Comparing nano-enabled copper formulations throughout the wood protection lifecycle:
transformations, releases, hazards, effectiveness and sustainability

Wendel Wohlleben + many FP7-SUN coauthors

UBA stakeholder conference, Dessau, 11. Sept. 2017

BASF
We create chemistry

Copper in non-nano-form has biocidal uses, with Cu^{2+} ions as regulated biocidal active

Wood after aging:
treated - untreated, moulded

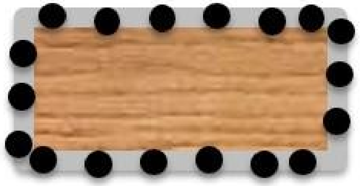
Brown rot and other fungi
UBA Dessau

Application examples: © BASF

BASF
We create chemistry

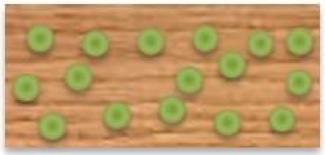
Conventional and nano-enabled wood protection

CuO acrylate
15 kg Cu/m³
in barrier



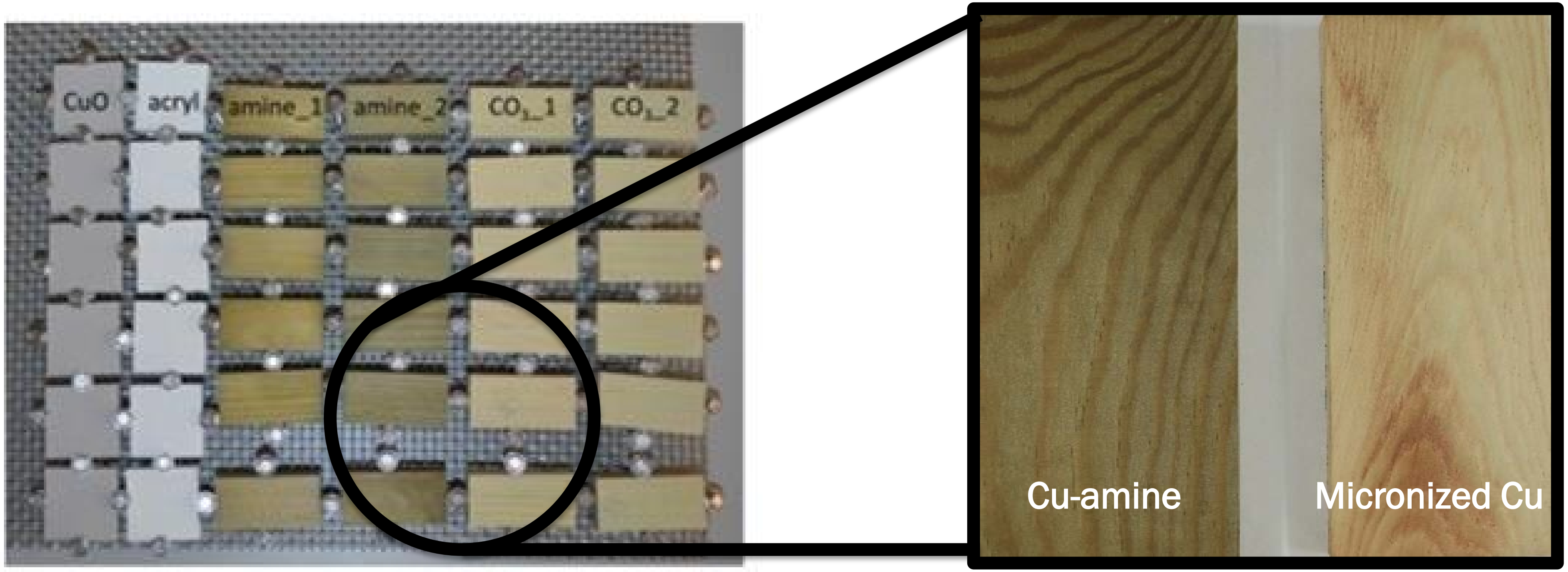
Cu-amine
1 kg Cu/m³
in bulk

Micronized Cu
1 kg Cu/m³
in bulk



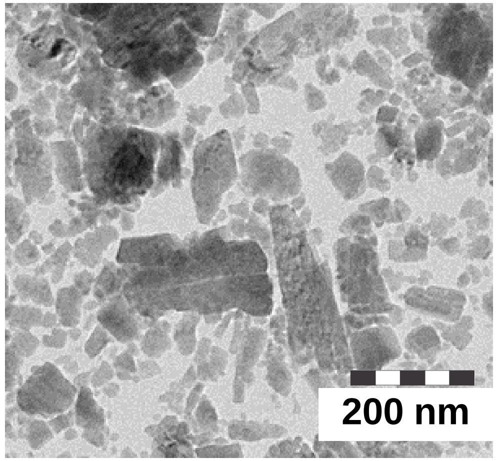
Motivation for CuO acrylate:
less Cu consumption: 0.1 kg Cu/m³ Cu in bulk

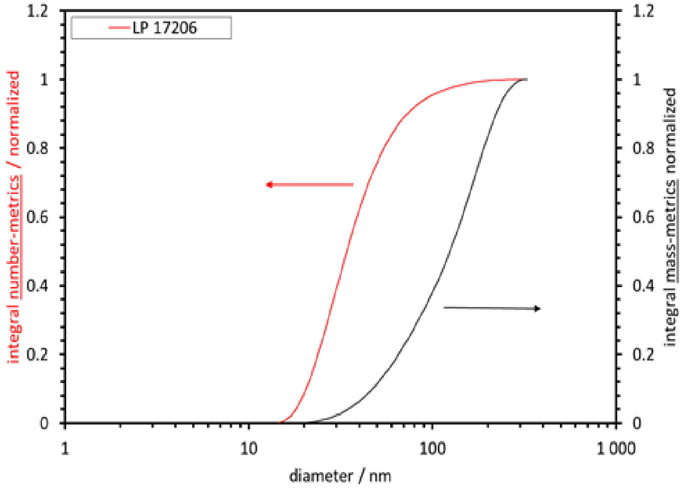
Motivation for "micronized Cu" = $Cu_2(OH)_2CO_3$
More natural wood appearance



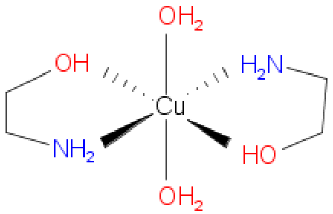
Solutions or nano-suspensions can penetrate deep into wooden pores

Micronized Cu suspension (US standard) (nano by nb%)



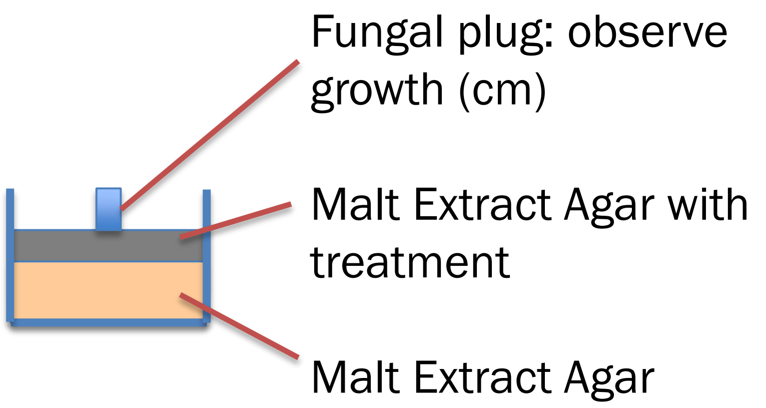


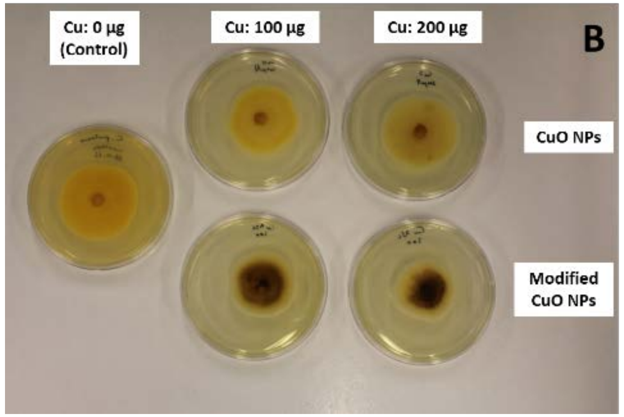
Cu-amine solution (EU standard) (non-nano)

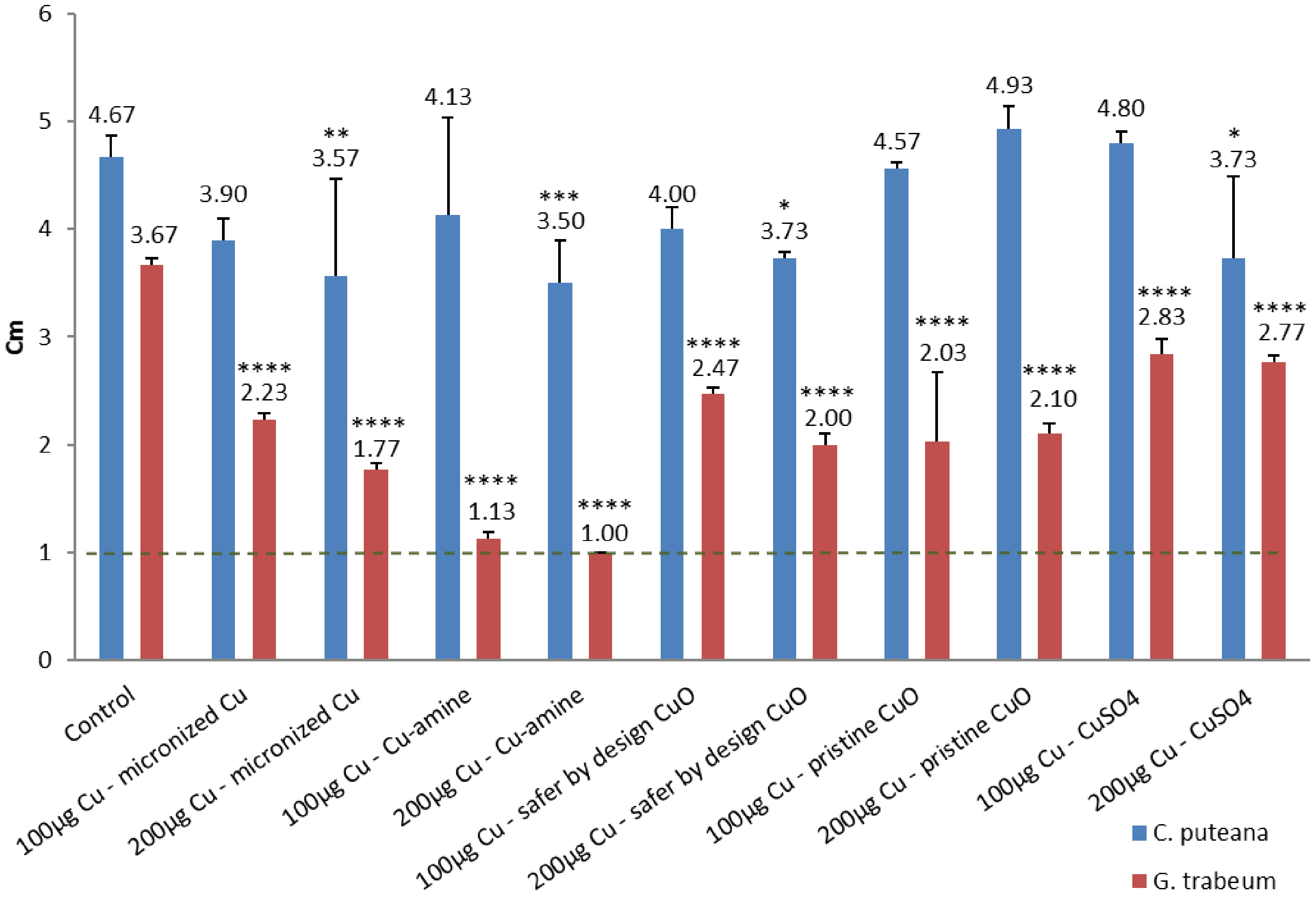


Vacuum-pressure impregnation for use class 3 and class 4 treated wood

Effects of *formulations* on fungi (*before* incorporation into wood) (Pantano, Stone: HWU)





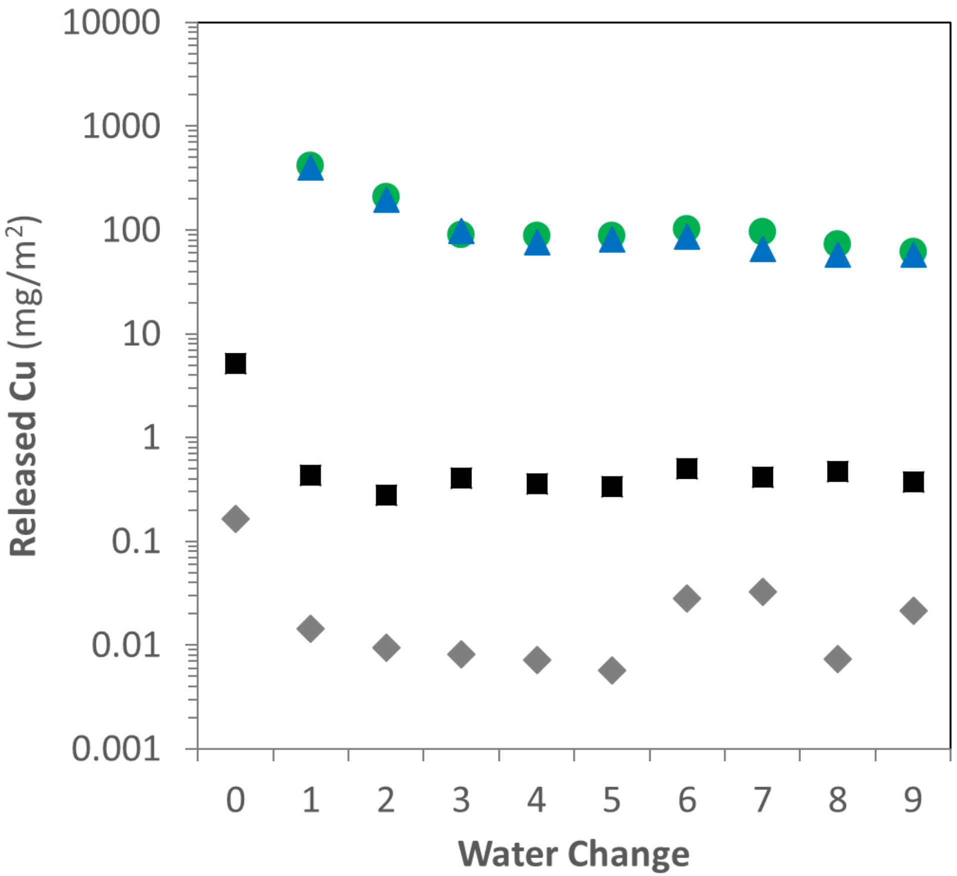


Cu-amine >> $Cu_2(OH)_2CO_3$ > $CuSO_4$ > CuO_ascorbate > CuO

Effects not primarily dissolution-mediated, and can be modulated by surface modifications

Leaching according to EN 84

(Navratilova, von der Kammer: UVIENNA)

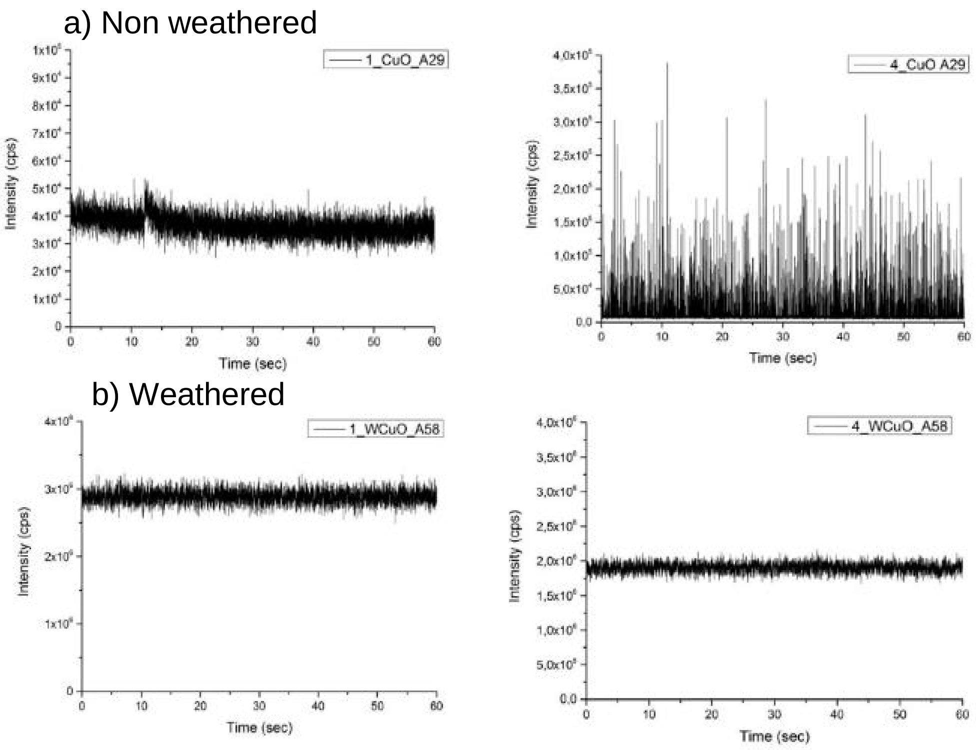


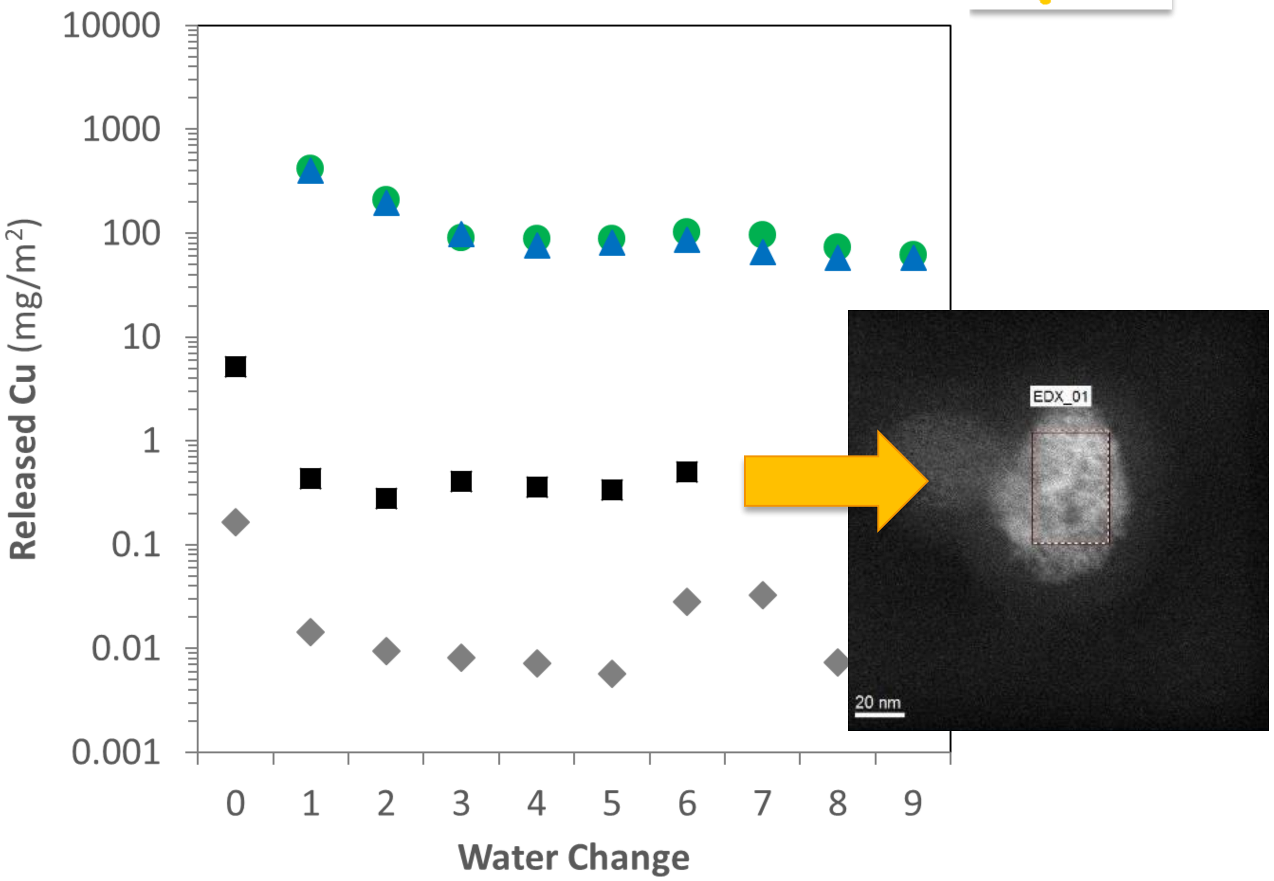
Total release (ICPMS integral):

Cu-amine ~ $Cu_2(OH)_2CO_3$ >> CuO > acrylic control

Leaching according to EN 84

(Navratilova, von der Kammer: UVIENNA)





<u>Total release (ICPMS integral):</u>

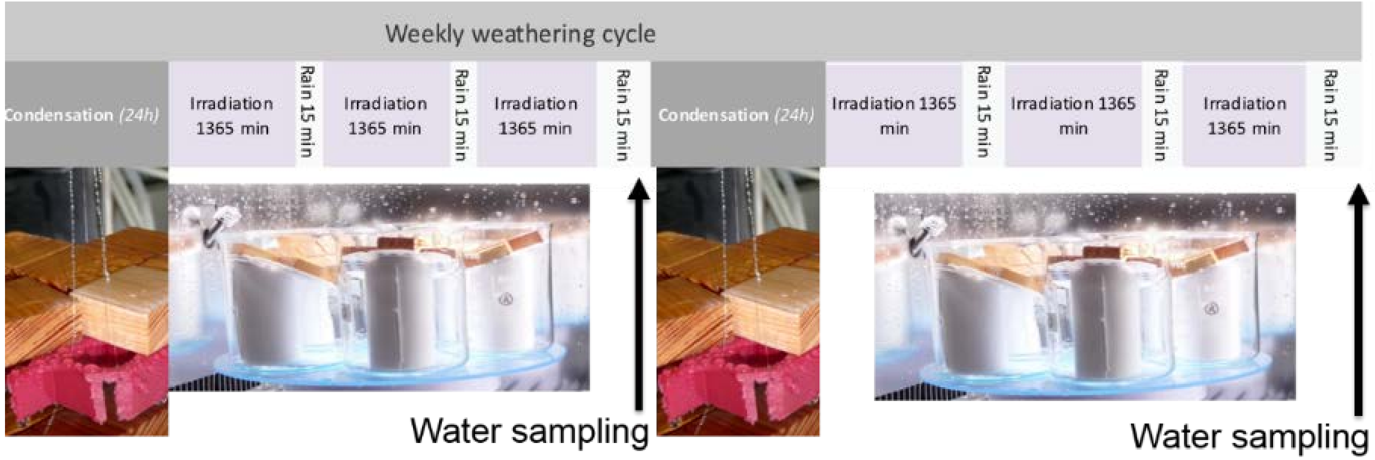
Cu-amine ~ $Cu_2(OH)_2CO_3$ >> CuO > acrylic control

<u>TEM + spICPMS spikes</u>:

Particulate spikes only found in leaching from aged CuO-acrylic-coating, not from other woods.

Nano-$Cu_2(OH)_2CO_3$@wood releases only *ionic* Cu.

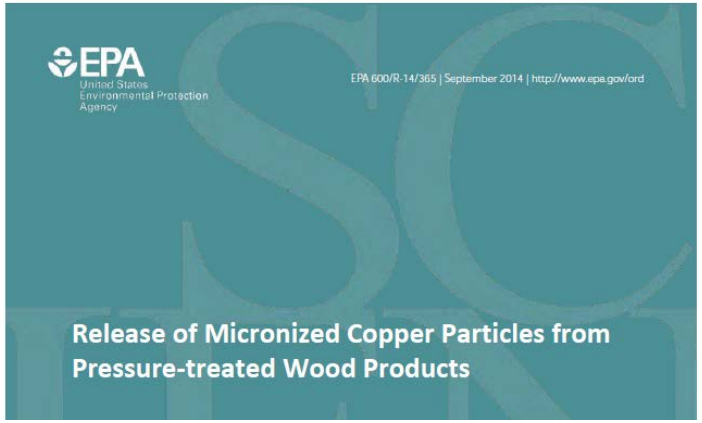
Aging of treated woods
(Scifo, Rose: CEREGE)

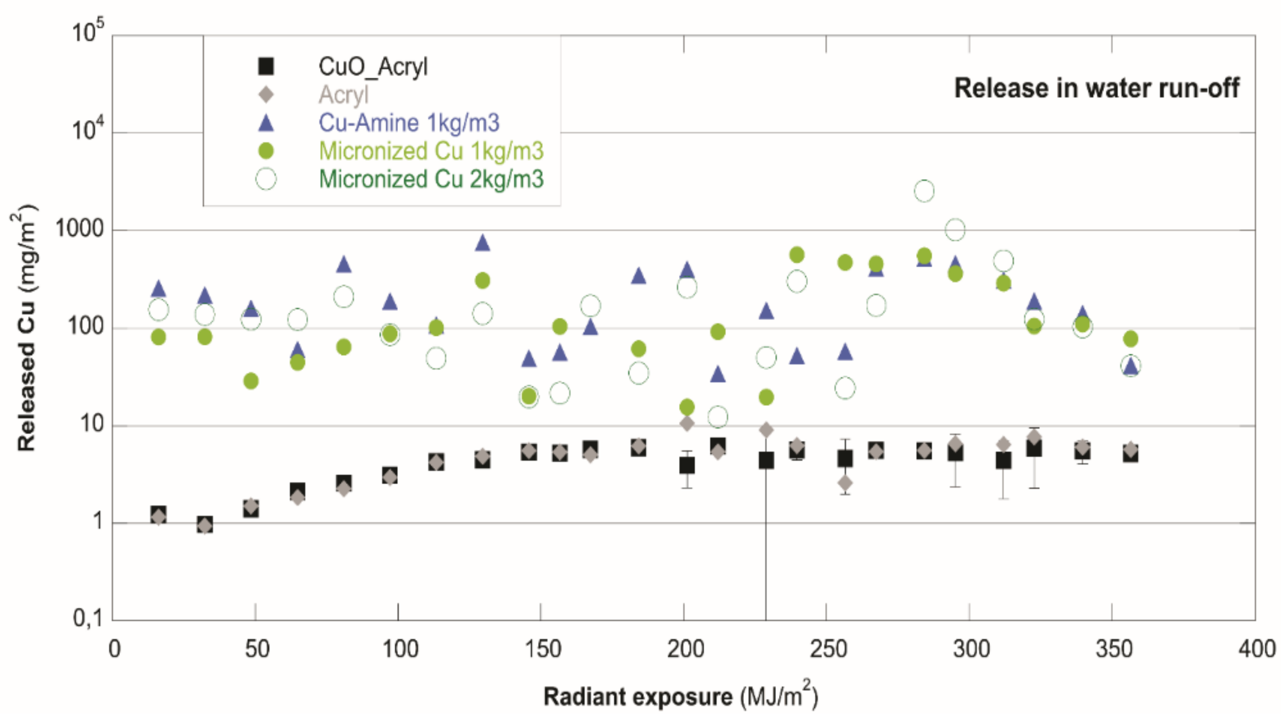


Higher release per treated wood surface during condensation (wood swelling) than during rain events.

Weak trends with UV dose.

Release levels consistent with EPA reports.



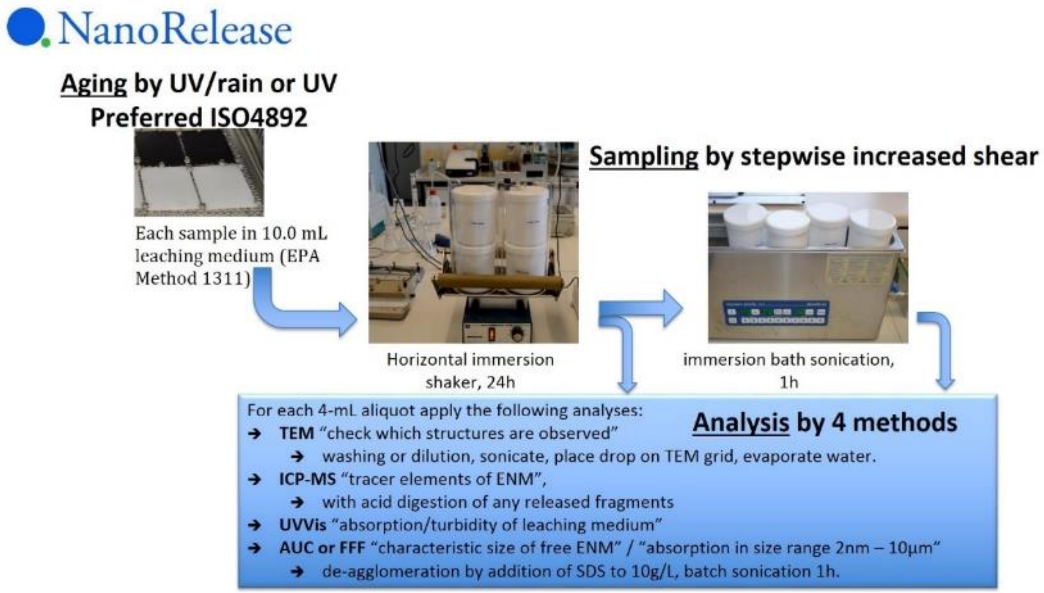


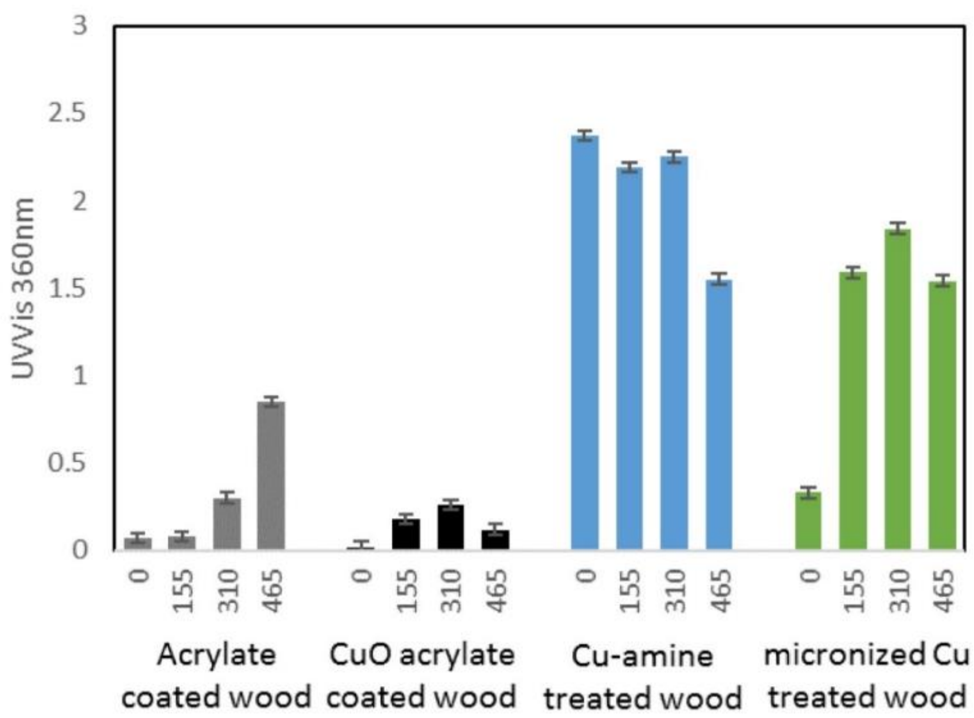
Cu-amine ~ $Cu_2(OH)_2CO_3$ >> CuO ~ acrylic control

Aging + mechanical stress on treated woods

(Neubauer: BASF)

NanoRelease protocol was globally reproducible (EPA, NRC, LEITAT, BASF) Carbon (**2017**) 113:346-360
all data open-access at NIST servers
TR development (2017-2019) at ISO TC229





Release from acrylic coatings increases with UV dose, with particulate releases.

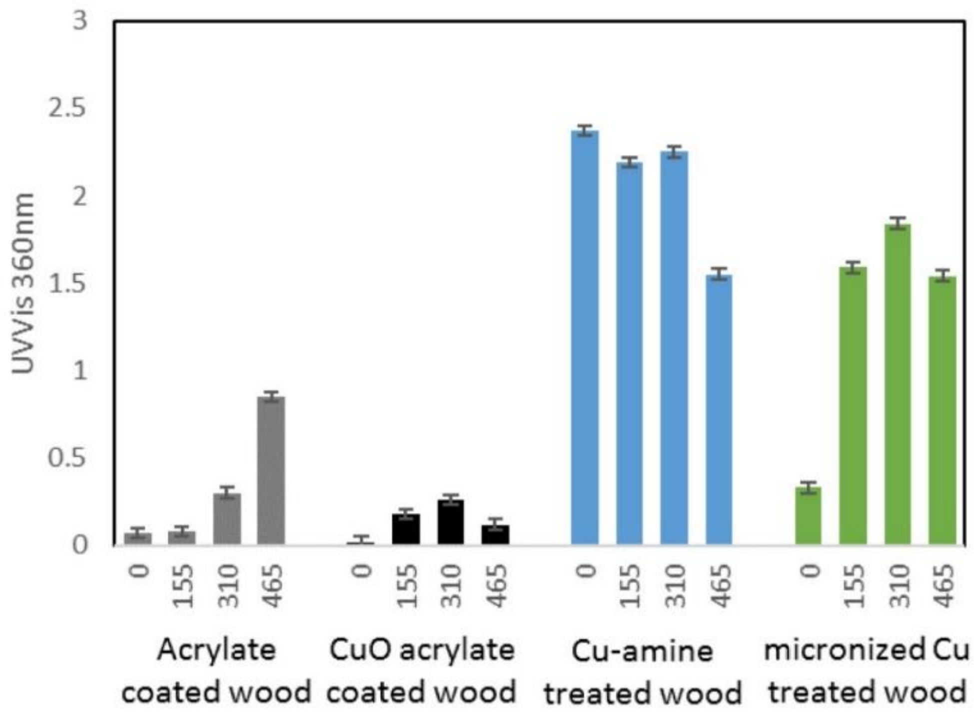
Cu-amine ~ $Cu_2(OH)_2CO_3$ >> CuO ~ acrylic control

Weak trends with UV dose from impregnated woods.

Aging + mechanical stress on treated woods

(Neubauer: BASF)

Wood		Cu, ppm	
	UV/rain weather, MJ/m²	total	<20 nm
Acrylate coated wood	0	0.1	
	155	0.2	0.1
	310	0.4	0.3
	465	1.5	1.4
CuO acrylate coated wood	0	0.1	0.1
	155	0.3	0.2
	310	0.5	0.3
	465	0.4	0.2
Cu amine impregnated wood	0	145	145
	155		90
	310		120
	465	50	48
Micronized Cu impregnated wood	0	27	29
	155		85
	310		100
	465	70	61



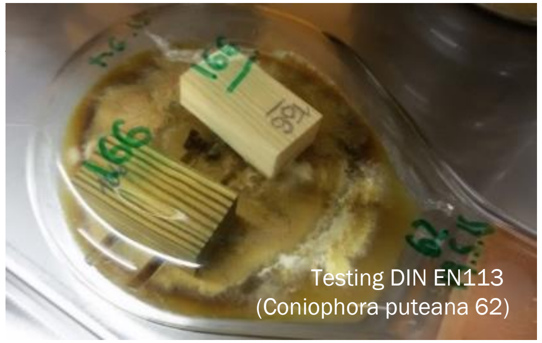
Release from acrylic coatings increases with UV dose, with particulate releases.

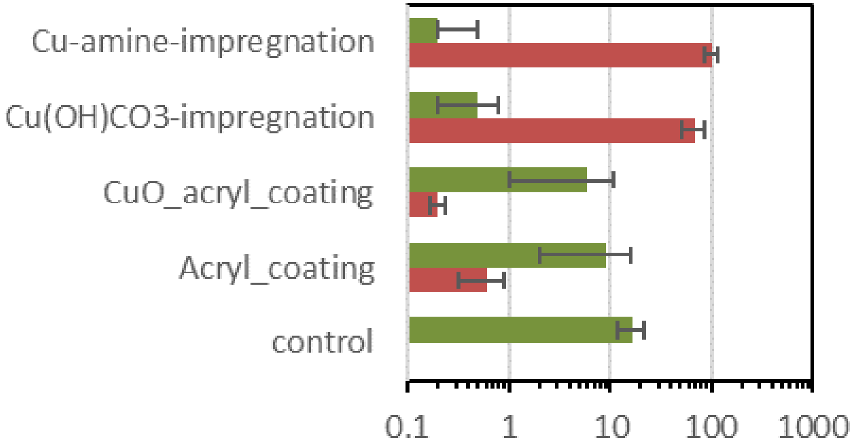
Cu-amine ~ $Cu_2(OH)_2CO_3$ >> CuO ~ acrylic control

Weak trends with UV dose from impregnated woods. Predominantly ionic releases from both Cu-amine and micronized Cu-Carbonate.

Product effectiveness: wood mass loss vs. ion release

(Civardi, EMPA)





Interim summary of technological alternatives for wood protection:

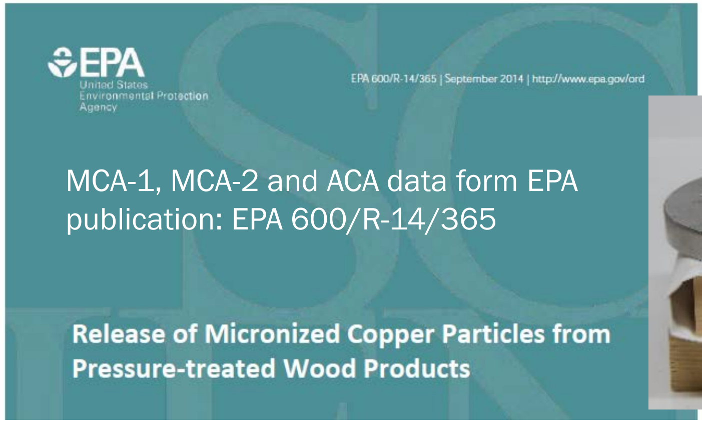
- Wood treated with $Cu_2(OH)_2CO_3$ nanoparticles releases *ions* as biocidal active
- The „safer-by-design“ **CuO** barrier technology (overall x10 less Cu) fails, because it does not release sufficient Cu ions.

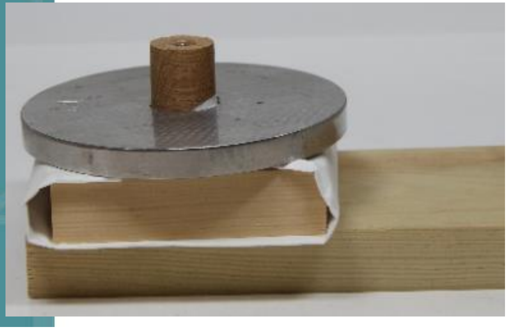
  - Effectiveness (agar): Cu-amine >> $Cu_2(OH)_2CO_3$ > $CuSO_4$ > **CuO**
  - Cu ions (at agar pH): Cu-amine ~ $CuSO_4$ >> $Cu_2(OH)_2CO_3$ ~ **CuO**
  - Effectiveness (treated wood): Cu-amine ~ $Cu_2(OH)_2CO_3$ >> **CuO** > control
  - Cu ion (released from treated wood): Cu-amine ~ $Cu_2(OH)_2CO_3$ >> **CuO** > control

→ Transformation in use phase govern both benefits and risks of nano-enabled biocides.

Handling exposure? Wipe releases from wood surface

Wood preservative	Copper concentration Kg/m³ wood	Copper concentration µg/ 25 cm² wood surface	Weathering	Copper content per wipe µg
$Cu_2(OH)_2CO_3$	0.95	6926	None	5.3
		6871	EN 927-6 8 weeks	6.8
	1.89	14191	None	5.0
Cu-amine	0.95	7278	None	2.0
		7200	EN 927-6 8 weeks	8.8
	1.89	15089	None	6.0
MCA-1*	0.61	4575	None	19.0
MCA-2*	0.73	5475	None	5.0
ACA*	1.77	13275	None	1.7





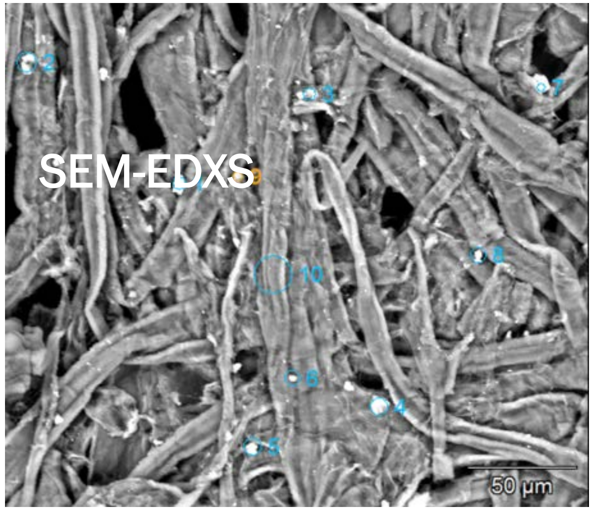
- ➪ Similar Copper release for Cu-amine and $Cu_2(OH)_2CO_3$ observed.
- ➪ Only ~ 0.1 % of Copper was transferred from the wood surface to the wipe.
- ➪ Copper release of un-weathered wood is similar to MCA-2-values from the EPA investigation.
- ➪ SEM-EDXS showed that for both systems Cu is co-localized with C and other metals. No identification as $Cu_2(OH)_2CO_3$

Human exposure? Wipes on treated woods (DTU + BASF)

release levels consistent with EPA reports, but transformation by sampling!

	C	O	Na	Mg	Al	Si	P	S	Cl	Ca	Cr	Fe	Cu
Messstelle 1	45,7	44,0	0,1	0,1	---	0,1	0,1	0,1	0,1	9,7	---	—	---
Messstelle 2	55,0	36,3	0,3	2,7	0,9	1,9	—	0,1	0,2	0,3	0,3	0,5	1,6
Messstelle 3	52,1	36,3	0,7	0,1	---	0,1	—	0,1	0,4	5,5	---	—	4,6
Messstelle 4	45,2	39,6	—	6,1	---	8,5	—	0,1	0,2	0,3	---	—	---
Messstelle 5	42,2	44,4	—	---	---	---	—	—	0,2	13,2	---	—	---
Messstelle 6	52,0	42,0	—	---	---	0,1	—	—	0,3	5,5	---	—	---
Messstelle 7	24,7	53,3	—	0,2	---	---	—	—	---	21,4	---	—	0,4
Messstelle 8	57,2	34,5	0,3	0,2	---	0,1	0,1	—	0,2	7,4	---	—	---
Messstelle 9	58,9	39,2	—	---	---	---	—	0,9	---	1,1	---	—	---
Messstelle 10	53,6	45,8	—	---	---	---	—	—	---	0,5	---	—	---

--- Element nicht nachgewiesen



Total ICPMS + Single-particle-ICPMS
Results on wood wipes

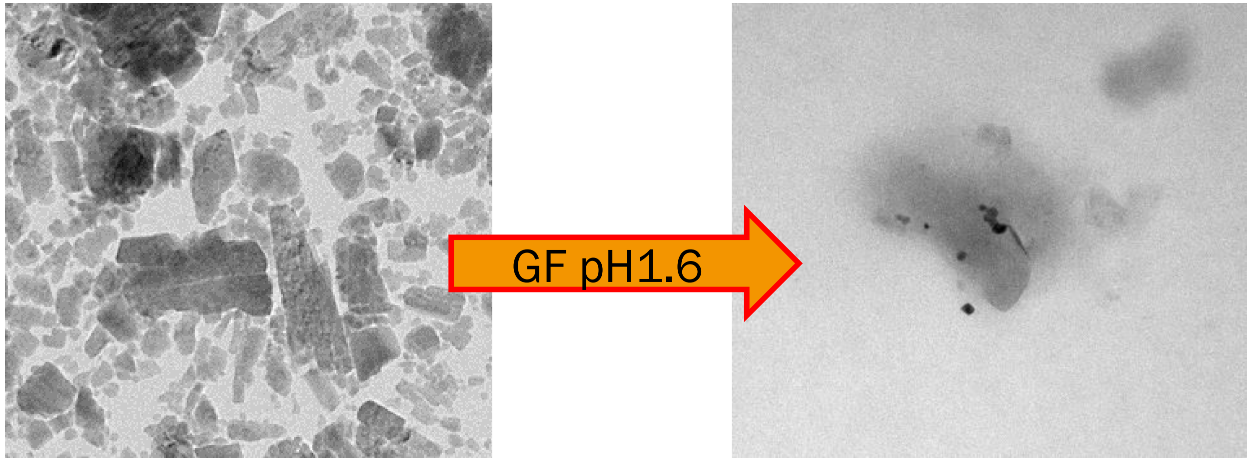
Wood treatement	Total Cu (µg/wipe)	Total extracted Cu (µg/wipe)	Extracted particulate Cu (µg/wipe)
2.7 % CuCO3	5.0	/	/
2.7 % CuCO3	/	0.077	0.0096
2.7 % CuCO3	/	0.826	< 0.0008
2.7 % CuAmine	6.0	/	/
2.7 % CuAmine	/	0.828	< 0.0008
2.7 % CuAmine	/	0.183	0.0002

Total ICPMS + Single-particle-ICPMS
Results on controls tissues with pure formulations

Formulation on wipe	Adjusted Cu content (µg/wipe)	Total extracted Cu (µg/wipe)	Extracted particulate Cu (µg/wipe)
CuCO3	30	0.652	< 0.0007
CuCO3	30	0.839	< 0.0008
CuAmine	30	0.035	0.0014
CuAmine	30	0.027	0.0017

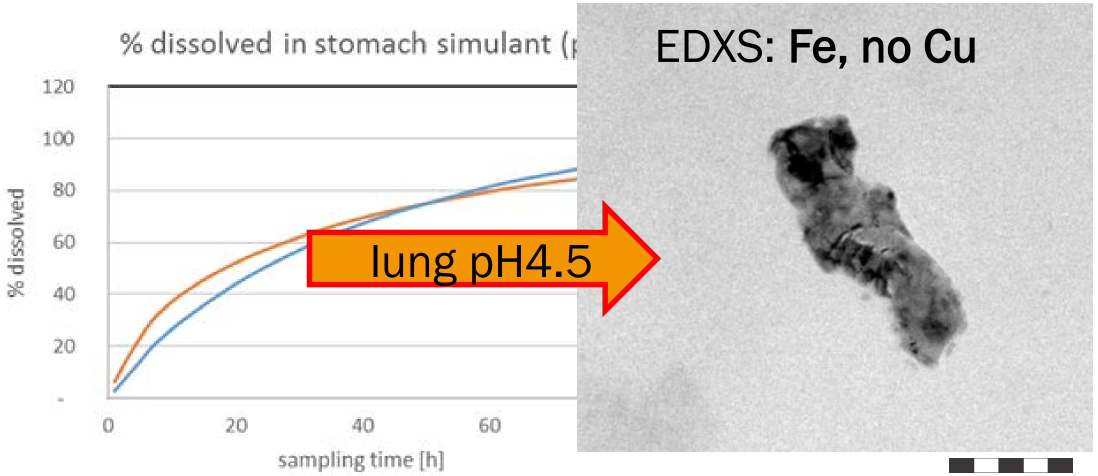
Dissolution after oral uptake: CuO and Cu-carbonate dissolve similarly in stomach, similar LOAEL

Cu-Carbonate, micronized



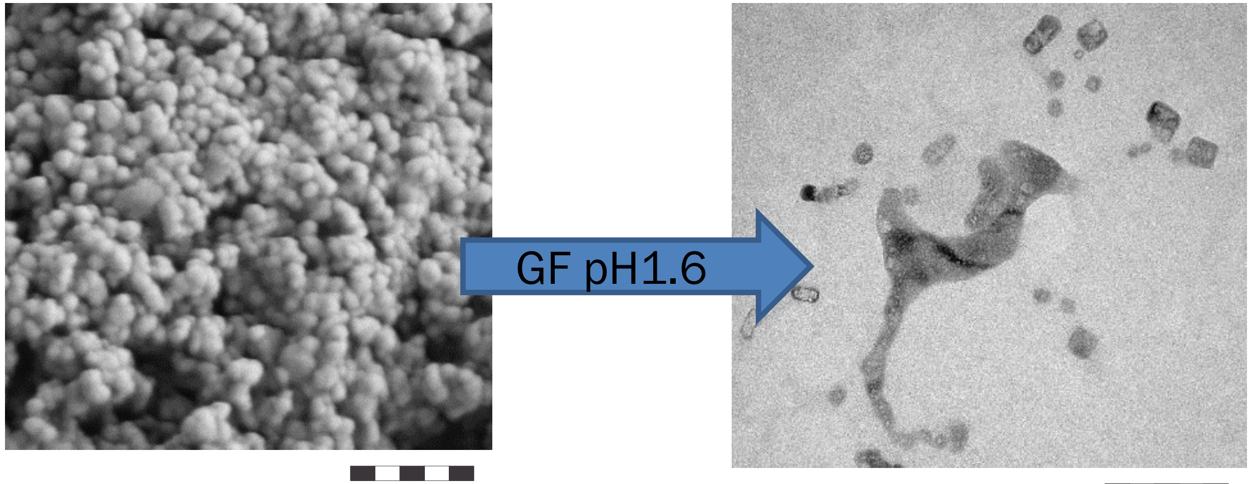
200 nm

200 nm



200 nm

CuO

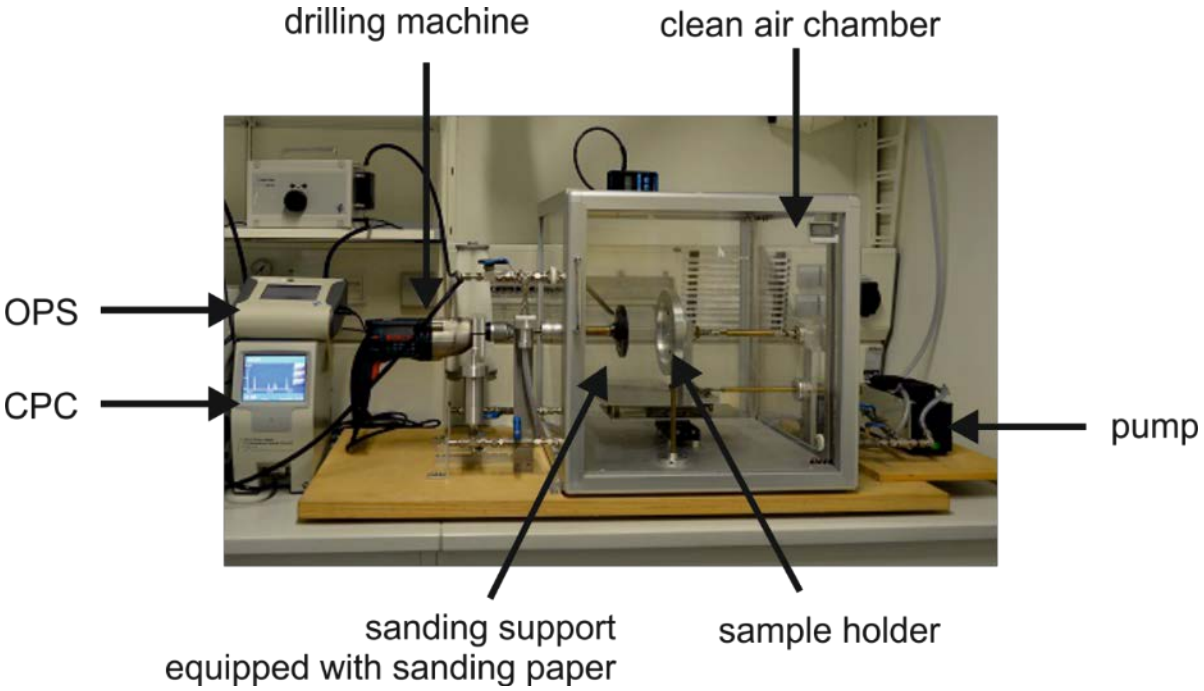


200 nm

200 nm

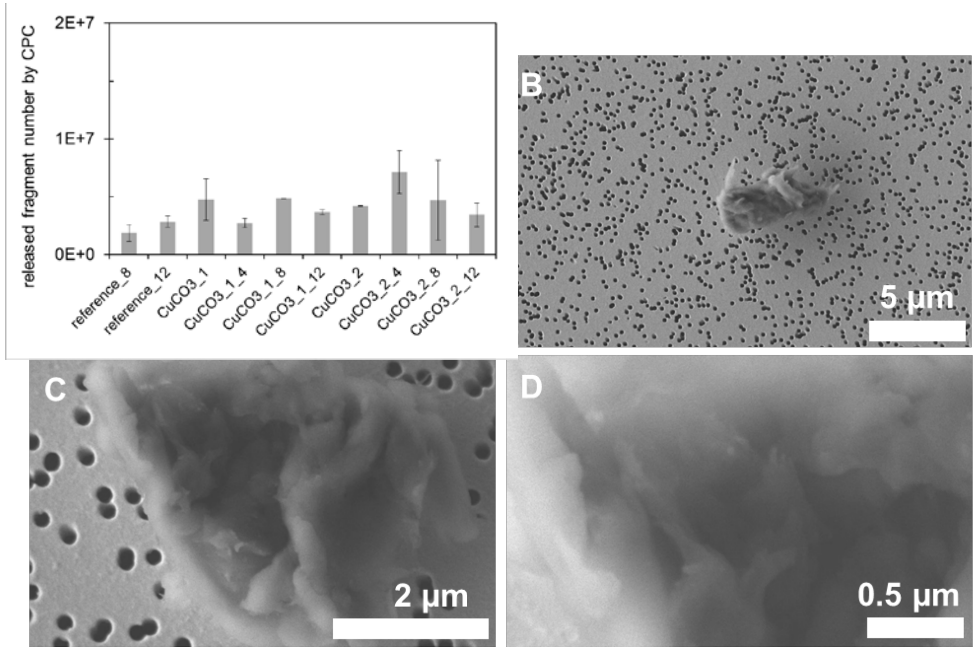
	CuO	$Cu_2(OH)_2CO_3$
What they are	80 % Cu	55% Cu
Where they go:	Dissolves fast in lungs & GIT, slow in env. surface water	Dissolves fast in lungs & GIT, slower in env. surface water
What they do:	active in lung (2 mg/m³), in GIT (128 mg/kg), on algae & daphnids	active in GIT (64 mg/kg), on microflora (n.d. on others)

Wood refurbishment: Release during sanding ?



- Release dominated by wood;
- Aerosol modal size around 200nm
- Cu content in dust lower from $Cu_2(OH)_2CO_3$ than from Cu-amine; high from CuO_acrylic: a consequence of the „barrier“ concept.

CPC/SEM of $Cu_2(OH)_2CO_3$ treated wood

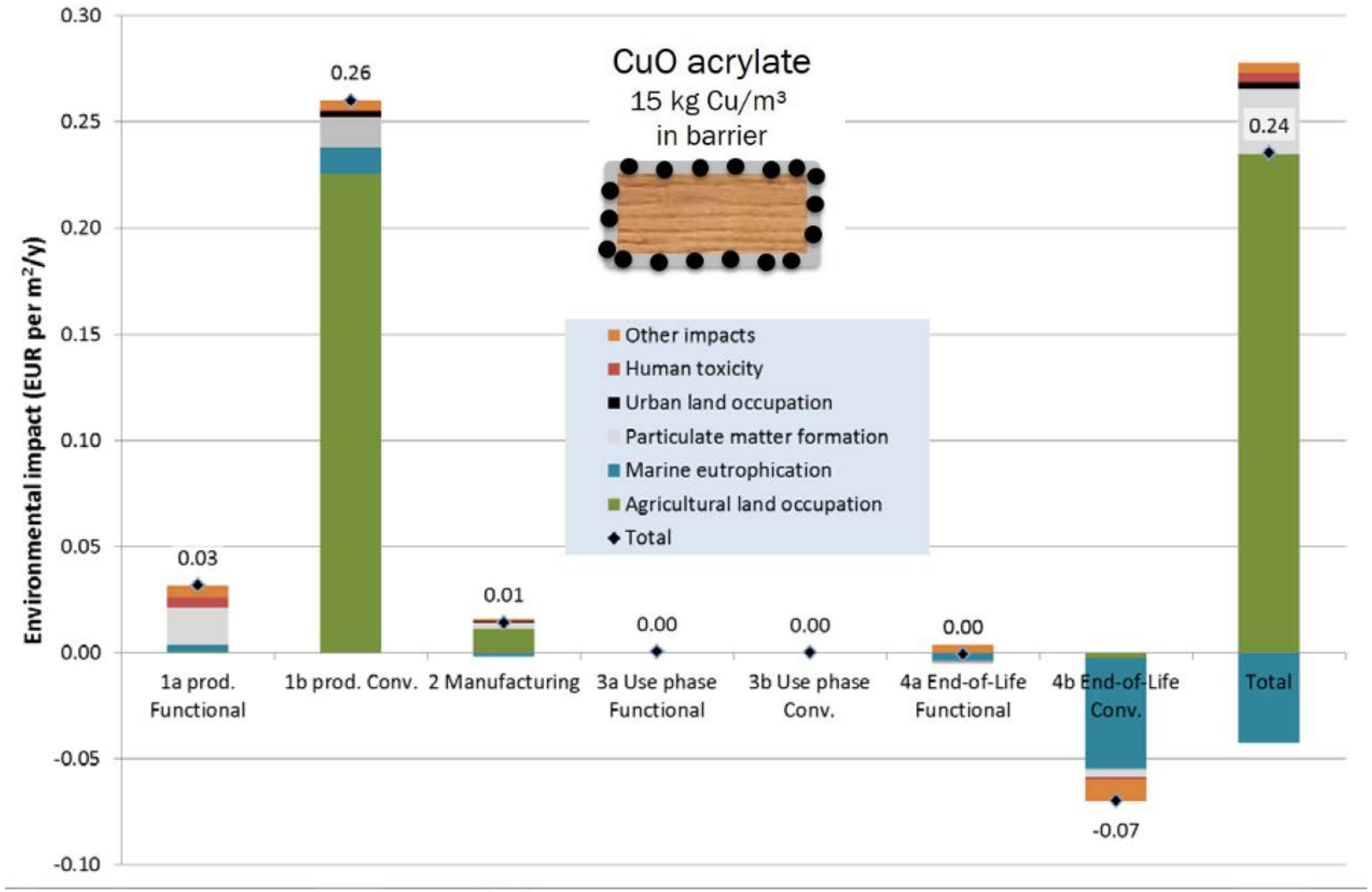


ICPMS of all wood sanding dusts

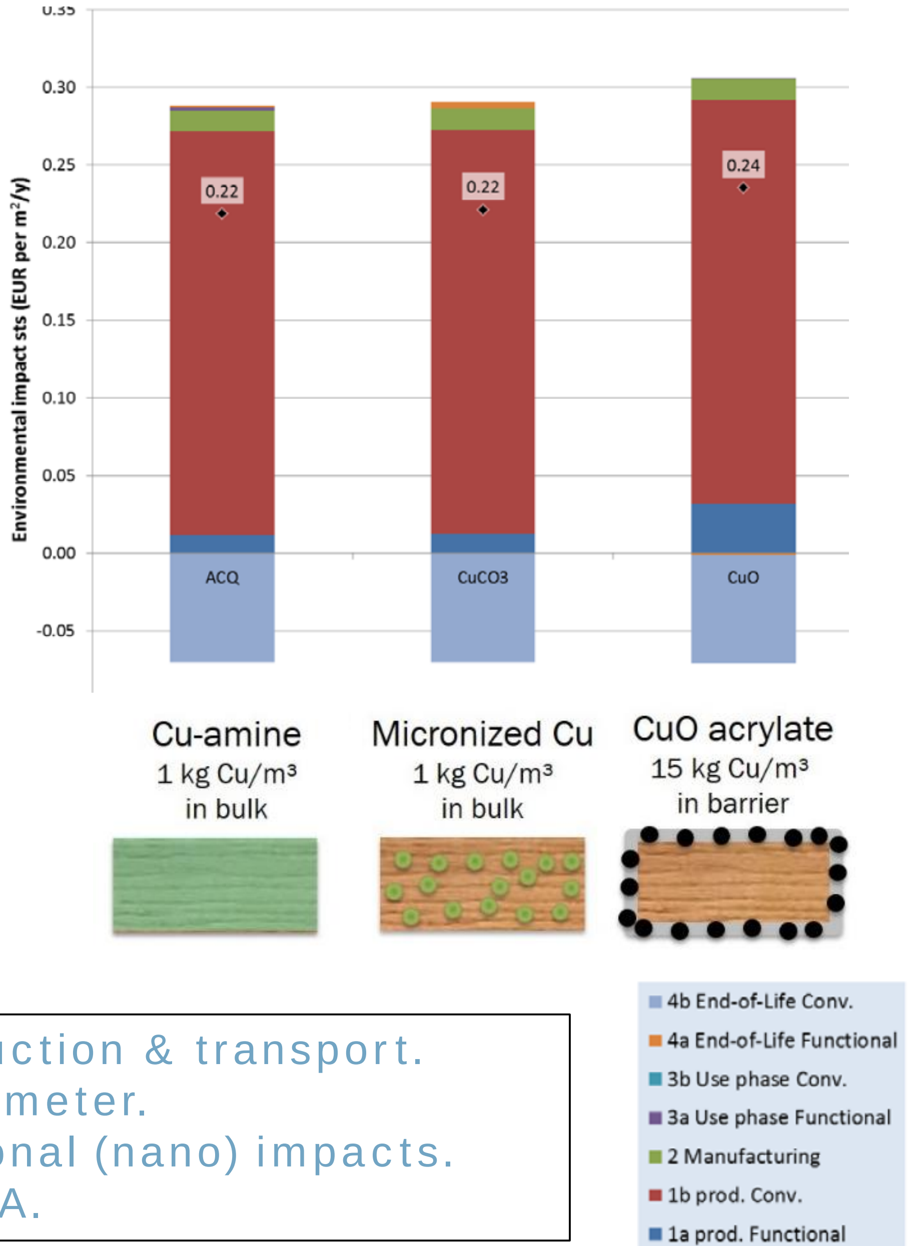
Sanded wood	Cu content of sanding dust (%)	Standard deviation by aging 0-1-2-3 months ISO4892
Cu amine 1kg/m³	0.27	0.02
Cu amine 2kg/m³	0.46	0.06
micronized Cu 1kg/m³	0.17	0.01
micronized Cu 2kg/m³	0.36	0.02
Acrylate	0.00	0.00
CuO acrylate 0.1kg/m³	0.33	0.10

LIFECYCLE ANALYSIS: CUO VS CU-CARBONATE VS ACQ

TNO innovation for life

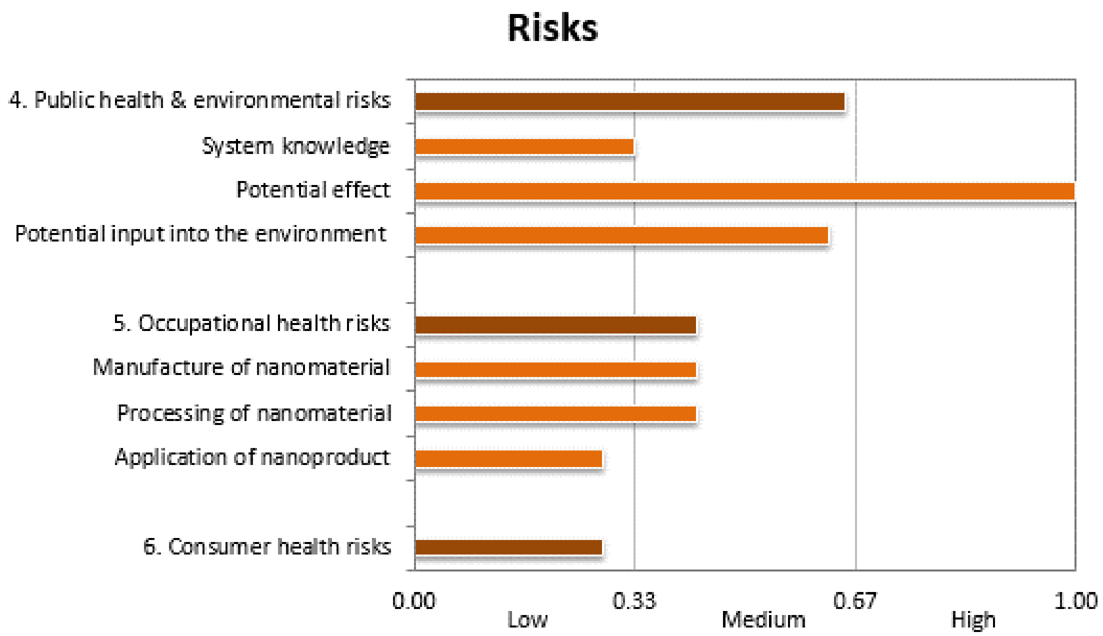


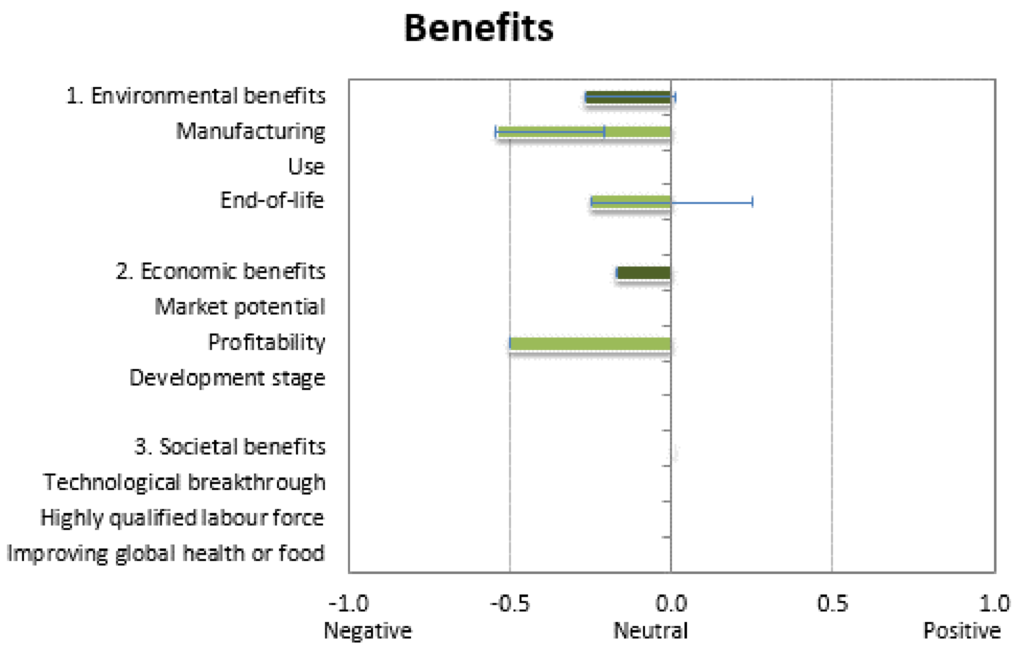
igure 24. Environmental impacts of 1 m².y⁻¹ CuO painted wooden cladding



…the use phase releases impacts are irrelevant compared to production & transport.
!! Assumed service life (=performance) is most sensitive input parameter.
…conventional (non-nano) impacts are a stronger lever than functional (nano) impacts.
…matching results for pigment LCA.

Integrating lifecycle analysis, hazard and exposure: LICARA nanoscan assessment of CuO-additive: <u>Production risk + Consumer performance in focus</u>



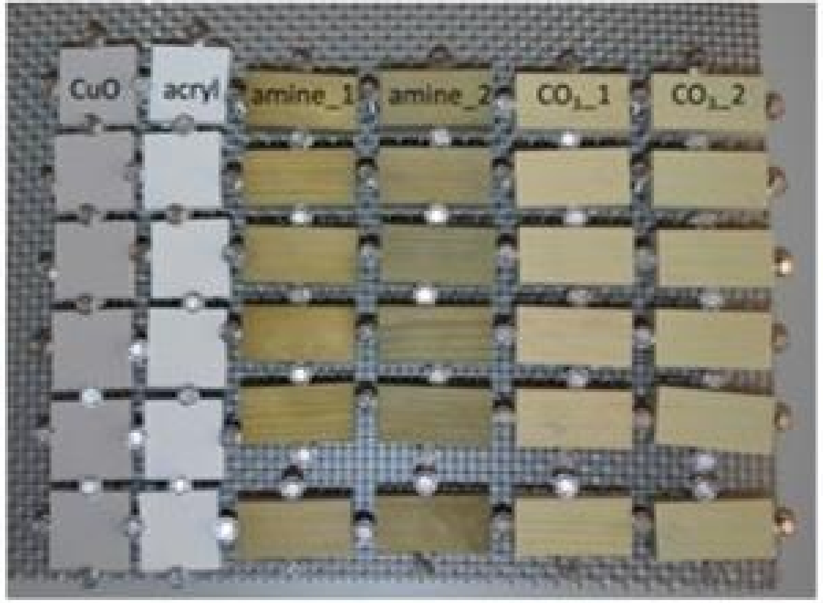


nanoSCAN compares technological alternatives by benefit or impact in:

- Environment
- Social, Occupational, Consumer
- Economical

CuO acrylic coating is less sustainable than the technological alternatives, and will not be developed into a commercial product.

Conclusions



- We compared: Solubilized Cu^{2+} in Cu-Amine vs. NP-$Cu_2(OH)_2CO_3$ as in bulk preservatives vs. NP-CuO embedded in surface barrier.
- Treatment with Cu-Amine and NP-$Cu_2(OH)_2CO_3$ showed sufficient efficacy against *Coniophora puteana*
- Surface coating with embedded NP-CuO was *not* effective.

- EN84-leaching of Cu-Amine and NP-$Cu_2(OH)_2CO_3$ was near-identical
  - both systems released Copper as ionic Cu^{2+}.
  - Matching results for combination of condensation / rain / shear

- Occupational and consumer exposure addressed by wipe & sanding tests, on fresh and aged woods. Hazards addressed by oral in vivo testing.
  - Similarity of (low) release rates from Cu-Amine and NP- $Cu_2(OH)_2CO_3$ woods.
  - Absence of pristine particles, but re-precipitation of Cu amine can occur.
  - NP- $Cu_2(OH)_2CO_3$ dissolves in stomach (hours) and environmental surface water (days) to ionic Cu^{2+}.

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