

Green manure and long-term fertilization effects on available soil zinc and cadmium and their accumulation by wheat (*Triticum aestivum* L.)

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Zinc (Zn) deficiency in humans due to imbalanced diets is a global nutritional problem. It is especially widespread in populations of low-income countries depending on cereals as staple food. Grain Zn concentrations are particularly low in cereals grown on soils with low phytoavailable Zn concentrations. Plant Zn uptake depends on soil properties such as pH, calcium carbonate, iron and manganese oxides, total Zn and organic matter content (OM). Soil pH, total Zn and OM can be influenced on farms with limited access to mineral fertilizers through organic matter management practises. In this study, we investigated to what extent green manure application could increase soil Zn availability and wheat grain Zn concentrations (biofortification) on soil with different long-term fertilizer management. Also cadmium (Cd) was included in the study, as wheat is a major source of Cd taken up by humans. Clover (*Trifolium alexandrinum* L.) and mustard (*Sinapis alba* L.) species were grown on split-plots of a Swiss long-term field trial either managed with farmyard manure (FYM) or mineral fertilizers (NPK). One week after incorporation of their residues into the soil as green manure, wheat (*Triticum aestivum* L.) was cultivated. Soil Zn and Cd availabilities were measured by the Diffusive Gradients in Thin Films (DGT) method at various stages of wheat growth along with dissolved organic carbon (DOC), total free amino acids (TFAA) and soil mineral nitrogen (N_{min}) extracted with 2 M KCl. Zn and Cd concentrations were also measured in the wheat shoots at various stages over the entire growing period, and additionally in the grains at harvest. Contrary to mustard, applying clover as green manure increased N_{min} concentrations and wheat biomass. However, neither increased grain Zn concentrations. DGT available Zn and Cd increased temporarily after application of farmyard manure and mineral nitrogen fertilizer. The input of Zn and Cd with farmyard manure resulted in higher grain Zn concentrations on the FYM than on the NPK soil. The concentrations of DOC and TFAA, which can complex and mobilize soil Zn, were also higher in the FYM soil at wheat tillering and flowering and positively correlated with DGT Zn and Cd, suggesting that the higher availability was due to the larger presence of manure-derived metal-binding soluble organic ligands in this treatment. Furthermore, DGT Zn and Cd concentrations correlated positively with Zn and Cd concentrations in wheat shoots and grains. This study revealed no wheat Zn biofortification effects of clover and mustard applied as green manures to soil containing sufficient phytoavailable Zn but that long-term farmyard manure application can increase grain Zn concentrations. In addition, it showed that DGT is sensitive to the temporal dynamics in Zn and Cd availability during wheat growth and has the potential to be used as a predictor of fertilizer effects on grain Zn and Cd accumulation.