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Metabolomic and Proteomic Analysis of Manganese Sensitivity and Tolerance in the Tropical Legume Cowpea (*Vigna unguiculata* L.)

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Manganese is a widely distributed plant disorder appearing on acidic and insufficiently drained soils of the (sub)tropics. In the tropical legume cowpea increased manganese (Mn) availability leads to typical toxicity symptoms in form of visible brown apoplastic depositions consisting of Mn oxides and polyphenols followed by chlorosis and leaf shedding. Silicon (Si) supply alleviates toxicity symptoms in Mn-sensitive cultivars. Here, Mn and Si-mediated apoplastic and symplastic modulations in the metabolome and proteome of two genotypes differing in Mn tolerance are described. The key role of apoplastic peroxidases in Mn toxicity was confirmed by the characterization of isoenzymes. The decisive role of specific phenols as NADH-*peroxidase* activity-modulators was substantiated. Modifications of photosynthesis were greater in the Mn-sensitive than in the Mn-tolerant cultivar. These changes also affected the primary carbohydrate and nitrogen metabolism reflecting its disturbance and need for rebalancing. Proteomic but also metabolomic results particularly after short-term Mn supply indicated coordinated stress-perception and signal-transduction processes to be triggered earlier more in the Mn-sensitive cultivar. Differences and changes in the abundance of other metabolites and enzymes of the primary and secondary metabolism and the antioxidative regeneration system not only in the symplast but also the apoplast may partly explain and contribute to genotypic and Si-mediated Mn tolerance. In conclusion, Mn toxicity seems to involve a coordinated interplay of apoplastic and symplastic metabolic pathways, whereas Mn tolerance seems to be based primarily on a constitutive higher antioxidative capacity.