Do long-term applications of organic residues promote copper ecotoxicity in soil?

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Amendments with organic residues (OR) are a major source of copper (Cu) contamination in agricultural soils. The chronic soil contamination with Cu raises the problem of potential toxic effects of Cu on soil organisms and then the long-term sustainability of OR recycling in agriculture. Contrary to heavy soil contaminations, Cu availability in soil and bioavailability to soil organisms remain poorly documented in the context of long-term OR recycling where soil contamination is moderate. The ecotoxicity of Cu depends both on its availability in soil and its bioavailability for soil organisms. In the case of long-term OR applications, Cu availability will be driven by the level of contamination and by temporal evolution of key soil physical-chemical properties such as pH and organic matter content. In the meantime Cu ecotoxicity will depend on the bio-influence of soil organisms on the soil volume they explore i.e. the rhizosphere for plants and the drilosphere for earthworms.

The aim of this study was to assess the effect of long-term OR applications on Cu availability in soil and Cu bioavailability to plants and earthworms. A hundred soil samples were selected from four decadal field trials (chronosequences) receiving either no fertilization, mineral fertilization, or organic fertilization and then exhibiting contrasted soil properties. In addition to soil properties we determined Cu availability in each soil sample following (i) a kinetic approach based on the diffusive gradient in thin films (DGT) and (ii) an equilibrium approach based on the measurements of total Cu concentration and Cu^{2+} activity in soil solution. The drivers of Cu speciation in soil solution were assessed by modelling using the windermere humic aqueous model (WHAM). On the hundred soil samples a sub-selection of thirty soil samples were then exposed to plants (*Festuca arrundinaceae*) and earthworms (*Dichogaster saliens*) in biotests. Copper availability in the rhizosphere and drilosphere was measured as detailed above and Cu bioavailability was determined by measuring Cu uptake flux in plants and earthworms.

The soil chronosequence analyses revealed a temporal increase of pH and dissolved organic matter (DOM) that led to an increase in Cu total concentration and a decrease of Cu^{2+} in soil solution, while DGT-available Cu was not significantly altered. The action of soil organisms, as compared to bulk soil, led to pH further increased while DOM decreased in the rhizosphere and the drilosphere. These evolutions of pH and DOM in the rhizosphere and the drilosphere led to a decrease in total Cu concentration and Cu^{2+} in soil solution compared to the bulk soil. Copper uptake flux in plants and earthworms revealed that Cu bioavailability to earthworms and plants were not significantly different under long-term organic or mineral or no fertilization.

All these results were consistent with the hypothesis that long-term applications of OR, while inducing a chronical soil Cu contamination, still have a protective effect towards Cu ecotoxicity in soil by decreasing Cu availability in soil under physical-chemical and biological control.