Supporting Information

Copper oxide nanoparticles mitigate cadmium-arsenic phytotoxicity to rice plants (*O.sativa*) and protect *Daphnia magna* via soil-water partitioning

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The following are included as supporting information for this paper:

Text S1 Visual MINTEQ speciation modeling of dissolved Cu in exposure media

Cu speciation in Hoagland solution and simulated drain waters was evaluated using Visual MINTEQ (version 4.0), incorporating the Stockholm Humic Model (SHM) to account for complexation with soil organic matter. Model inputs included measured pH and the major-ion composition of each medium (Table S1). In the Visual MINTEQ output (Table S3-S10), prefix codes are utilized to distinguish between different adsorption states of chemical species. Species without a prefix represent free ions in the bulk solution. The prefix '(6)' denotes Donnan-sorbed ions, which are enriched near the organic matter surface due to electrostatic attraction within the Donnan phase. The prefix '/' indicates specific complexation, representing metal ions that are chemically bound (complexed) to the functional groups of the soil organic matter.

Text S2 Sample digestion methods

1. Plant tissues

The dried root and shoot samples were cut into segments of approximately 2 cm and placed into digestion tubes. The samples were moistened with 0.5 mL of pure water and allowed to stand for 24 h. Subsequently, 4 mL of dilute nitric acid (1:1, v/v) was added into the mixture and heated at 96°C for 15 min. After cooling, 0.2 mL of concentrated nitric acid was added, followed by heating for 2.5 h. Additional nitric acid was added until there was no brown gas emission produced. Finally, 0.5 mL of 30% H_2O_2 were added, and the mixture was heated for 50 min. Upon completion of digestion, the solution was filtered and diluted to a final volume of 50 mL.

2. Soil samples

Approximately 0.5 g of soil sample was accurately weighed into a digestion tube. Then, 5 mL of dilute nitric acid (1:1, v/v) was added, and the sample was heated at 96°C for 15 min under reflux digestion. After cooling, 11 mL of concentrated nitric acid was added, and heating continued for 11.5 h. Additional nitric acid was added until there was no brown gas emission produced. Finally, 1.5 mL of 30% H_2O_2 were added, and the mixture was heated at 95 ± 5°C for 2 h. After cooling, the digested solution was filtered and made up to a final volume of 50 mL.

3. Water samples

A 2 mL aliquot of the water sample was mixed with 8 mL of pure water in a digestion tube.

Then, 0.2 mL of HNO_3 and 0.1 mL of HCl were added, and the mixture was digested at 85°C for 6 h. After cooling, the solution was filtered and diluted to a final volume of 50 mL.

Text S3 Theoretical settling velocity calculation

The gravitational settling velocity of nCuO aggregates was estimated using Stokes' law for a spherical particle in a viscous fluid:

$$v = \frac{2(\rho_p - \rho_f)gr^2}{9 \quad \eta}$$

where ρ_p is the particle density, ρ_f is the fluid density (1000 kg m^{-3} for water), g is the gravitational acceleration (9.8 m s^{-2}), r is the aggregate radius, and η is the dynamic viscosity of water (8.9×10^{-4} Pa s at 25°C).

The hydrodynamic diameter of nCuO aggregates at 100 mg L^{-1} was 426.6 nm, giving a radius r of 2.133×10^{-7} m. The density of nCuO aggregates (ρ_p) is a critical parameter. Due to the challenges in measuring the effective density of nanoscale aggregates, the theoretical density of bulk CuO (6400 kg m^{-3}) was used in this calculation. It is important to note that this likely represents a maximum estimate for the settling velocity, as the porous nature of aggregates could result in a lower effective density and consequently a slower settling rate. Nevertheless, even if the effective density were significantly lower, the calculated velocity for micron-sized aggregates would still be substantial enough to confirm that gravitational settling is a dominant process over experimental timescales.

Text S4 Acute Daphnia magna toxicity assays and EC50 estimation

Acute toxicity of nCuO and $CuCl_2 \cdot 2H_2O$ to *Daphnia magna* was evaluated in Hoagland solution using a dose–response design. Dose–response curves were fitted for each Cu source; nCuO yielded a robust fit and an EC_{50} of 9.66 mg L^{-1} (Figure S4). In contrast, the $CuCl_2 \cdot 2H_2O$ dataset did not meet the fitting acceptance criterion within the 95% confidence interval. Thus, its EC_{50} was estimated as the geometric mean of the two bounding concentrations corresponding to 100% survival (0.01 mg L^{-1}) and 100% mortality (1.0 mg L^{-1}), resulting in an EC_{50} of 0.10 mg L^{-1}.

Text S5 Simulated drain-water preparation, effective Cu exposure, and *Daphnia* outcomes

Simulated drain waters were prepared by mixing surface water with centrifuged porewater collected from red and brown paddy soils. Effective Cu concentrations were calculated based on measured dissolved Cu to compare against EC_{50} values derived in Hoagland solution (Table S2). In drain water derived from red soil, effective nCuO concentrations exceeded the Hoagland EC_{50} across treatments; however, mortality in the nCuO 10 and 100 mg L^{-1} groups remained comparable to or lower than the control, and consistently lower than the corresponding $CuCl_2 \cdot 2H_2O$ treatments at equivalent nominal Cu. In drain water derived from brown soil, effective nCuO concentrations similarly exceeded the Hoagland EC_{50}, yet several high-concentration nCuO treatments again showed mortality lower than the control, consistent with stronger medium buffering via complexation and precipitation that reduces free Cu^{2+} exposure.

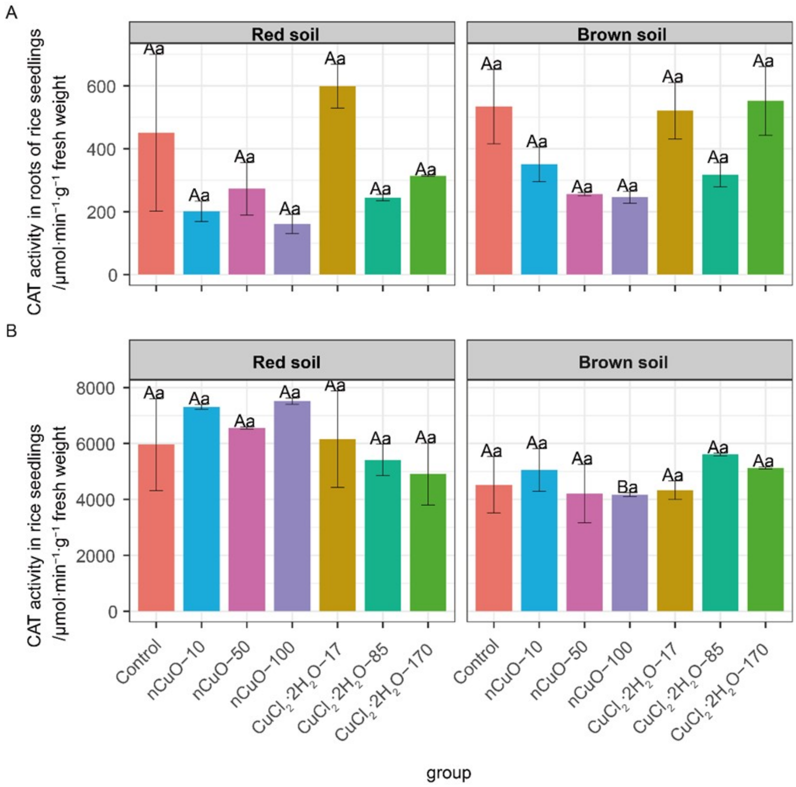

Figure S1. The activity of CAT in the roots and shoots of rice seedlings grown in a red soil collected from Jiangxi Province and a brown soil from Shandong Province treated with nCuO and $CuCl_2 \cdot 2H_2O$**.** Capital letters indicate comparisons between different soil types under identical treatment. Lowercase letters indicate comparisons between different treatments within the same soil on the same sampling day. A statistically significant difference is considered when two groups do not share common letters ($p < 0.05$). N=8; error bars represent mean ± standard error.

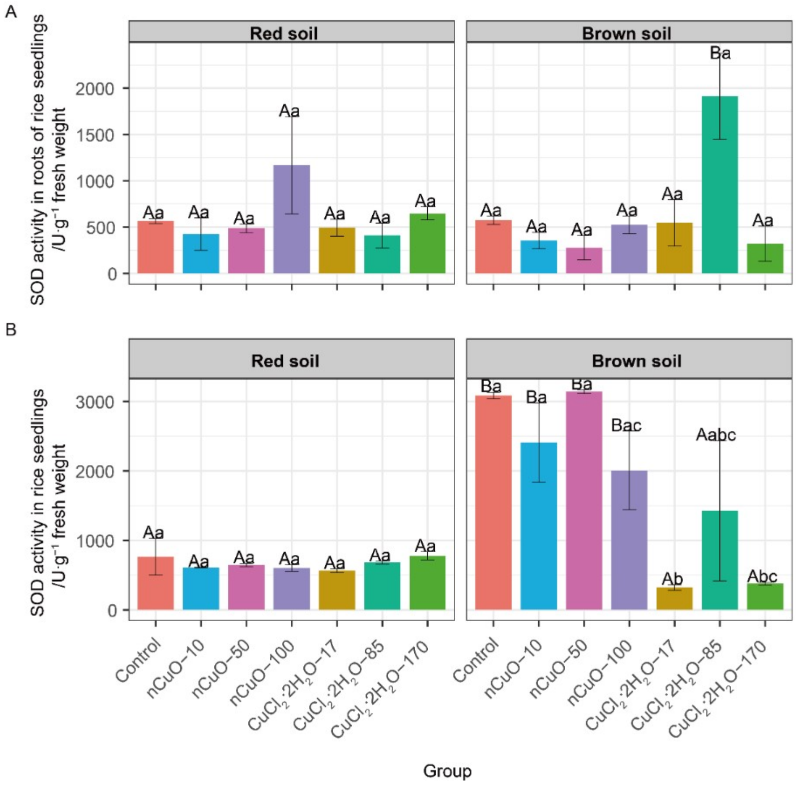

Figure S2. The activity of SOD enzyme in the roots and shoots of rice seedlings grown in a red soil collected from Jiangxi Province and a brown soil from Shandong Province treated with nCuO and $CuCl_2 \cdot 2H_2O$. Capital letters indicate comparisons between different soil types under identical treatment. Lowercase letters indicate comparisons between different treatments within the same soil on the same sampling day. A statistically significant difference is considered when two groups do not share common letters ($p < 0.05$). N=8; error bars represent mean±standard error.

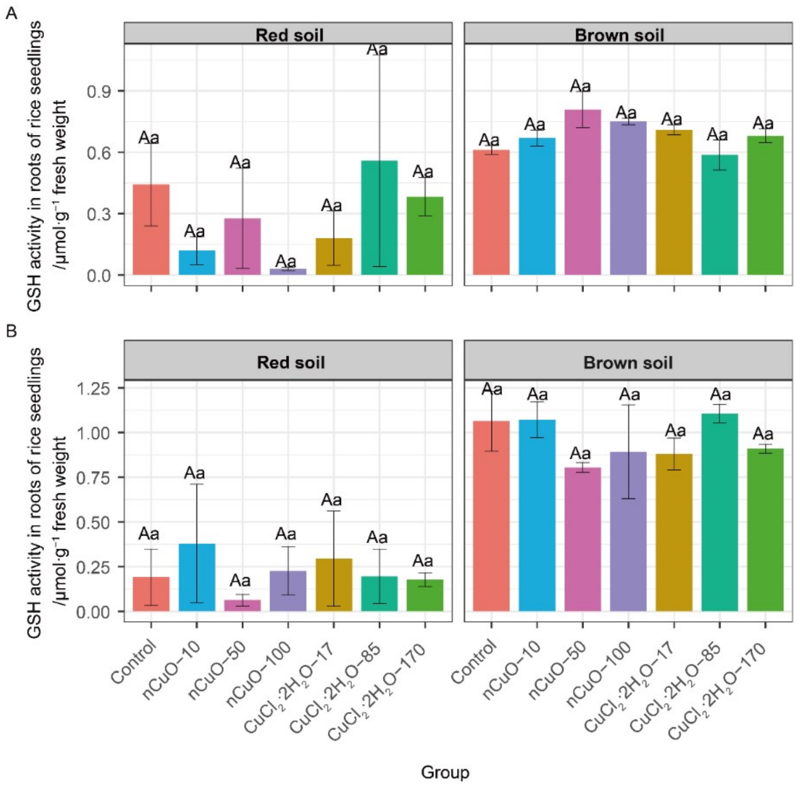

Figure S3. The content of GSH in the roots and shoots of rice seedlings grown in a red soil collected from Jiangxi Province and a brown soil from Shandong Province treated with nCuO and $CuCl_2 \cdot 2H_2O$. Capital letters indicate comparisons between different soil types under identical treatment for the same treatment. Lowercase letters indicate comparisons between different treatments within the same soil on the same sampling day. A statistically significant difference is considered when two groups do not share common letters (p < 0.05). N=8; error bars represent mean±standard error.

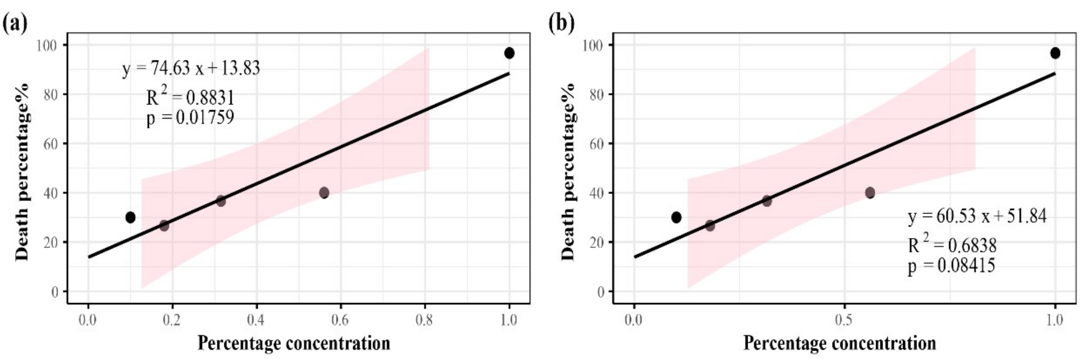

Figure S4. Dose–response curves for *Daphnia magna* exposed to (a) nCuO and (b) $CuCl_2 \cdot 2H_2O$ in Hoagland solution

Table S1 1/5 Hoagland nutrient solution components

Types of drugs	Concentration/ (mg mL-1)
$MgCl_2$	19.04
$CaCl_2·2H_2O$	147.01
KCl	37.28
Fe-EDTA	7.76
$Na_2SiO_3·9H_2O$	213.15
H_3BO_3	2.78
$MnCl_2·4H_2O$	1.78
$ZnSO_4·7H_2O$	2.88
$CuSO_4·5H_2O$	3.75
MoO_3	1.01

Table S2 Survival of *Daphnia magna* in simulated rice paddy drainage water derived from a red soil from Jiangxi Province and a brown soil from Shandong Province

Soil type	**Group**	**Percentage of deaths/%**	**Corresponding concentration / mg L-1**
Red soil from Jiangxi Province	Control	64.29	/
	nCuO 10 mg L-1	57.14	＞EC50
	nCuO 50 mg L-1	71.43	＞EC50
	nCuO 100 mg L-1	57.14	＞EC50
	nCuO 500 mg L-1	100.00	＞EC50
	$CuCl_2·2H_2O$ 17 mg L-1	42.86	＜EC50
	$CuCl_2·2H_2O$ 85 mg L-1	57.14	＞EC50
	$CuCl_2·2H_2O$ 170 mg L-1	57.14	＞EC50
	$CuCl_2·2H_2O$ 850 mg L-1	100.00	＞EC50
Brown soil from Shandong Province	Control	72.02	/
	nCuO 10 mg L-1	71.43	＞EC50
	nCuO 50 mg L-1	58.57	＞EC50
	nCuO 100 mg L-1	62.50	＞EC50
	nCuO 500 mg L-1	52.73	＞EC50
	$CuCl_2·2H_2O$ 17 mg L-1	47.73	＜EC50
	$CuCl_2·2H_2O$ 85 mg L-1	50.00	= EC50
	$CuCl_2·2H_2O$ 170 mg L-1	47.73	＜EC50
	$CuCl_2·2H_2O$ 850 mg L-1	45.45	＜EC50

Table S3 Mineral speciation and concentration in soil solution treated with 500 mg/L nCuO

Mineral species	Concentration (mol/L)	Mineral species	Concentration (mol/L)
(6)Cd^{+2}D(s)	6.96E-10	$Cu(OH)_4^{-2}$	6.64E-25
(6)Cu^{+2}D(s)	1.46E-4	Cu^{+2}	1.29E-10
(6)Fe^{+2}D(s)	1.20E-06	$Cu_2(OH)_2^{+2}$	2.81E-18
(6)H^{+1}D(s)	1.15E-5	Cu_2OH^{+3}	7.48E-21
(6)Mn^{+2}D(s)	4.94E-07	$Cu3(OH)_4^{+2}$	9.68E-26
(6)Pb^{+2}D(s)	1.76E-10	$CuOH^{+}$	9.42E-12
(6)Zn^{+2}D(s)	3.22E-08	$Fe(OH)_2$ (aq)	1.79E-20
/HA-(s)	6.28E-3	$Fe(OH)^{3-}$	1.31E-24
/HA2Cd(s)	1.70E-13	Fe^{+2}	1.07E-12
/HA2Cu(s)	2.11E-4	$FeOH^{+}$	9.79E-16
/HA2CuOH(s)	4.30E-09	H^{+1}	4.37E-07
/HA2Pb(s)	7.29E-10	H_2AsO^{4-}	2.03E-08
/HA2Zn(s)	2.40E-11	H_3AsO_4	1.77E-12
/$HACd^{+}$(s)	1.67E-09	$HAsO_4^{-2}$	4.77E-09
/HA-Cd^{+2}G(s)	2.01E-10	HFA^{-}dum(s)	3.07E-4
/$HACu^{+}$(s)	5.89E-3	$Mn(OH)_4^{-2}$	1.10E-35
/HA-Cu^{+2}G(s)	4.21E-5	Mn^{+2}	7.78E-13
/HAFe(II)$^{+}$(s)	8.55E-07	$Mn_2(OH)^{3+}$	9.32E-30
/HA-Fe^{+2}G(s)	3.48E-07	Mn_2OH^{+3}	3.51E-29
/HA-H^{+1}G(s)	3.32E-06	$MnOH^{+}$	4.50E-17
/$HAMn^{+}$(s)	2.48E-07	OH^{-}	2.31E-08
/HA-Mn^{+2}G(s)	2.53E-07	$Pb(OH)_2$ (aq)	6.57E-21
/$HAPb^{+}$(s)	8.28E-09	$Pb(OH)^{3-}$	1.52E-25
/HA-Pb^{+2}G(s)	5.07E-11	Pb^{+2}	1.56E-16
/$HAZn^{+}$(s)	5.87E-08	Pb_2OH^{+3}	2.23E-32
/HA-Zn^{+2}G(s)	9.30E-09	$Pb_3(OH)_4^{+2}$	1.34E-46
/HHA(s)	0.025	$Pb_4(OH)_4^{+4}$	2.09E-59
AsO_4^{-3}	1.74E-14	$PbOH^{+}$	9.01E-18
$Cd(OH)_2$ (aq)	1.64E-23	Z-(6)(s)	-3.95E-4
$Cd(OH)^{3-}$	3.71E-30	$Zn(OH)_2$ (aq)	1.91E-18
$Cd(OH)_4^{-2}$	8.76E-38	$Zn(OH)^{3-}$	1.39E-23
Cd^{+2}	6.17E-16	$Zn(OH)_4^{-2}$	5.10E-30
Cd_2OH^{+3}	3.50E-34	Zn^{+2}	2.86E-14
$CdOH^{+}$	1.13E-19	Zn_2OH^{+3}	1.88E-30
$Cu(OH)_2$ (aq)	3.99E-14	$ZnOH^{+}$	6.58E-17
$Cu(OH)^{3-}$	3.56E-18		

Table S4 Mineral speciation and concentration in soil solution treated with 100 mg/L nCuO

Mineral species	Concentration (mol/L)	Mineral species	Concentration (mol/L)
(6)Cd+2D(s)	2.20E-09	Cu(OH)4-2	2.36E-27
(6)Cu+2D(s)	3.75E-4	Cu+2	4.61E-13
(6)Fe+2D(s)	2.49E-06	Cu2(OH)2+2	3.56E-23
(6)H+1D(s)	6.65E-4	Cu2OH+3	9.49E-26
(6)Mn+2D(s)	5.97E-07	Cu3(OH)4+2	4.36E-33
(6)Pb+2D(s)	3.44E-09	CuOH+	3.35E-14
(6)Zn+2D(s)	2.60E-07	Fe(OH)2 (aq)	5.13E-23
/HA-(s)	2.47E-3	Fe(OH)3-	3.74E-27
/HA2Cd(s)	2.74E-14	Fe+2	3.06E-15
/HA2Cu(s)	3.54E-5	FeOH+	2.80E-18
/HA2CuOH(s)	7.35E-11	H+1	4.37E-07
/HA2Pb(s)	1.37E-09	H2AsO4-	3.26E-07
/HA2Zn(s)	3.58E-12	H3AsO4	2.84E-11
/HACd+(s)	2.74E-10	HAsO4-2	7.67E-08
/HA-Cd+2G(s)	4.30E-10	HFA-dum(s)	1.42E-3
/HACu+(s)	7.74E-4	Mn(OH)4-2	1.85E-38
/HA-Cu+2G(s)	7.31E-5	Mn+2	1.30E-15
/HAFe(II)+(s)	4.48E-08	Mn2(OH)3+	2.61E-35
/HA-Fe+2G(s)	4.85E-07	Mn2OH+3	9.87E-35
/HA-H+1G(s)	1.30E-4	MnOH+	7.54E-20
/HAMn+(s)	7.61E-09	OH-	2.31E-08
/HA-Mn+2G(s)	2.07E-07	Pb(OH)2 (aq)	1.78E-22
/HAPb+(s)	1.20E-08	Pb(OH)3-	4.11E-27
/HA-Pb+2G(s)	6.71E-10	Pb+2	4.22E-18
/HAZn+(s)	1.77E-08	Pb2OH+3	1.64E-35
/HA-Zn+2G(s)	5.08E-08	Pb3(OH)4+2	2.67E-51
/HHA(s)	0.03	Pb4(OH)4+4	1.14E-65
AsO4-3	2.80E-13	PbOH+	2.44E-19
Cd(OH)2 (aq)	7.20E-26	Z-(6)(s)	-1.70E-3
Cd(OH)3-	1.63E-32	Zn(OH)2 (aq)	2.14E-20
Cd(OH)4-2	3.85E-40	Zn(OH)3-	1.56E-25
Cd+2	2.71E-18	Zn(OH)4-2	5.72E-32
Cd2OH+3	6.75E-39	Zn+2	3.20E-16
CdOH+	4.95E-22	Zn2OH+3	2.36E-34
Cu(OH)2 (aq)	1.42E-16	ZnOH+	7.36E-19
Cu(OH)3-	1.27E-20		

Table S5 Mineral speciation and concentration in soil solution treated with 50 mg/L nCuO

Mineral species	Concentration (mol/L)	Mineral species	Concentration (mol/L)
(6)Cd+2D(s)	1.66E-09	Cu(OH)4-2	5.74E-28
(6)Cu+2D(s)	1.75E-4	Cu+2	1.12E-13
(6)Fe+2D(s)	1.76E-06	Cu2(OH)2+2	2.10E-24
(6)H+1D(s)	8.47E-4	Cu2OH+3	5.60E-27
(6)Mn+2D(s)	3.55E-07	Cu3(OH)4+2	6.27E-35
(6)Pb+2D(s)	1.30E-09	CuOH+	8.15E-15
(6)Zn+2D(s)	9.46E-08	Fe(OH)2 (aq)	1.89E-23
/HA-(s)	1.84E-3	Fe(OH)3-	1.38E-27
/HA2Cd(s)	2.69E-14	Fe+2	1.13E-15
/HA2Cu(s)	2.23E-5	FeOH+	1.03E-18
/HA2CuOH(s)	2.92E-11	H+1	4.37E-07
/HA2Pb(s)	7.36E-10	H2AsO4-	1.67E-08
/HA2Zn(s)	1.32E-12	H3AsO4	1.45E-12
/HACd+(s)	2.26E-10	HAsO4-2	3.92E-09
/HA-Cd+2G(s)	3.28E-10	HFA-dum(s)	1.20E-3
/HACu+(s)	3.97E-4	Mn(OH)4-2	5.73E-39
/HA-Cu+2G(s)	3.45E-5	Mn+2	4.04E-16
/HAFe(II)+(s)	2.83E-08	Mn2(OH)3+	2.51E-36
/HA-Fe+2G(s)	3.48E-07	Mn2OH+3	9.46E-36
/HA-H+1G(s)	1.67E-4	MnOH+	2.34E-20
/HAMn+(s)	4.03E-09	OH-	2.31E-08
/HA-Mn+2G(s)	1.25E-07	Pb(OH)2 (aq)	3.50E-23
/HAPb+(s)	5.58E-09	Pb(OH)3-	8.08E-28
/HA-Pb+2G(s)	2.56E-10	Pb+2	8.30E-19
/HAZn+(s)	6.32E-09	Pb2OH+3	6.33E-37
/HA-Zn+2G(s)	1.87E-08	Pb3(OH)4+2	2.03E-53
/HHA(s)	0.03	Pb4(OH)4+4	1.69E-68
AsO4-3	1.43E-14	PbOH+	4.80E-20
Cd(OH)2 (aq)	2.83E-26	Z-(6)(s)	-1.44E-3
Cd(OH)3-	6.39E-33	Zn(OH)2 (aq)	4.05E-21
Cd(OH)4-2	1.51E-40	Zn(OH)3-	2.95E-26
Cd+2	1.06E-18	Zn(OH)4-2	1.08E-32
Cd2OH+3	1.04E-39	Zn+2	6.05E-17
CdOH+	1.94E-22	Zn2OH+3	8.45E-36
Cu(OH)2 (aq)	3.45E-17	ZnOH+	1.39E-19
Cu(OH)3-	3.08E-21		

Table S6 Mineral speciation and concentration in soil solution treated with 10 mg/L nCuO

Mineral species	**Concentration (mol/L)**	**Mineral species**	**Concentration (mol/L)**
(6)Cd+2D(s)	2.05E-09	Cu(OH)4-2	3.64E-29
(6)Cu+2D(s)	3.40E-5	Cu+2	1.78E-14
(6)Fe+2D(s)	1.72E-06	Cu2(OH)2+2	3.37E-26
(6)H+1D(s)	1.22E-3	Cu2OH+3	1.13E-28
(6)Mn+2D(s)	2.09E-07	Cu3(OH)4+2	1.01E-37
(6)Pb+2D(s)	1.03E-09	CuOH+	1.03E-15
(6)Zn+2D(s)	2.23E-07	Fe(OH)2 (aq)	9.54E-24
/HA-(s)	1.60E-3	Fe(OH)3-	5.53E-28
/HA2Cd(s)	5.91E-14	Fe+2	9.00E-16
/HA2Cu(s)	7.93E-06	FeOH+	6.56E-19
/HA2CuOH(s)	8.57E-12	H+1	5.50E-07
/HA2Pb(s)	1.10E-09	H2AsO4-	1.48E-08
/HA2Zn(s)	4.53E-12	H3AsO4	1.62E-12
/HACd+(s)	2.66E-10	HAsO4-2	2.75E-09
/HA-Cd+2G(s)	3.64E-10	HFA-dum(s)	1.30E-3
/HACu+(s)	7.78E-5	Mn(OH)4-2	1.10E-39
/HA-Cu+2G(s)	6.03E-06	Mn+2	1.95E-16
/HAFe(II)+(s)	1.80E-08	Mn2(OH)3+	2.93E-37
/HA-Fe+2G(s)	3.05E-07	Mn2OH+3	1.75E-36
/HA-H+1G(s)	2.17E-4	MnOH+	8.96E-21
/HAMn+(s)	1.55E-09	OH-	1.83E-08
/HA-Mn+2G(s)	6.60E-08	Pb(OH)2 (aq)	1.44E-23
/HAPb+(s)	4.97E-09	Pb(OH)3-	2.63E-28
/HA-Pb+2G(s)	1.83E-10	Pb+2	5.40E-19
/HAZn+(s)	1.17E-08	Pb2OH+3	2.13E-37
/HA-Zn+2G(s)	3.95E-08	Pb3(OH)4+2	2.22E-54
/HHA(s)	0.04	Pb4(OH)4+4	1.21E-69
AsO4-3	7.96E-15	PbOH+	2.48E-20
Cd(OH)2 (aq)	1.81E-26	Z-(6)(s)	-1.53E-3
Cd(OH)3-	3.24E-33	Zn(OH)2 (aq)	4.92E-21
Cd(OH)4-2	6.08E-41	Zn(OH)3-	2.85E-26
Cd+2	1.08E-18	Zn(OH)4-2	8.30E-33
Cd2OH+3	8.46E-40	Zn+2	1.17E-16
CdOH+	1.56E-22	Zn2OH+3	2.50E-35
Cu(OH)2 (aq)	3.47E-18	ZnOH+	2.13E-19
Cu(OH)3-	2.46E-22		

Table S7 Mineral speciation and concentration in soil solution treated with 850 mg/L $CuCl_2 \cdot 2H_2O$

Mineral species	Concentration (mol/L)	Mineral species	Concentration (mol/L)
(6)Cd+2D(s)	3.52E-09	Cu(OH)4-2	1.35E-31
(6)Cu+2D(s)	9.60E-08	Cu+2	2.64E-17
(6)Fe+2D(s)	1.40E-06	Cu2(OH)2+2	1.17E-31
(6)H+1D(s)	1.39E-3	Cu2OH+3	3.11E-34
(6)Mn+2D(s)	2.02E-07	Cu3(OH)4+2	8.18E-46
(6)Pb+2D(s)	1.38E-09	CuOH+	1.92E-18
(6)Zn+2D(s)	1.34E-07	Fe(OH)2 (aq)	6.45E-24
/HA-(s)	1.63E-3	Fe(OH)3-	4.71E-28
/HA2Cd(s)	1.23E-13	Fe+2	3.85E-16
/HA2Cu(s)	2.74E-08	FeOH+	3.52E-19
/HA2CuOH(s)	3.03E-14	H+1	4.37E-07
/HA2Pb(s)	1.81E-09	H2AsO4-	5.32E-08
/HA2Zn(s)	3.21E-12	H3AsO4	4.63E-12
/HACd+(s)	4.25E-10	HAsO4-2	1.25E-08
/HA-Cd+2G(s)	5.81E-10	HFA-dum(s)	1.40E-3
/HACu+(s)	2.11E-07	Mn(OH)4-2	1.40E-39
/HA-Cu+2G(s)	1.58E-08	Mn+2	9.87E-17
/HAFe(II)+(s)	1.20E-08	Mn2(OH)3+	1.50E-37
/HA-Fe+2G(s)	2.31E-07	Mn2OH+3	5.65E-37
/HA-H+1G(s)	2.30E-4	MnOH+	5.71E-21
/HAMn+(s)	1.23E-09	OH-	2.31E-08
/HA-Mn+2G(s)	5.94E-08	Pb(OH)2 (aq)	1.60E-23
/HAPb+(s)	6.50E-09	Pb(OH)3-	3.69E-28
/HA-Pb+2G(s)	2.28E-10	Pb+2	3.79E-19
/HAZn+(s)	6.22E-09	Pb2OH+3	1.32E-37
/HA-Zn+2G(s)	2.21E-08	Pb3(OH)4+2	1.93E-54
/HHA(s)	0.04	Pb4(OH)4+4	7.36E-70
AsO4-3	4.55E-14	PbOH+	2.19E-20
Cd(OH)2 (aq)	2.57E-26	Z-(6)(s)	-1.63E-3
Cd(OH)3-	5.81E-33	Zn(OH)2 (aq)	2.46E-21
Cd(OH)4-2	1.37E-40	Zn(OH)3-	1.80E-26
Cd+2	9.66E-19	Zn(OH)4-2	6.58E-33
Cd2OH+3	8.58E-40	Zn+2	3.68E-17
CdOH+	1.77E-22	Zn2OH+3	3.13E-36
Cu(OH)2 (aq)	8.13E-21	ZnOH+	8.47E-20
Cu(OH)3-	7.25E-25		

Table S8 Mineral speciation and concentration in soil solution treated with 170 mg/L $CuCl_2 \cdot 2H_2O$

Mineral species	**Concentration (mol/L)**	**Mineral species**	**Concentration (mol/L)**
(6)Cd+2D(s)	1.83E-09	Cu(OH)4-2	3.60E-31
(6)Cu+2D(s)	1.04E-07	Cu+2	1.11E-17
(6)Fe+2D(s)	1.41E-06	Cu2(OH)2+2	5.23E-32
(6)H+1D(s)	1.42E-3	Cu2OH+3	8.79E-35
(6)Mn+2D(s)	6.84E-07	Cu3(OH)4+2	3.90E-46
(6)Pb+2D(s)	9.10E-10	CuOH+	1.29E-18
(6)Zn+2D(s)	1.48E-07	Fe(OH)2 (aq)	6.40E-24
/HA-(s)	1.65E-3	Fe(OH)3-	7.40E-28
/HA2Cd(s)	6.29E-14	Fe+2	1.52E-16
/HA2Cu(s)	2.90E-08	FeOH+	2.20E-19
/HA2CuOH(s)	3.27E-14	H+1	2.76E-07
/HA2Pb(s)	1.17E-09	H2AsO4-	2.57E-08
/HA2Zn(s)	3.47E-12	H3AsO4	1.41E-12
/HACd+(s)	2.13E-10	HAsO4-2	9.57E-09
/HA-Cd+2G(s)	2.97E-10	HFA-dum(s)	1.42E-3
/HACu+(s)	2.19E-07	Mn(OH)4-2	1.17E-38
/HA-Cu+2G(s)	1.68E-08	Mn+2	1.31E-16
/HAFe(II)+(s)	1.16E-08	Mn2(OH)3+	1.05E-36
/HA-Fe+2G(s)	2.28E-07	Mn2OH+3	1.57E-36
/HA-H+1G(s)	2.30E-4	MnOH+	1.20E-20
/HAMn+(s)	3.98E-09	OH-	3.66E-08
/HA-Mn+2G(s)	1.97E-07	Pb(OH)2 (aq)	1.04E-23
/HAPb+(s)	4.12E-09	Pb(OH)3-	3.79E-28
/HA-Pb+2G(s)	1.47E-10	Pb+2	9.78E-20
/HAZn+(s)	6.58E-09	Pb2OH+3	1.39E-38
/HA-Zn+2G(s)	2.39E-08	Pb3(OH)4+2	2.10E-55
/HHA(s)	0.04	Pb4(OH)4+4	2.06E-71
AsO4-3	5.52E-14	PbOH+	8.97E-21
Cd(OH)2 (aq)	1.32E-26	Z-(6)(s)	-1.65E-3
Cd(OH)3-	4.71E-33	Zn(OH)2 (aq)	2.67E-21
Cd(OH)4-2	1.76E-40	Zn(OH)3-	3.09E-26
Cd+2	1.97E-19	Zn(OH)4-2	1.79E-32
Cd2OH+3	5.64E-41	Zn+2	1.59E-17
CdOH+	5.71E-23	Zn2OH+3	9.24E-37
Cu(OH)2 (aq)	8.63E-21	ZnOH+	5.80E-20
Cu(OH)3-	1.22E-24		

Table S9 Mineral speciation and concentration in soil solution treated with 85 mg/L $CuCl_2 \cdot 2H_2O$

Mineral species	Concentration (mol/L)	Mineral species	Concentration (mol/L)
(6)Cd+2D(s)	2.41E-09	Cu(OH)4-2	1.50E-30
(6)Cu+2D(s)	4.32E-7	Cu+2	4.64E-17
(6)Fe+2D(s)	1.55E-06	Cu2(OH)2+2	9.08E-31
(6)H+1D(s)	1.43E-3	Cu2OH+3	1.52E-33
(6)Mn+2D(s)	4.71E-6	Cu3(OH)4+2	2.82E-44
(6)Pb+2D(s)	1.22E-09	CuOH+	5.36E-18
(6)Zn+2D(s)	1.29E-07	Fe(OH)2 (aq)	7.01E-24
/HA-(s)	0.0016765	Fe(OH)3-	8.10E-28
/HA2Cd(s)	8.23E-14	Fe+2	1.66E-16
/HA2Cu(s)	1.20E-07	FeOH+	2.41E-19
/HA2CuOH(s)	1.38E-13	H+1	2.76E-07
/HA2Pb(s)	1.55E-09	H2AsO4-	3.27E-08
/HA2Zn(s)	3.00E-12	H3AsO4	1.80E-12
/HACd+(s)	2.74E-10	HAsO4-2	1.22E-08
/HA-Cd+2G(s)	3.85E-10	HFA-dum(s)	1.44E-3
/HACu+(s)	8.94E-07	Mn(OH)4-2	8.06E-38
/HA-Cu+2G(s)	6.90E-08	Mn+2	9.00E-16
/HAFe(II)+(s)	1.25E-08	Mn2(OH)3+	4.96E-35
/HA-Fe+2G(s)	2.47E-07	Mn2OH+3	7.44E-35
/HA-H+1G(s)	2.29E-4	MnOH+	8.25E-20
/HAMn+(s)	2.69E-08	OH-	3.66E-08
/HA-Mn+2G(s)	1.34E-06	Pb(OH)2 (aq)	1.39E-23
/HAPb+(s)	5.39E-09	Pb(OH)3-	5.08E-28
/HA-Pb+2G(s)	1.95E-10	Pb+2	1.31E-19
/HAZn+(s)	5.61E-09	Pb2OH+3	2.50E-38
/HA-Zn+2G(s)	2.06E-08	Pb3(OH)4+2	5.03E-55
/HHA(s)	0.04	Pb4(OH)4+4	6.62E-71
AsO4-3	7.02E-14	PbOH+	1.20E-20
Cd(OH)2 (aq)	1.73E-26	Z-(6)(s)	-1.68E-3
Cd(OH)3-	6.21E-33	Zn(OH)2 (aq)	2.32E-21
Cd(OH)4-2	2.32E-40	Zn(OH)3-	2.69E-26
Cd+2	2.59E-19	Zn(OH)4-2	1.56E-32
Cd2OH+3	9.79E-41	Zn+2	1.38E-17
CdOH+	7.52E-23	Zn2OH+3	6.99E-37
Cu(OH)2 (aq)	3.59E-20	ZnOH+	5.05E-20
Cu(OH)3-	5.08E-24		

Table S10 Mineral speciation and concentration in soil solution treated with 17 mg/L $CuCl_2 \cdot 2H_2O$

Mineral species	Concentration (mol/L)	Mineral species	Concentration (mol/L)
(6)Cd+2D(s)	2.18E-09	Cu(OH)4-2	1.00E-31
(6)Cu+2D(s)	2.87E-08	Cu+2	3.09E-18
(6)Fe+2D(s)	1.79E-06	Cu2(OH)2+2	4.04E-33
(6)H+1D(s)	1.41E-3	Cu2OH+3	6.78E-36
(6)Mn+2D(s)	3.14E-07	Cu3(OH)4+2	8.34E-48
(6)Pb+2D(s)	9.42E-10	CuOH+	3.57E-19
(6)Zn+2D(s)	2.14E-07	Fe(OH)2 (aq)	8.13E-24
/HA-(s)	1.65E-3	Fe(OH)3-	9.40E-28
/HA2Cd(s)	7.50E-14	Fe+2	1.93E-16
/HA2Cu(s)	8.06E-09	FeOH+	2.80E-19
/HA2CuOH(s)	9.07E-15	H+1	2.76E-07
/HA2Pb(s)	1.21E-09	H2AsO4-	2.43E-08
/HA2Zn(s)	5.03E-12	H3AsO4	1.33E-12
/HACd+(s)	2.55E-10	HAsO4-2	9.03E-09
/HA-Cd+2G(s)	3.54E-10	HFA-dum(s)	1.42E-3
/HACu+(s)	6.10E-08	Mn(OH)4-2	5.40E-39
/HA-Cu+2G(s)	4.66E-09	Mn+2	6.03E-17
/HAFe(II)+(s)	1.48E-08	Mn2(OH)3+	2.23E-37
/HA-Fe+2G(s)	2.91E-07	Mn2OH+3	3.34E-37
/HA-H+1G(s)	2.30E-4	MnOH+	5.53E-21
/HAMn+(s)	1.84E-09	OH-	3.66E-08
/HA-Mn+2G(s)	9.09E-08	Pb(OH)2 (aq)	1.08E-23
/HAPb+(s)	4.29E-09	Pb(OH)3-	3.94E-28
/HA-Pb+2G(s)	1.53E-10	Pb+2	1.02E-19
/HAZn+(s)	9.58E-09	Pb2OH+3	1.50E-38
/HA-Zn+2G(s)	3.47E-08	Pb3(OH)4+2	2.35E-55
/HHA(s)	0.04	Pb4(OH)4+4	2.40E-71
AsO4-3	5.21E-14	PbOH+	9.31E-21
Cd(OH)2 (aq)	1.57E-26	Z-(6)(s)	-0.0016503
Cd(OH)3-	5.62E-33	Zn(OH)2 (aq)	3.87E-21
Cd(OH)4-2	2.10E-40	Zn(OH)3-	4.47E-26
Cd+2	2.35E-19	Zn(OH)4-2	2.60E-32
Cd2OH+3	8.02E-41	Zn+2	2.30E-17
CdOH+	6.80E-23	Zn2OH+3	1.94E-36
Cu(OH)2 (aq)	2.40E-21	ZnOH+	8.41E-20
Cu(OH)3-	3.39E-25		