Long-term Natural Attenuation of Cu Added to Soils Predicted by Soil pH and Time

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INTRODUCTION

Natural attenuation of Cu added to soil refers to the processes by which the mobility and bioavailability/toxicity of Cu in soil declines with time. The processes of natural attenuation can be attributed to micropore diffusion, occlusion in solid phases by co-precipitation and co-flocculation, cavity entrapment, and solid solution formation. Although natural attenuation plays a key role in metal risk assessment of field soils, long-term attenuation of Cu added to soils has not been studied in detail (Lock and Janssen 2003). In this study, an isotope dilution technique was used to determine long-term changes in lability of Cu added to soils incubated outdoors and a model was developed based on incubation time and soil pH.

METHODS

A set of 19 soils were collected from 9 European countries and spiked with different amounts of Cu which were determined in a preliminary experiment from the total concentration of Cu able to decrease plant growth by 10% (EC_{10}) and 90% (EC_{90}) in the different soils (data provided by Rothamsted). The spiked soils were leached with "artificial rain water" in order to avoid salt effects on metal partitioning (Stevens et al. 2003) and to replace nutrients that were leached. After leaching, the soils were equilibrated in an outdoor environment for different times (3 weeks, 3, 6 and 12 months). An isotopic dilution technique was used to determine the labile Cu in soils (E value).

RESULTS AND DISCUSSION

When water soluble Cu is added to soils, it partitions quickly between solution and solid phases in soil, followed by slow processes that gradually decrease the lability of the added Cu. The fast processes, which led to decreased lability of the added Cu (E value), are probably attributed to the precipitation/nucleation of Cu on soil surfaces. This is considered to be related to the formation of $Cu(OH)^{+}$ in soil solution and on the surfaces of soil solid phases where proton dissociation from water molecules often takes place more readily than in bulk solutions (Ma and Uren 1998). The slow processes could be described by a diffusion-based equation. Based on the processes of Cu precipitation/nucleation and micropore diffusion, a semi-mechanistic model of long-term natural attenuation of Cu spiked to soils was developed:

$$\text{E value (\%)} = A - \frac{B}{10^{(pK^\circ - pH)} + 1} \times t^{C/t} - 600\sqrt{D/\pi r^2}\ \sqrt{t},$$

where A is a coefficient which represents the E value of added Cu at time zero (=100%); B is a coefficient which is considered to be related to the effect of precipitation/nucleation; t is incubation time (day); pK° is the first hydrolysis constant of Cu (=7.7); D/r^2 expresses the apparent diffusion rate coefficient; the reciprocal power exponential equation $t^{C/t}$ is used to describe the relatively fast reactions led by precipitation/nucleation; and pH is the soil pH measured in 0.01 M $CaCl_2$.

The coefficient B in the model for EC_{10}-spiked soils (88.3) was lower than that for EC_{90}-spiked soils (106.9) and the difference was significant at $P<0.01$. These results suggest a greater possibility of precipitation/nucleation of Cu when spiked at higher concentrations (EC_{90}). To simplify the model, we ignored the difference between spiking rates.

The model with parameters was as follows:

$$\text{E value (\%)} = 100 - \frac{97.6}{10^{(pK^\circ - pH)} + 1} \times t^{1/t} - 1.74\sqrt{t} \qquad (t \le 1 \text{ year})$$

The measured E values and the E values estimated by the model are shown in Figure 1. The correlation coefficient ($R^2 = 0.844$) for the model is highly significant ($P<0.00001$).

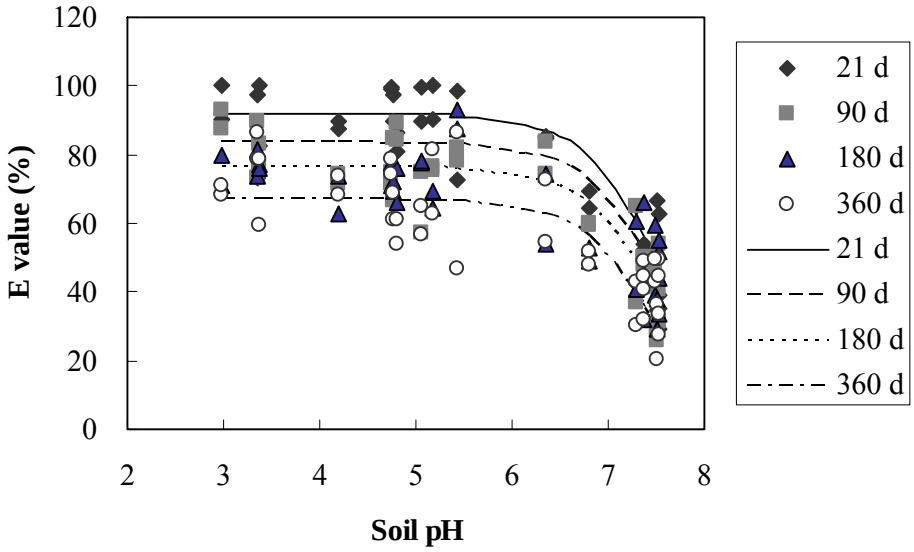

Fig. 1. The E values (%) for added Cu measured in the EC_{10}- and EC_{90}-spiked soils incubated for different times and the curves predicted by the model.

Because the long-term diffusion processes can be linearly related to the logarithm of time after the initial stage, the following model can be used to predict the E values when the incubation time is greater than 1 year after Cu addition.

$$\text{E value (\%)} = 100 - \frac{89.8}{10^{(pK^\circ - pH)} + 1} \times t^{1/t} - 11.3 \times \log(t) \qquad (t > 1 \text{ year})$$

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