Heavy metal exposure risks from filaments used in 3D printing

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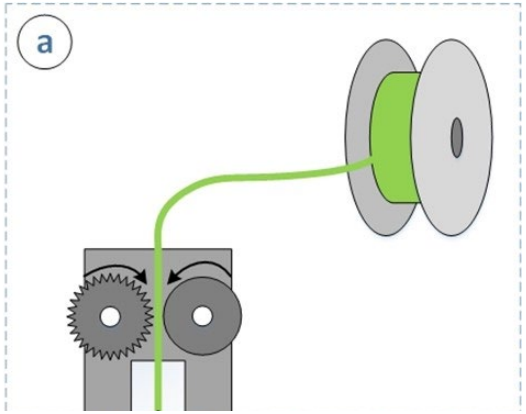
What is fused filament fabrication (FFF)?

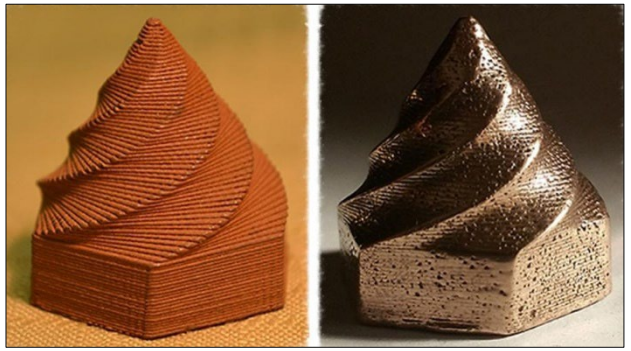


- A material extrusion process
  - Thermoplastic material pushed through heated nozzle to create objects layer by layer
- Most popular type of additive manufacturing (AM)
- Ideal for small-scale production and household use

PC: https://euroceram.org

Metal AM on the rise

Metal additives can be incorporated into thermoplastic “feedstock” anywhere from 10-80% by weight and printed on desktop computers



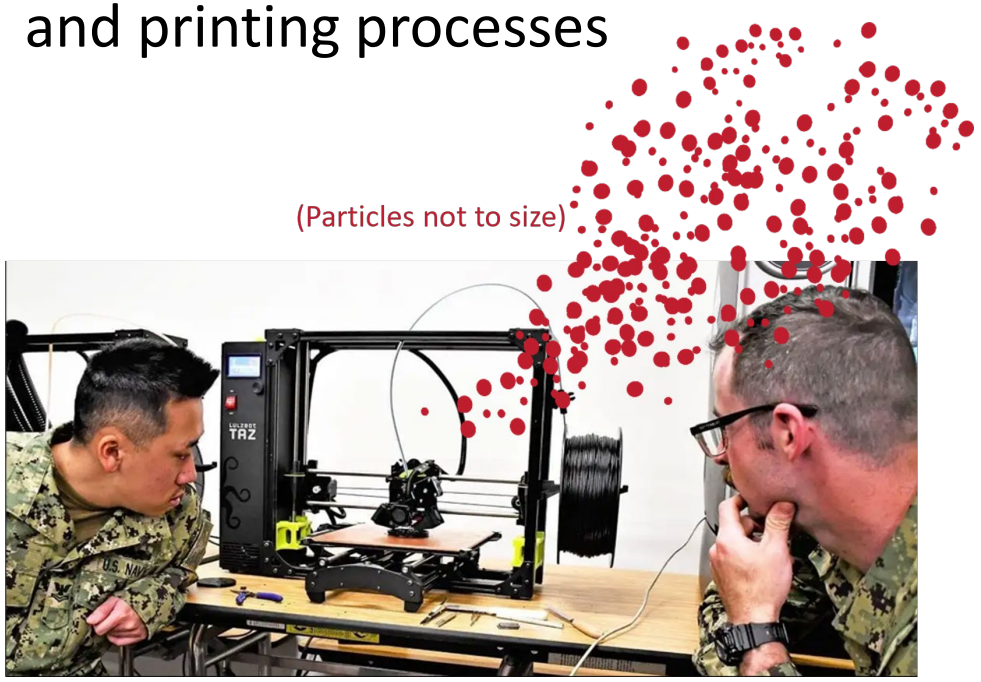
Pre- and post-sintering

Pre- and post-polishing

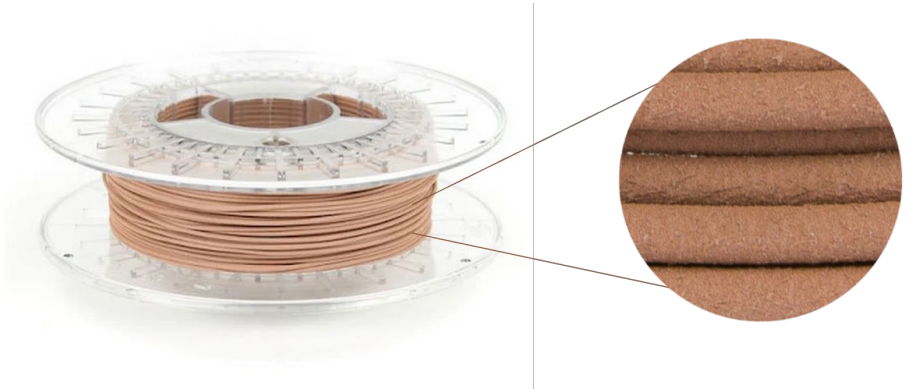
PC: Defense Media Network, 3Dprint.com, colorfabb.com

Metal AM on the rise (cont.)

Need to assess the potential health effects from thermoplastic materials and printing processes



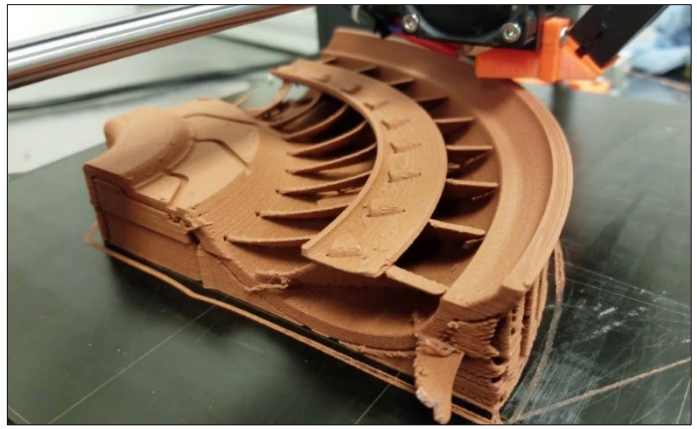
- Focus on the ultrafine particles (UFP, <100 nm) and hazardous VOCs emitted during printing processes
- Dermal contact and oral ingestion understudied exposure pathways



PC: Defense Media Network, colorfabb.com

How might dermal contact and subsequent ingestion be important exposure pathways?

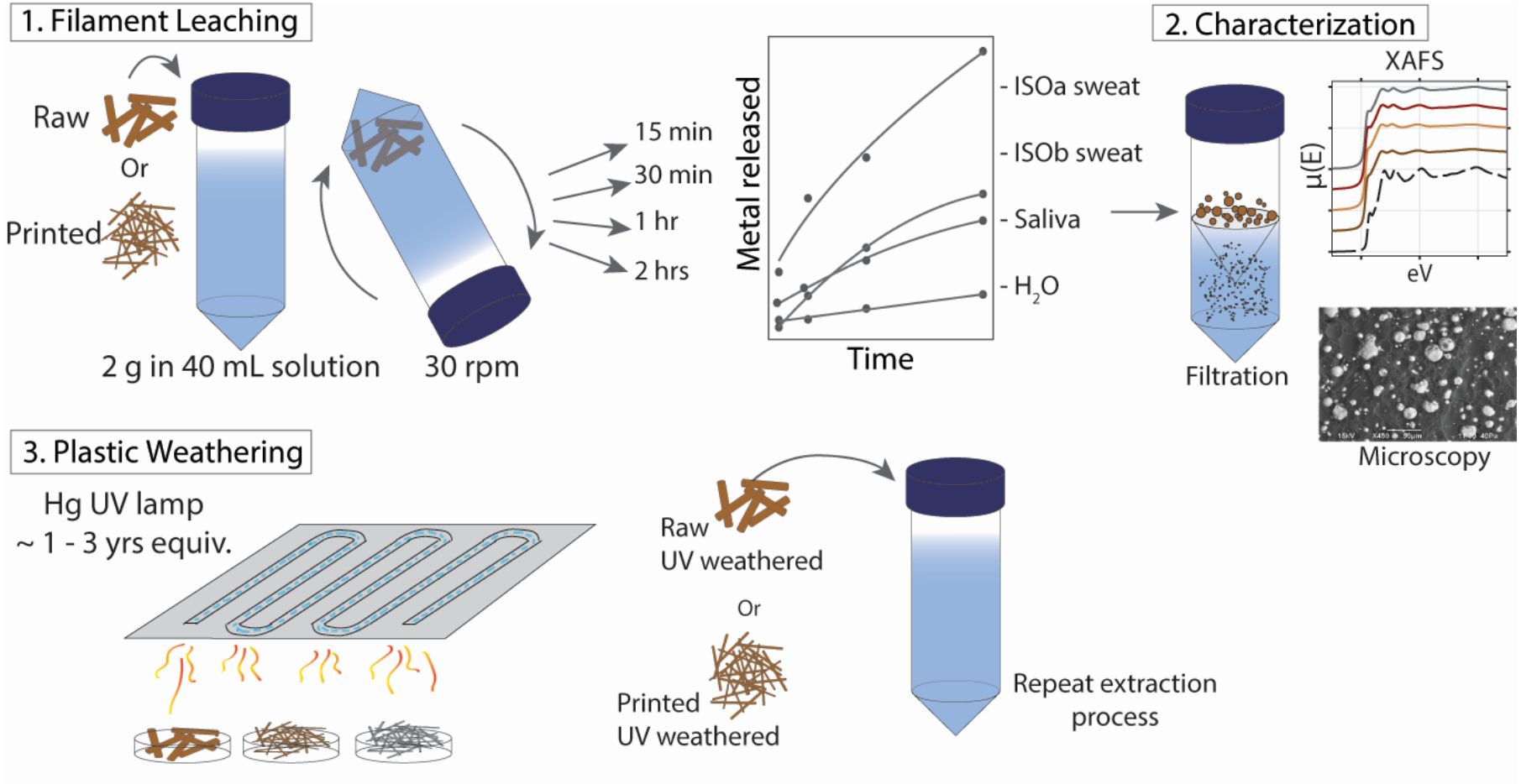
colorFabb (CF) filaments
(Copperfill pictured, unpolished vs. polished)



Virtual Foundry (VF) filaments
(Copperfill pictured, pre-sintered)

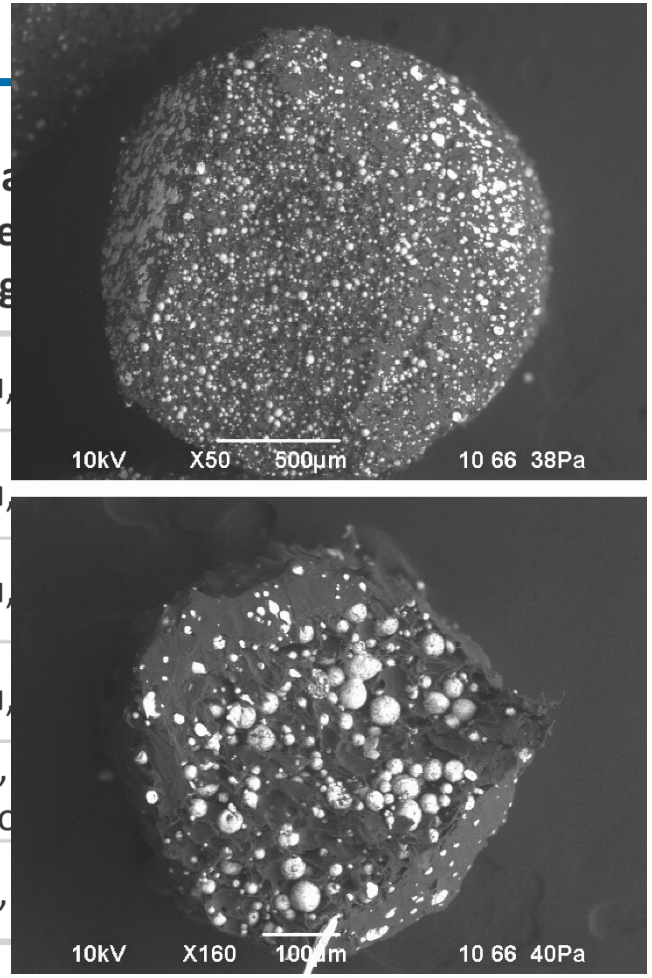
PC: colorfabb.com,
Virtual Foundry, Inc.

Study overview



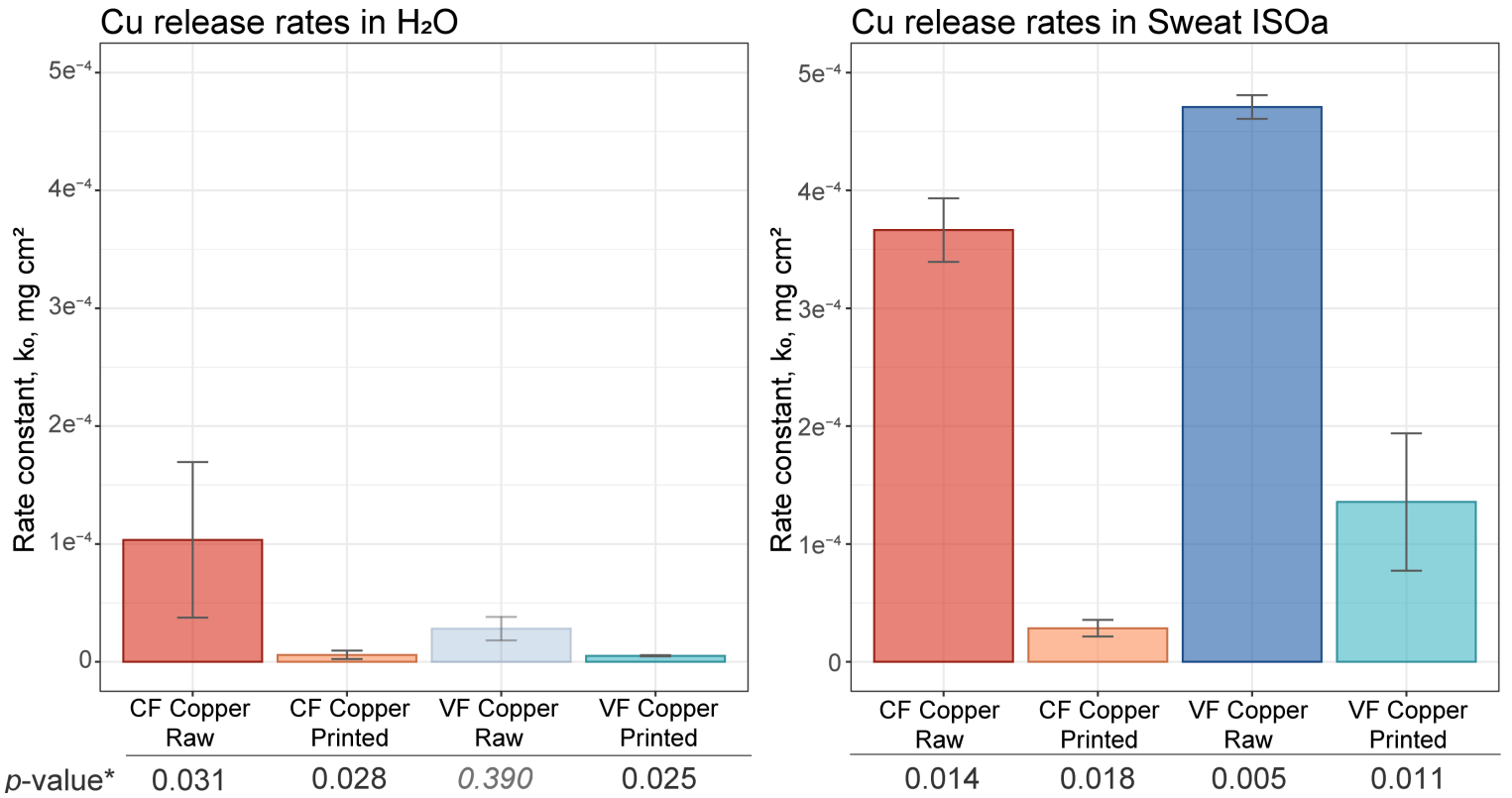
1. Metal infill is micro-sized metallic spheres dispersed as powder through the polymer matrix

Filament	Metallic particle diameters: Mean, µm	Median, µm	CV, %	Density dist.	Total metal, %	Ma ele mg
CF Copper	9.4	7.8	61		77 ± 3	Cu,
VF Copper	12.4*	7.7	101		83 ± 3	Cu,
CF Bronze	19.8*	16.5	62		77 ± 3	Cu,
VF Bronze	12.3	9.3	76		87 ± 6	Cu,
CF Steel	7.8	5.0	91		79 ± 3*	Cr, Mo
VF Steel	24.0*	23.1	39		65 ± 5	Cr,



Cross-diagram SEM images of CF Copper filament raw (top) and printed (bottom).

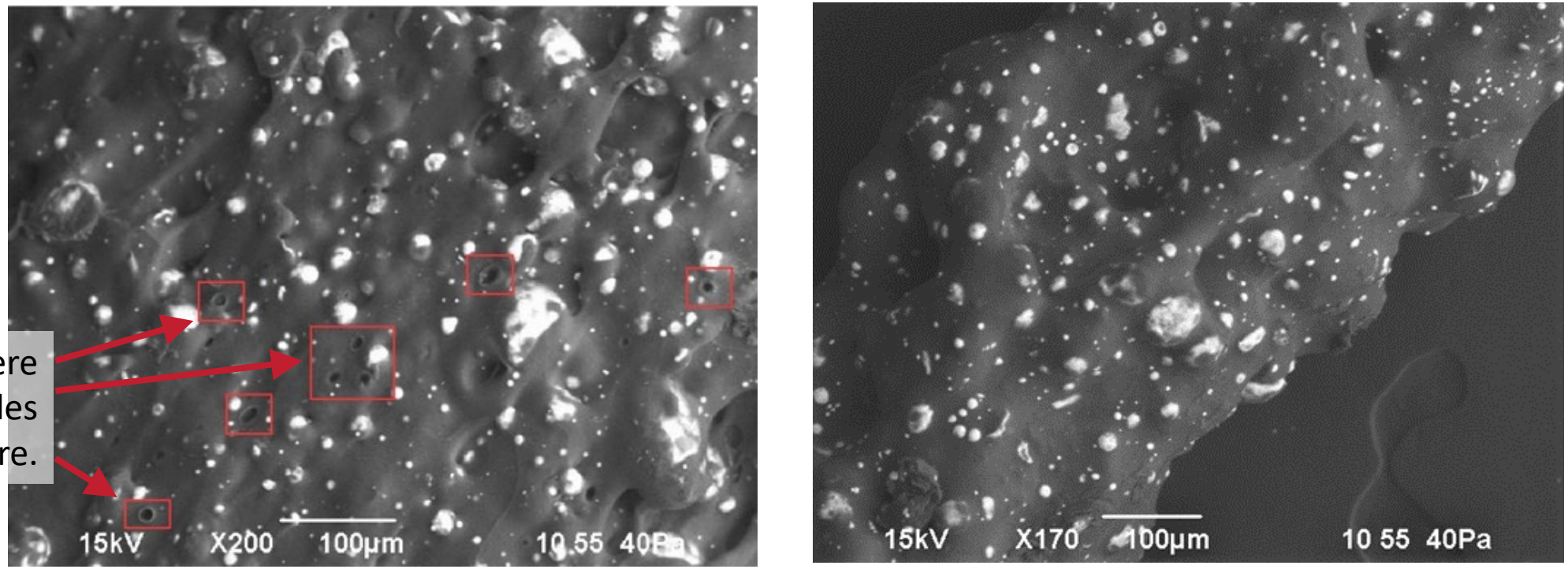
2. Filaments released more metal additives in raw form than printed forms



Synthetic solutions also have greater impact on certain metals, such as Cu

2. Why might raw filaments release more metal particles?

Holes where metal particles likely were.

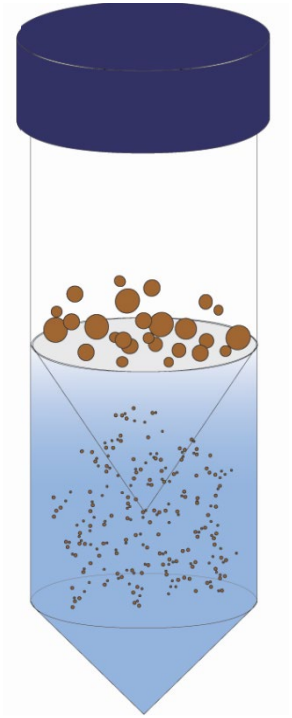


SEM images of VF copper filament (left) raw and (right) printed.

A “leachable” metal layer at the plastic surface may be causing a pulse of initial metal release.

(Filella 2020, Turner and Filella 2021)

3. Metal additives primarily released as particles > 0.45 µm

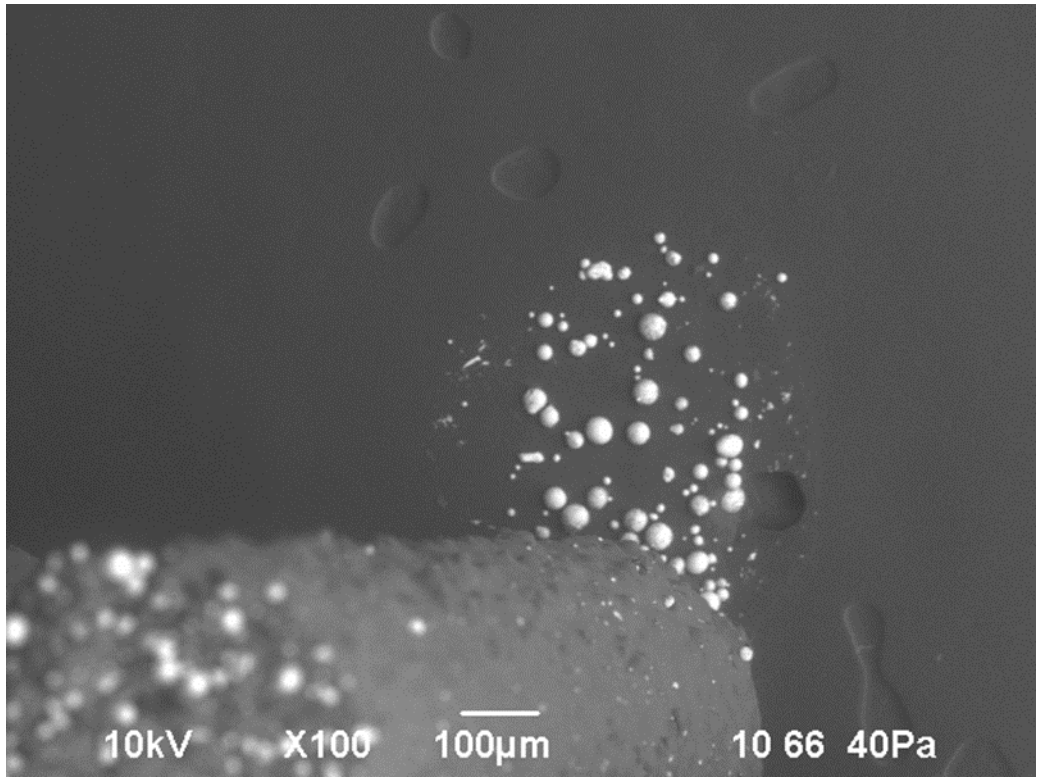


Sn (Bronze)

Cr (Steel)

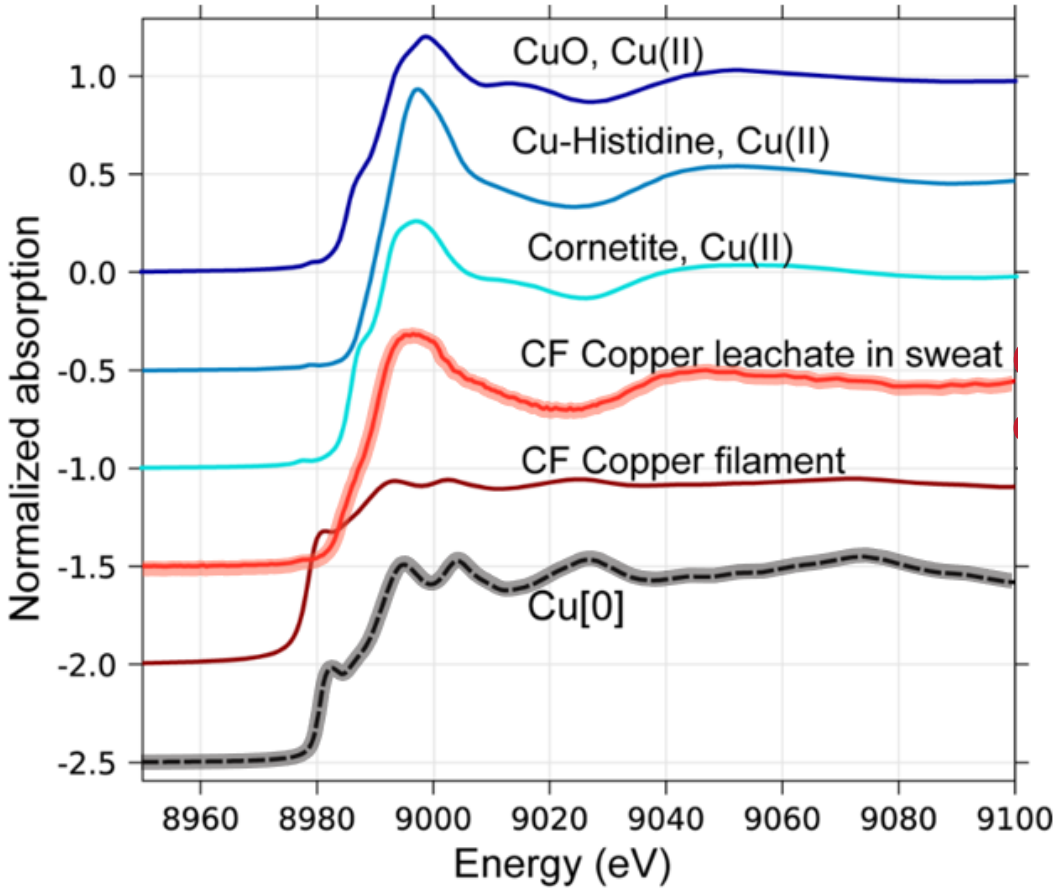
Cu (Copper, Bronze)

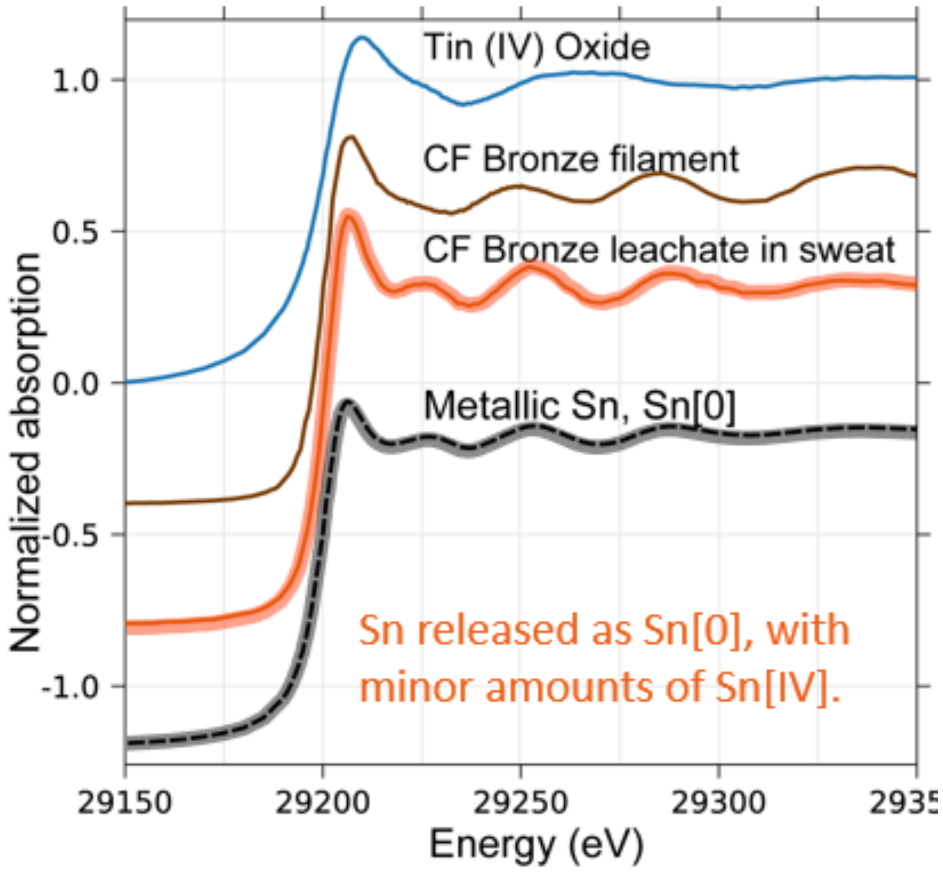
Higher Cu solubility allows greater absorption and possible ingestion.



SEM image of CF bronze filament showing metallic particles that stuck to the carbon adhesive tab.

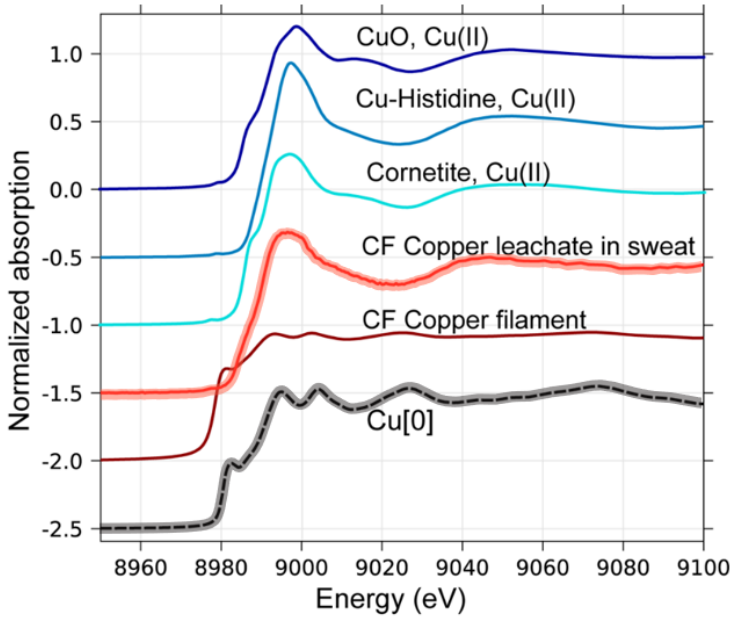
3. XANES data shows oxidation of metallic particles.





Preliminary conclusions:

- Metal filaments release microparticles pre- and post-printing.
- Particles within size range capable of dermal adherence (< 150 µm).
- Raw filaments release more particles than printed, and synthetic solutions such as sweat have greater impact on certain elements.
- Fraction of the metal particles appear to be oxidized. Change in oxidation state may impact solubility and subsequent bioavailability.

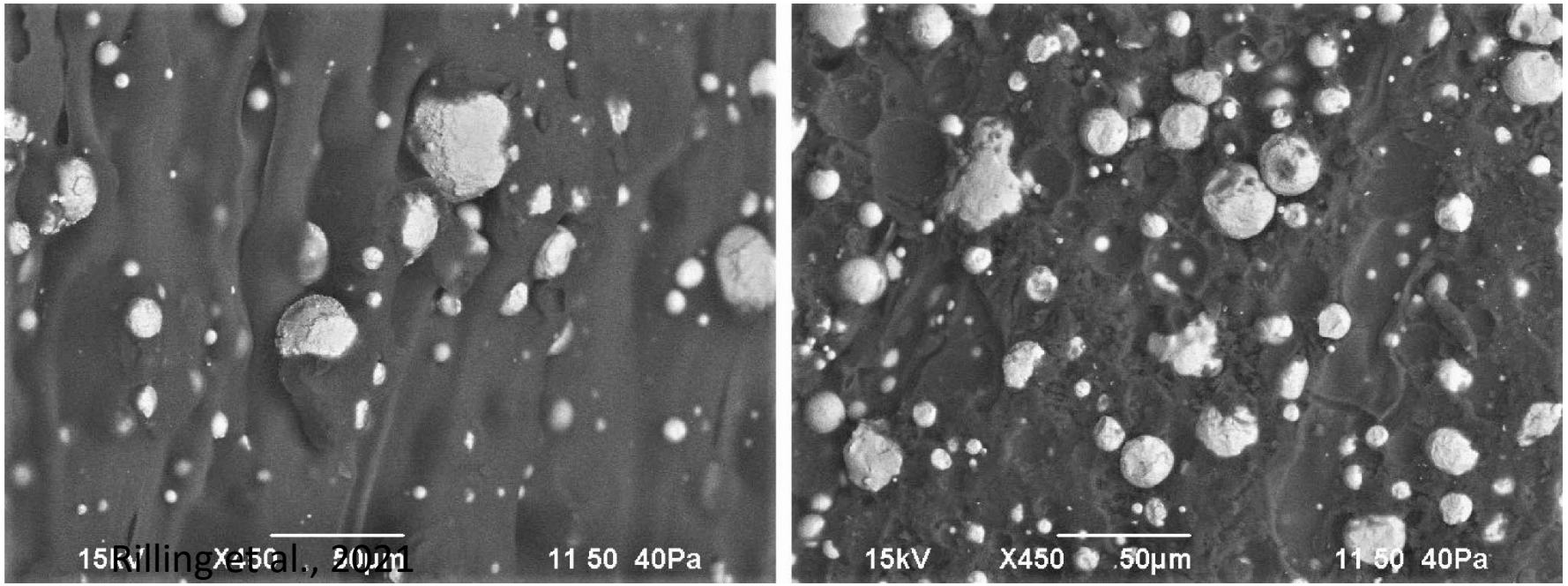


Next steps:

- Incorporate toxicology data and exposure limits and guidelines
- Apply findings to realistic exposure scenarios

Final note: The long-term view

UV weathering of the thermoplastic increased porosity and surface area of the polymer, accelerating loss of metal particles



Rilling et al., 2021

SEM images of CF Copper filament (left) unweathered and (right) weathered.

Thank you!

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References:

Filella, M. (2020). "Antimony and PET bottles: Checking facts." Chemosphere 261: 127732.

Rillig, M. C., et al. (2021). "The Global Plastic Toxicity Debt." Environmental science & technology 55(5): 2717-2719.

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