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Advanced X-ray spectroscopy and mass spectrometry techniques for characterizing mesoporous silica-based nanomaterials at the plant-soil continuum

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Engineered nanomaterials applied as foliar sprays are increasingly investigated to improve micronutrient-use efficiency and reduce off-target losses, yet the in planta fate of silica-based carriers remains difficult to resolve because (i) silicon is ubiquitous in plants and soils and (ii) nanoparticles can transform during transport. Here we advance a correlative characterization framework for mesoporous silica-based nanomaterials at the plant–soil continuum using a ~70 nm core-shell ZnO encapsulated in a silica nanocarrier (ZnO@MSN) applied to tomato leaves.

Synchrotron-based nanoholotomography demonstrates that MSNs traverse the leaf epidermis and reach vascular tissues via an apoplastic route. Mass spectrometry imaging and synchrotron (micro)-X-ray fluorescence provide cross-validation of long-distance redistribution from the treated leaf to distal organs, consistent with phloem-mediated transport. Along the translocation pathway, Si speciation evolves from particulate silica toward more soluble silicate and other assimilated Si species, indicating substantial in vivo transformation. Collectively, these observations show that silica-based nanomaterials up to ~70 nm can be systemically translocated, larger than the commonly assumed <20 nm size-exclusion limit.

We then outline how stable isotopes can close this gap and enable unequivocal tracking across the plant-soil continuum. Enriching the silica in 29Si or 30Si provides an isotopic fingerprint in contrast to the background Si, enabling isotope-dilution mass balances in tissues, xylem/phloem exudates, and rhizosphere porewaters. Coupling bulk isotope ratios with spatially resolved mapping using our LA-ICP-MS and TOF-SIMS equipments will quantify where the carrier persists as particles, dissolves to silicic acid, or becomes incorporated into biogenic silica pools. This integrated ‘isotope + correlative imaging’ strategy links nanocarrier design (porosity, surface functionalization) to nutrient delivery efficiency and environmental persistence and offers a general method for tracing silica-based nanomaterials in complex biological and soil matrices.