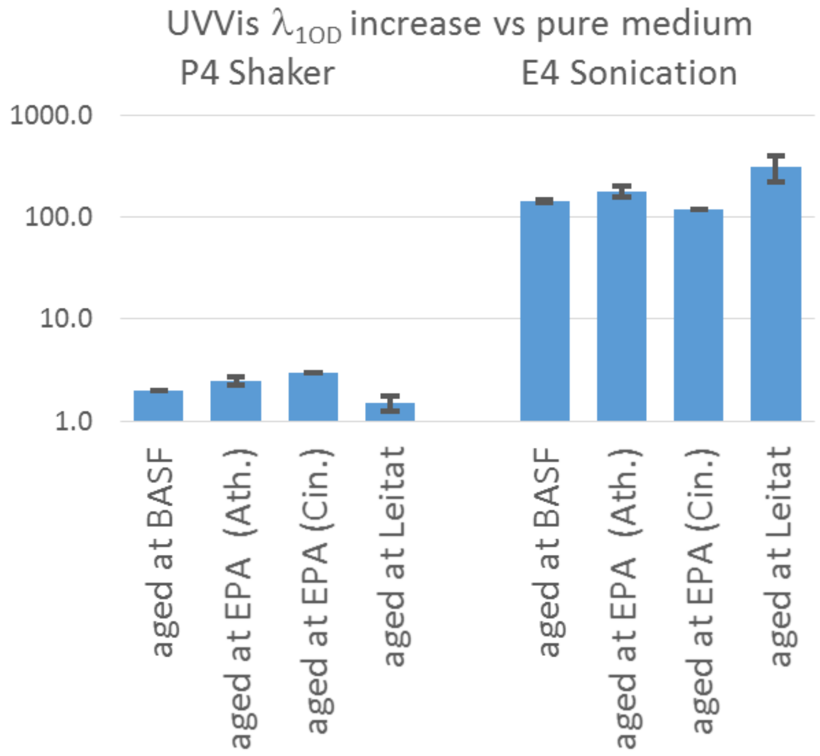
Rate of Release: UVVis spectroscopy

both absorbance (260nm) and turbidity ($\Delta\lambda_{1OD}$) evaluations are consistent

- High dynamic range, same ranking as conventional absorbance reading
- Excellent discrimination of low-high release





NanoRelease

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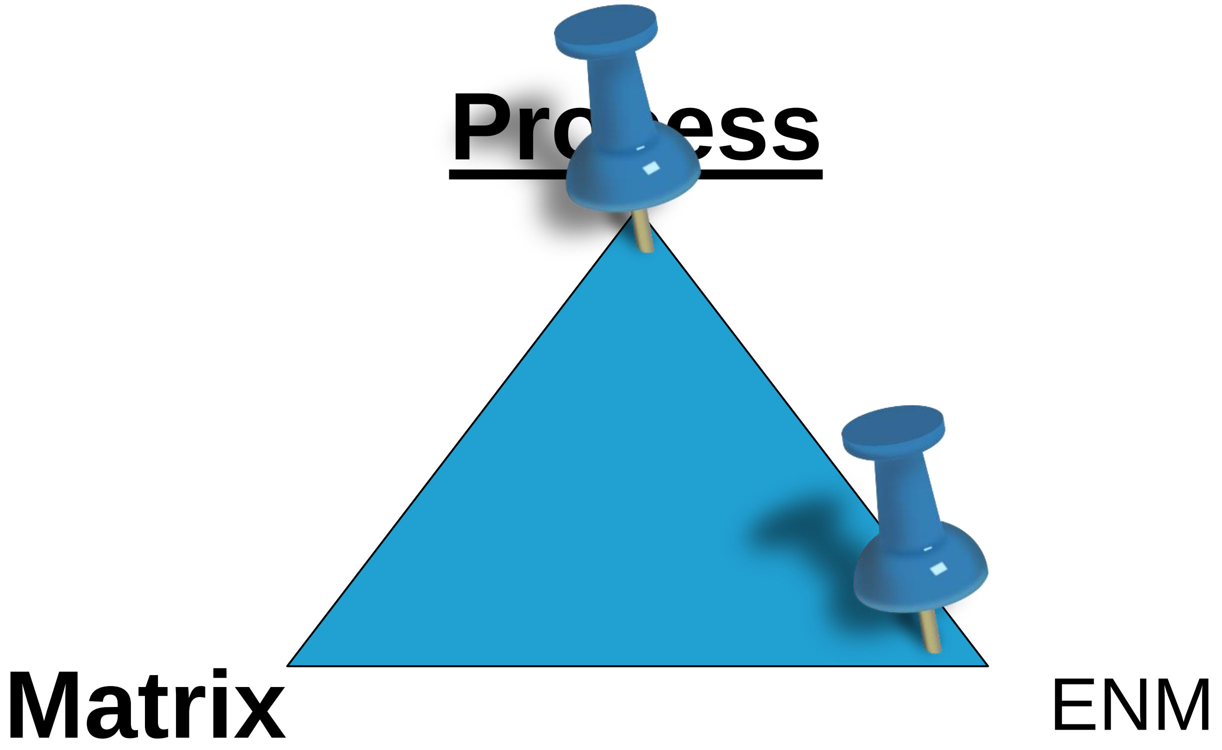
Pilot inter-laboratory weathering test: Conclusions

- 160 specimen of epoxy (0%, 0.25% CNT) and PA (0%, 4% CNT); **no UV stabilizer**
- 4 labs (2 US, 2 EU) aging by UV and rain (ISO 4892), then shipping for analysis.
  - 1 lab (CAN) dry sampling by tape → SEM, EDXS
  - 2 labs (1 US, 1 EU) immersion fluid sampling → TEM, ICPMS, UVVis, AUC, FFF
- **Quantitative agreement, often within error bars, within factor 2 in worst case.**
  - ICPMS, UVVis, TEM, AUC consistent. Immersion protocol recommended as voluntary standard. Epoxy-CNT recommended as high-release control material, PA-CNT as low-release material differing in “form” and “rate” of release.
  - Remaining deviations relate *primarily* to differences of the aging (inhomogeneity of UV and spray, surface contaminations (EDXS))

- ***Form* and *rate* of release can be *quantified* using ISO-aging/processing + sophisticated sampling + ISO-analytics.**

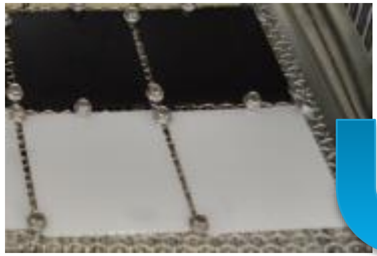
Wohlleben, Kingston, Zepp et al., Carbon (**2016**), accepted

Stick to a single protocol, explore materials, extract rules of release



NanoRelease weathering protocol applied to 27 materials of PE, PU, PA, POM, epoxy, cement with organic, metal-oxide, carbonaceous nanomaterials

Aging all by ISO 4892-2, pure matrix in parallel to nanocomposite



Sampling by worst-case approach

immersion bath sonication, 1h

- ➔ **TEM** "check which structures are observed"
- ➔ **AUC** "fragment mass in size ranges 2nm-150nm and 2nm-10µm"
  - ➔ Size-selective quantification

Where applicable, supported by rankings by:

- ➔ **ICP-MS** with acid digestion of any released fragments
- ➔ **UVVis** "absorption/turbidity of leaching medium"

NanoRelease

Analysis by a sub-set of the NanoRelease protocol

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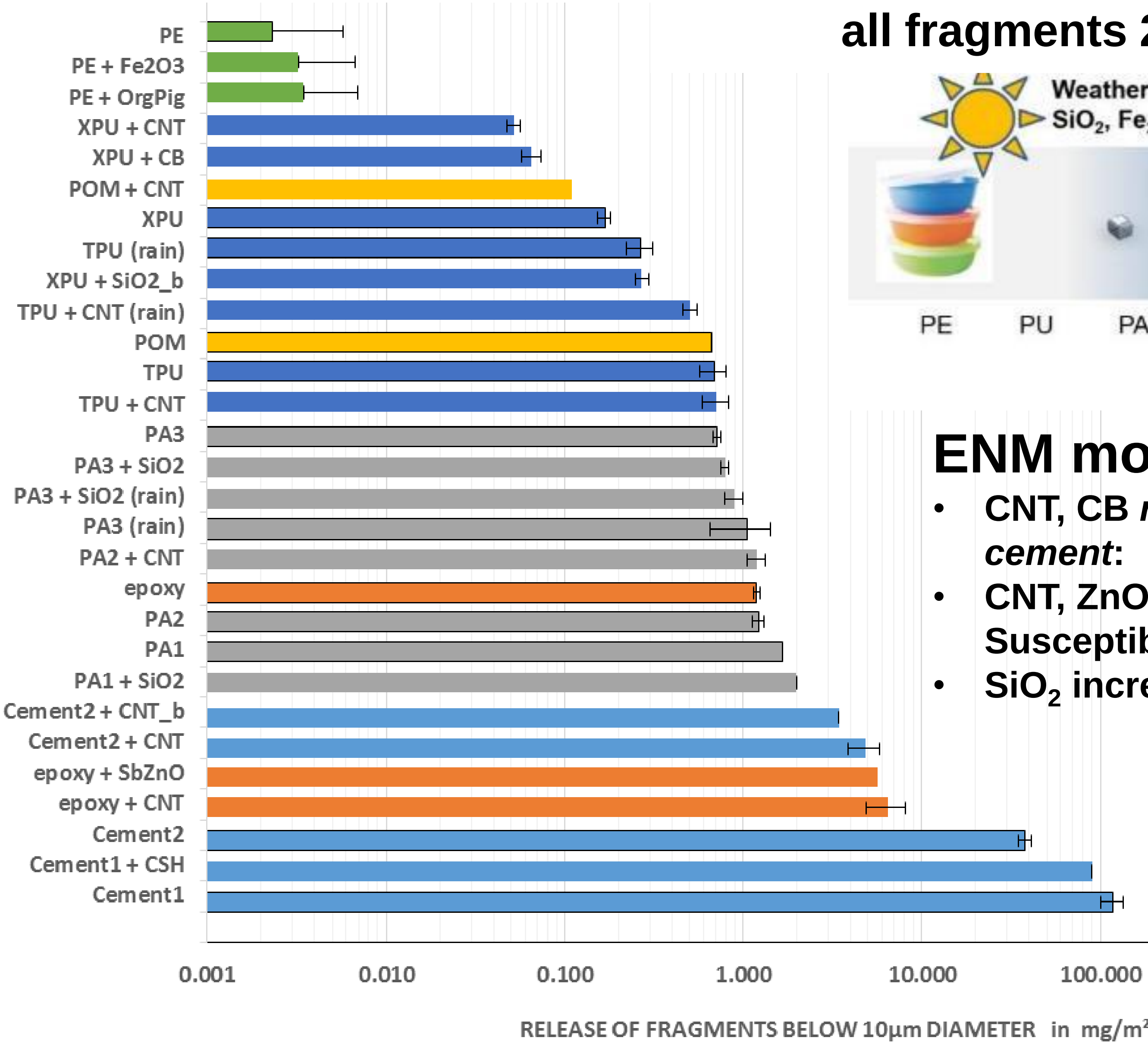
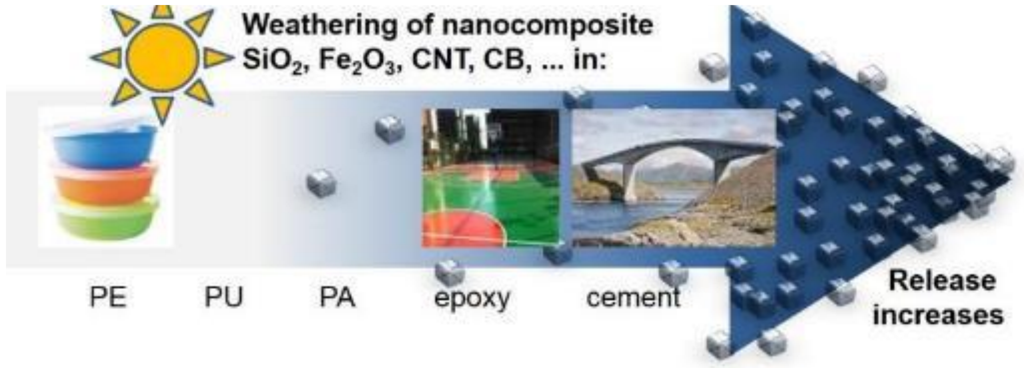
Wohlleben & Neubauer (**2016**). NanoImpact DOI 10.1016/j.impact.2016.01.001

Matrix determines weathering release rates



all fragments 2nm – 10µm



ENM modulates

- CNT, CB *reduce* release from *PA, PU, POM, cement*: → entanglement, passivation
- CNT, ZnO *increase* from *epoxy* → Susceptible matrix for temperature, radicals
- SiO_2 increase release from PA, PU

Wohlleben & Neubauer (**2016**). NanoImpact DOI 10.1016/j.impact.2016.01.001

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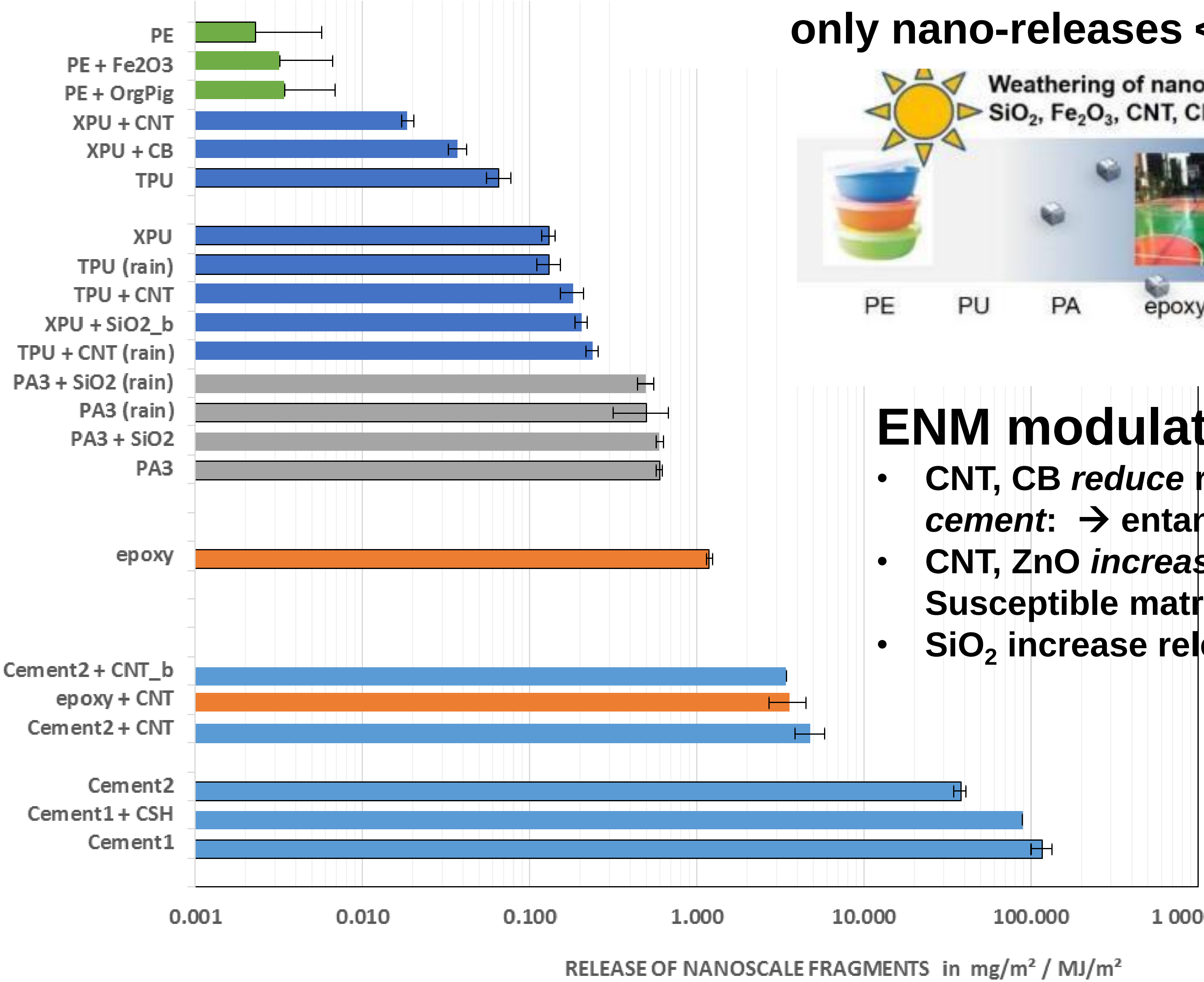
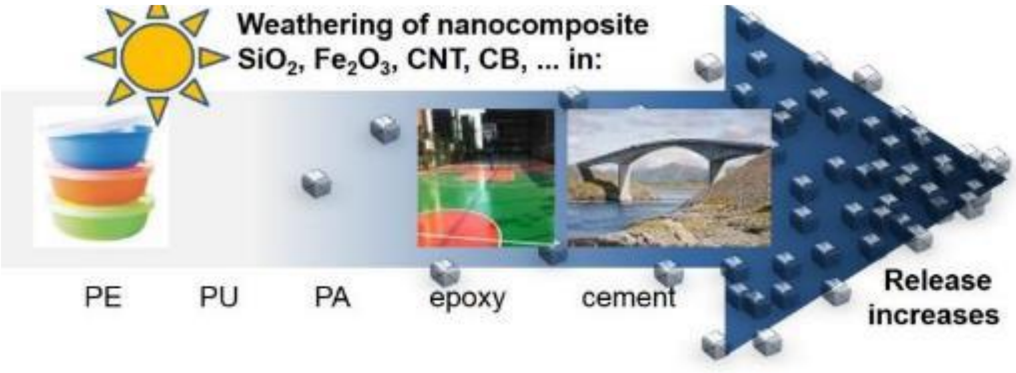
Matrix determines weathering release rates



only nano-releases < 150 nm



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Wohlleben & Neubauer (**2016**). NanoImpact DOI 10.1016/j.impact.2016.01.001

Key parameters that rule form and rate of release from nano-enabled products

Process

Mechanical machining:
→ Dominated by composite fragments
→ ENM protrude if matrix is cross-linked
→ Release rates scale x 10^4 with shear

No release of free ENM by machining, unless composite contains agglomerates

Chemical degradation:
→ Release rates scale x 10^5 with matrix

Reduction x 10 of aging-induced release, if ENM form a network upon matrix removal

Matrix

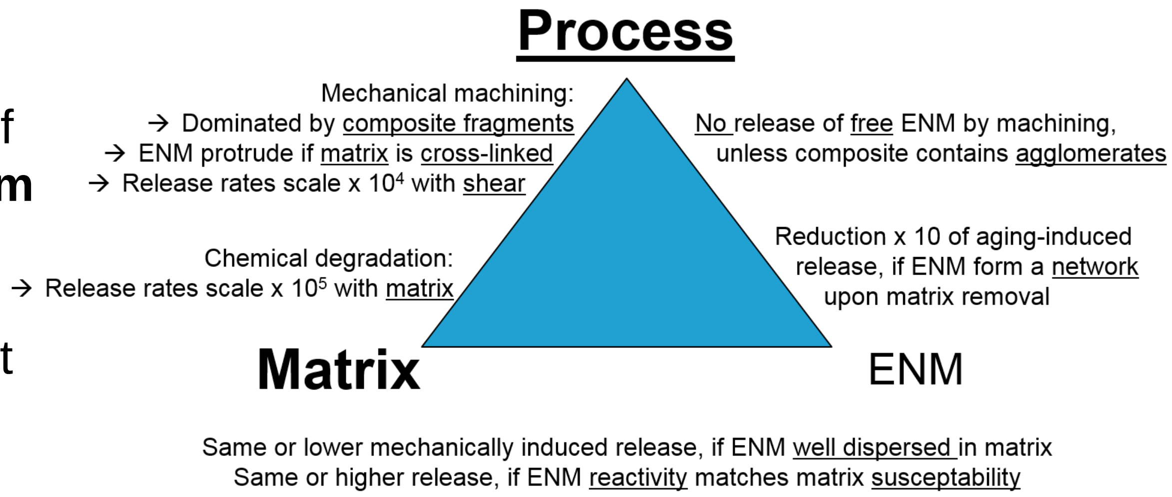
ENM

Same or lower mechanically induced release, if ENM well dispersed in matrix
Same or higher release, if ENM reactivity matches matrix susceptibility

Exploit similarities in *form* and *rate* of release for grouping & modeling

1. Compare to established simulation of similar **process: → metrics** and **form**

2. Compare to data on similarly resilient **matrix: → rate** (order of magnitude) and → **toxicity** (of fragments)



3. **ENM** release modulation for each process:
   - Washing/leaching: potential **to transform** (**ion** release vs **particle** release)
   - Machining: potential to **agglomerate** or to **mechanically stiffen** (release **sizes**)
   - Weathering & incineration: ENM reactivity matching matrix susceptibility:
     - **catalytically** accelerate matrix degradation (ZnO by UV; Fe_2O_3 by incineration)
     - **passivate** the underlying matrix (CB, CNT by UV, clays by incineration)

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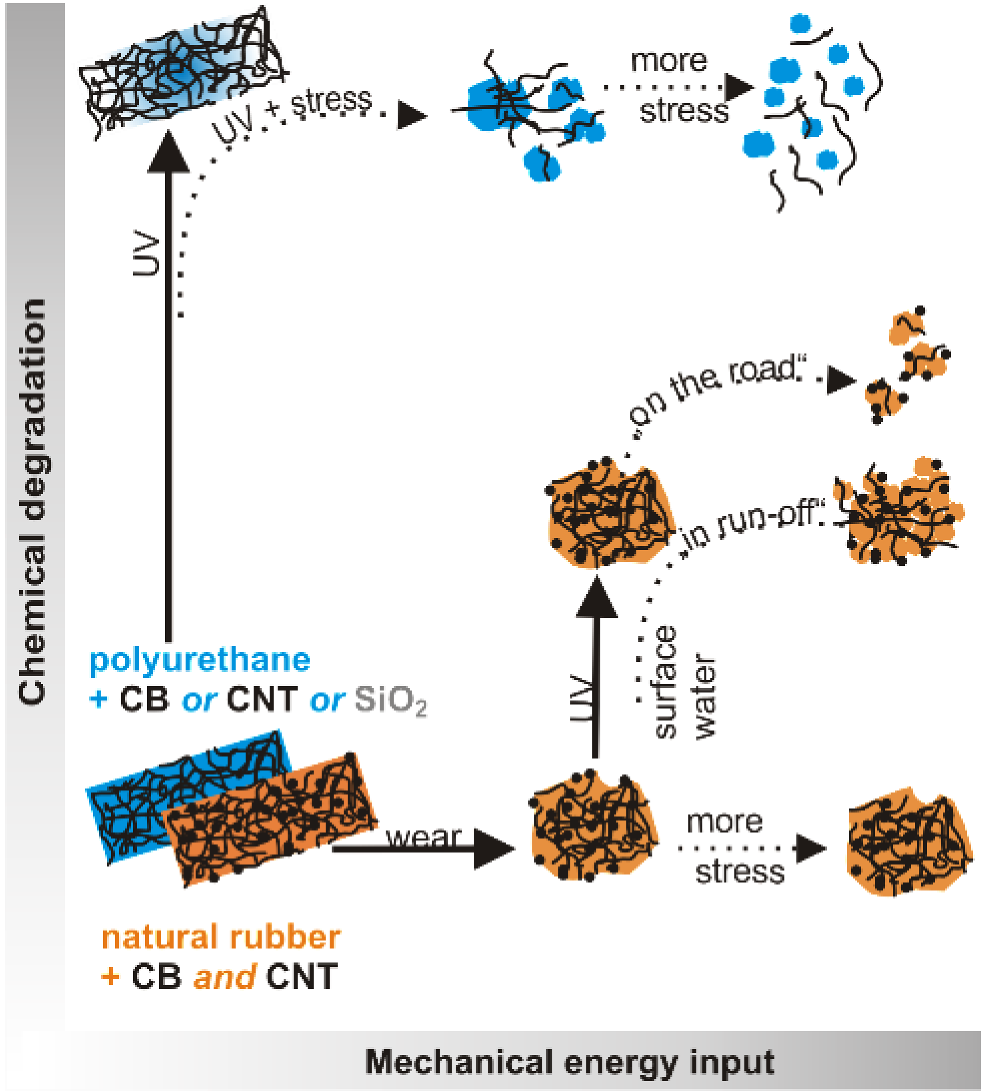
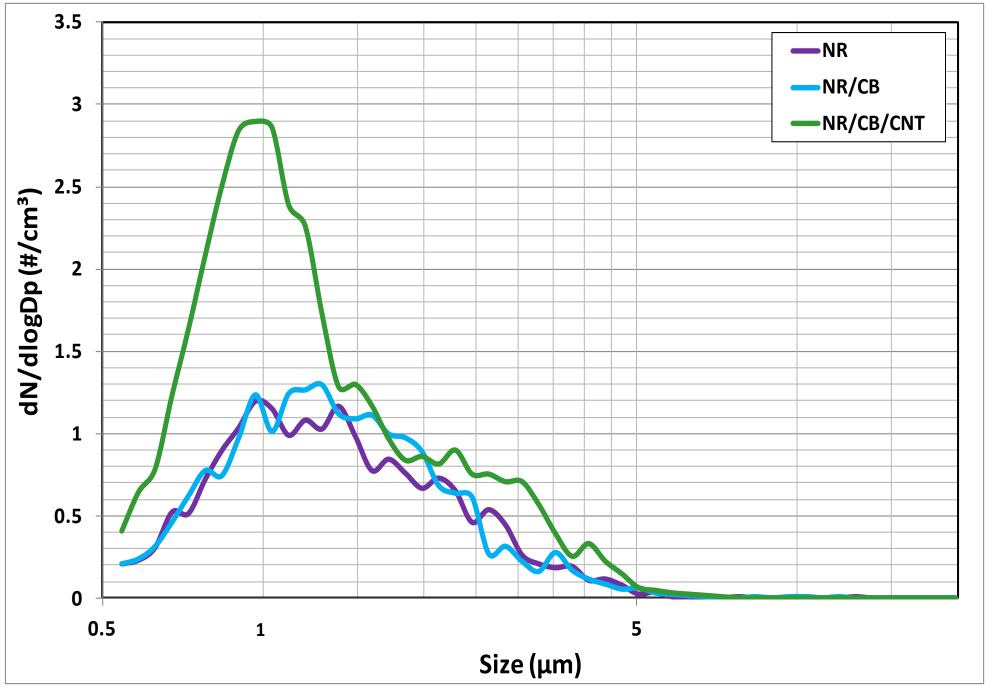
Where next? → Complex scenarios, secondary fragmentation

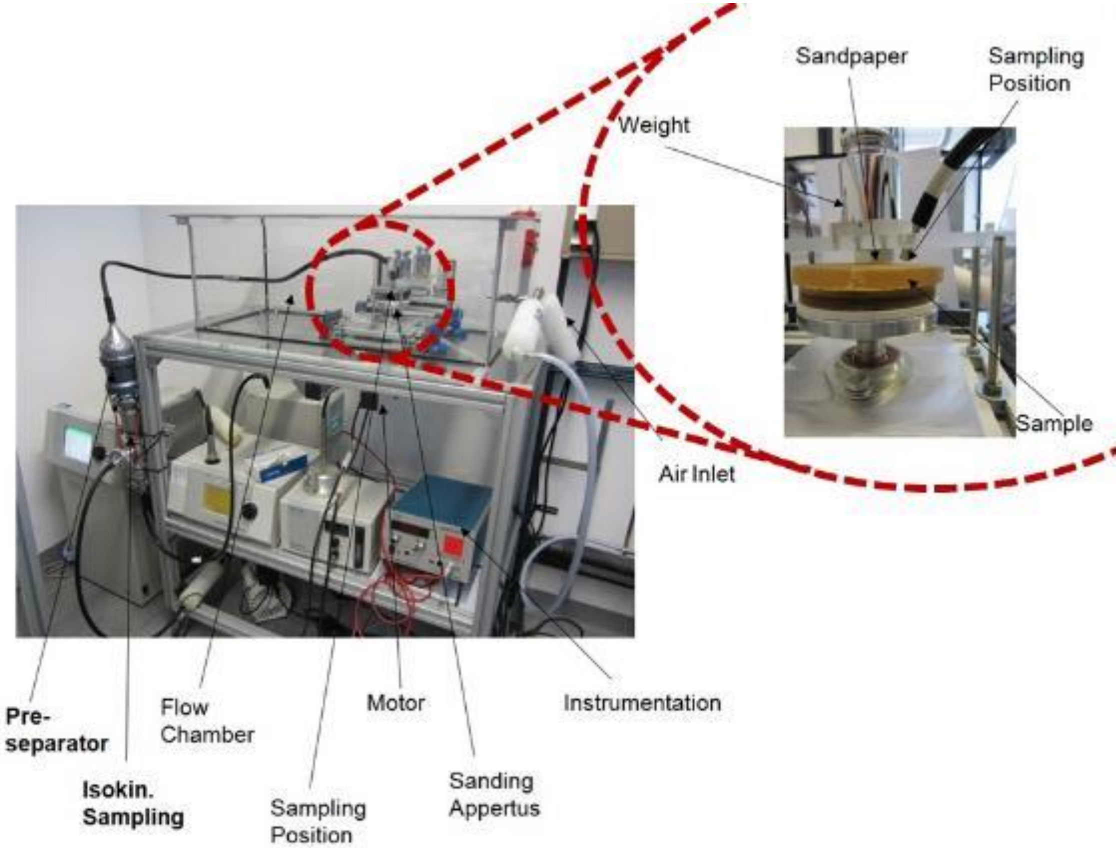


Primary fragmentation

Natural rubber
+ 40% Carbon Black
+ 4% mwCNT

1. Sanding to simulate "full stop"



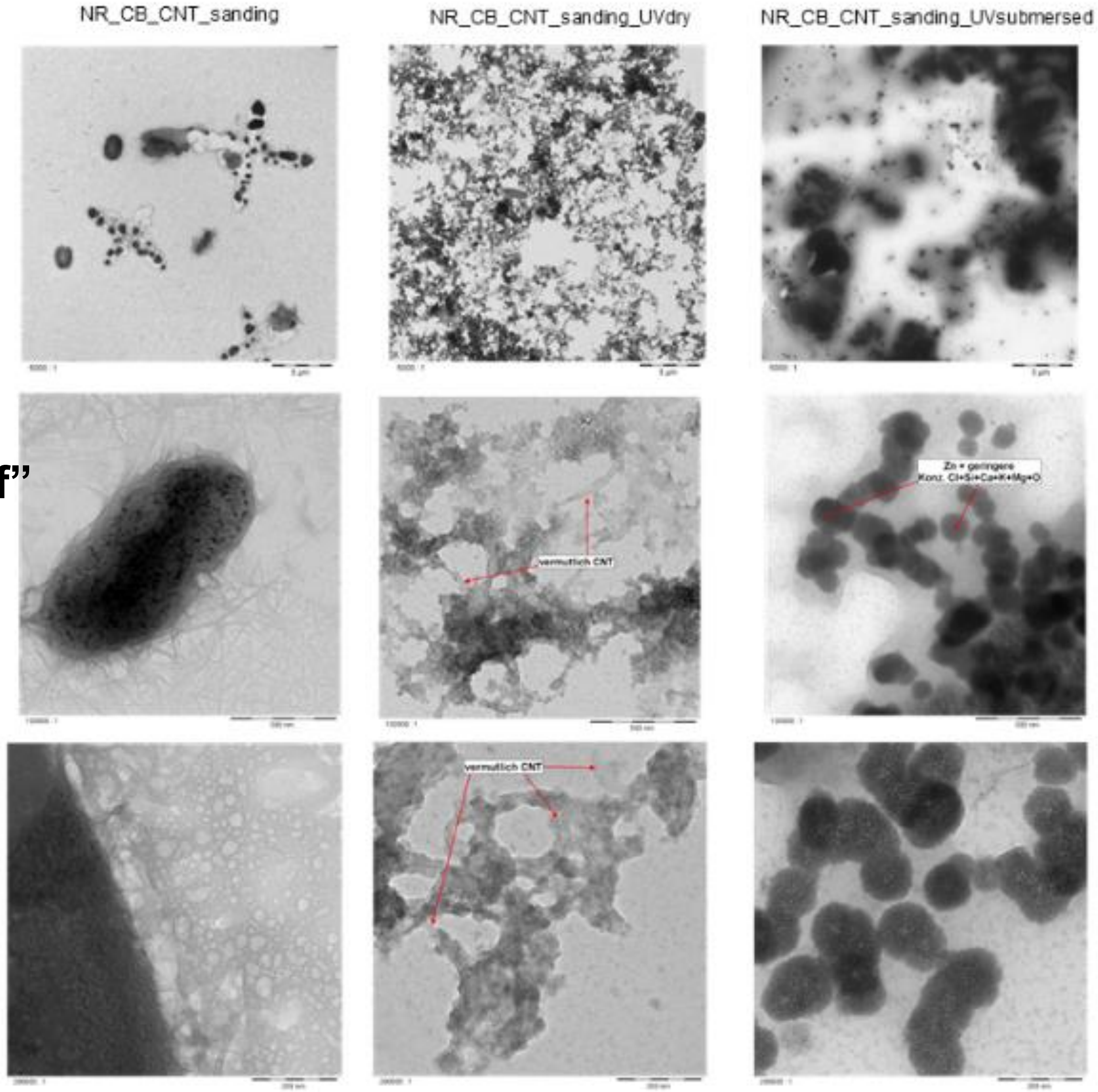


MARINA
MANAGING RISKS OF NANOMATERIALS

Secondary fragmentation

1. Sanding to simulate "full stop"

2. **Aging**
   - **UV submersed in M4 = "in run-off"**
   - **UV dry = "on the road"**
3. Sonication in M4 medium
4. Filtration 5µm
5. Analysis as in NanoRelease
   - TEM
   - UVVis
   - AUC
   - EDX



Wohlleben, Kuhlbusch and teams,
Environ Sci nano (**2016**) 3:1036

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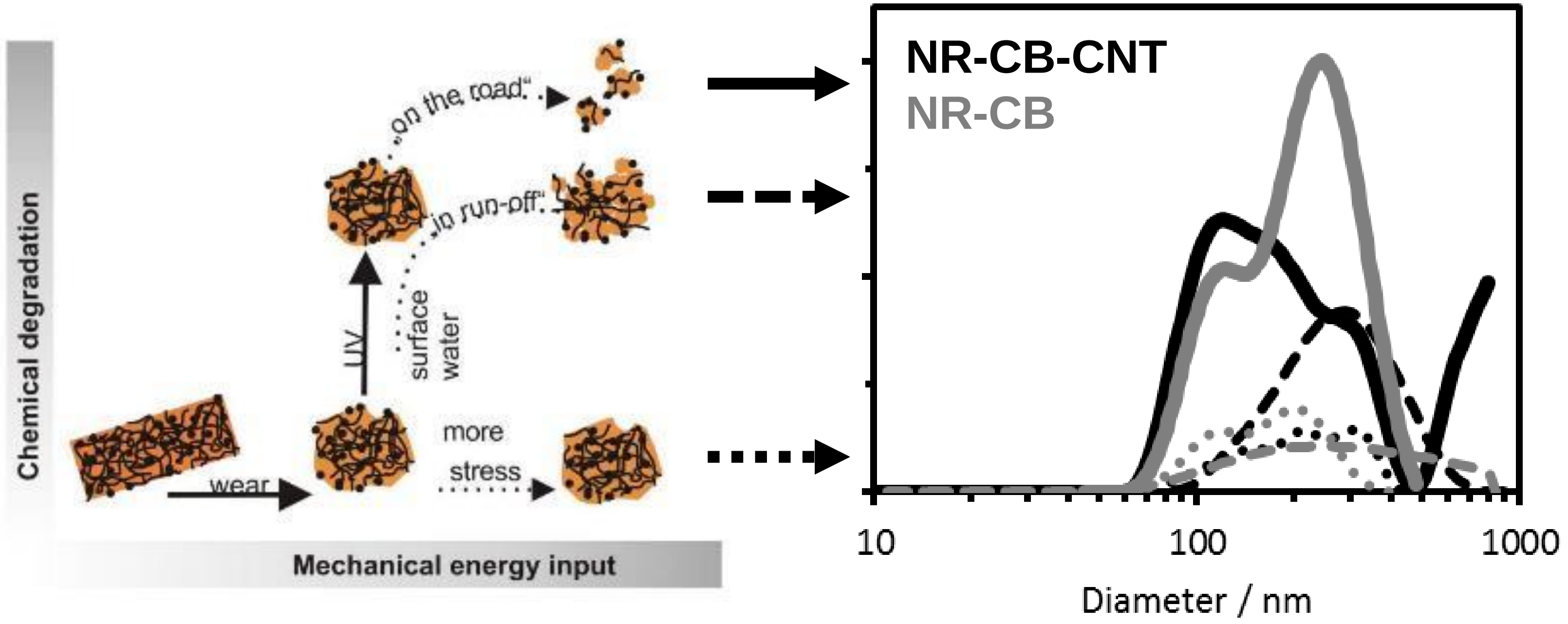
Sample	Scenario to be simulated	Fraction below 5µm % of total solids (gravimetry)	
		NR_CB	NR_CB_CNT
sanding fragments, sonicated in M4	Freshly generated tread wear	0.7 %	0.7 %
sanding fragments, UV irradiated in M4, sonicated	Tread wear with direct run-off into surface water	1.6 %	1.7 %
sanding fragments, UV irradiated, sonicated in M4	Tread wear with delayed run-off into surface water	4.0 %	4.5 %

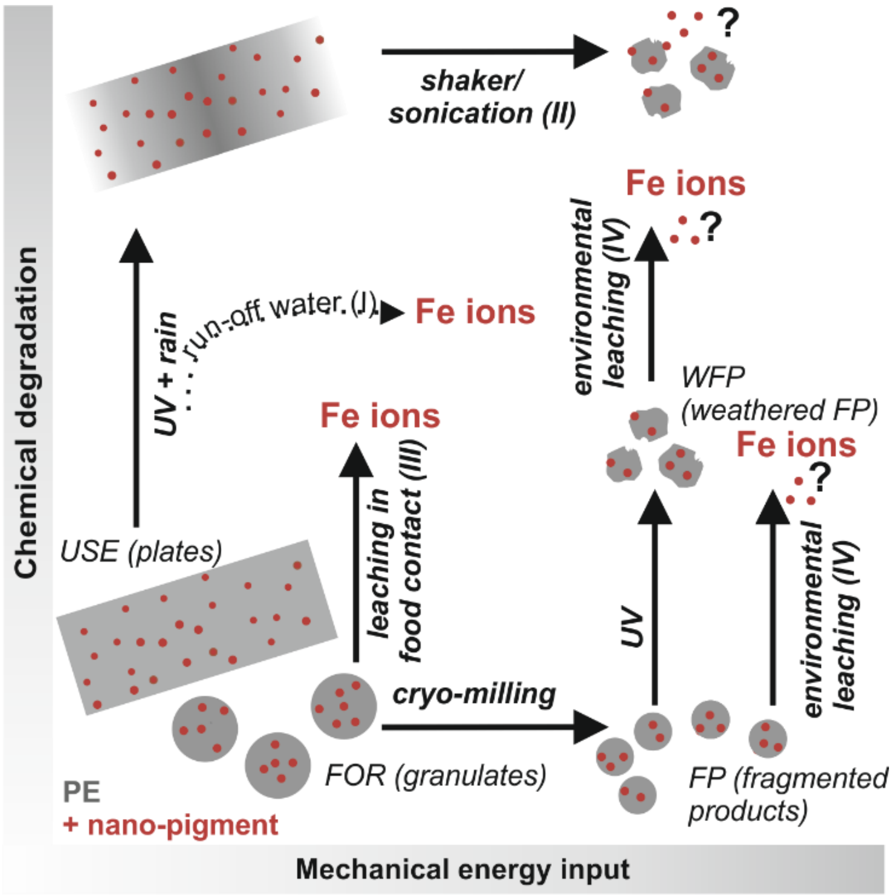
- UV aging does induce secondary fragmentation.
- **“in run-off” aging significantly less secondary fragmentation vs. “on the road”**
- maximum free ENM is 0.045 % of the tread wear.

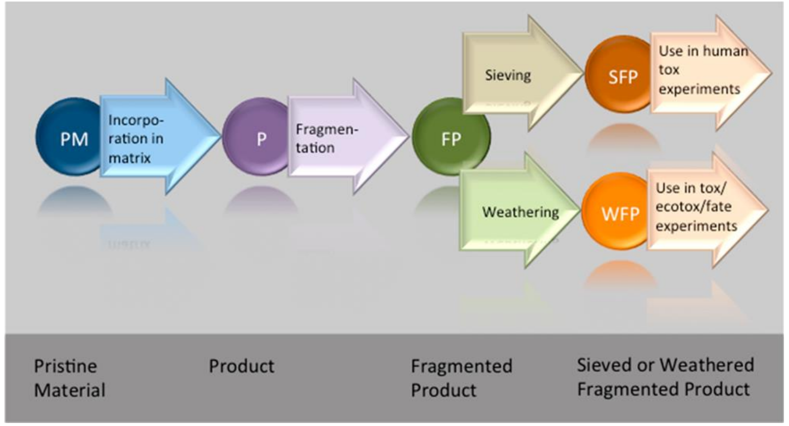


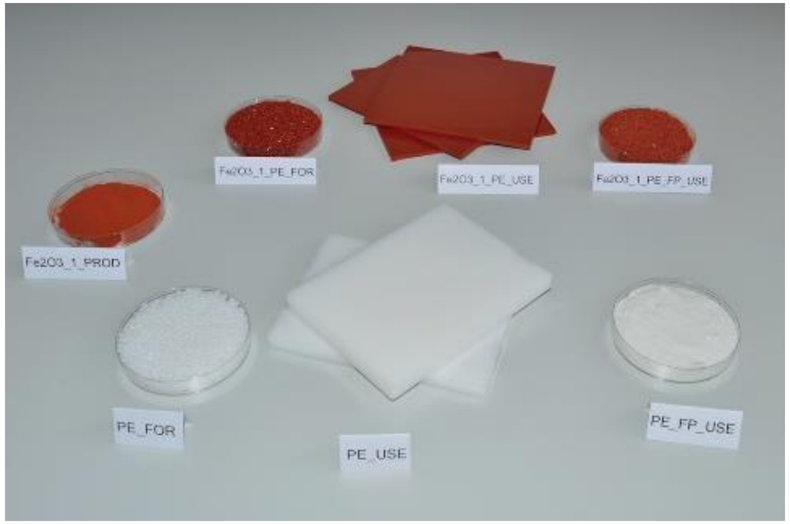
Environ Sci nano (**2016**) 3:1036

Complexe scenarios based on Nowack et al. **Environ. Sci. Technol. 2016**, 50, 2747

full life cycles, secondary fragmentation / leaching, ecotox effects of pigmented plastics





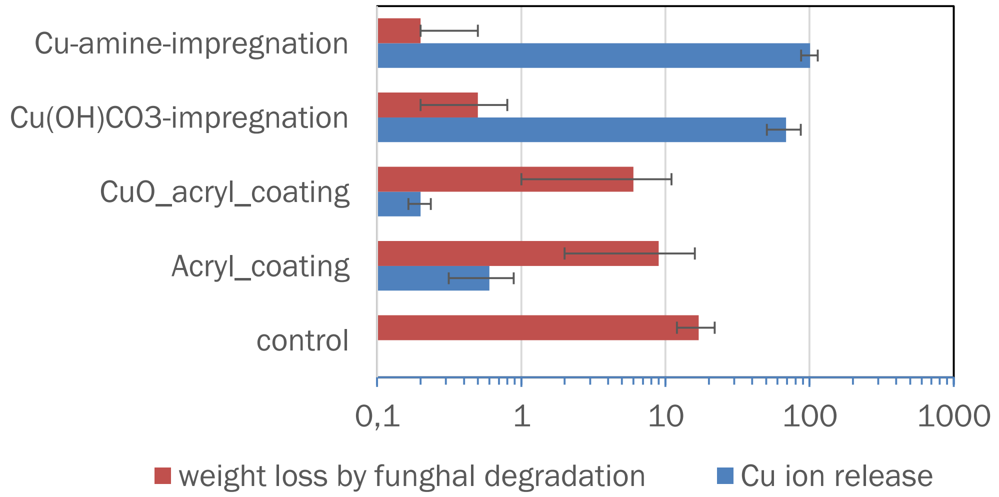


	MANUFACTURING		USE		DISPOSAL
→ Presentations	Koivisto et al. (now)	+	Scifo et al, 14.15 session	+	Soritiou et al, 17.15 session

Complex scenarios:

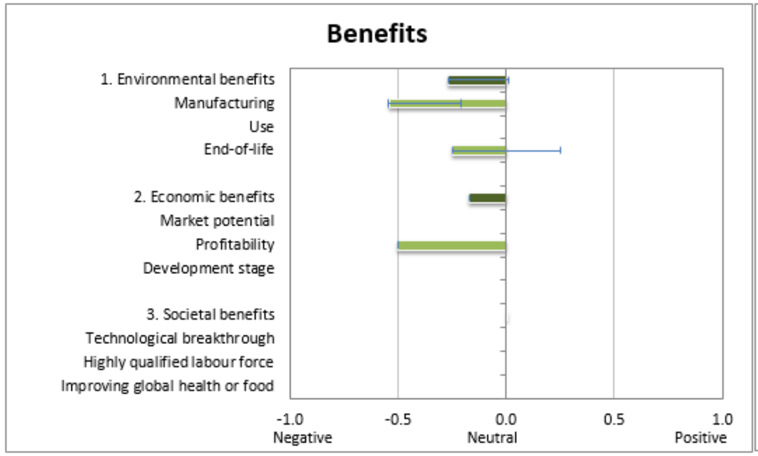
CuO vs Cu-amine vs. $Cu(OH)CO_3$

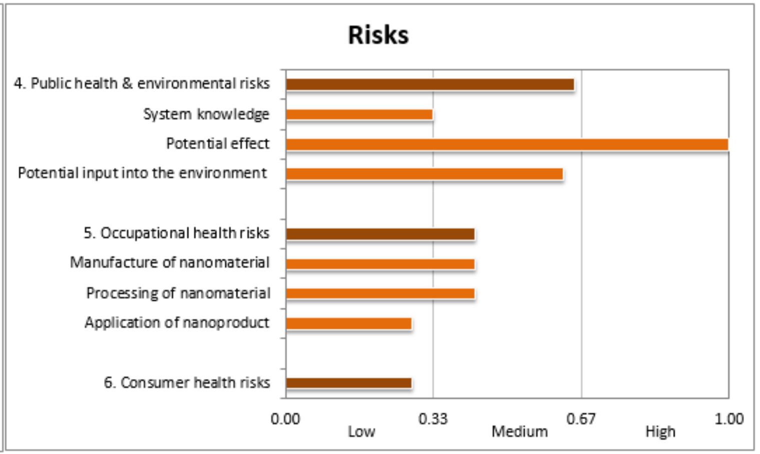
Transformation to ions and release determines effectiveness of wood protection



Testing DIN EN113 (Coniophora puteana 62)

insufficient sustainability of CuO_coating (LICARA nanoscan) → stop development.





→ Presentation Neubauer et al, 14.15 session !

Please join the release sessions today

MANUFACTURING 11.15 h
Auditorium Platine

WANG Jing
SCOTT Keana
KOIVISTO Antti Joonas
GÖHLER Daniel
BOUTRY Delphine

USE 14.45 h
Chrome 1

SUNG Li-Piin
JOSE LUIS Muñoz
SCIFO Lorette
NEUBAUER Nicole
MITRANO Denise

FAIRBROTHER Howard

DISPOSAL 17.15 h
Chrome 1

SOTIRIOU Georgios A.
PAUR Hanns-R.
KUHLBUSCH Thomas A.J.
CABALLERO-GUZMAN Alejandro

CONCLUDING CONCEPTS

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Sincere Acknowledgements to:

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Hubert Rauscher, JRC-Ispra

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Nicole Neubauer
Philipp Müller
Sabine Hirth
Robert Landsiedel
…many more…

SUN

Jerome Rose & Lorette Scifo, CEREGE
Bernd Nowack, EMPA
Joonas Koivisto, Keld Jensen, NRCWE
Many more…

Harvard

George Sotiriou,
Phil Demokritou

MARINA – Managing Risks of Nanomaterials

Thomas Kuhlbusch, IUTA
Yaobo Ding, IST
Julie Mueller, Nanocyl
Iňigo Larraza Alvarez, Acciona

NanoRelease

300 experts… some from the core team here:

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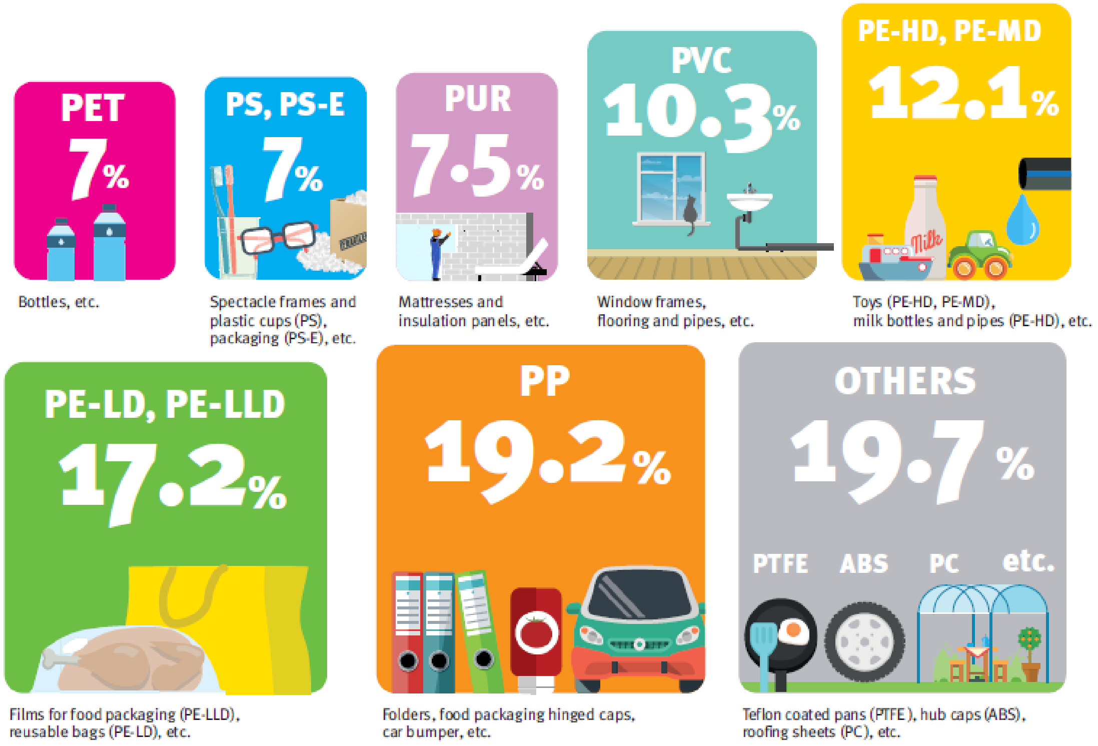
Scratching at the tip of the iceberg?
Matrix materials compared to production volumes

The tip: high-performance composites: $ 5 bn epoxy
Freedonia, *High-Performance composites (US) (2016)*

The iceberg: Consumer goods: € 350 bn other plastics
Plastics Europe, Fact Sheet (2015)



European plastics demand* by polymer type 2014
Source: PlasticsEurope (PEMRG) / Consultic / myCeppi
* EU-28+NO/CH

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