

## Supporting Information

### Fate of copper in soil: effect of agrochemical (nano)formulations and soil properties

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Table S1. Parameters derived by nonlinear curve fitting with a pseudo first order kinetics (one phase association)

$$y_t = y_0 + (\text{plateau} - y_0) \times (1 - e^{-kt})$$

<b>S1</b>	<b>Si50</b>	<b>Si500</b>	<b>CuSO<sub>4</sub></b>	<b>Tribasic*</b>	<b>nCuO</b>	<b>Kocide</b>	<b>Cu(OH)<sub>2</sub></b>	<b>ChampDP</b>	<b>GO</b>
<b>Y<sub>0</sub></b> (mg/kg)	0.132	0.121	0.150	0.193	0.011	0.096	0.124	0.175	0.044
<b>Plateau</b> (mg/kg)	0.074	0.080	0.075	~ -62.90	0.053	0.051	0.059	0.076	0.025
<b>k</b> (day <sup>-1</sup> )	0.325	0.333	0.403	~ 4.630e-005	0.064	0.418	0.418	0.660	0.373
<b>Half-time</b> (day)	2.131	2.081	1.721	~ 14971	10.880	1.657	1.657	1.050	1.858
<b>R<sup>2</sup></b>	0.973	0.855	0.967	0.598	0.973	0.962	0.954	0.937	0.932

\*ambiguous fit

<b>S2</b>	<b>Si50</b>	<b>Si500</b>	<b>CuSO<sub>4</sub></b>	<b>Tribasic</b>	<b>nCuO</b>	<b>Kocide</b>	<b>Cu(OH)<sub>2</sub></b>	<b>ChampDP</b>	<b>GO</b>
<b>Y<sub>0</sub></b> (mg/kg)	0.815	0.599	0.903	1.020	0.040	0.560	0.544	0.541	0.173
<b>Plateau</b> (mg/kg)	0.364	0.436	0.557	0.673	0.332	0.409	0.410	0.411	0.135
<b>k</b> (day <sup>-1</sup> )	0.295	0.780	0.518	0.455	0.238	0.621	0.666	0.791	0.270
<b>Half-time</b> (day)	2.348	0.888	1.337	1.523	2.915	1.117	1.041	0.877	2.566
<b>R<sup>2</sup></b>	0.858	0.408	0.892	0.832	0.969	0.863	0.876	0.883	0.852

<b>S3</b>	<b>Si50</b>	<b>Si500</b>	<b>CuSO<sub>4</sub></b>	<b>Tribasic</b>	<b>nCuO</b>	<b>Kocide</b>	<b>Cu(OH)<sub>2</sub></b>	<b>ChampDP</b>	<b>GO</b>
<b>Y<sub>0</sub></b> (mg/kg)	0.101	0.097	0.094	0.145	0.012	0.072	0.108	0.114	0.045
<b>Plateau</b> (mg/kg)	0.047	0.045	0.043	0.051	0.034	0.033	0.046	0.048	0.021
<b>k</b> (day <sup>-1</sup> )	0.250	0.319	0.227	0.179	0.211	0.338	0.318	0.265	0.257
<b>Half-time</b> (day)	2.776	2.175	3.053	3.884	3.286	2.049	2.179	2.614	2.697
<b>R<sup>2</sup></b>	0.980	0.974	0.982	0.978	0.952	0.978	0.959	0.960	0.982

Table S2. Multi-surface equilibrium modelling parameters and predictions

Soil	pH <sup>a</sup>	Soil model			Solution model		Plateau/ Cu-CaCl <sub>2</sub> at t=∞ (mg kg <sup>-1</sup> ) <sup>b</sup>	Predicted equilibrium CaCl <sub>2</sub> -extractable Cu conc. (mg kg <sup>-1</sup> ) <sup>c</sup>
		Reactive Cu (mg kg <sup>-1</sup> )	Cu-OM %	Cu- FeOx %	log free Cu <sup>2+</sup>	log free Cu <sup>2+</sup>		
<u>No added Cu</u>								
S1	6.92	0.21	100.00	0.00	-13.6	-10.8		
S2	5.54	2.17	99.83	0.17	-9.1	-9.2		
S3	5.89	4.08	99.99	0.01	-11.8	-11.0		
<u>With Cu application</u>								
S1	6.4	50.21	92.06 <sup>d</sup>	7.67	-6.5	-7.3	0.06	0.26
S2	5.0	52.17	97.07	1.52	-5.8	-6.2	0.41	0.76
S3	6.1	54.08	99.34	0.66	-9.2	-8.9	0.04	0.04

<sup>a</sup>pH value measured for each soil in CaCl<sub>2</sub>; Lower pH value measured in each soil at t=29 days (see Figure S2 and S3)

<sup>b</sup>Derived from fitting the kinetics. Average value for the nine formulations considered

<sup>c</sup>Predicted equilibrium CaCl<sub>2</sub>-extractable Cu concentration; determined by predicting the free Cu<sup>2+</sup> concentration using the Soil model, and implementing this free Cu<sup>2+</sup> concentration into the solution model to predict the total dissolve Cu concentration. (This is the inverse modelling route as by which the free Cu<sup>2+</sup> concentration was determined from the measured total Cu concentration in CaCl<sub>2</sub> extracts at 28 days)

<sup>d</sup>Percentages do not add up to 100% because of the contribution of Cu not associated with soil organic matter and Fe(hydr)oxide minerals (e.g. Cu<sup>2+</sup> (aq), Cu(OH)<sup>+</sup>(aq)) to the total reactive Cu pool.

- Before Cu amendment, the Soil and Solution models are in reasonable agreement (within 1 log unit) for S2 and S3.
- For S1, the Soil model underestimates the free Cu concentration computed by the Solution model (2.8 log units). The cause for the discrepancy is unclear.
- After Cu amendment, the Soil and Solution models are again in good agreement for S2 and S3 (up to 0.4 log units difference).
- The Soil model for S1 overestimates the free Cu concentration in solution by 0.8 log units.
- A possible explanation for the overestimation could be of Cu-bearing minerals. However, Figure S4 showing the free Cu<sup>2+</sup> concentration in equilibrium with Cu(OH)<sub>2</sub> and Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> as a function of pH suggests that precipitation is unlikely to play an important role under the conditions measured in S1. The reasons why the model overestimated the dissolved Cu thus remain uncertain.
- The CaCl<sub>2</sub> extractable concentration at t=∞ from the kinetic model (Plateau) and the predicted equilibrium CaCl<sub>2</sub>-extractable Cu concentration are in reasonable agreement, with a difference by a factor of 4.2 for S1, 1.8 for S2 and 1.1 for S3. The ranking of the measured Cu concentrations corresponds with the modelled results (i.e. higher Cu concentration in S2 than in S3).

Figure S1. Extractable Cu over a 29 days incubation for three soils (S1-S3) spiked with nine different forms of Cu.

Results are expressed in mg/kg (data on Figure 1 are in % of Cu added). Error bars are the standard deviation between triplicates (often smaller than the symbols). The dashed lines are fits with a one-phase association model. Fitted parameters are presented in Table S1.

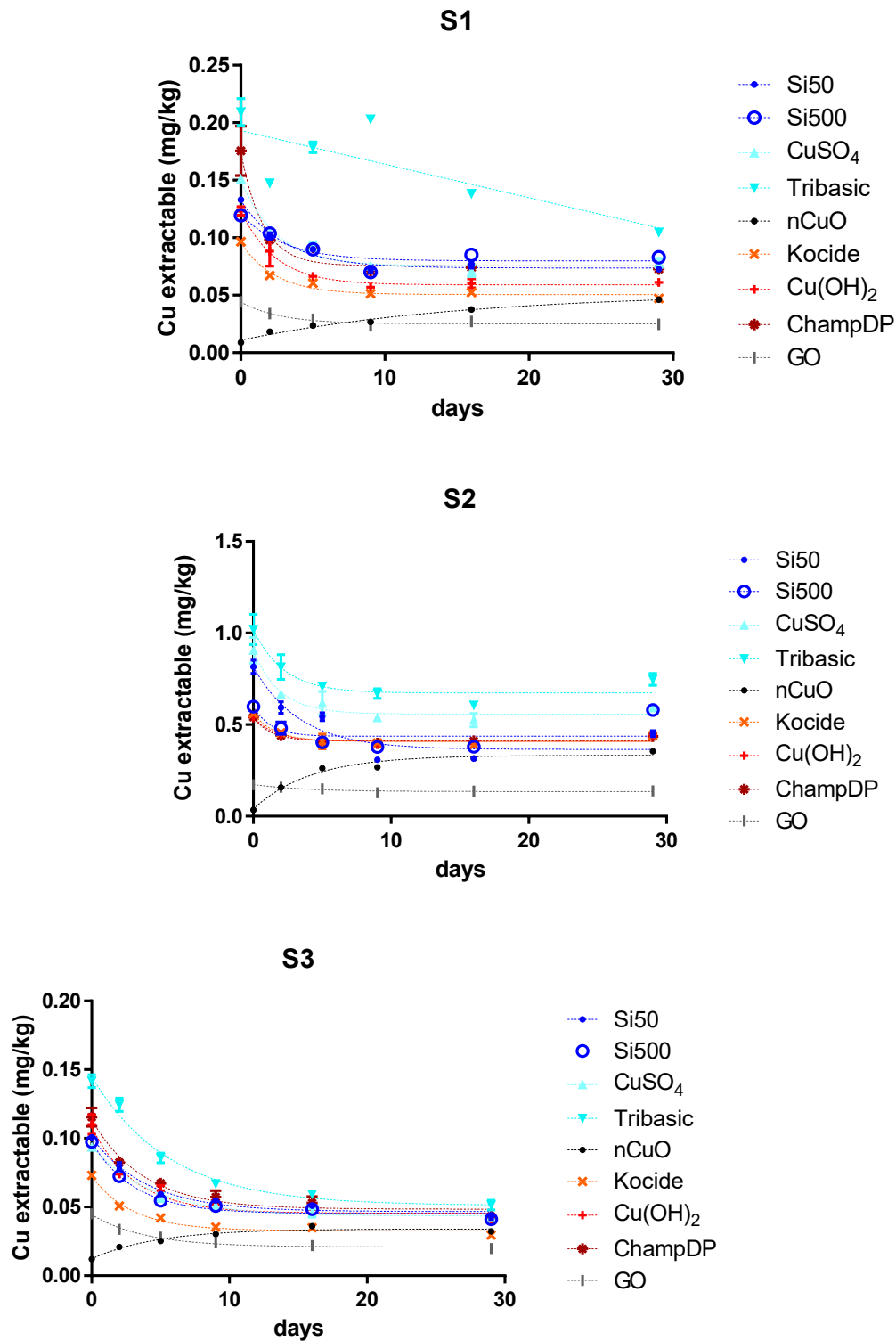


Figure S2. pH measured in CaCl<sub>2</sub> 0.01M suspensions after the addition of different forms of Cu.

The dashed line shows the pH of soil controls, which did not receive Cu additions. Error bars are for triplicates (often smaller than the symbols)

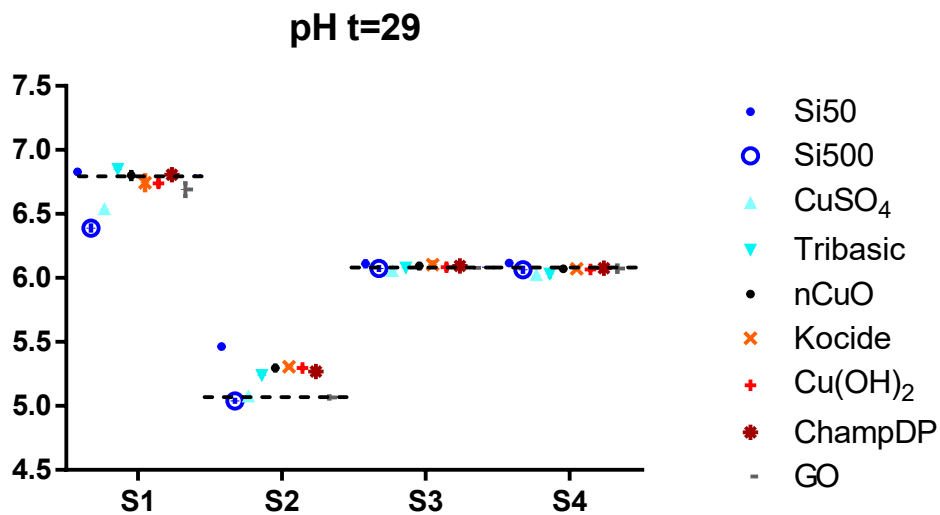
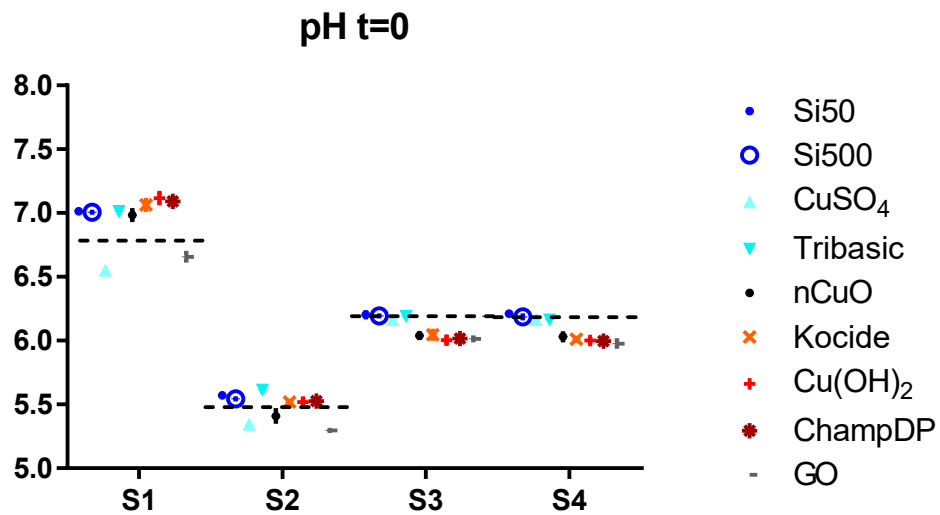
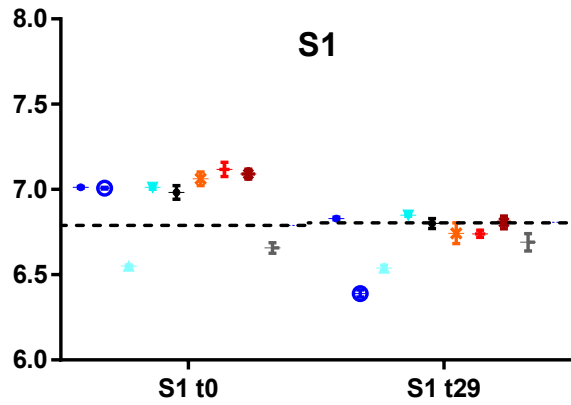
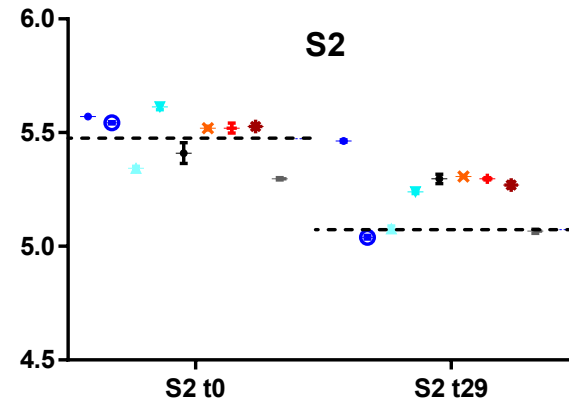


Figure S3. pH measured in CaCl<sub>2</sub> 0.01M suspensions after the addition of different forms of Cu.

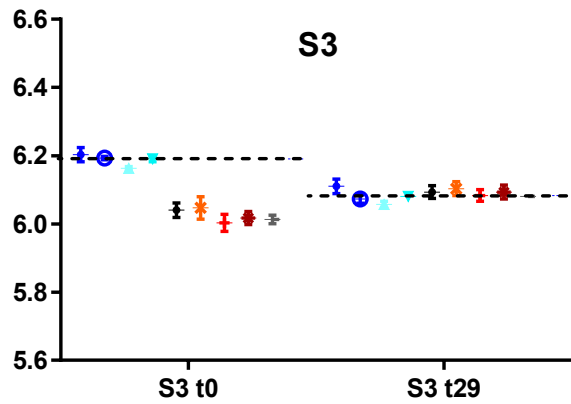
The dashed line shows the pH of soil controls, which did not receive Cu additions. The data is the same as Figure S2 but allows an easier comparison between pH values measured at t=0 and t=29. Error bars are for triplicates (often smaller than the symbols).



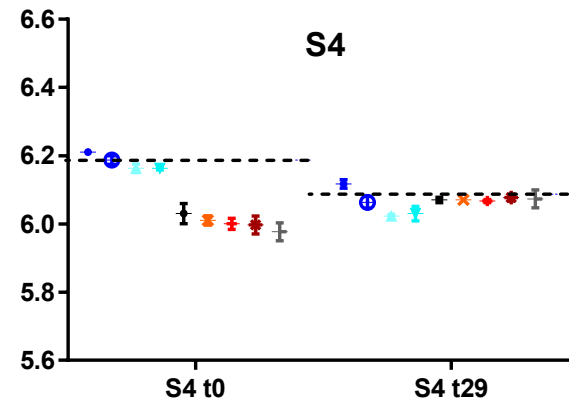
- Si50
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- ▲ CuSO<sub>4</sub>
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- nCuO
- × Kocide
- + Cu(OH)<sub>2</sub>
- ChampDP
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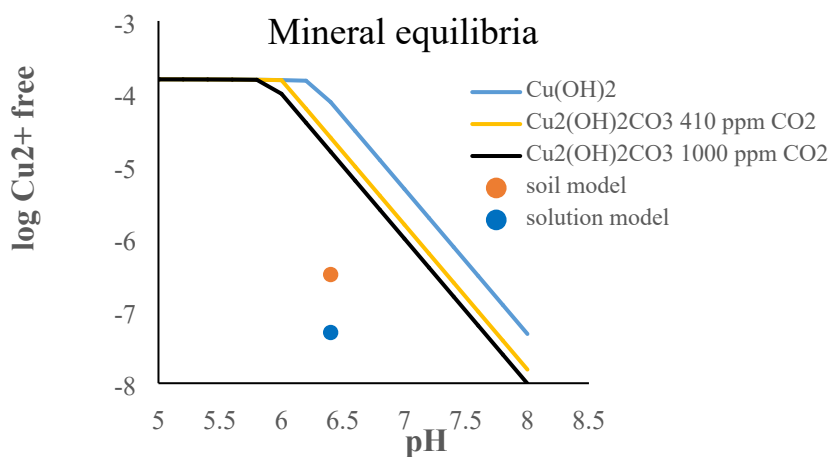


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Figure S4. Free  $\text{Cu}^{2+}$  concentration in equilibrium with  $\text{Cu}(\text{OH})_2(\text{s})$  and  $\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s})$  as a function of pH.



For  $\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s})$ , two gas phase  $\text{CO}_2$  concentrations (410 ppm (=atmospheric) and 1000 ppm) were included. 10 mM  $\text{CaCl}_2$  was included as background electrolyte. The maximum Cu concentration equals the total reactive Cu concentration in S1 after Cu addition ( $1.57 \cdot 10^{-4}$  M). The predictions of the free  $\text{Cu}^{2+}$  concentration in S1 after application of the Cu treatments by the soil and the solution model (indicated with the orange and blue dot, respectively) are well below the concentrations in equilibrium with the minerals. This suggests that these Cu-bearing minerals did not form (and limit the free  $\text{Cu}^{2+}$  concentration) as a result of Cu application.

Figure S5.  $\text{CaCl}_2$ -extractable Cu over a 29 days incubation for three soils (S1-S3) spiked with nine different forms of Cu. Results are expressed as the % of Cu added. Error bars are the standard deviation between triplicates (often smaller than the symbols). The data is the same as that presented to Figure 1 in the main document.

