Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.29076

Unravelling hydrophobic interactions allowing Cu-based nanoparticles to cross tomato leaf cuticle

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Understanding the interactions between plant leaves and (nano)particles (NPs) is crucial to address phytochemical and environmental challenges. Recent studies are revealing how NPs adhesion, uptake, and transformation on leaf surfaces are influenced by environmental factors, plant surface, and NPs properties. Cu-based fungicidal and nutrient foliar applications are widely used but often face wash-off issues. Cu-based NPs can reduce this loss by enhancing surface affinity and help tuning absorption. The hydrophobic plant cuticle, covering aerial plant parts, presents great potential for NP adhesion and uptake. Yet, the role of hydrophobic interactions between leaf' cuticle and NPs, as NPs' ability to cross cuticle is not clearly established.

The role of hydrophobic interactions in NPs adhesion, leaf absorbtion and translocation in plant part has been studied. Leaf surface properties was varied trough mutant approach (Wild-type, *Cyp86a69*, *Shine2*, *Cus1*). The leaf was characterized for their cuticle and cell-wall thickness (TEM), surface-hydrophobicity (contact-angle) and epicuticular wax and cutin composition and amount (GC-MS/FID). Hydrophilic CuO NPs were compared to hydrophobic CuO coated with MUA (11-mercaptoundecanoic acid) after 21 days of exposure. NPs translocation was followed by Cu content in rinsing solvent, wax, and plant parts by ICPMS. Cu distribution on and in leaves as well as Cu chemical speciation was evaluated by synchrotron source (ID21, ESRF) X-Ray fluorescence (µXRF) and absorption (µXANES).

The results allow to determine the fate of CuO and hydrophobic CuO-MUA on/in the leaf after exposure. For all plants and NPs, half of Cu is washed off by rinsing, yet a 10% fraction of hydrophobic NPs are associated to wax. X-Rays fluorescence mapping shows Cu association to the cuticle, and accumulation in the anticlinal cell-wall of the epidermis (fig.2). Overall, results suggest that after leaf uptake, used CuO NPs are rapidly translocated to other plants parts. The higher hydrophobicity of the NPs modifies the interaction with the plant thanks to the affinity for wax lipids, which could be useful to increase the protection of crops against fungi. These results offer new insights into the role of hydrophobic interactions between plant surfaces and NPs in the development of more efficient and sustainable phytochemicals.

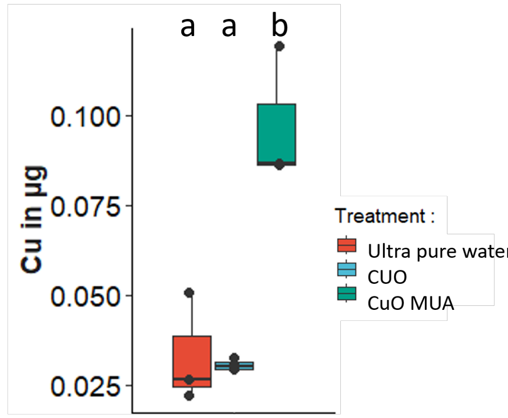

Fig. 1 : Cu in wax of leaves of tomato wild-type extracted with chloroform. Different letters indicate significant differences under post-hoc pairwise t-test (p-value < 0,01).

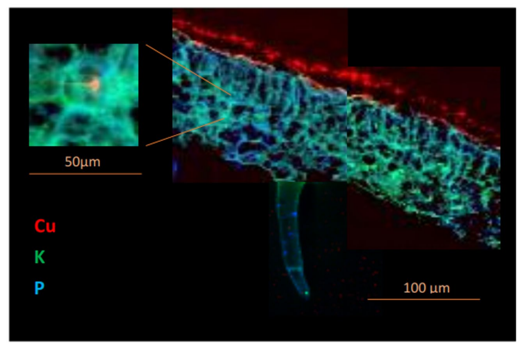

Fig. 2 : Cu in the vasculature and leaf surface. Leaf cuts µXRF mapping. Tomato Cus exposed to CuO bare NPs.