Copper toxicity in soils amended with copper containing fungicides

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Introduction

The long-term application of copper containing pesticides can cause a significant accumulation of Cu in soils. It can however be expected that such a long-term accumulation of Cu in soils due to the annual application of small amounts of Cu will result in strong attenuation of Cu availability and hence a lower toxicity of Cu in soils compared to assumptions in the Voluntary Risk Assessment Report (VRAR) on Cu and its compounds (2009). The aim of this work was to compare Cu toxicity in soils with high Cu concentrations due to the application of Cu fungicides with Cu toxicity in corresponding reference soils spiked with $CuCl_2$ and with Predicted No Effect Concentrations (PNEC) derived according to the VRAR for Cu.

Materials and Methods



- Soils with high Cu content due to a long history of application of Cu containing fungicides were sampled at 11 vineyards in Europe, covering a representative range in soil properties (pH: 6.8-7.5; eCEC: 17-37 $cmol_c$/kg, clay: 10-39%; Organic C: 2.5-11.8%; maximal Cu concentration: 349-689 mg Cu/kg).
- At each site, a field gradient with increasing Cu concentrations was collected, together with an uncontaminated control soil outside the vineyard.
- Cu toxicity was measured in the field gradient and the control soil spiked with $CuCl_2$ (approx. 100-1600 mg Cu/kg) according to standard ecotoxicity tests for sensitive species and endpoints representing the 3 trophic levels of terrestrial organisms: plant yield (tomato, according to ISO 11269-2 (2005)), root length (barley, according to ISO 11269-1 (2005)), microbial activity (nitrification, ISO 14238-1 (1997) and Smolders et al., 2001) and invertebrates (*Enchytraeus albidus* reproduction, according to OECD 220 (2004)).

Results and Discussion



- No clear dose-response curves could be derived for the field gradients. Only in 4 cases, there is a potential effect of Cu at the largest concentration, and in the other cases no significant effect of Cu could be detected up to the highest concentration. In contrast, freshly spiked control soils always showed a clear dose-response relationship and ED10 values ranged between 45 and 637 mg Cu/kg (Table 1, Figure 1).
- The discrepancy between the toxicity in the spiked gradient and field gradient is commonly quantified as the 'Leaching/Ageing' (L/A) factor, i.e. the ratio of the ED10 in the vineyard (where Cu can be leached and aged) and that in the freshly spiked gradient. After correction for potential differences in bioavailability between field soils and control soil due to differences in soil properties (eCEC), these factors vary between >0.4 and 6.8 (Table 1).
- PNEC values for these vineyard soils calculated according to the VRAR (based on a generic L/A factor of 2) vary between 100 and 158 mg Cu/kg and are a factor 2.2 to 5.7 below the corresponding NOEC values (Figure 2).
- Increasing the L/A factor to 4 results in soil-specific PNEC values between 159 and 255 mg Cu/kg, still a factor 1.4 to 3.6 smaller than the NOEC values observed in the vineyard soils (Figure 2).

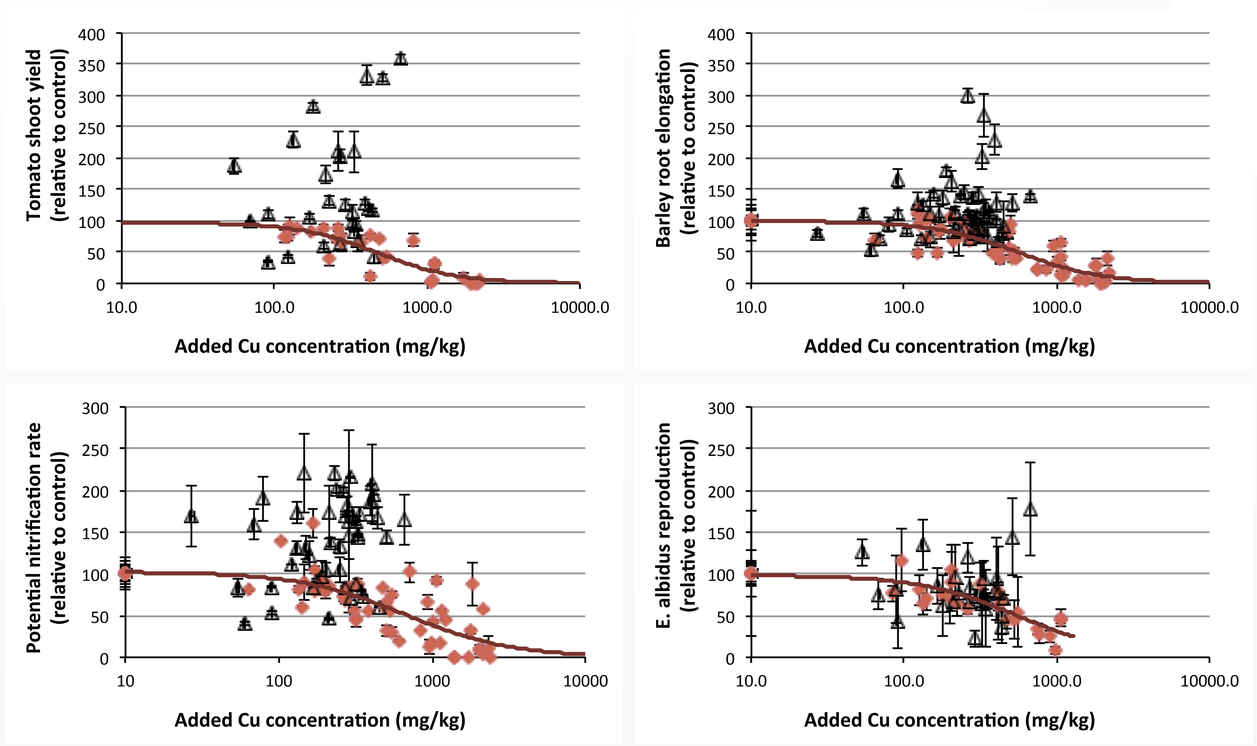

Figure 1: Dose-response graphs for field gradients and corresponding freshly spiked control soils. Curves are based on data for all freshly spiked soils.

Table 1: NOEC/ED10 values (based on added or background corrected Cu concentrations) for the field gradients and corresponding spiked control soils

Endpoint	NOEC Field gradient (mg/kg)	ED10 Freshly spiked (mg/kg)	Leaching-ageing (L/A) factor (/)
Tomato shoot yield	≥345 - ≥666	80 - 321	>0.8 - >3.9
Barley root elongation	≥248 - ≥666	86 - 637	>0.4 - >4.7
Nitrification	320 - ≥666	103 - 396	>0.7 - >4.1
Enchytraeus albidus reproduction	≥345 - ≥666	45 - 332	>0.7 - 6.8

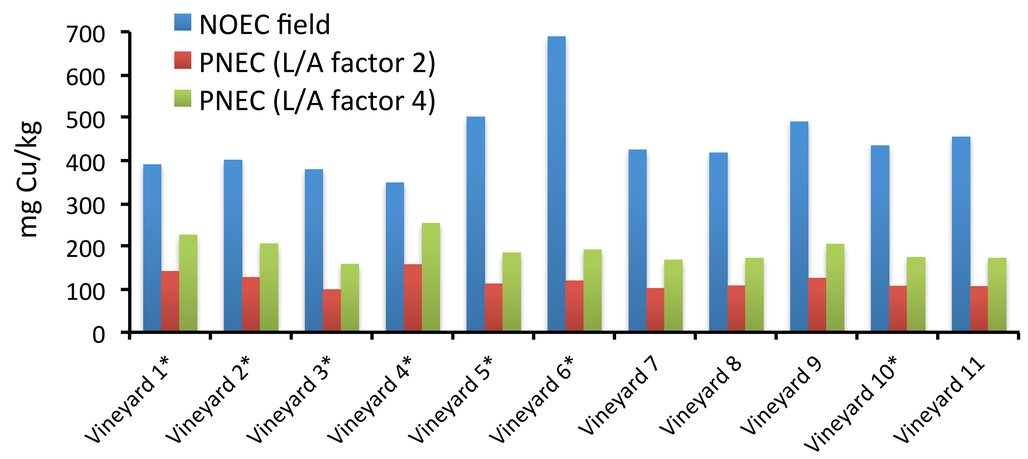

Figure 2: Comparison of field NOECs with PNEC values corrected for bioavailability due to varying soil properties and with different correction for ageing. In vineyards marked with * no toxicity was observed up to the highest Cu concentration tested.

Conclusions



- No significant Cu toxicity was observed below a total Cu concentration in soil of 418 mg Cu/kg (or added Cu dose of 320 mg Cu/kg) in surface horizons of 11 vineyard soils with a long history of application of Cu containing fungicides and covering a representative range in soil properties.
- Results confirm the conservative nature of PNEC values based on a generic leaching/ageing factor of 2.0 selected in the VRAR for Cu.
- Application of Cu-based plant protection products results in a small annual increase in Cu and hence most of the Cu will be redistributed to less available fractions in soil ("ageing") by the time the total Cu concentration reaches the threshold concentrations for Cu in soil. A scenario-specific L/A factor of 4.0 is still conservative and is considered more appropriate for risk assessment of Cu in soils affected by the long-term use of Cu as plant protection products.

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References: Voluntary Risk Assessment Report on Cu and its compounds, 2009; http://echa.europa.eu/chem_data/transit_measures/vrar_en.asp; Smolders, E., Brans K., Coppens F., and Merckx R., 2001. Potential nitrification rate as a tool for screening toxicity in metal-contaminated soils. Environmental Toxicology and Chemistry 20(11): 2469-2474.