Release from copper-treated wood – a summary of results from the SUN project

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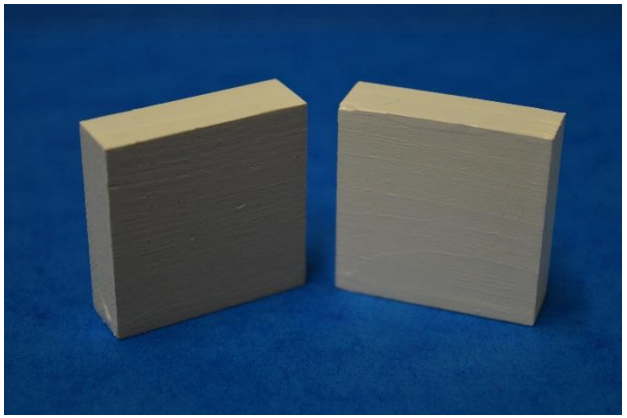
Materials

As copper (Cu) is a major fungicide used for wood protection, it was chosen as a case study in the ***EU project SUN*** (Sustainable Nanotechnologies) to investigate environmental and health risks during the lifecycle of Cu-containing wood preservatives.



3 types of Cu-treated wood:

- acrylic paint containing ***CuO nanoparticles***

  → *CuO_acryl, reference: acryl*

- water-based impregnations solution containing ***soluble Cu-amine***

  → *CuAmine*

- water-based impregnations solution containing basic ***copper carbonate*** ($CuCO_3$ x $Cu(OH)_2$) ***nanoparticles***

  → *CuCO3*

Release scenarios

I) ***Spontaneous release*** during weathering [EN 927-6]

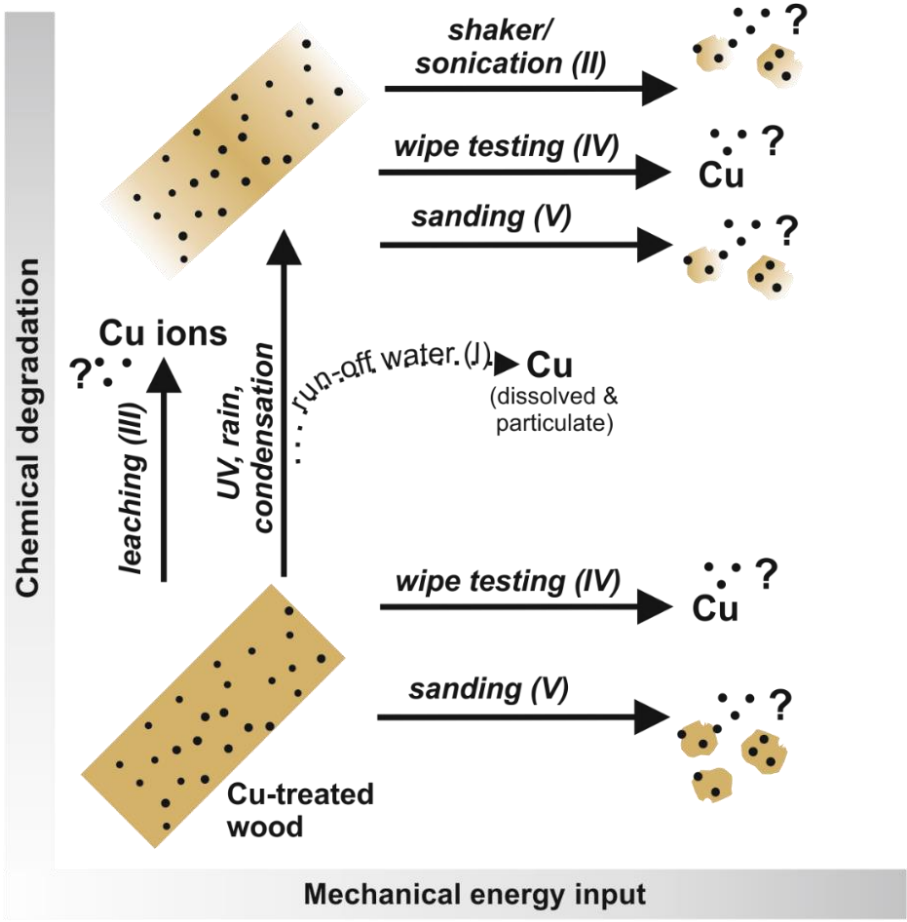
II) ***Release induced*** by immersion & mechanical stress [validated protocol from NanoRelease initiative (1)]

III) ***Leaching*** in water [EN 84]

IV) ***Wipe testing*** [NIOSH guideline 9102]

V) Release during ***sanding***

+ ***Effectiveness testing*** [EN 113, Pinus sylvestris L., 16 weeks]



(1) W. Wohlleben, C. Kingston, J. Carter, E. Sahle-Demessie, S. Vázquez-Campos, B. Acrey, C.-Y. Chen, E. Walton, H. Egenolf, P. Müller and R. Zepp, NanoRelease: Pilot interlaboratory comparison of a weathering protocol applied to resilient and labile polymers with and without embedded CNTs (to be submitted to Carbon)

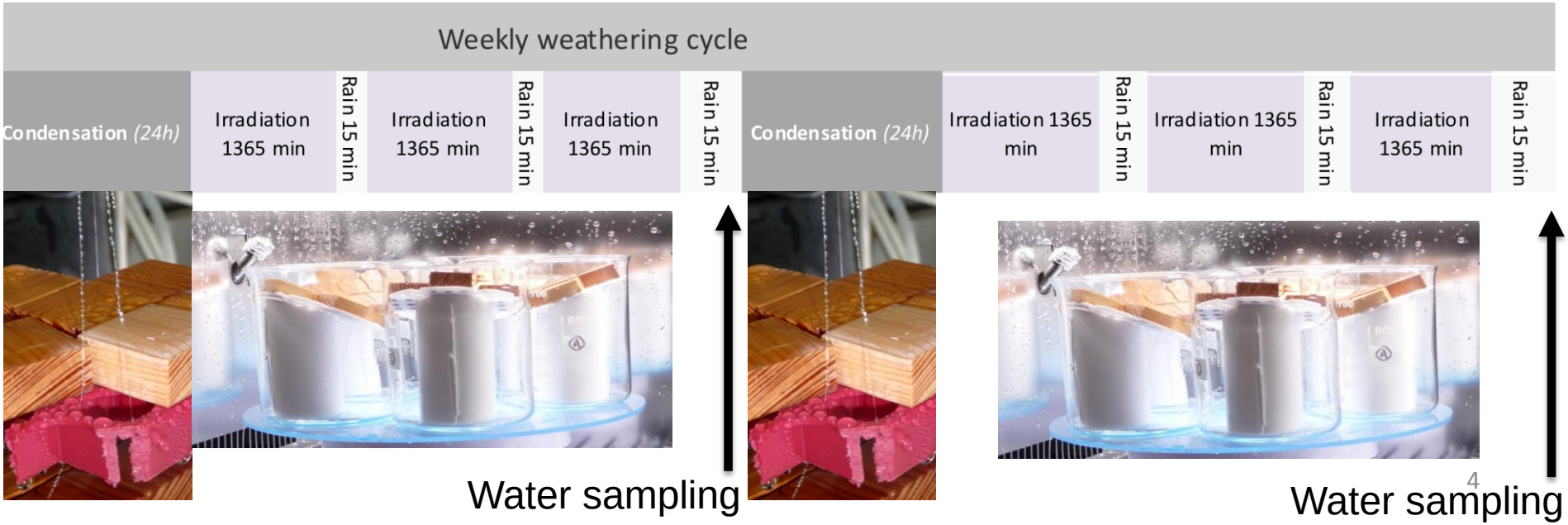
Scenario 1: Spontaneous release during weathering (CEREGE)

- ***Weathering*** adapted from EN 927-6 (12 weeks)
- ***Release sampling method:***

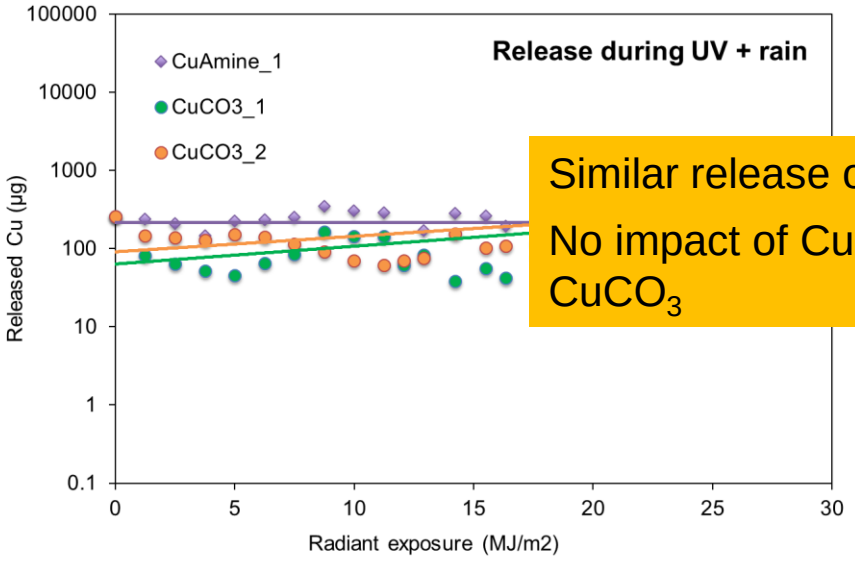
  run-off water sampling
- ***Detection & characterization:***

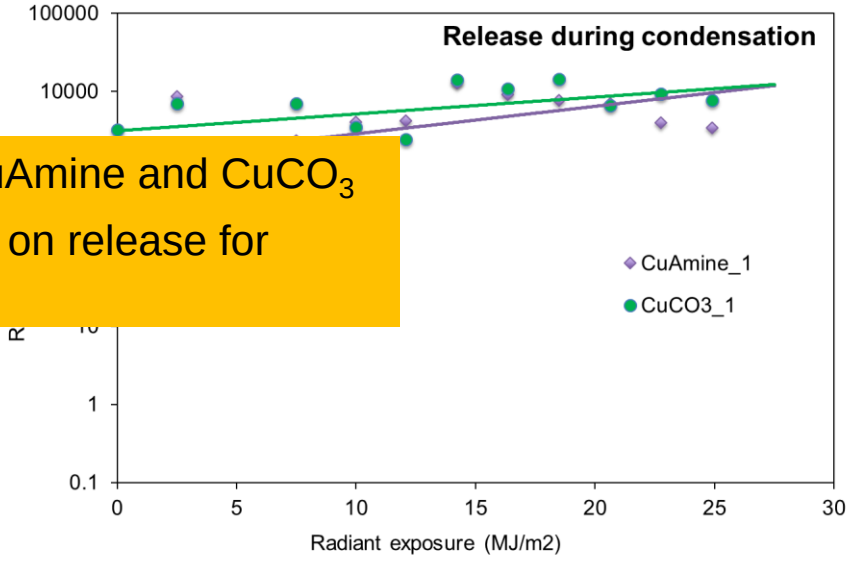
  ICP-MS of run-off waters (dissolved and particulate Cu)

source: atlas-mts.de



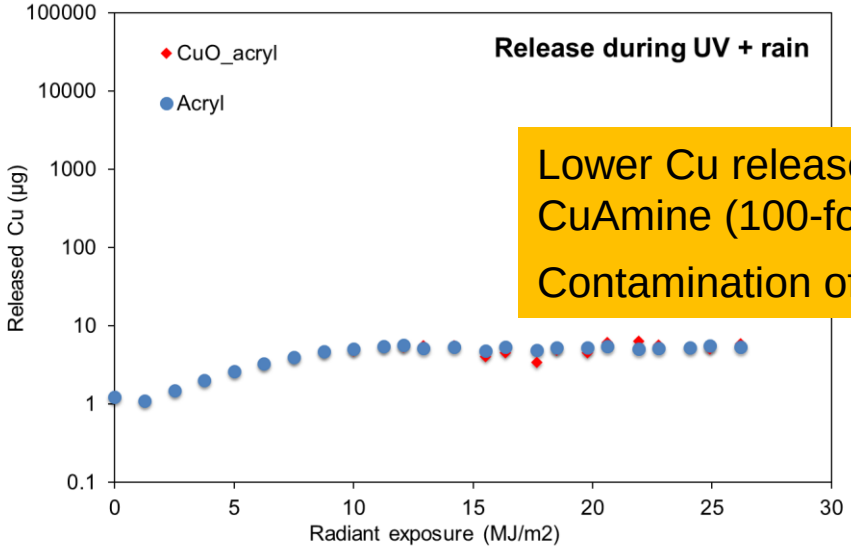
Scenario 1: Spontaneous release during weathering (CEREGE)

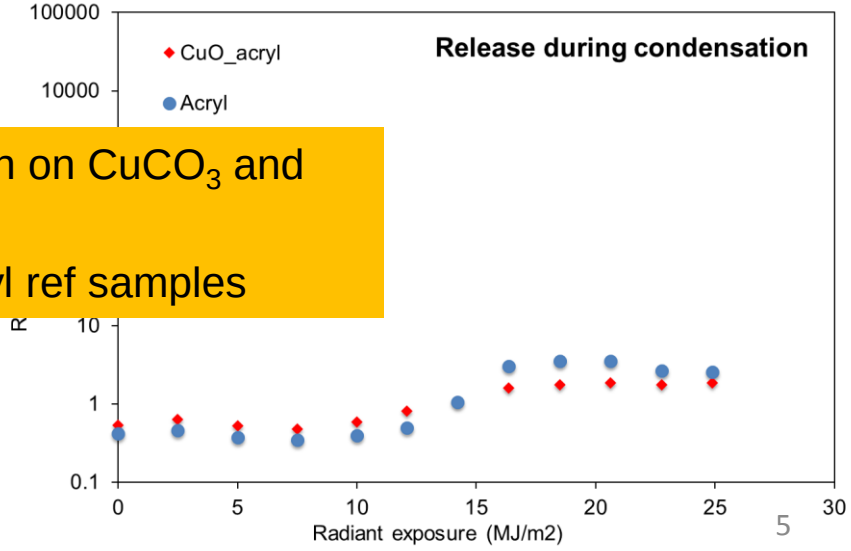




Similar release on CuAmine and $CuCO_3$

No impact of Cu load on release for $CuCO_3$





Lower Cu release than on $CuCO_3$ and CuAmine (100-fold)

Contamination of Acryl ref samples

Scenario 2: Release induced by immersion & mechanical stress (BASF)

- ***Weathering*** according to EN 927-6 (12 weeks) with mimicked condensation step in climate chamber (24h, 0 W/m^2, dry/wet 116/4 min)
- ***Release sampling method:*** (Wohlleben et al., 2014)

  Immersion of aged surface in H_2O (+ 0.5 g/l SDS)

  1) Shaker (24)

  2) Sonication (1h)

  NanoRelease

- **Detection & characterization of released fragments:**

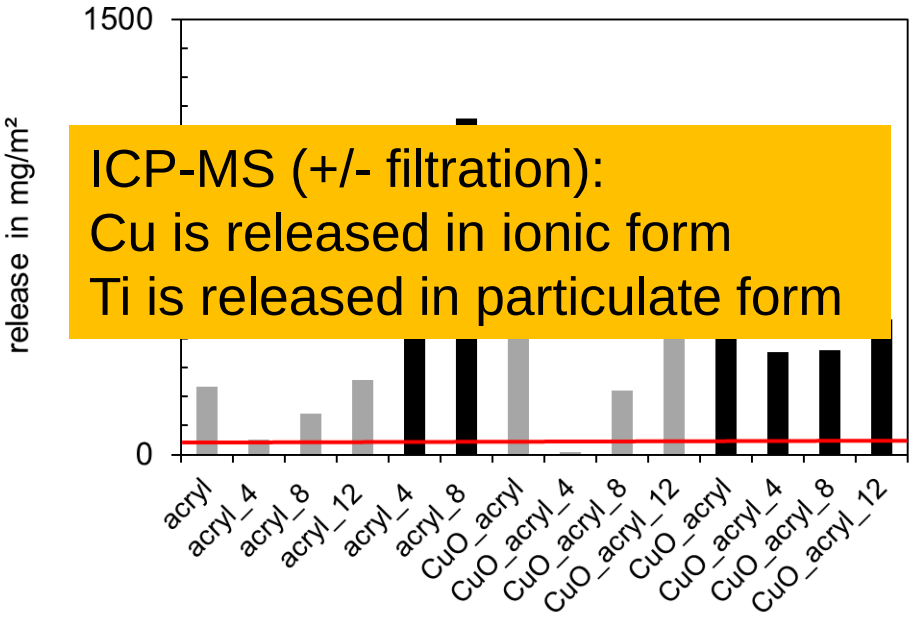
  analytical ultracentrifuge (AUC)

  ICP-MS

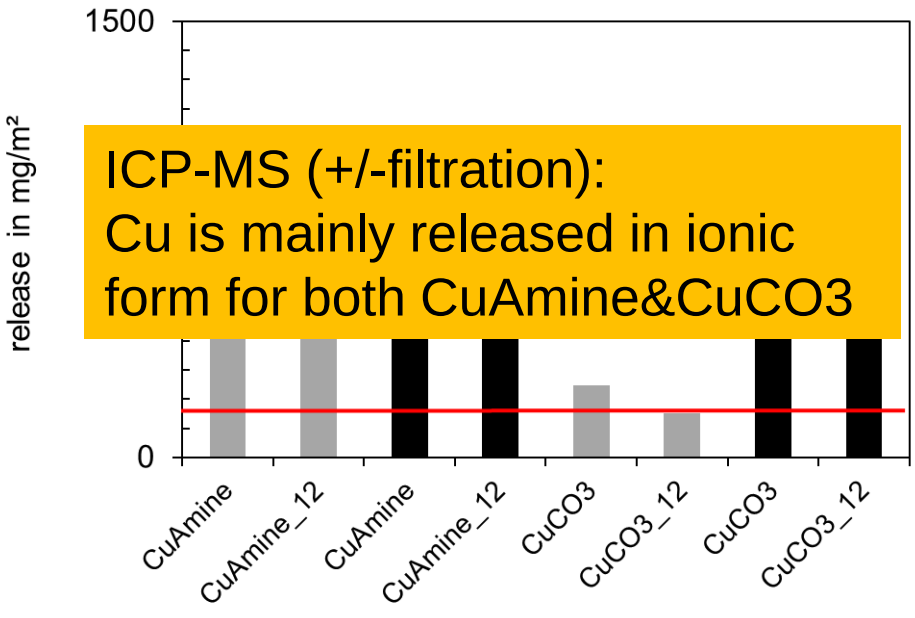
Scenario 2: Release induced by immersion & mechanical stress (BASF)

shaker
sonication

Quantification of release by AUC



ICP-MS (+/- filtration):
Cu is released in ionic form
Ti is released in particulate form



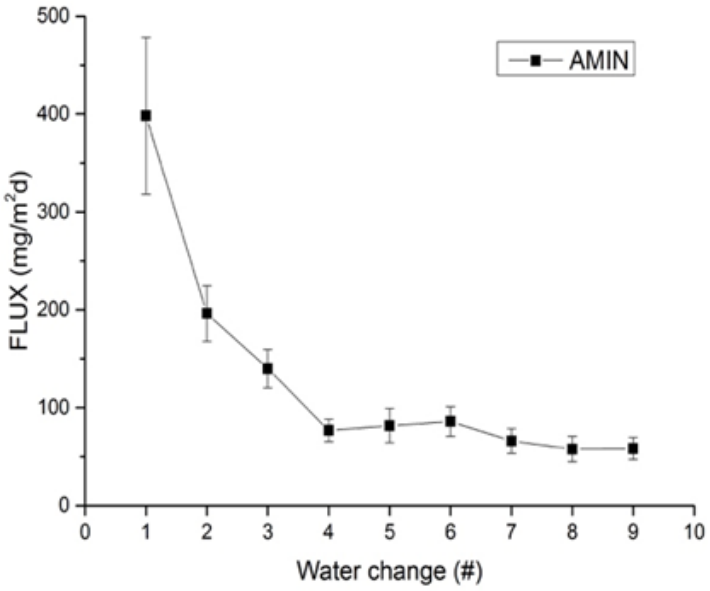
ICP-MS (+/-filtration):
Cu is mainly released in ionic form for both CuAmine&CuCO3

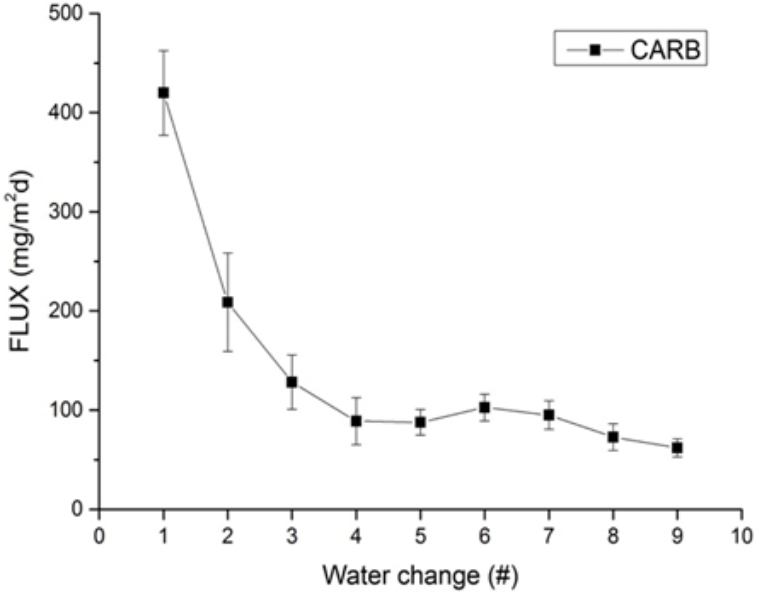
- Acryl: sonication > shaker
- CuO_acryl: sonication ~ shaker
- Release increases with aging

- sonication > shaker
- CuCO3 < CuAmine
- CuAmine: as-produced = aged
- CuCO3: aged < as-produced

Scenario 3: Leaching according to EN 84 (UVIENNA)

ICP-MS:



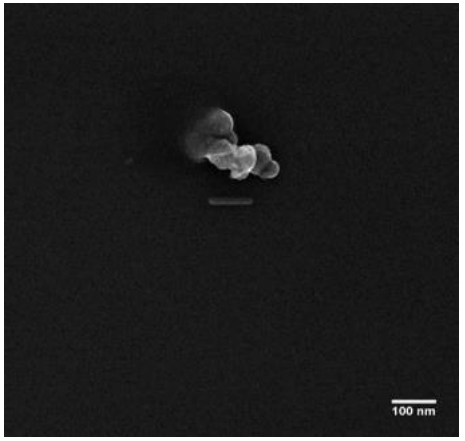


daily flux of ***116 mg Cu/m²d*** for CuAmine_1 (***4.2%*** of initial Cu within 14d)
and ***127 mg Cu/m²d*** for $CuCO_3$_1 (***4.0%*** of initial Cu within 14d)

- daily flux of CuO_acryl & reference acryl is significantly lower (100 fold)
- higher flux for weathered sample (2.4% of initial Cu, 21% after aging), also for reference → contamination during weathering

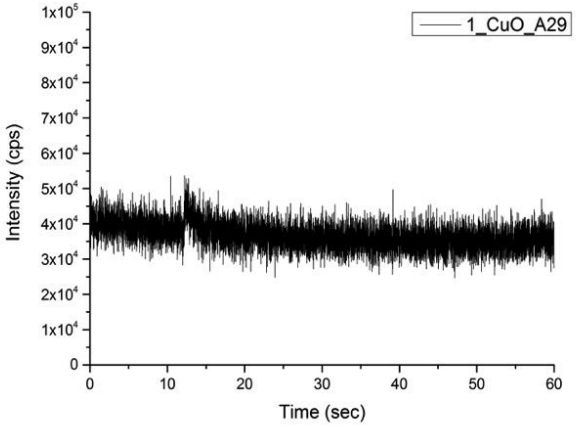
Scenario 3: Leaching according to EN 84 (UVIENNA)

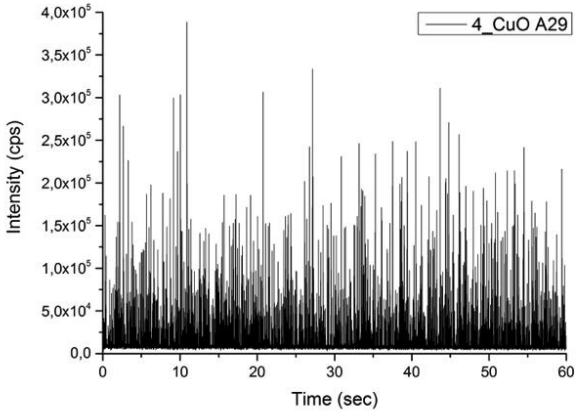
single particle ICP-MS:



CuO_acryl

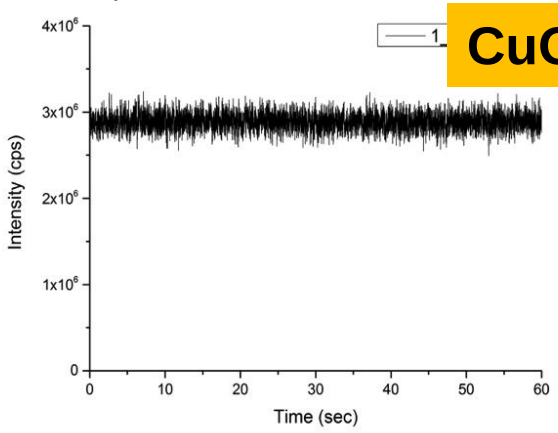
a) Non weathered

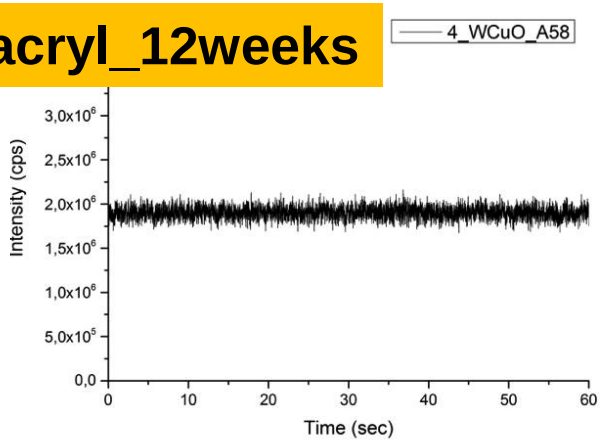




b) Weathered

CuO_acryl_12weeks

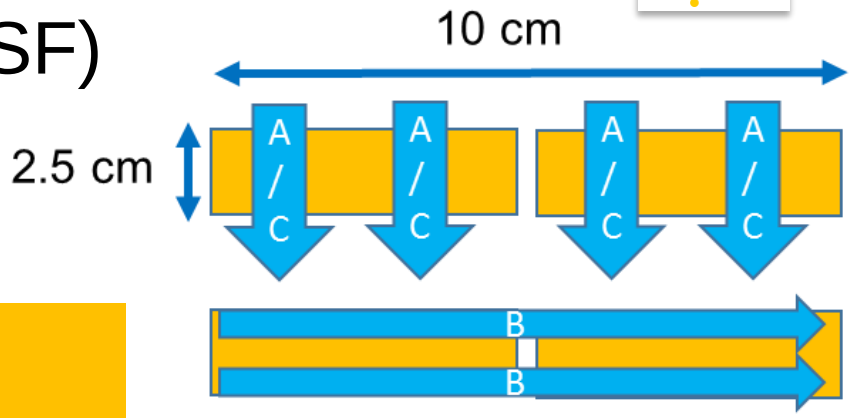




- No particulate release for CuCO3_1
- Particulate release for CuO_acryl
- Released particle number dependant on sampling time point
- Cu release from aged samples solely in ionic form

Scenario 4: Wipe testing (BASF)

according to NIOSH guideline 9102



SEM-EDX: no evidence for Cu particles
ICP-MS:

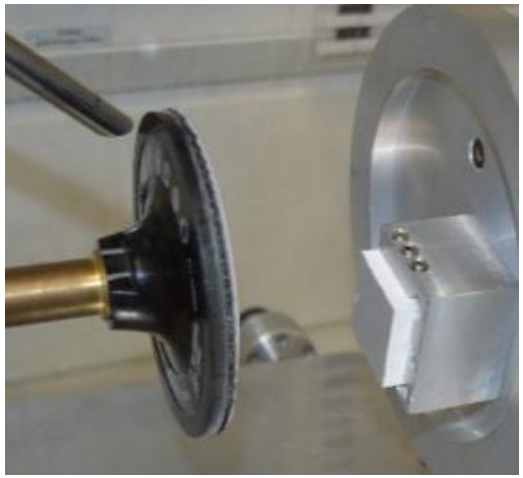
formulation	weathering	Cu content [mg Cu/l]	Cu content [mg Cu/m$^{2]}$
CuAmine_1	no	0.06	0.8
CuAmine_1	8 weeks	-	3.5
CuAmine_2	no	0.18	2.4
CuCO3_1	no	0.16	2.1
CuCO3_1	8 weeks	-	2.7
CuCO3_2	no	0.15	2.0

Cu release higher at higher Cu conc.

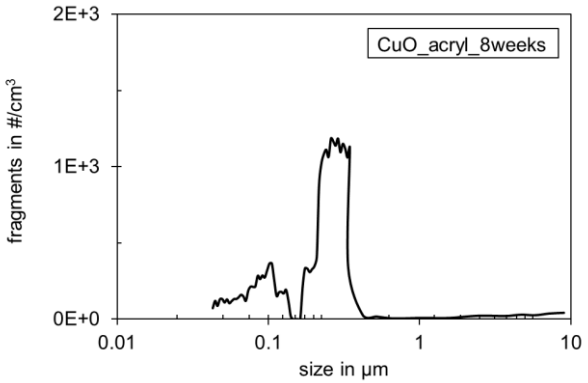
Constant Cu release

Higher Cu release after aging, more pronounced for soluble Cu

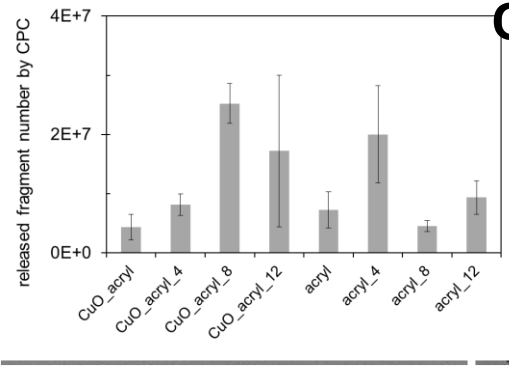
Scenario 5: Release during sanding (BASF)

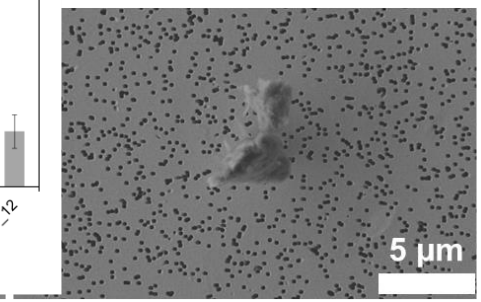


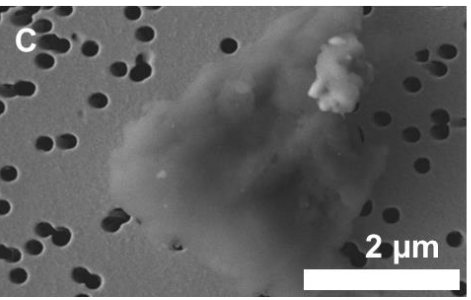
- Release dominated by wood
- ICPMS of aerosol & sampled dust: high Cu from CuO_acrylic despite low total mass

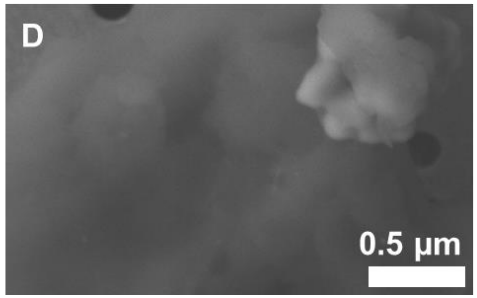


CuO_acryl_wood

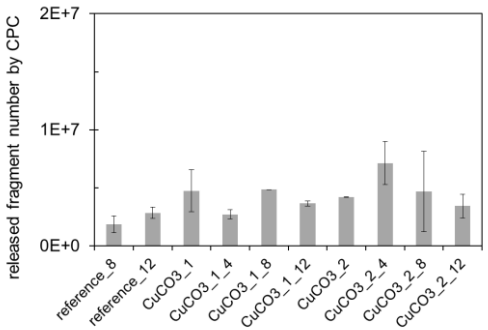


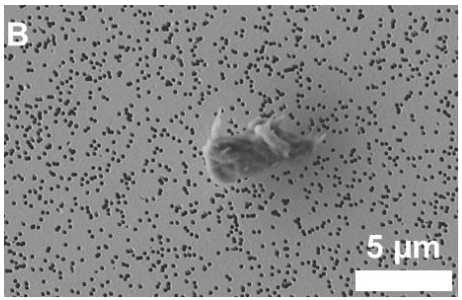


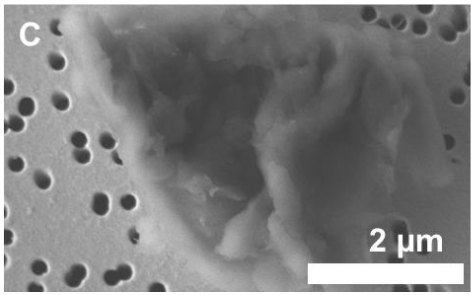


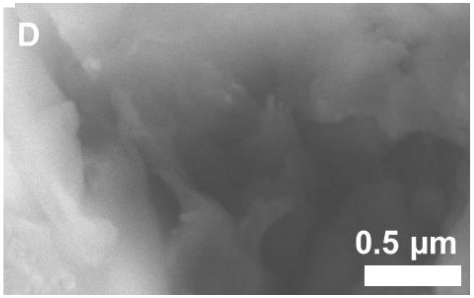


CuCO3_1_wood









Summary

- Particulate release seems to be **dominated by wood** *(immersion, sanding)*

- Cu release evidenced in all case but mainly in ***ionic form***, (except for as-produced CuO_acryl)

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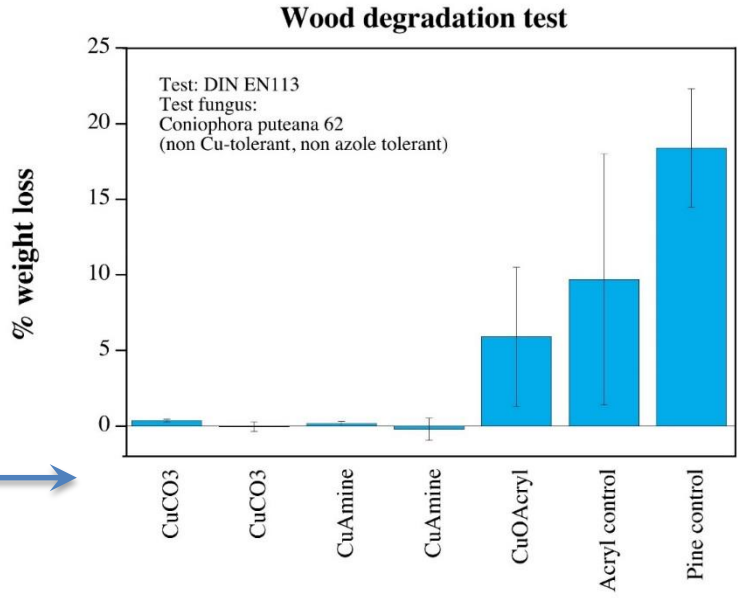
- Cu release from acrylic paint is significantly lower compared to impregnated wood.

- Ionic release correlates strongly with ***effectiveness***



Thank you for your attention!

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