The role of Cd storage forms on the mobility of Cd in soil-rice systems during grain filling stage

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Rice is a major source of the toxic contaminant cadmium (Cd) for humans. Here, we aimed to elucidate the role of Cd storage forms (*i.e.* Cd solid state speciation) during Cd remobilization from root and shoot into rice grain. In a pot trial, we grew rice on a Cd contaminated soil in non-flooded conditions. Soil and rice parts were sampled at flowering and maturity stages and Cd and micronutrient concentrations, Cd stable isotope ratios, and Cd speciation (XANES, EXAFS) were analyzed. The latter provided snapshots of Cd storage forms while Cd mass balances and isotope fractionation provided information on how the storage form controls the mobility of Cd during grain filling. In roots, Cd was fully bound to sulfur (S) at both growth stages and only a minor fraction of Cd was estimated to be remobilized from root to shoot during grain filling (2 to 9%). This corresponded with a retention of light isotopes in roots and a remobilization of heavy isotopes from roots to shoots that enriched the shoots in heavy isotopes ($\Delta^{114/110}Cd_{maturity\text{-}flowering}$ = 0.14 ± 0.04 ‰). The Cd speciation in the shoots changed from predominantly Cd-S (72%) to Cd-O (80%) during grain filling and only 0.77% of Cd in the shoots accumulated in the grains, which were strongly enriched in heavy isotopes ($\Delta^{114/110}Cd_{grains\text{-}straw}$ = 0.66 ± 0.03‰). Together, Cd isotopes showed that Cd-S complexes immobilize Cd in the straw, however, mass balances and Cd speciation suggest that most Cd-O storage forms also retained Cd in the straw. In addition, Cd was fully bound to S in the nodes and predominantly bound to S in the grains (84%) while Cd isotopes in the nodes and grains were not distinguishable. Hence, Cd-S may be mostly conserved in the path from node to grain. Generally, Cd was less mobile than zinc within the rice plant during grain filling. Our results showed that distinct Cd storage forms are involved in the immobilization of Cd in root and shoot and these storage forms may contribute to separate the contaminant Cd from chemically similar micronutrients.