Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary Information: Copper Oxide Nanoparticle Dissolution at Alkaline pH is Controlled by Dissolved Organic Matter: Influence of Soil-Derived Organic Matter, Wheat, Bacteria, and Nanoparticle Coating

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Table S1: Dissolved Cu from CuO NPs as affected by ligands from published studies. Arrow indicates whether natural organic matter from the treatment solutions increased or decreased solubility compared to the best available control(s).

Author	Solution, pH	Cu concentration (mg/L)
Conway et al. (2015)	Hydroponic media, pH 5.9	~0.45
	Wastewater, pH 7.6	~0.38
	Storm Runoff, pH 6.6	~0.32
	Freshwater, pH 6.32	~0.28 ↓
Pradhan et al. (2016) Sigma Aldrich NPs only	Stream water, pH 5.8	4.04
	Stream water + humic acid, pH 5.8	0.45 ↓
Peng et al. (2015)	Water, pH 7	<0.25
	Water + humic acid, pH 7	~1.5 ↑
Jiang et al. (2017)	Water, pH 7	~0.05
	Water + humic acid, pH 7	~0.3 ↑
	Water + fulvic acid, pH 7	~0.1 ↑
Peng et al. (2017)	Water, pH 7	0.19
	Water + humic acid	2.80 ↑

Table S2: Visual schematic of the treatments in this study. Each cell contains 6 replicates. The two cells marked with * indicate that these treatments were the only treatments with low dissolved organic carbon and CuO NPs, resulting in difficulty removing the NPs by centrifugation. See Fig. S2 for quantitative measurements of NP removal by single centrifugation, double centrifugation, and ultrafiltration.

Each cell contains 6 replicates		3.34 mM $Ca(NO_3)_2$ ("Electrolyte")		OrgM SPE		AgrM SPE		GarM SPE	
		Un-planted	Planted	Un-planted	Planted	Un-planted	Planted	Un-planted	Planted
No *Pc*O6	No CuO NPs								
	CuO NPs	*							
*Pc*O6	No CuO NPs								
	CuO NPs	*							

Table S3: Characteristics of soils. Soil samples were collected in 2014 for preliminary experiments in 2015-2016 and tested at a laboratory certified under the North American Proficiency Testing Program for Agricultural Labs. Soils were re-collected in 2016 for use in this study.

Soil characteristics			
Soil abbreviation	OrgM	AgrM	GarM
Name origin	Organic farm, Millville	Agricultural field, Millville	Community garden, Millville
Soil series, texture	Millville silt loam	Millville silt loam	Millville silt loam
Particle size distribution (% sand/silt/clay)	19/56/26	22/56/23	13/59/28
Cultivation	organic certified	commercial production	unknown amendments
Crop	continuous green cover and periodic compost amendments	winter wheat/alfalfa rotation	varied (community garden)
pH	7.7	7.8	7.8
EC (µS/cm)	1040	500	600
Phosphorus (mg/kg)	52.1	10.1	19.3
Potassium (mg/kg)	434	111	369
Ammonium (mg/kg N)	2.01	2.43	< 1.25
Nitrate (mg/kg N)	31.8	11.5	10.4
Sulfate (mg/kg S)	6.5	3.6	3.3
Organic matter (% of whole soil)	5.6	3.0	4.1
Cation exchange capacity (cmol/kg)	20.0	13.8	21.0
Calcium carbonate (%)	14.6	14.1	16.1
Saturated water content (m/m %)	46.5	41.0	45.5
DTPA – Fe (mg/kg)	9.8	8.95	10.5
DTPA – Cu (mg/kg)	1.44	1.29	2.72
DTPA – Mn (mg/kg)	16.3	14.1	13.8
DTPA – Zn (mg/kg)	3.07	1.66	1.62

Table S4: Full characterization of SPEs. Measurements = average of 3 replicates. Blank = below detection.

Soil name	OrgM	AgrM	GarM
Na (mg/L)	11.8	9.4	27.5
Mg (mg/L)	55.7	17.9	145.9
Al (μg/L)	8.3	6.9	<4
K (mg/L)	28.7	4.2	299.1
Ca (mg/L)	167.6	97.4	372.3
V (μg/L)	5.2	5.4	7.5
Cr (μg/L)	9.6	1.1	1.5
Mn (μg/L)	5.5	12.4	118.0
Fe (μg/L)	67.1	14.6	53.9
Co (μg/L)	1.6	1.5	11.1
Ni (μg/L)	5.7	6.7	20.3
Cu (μg/L)	13.4	22.8	48.4
Zn (μg/L)	51.1	34.1	48.7
As (μg/L)	7.2	6.1	18.8
Se (μg/L)	1.0	4.3	1.8
Sr (μg/L)	668.7	97.7	1124.0
Ba (μg/L)	402.0	161.6	640.4
Gluconate (mg/L)	1.9	3.9	< 0.5
Lactate (mg/L)	< 0.5	< 0.5	< 0.5
Acetate (mg/L)	0.7	< 0.5	< 0.5
Isobutyrate (mg/L)	< 0.5	< 0.5	<0.5
Butyrate (mg/L)	< 0.5	< 0.5	1.03
Isovalerate (mg/L)	< 0.5	< 0.5	<0.5
Valerate (mg/L)	< 0.5	< 0.5	< 0.5
Chloride (mg/L)	50.2	5.6	61.6
Nitrite (mg/L N)	5.7	11.8	2.80
Nitrate (mg/L N)	148.6	12.6	573.8
Sulfate (mg/L)	36.8	18.4	194.8
Oxalate (mg/L)	< 0.5	< 0.5	< 0.5
Phosphate (mg/L P)	< 0.5	< 0.5	1.99
Citrate (mg/L)	< 0.5	< 0.5	< 0.5
Alkalinity (mg /L $CaCO_3$)	340	450	490
EC (μS/cm)	735	391	3380
DOC (mg/L C)	42.7	73.4	305
Humic acids (mg/L C)	<0.8	<0.8	4.3
Fulvic acids (mg/L C)	28.3	38.0	165

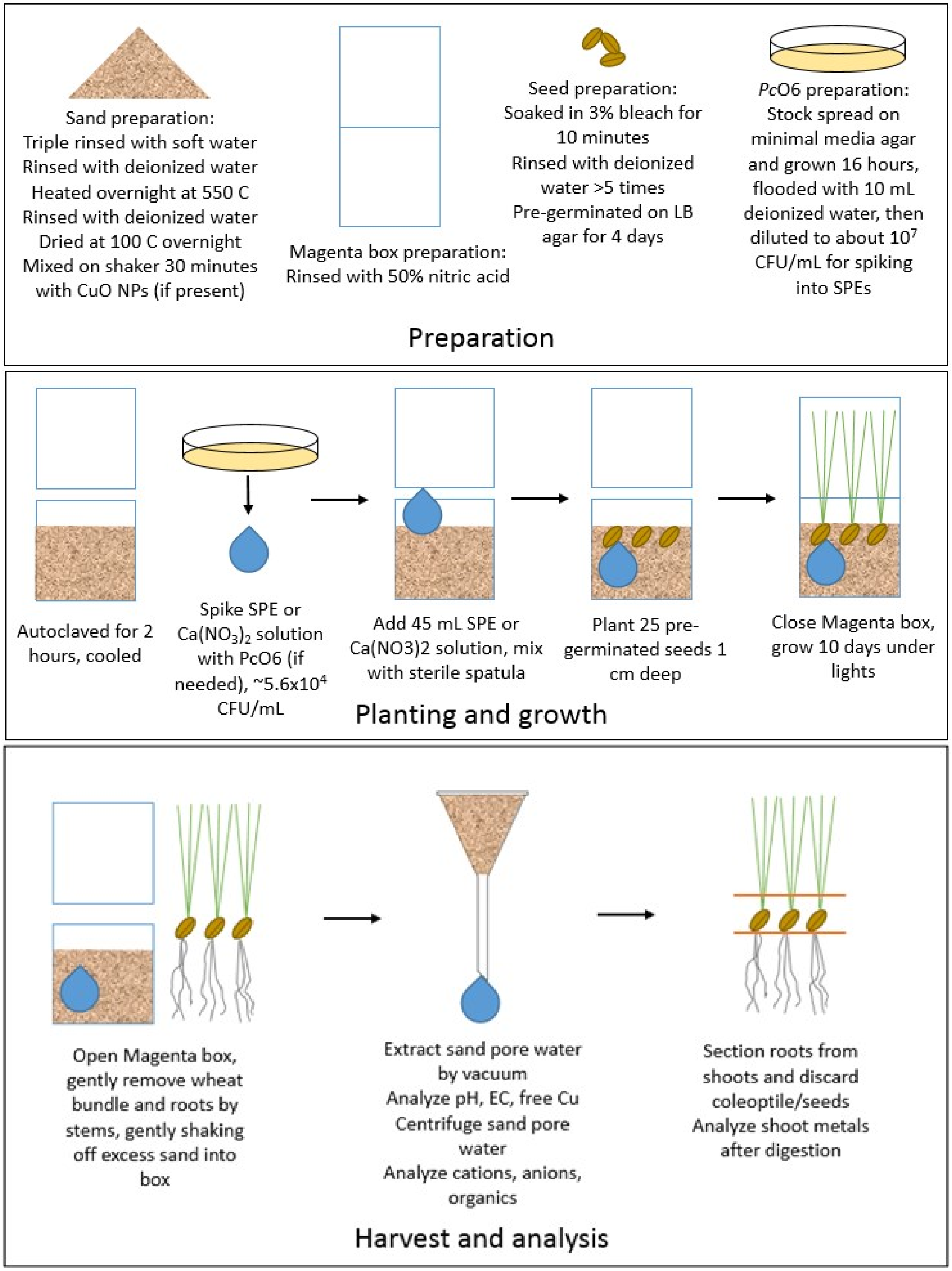

Fig. S1: Flow diagram of wheat preparation, planting/growth, and harvest/analysis.

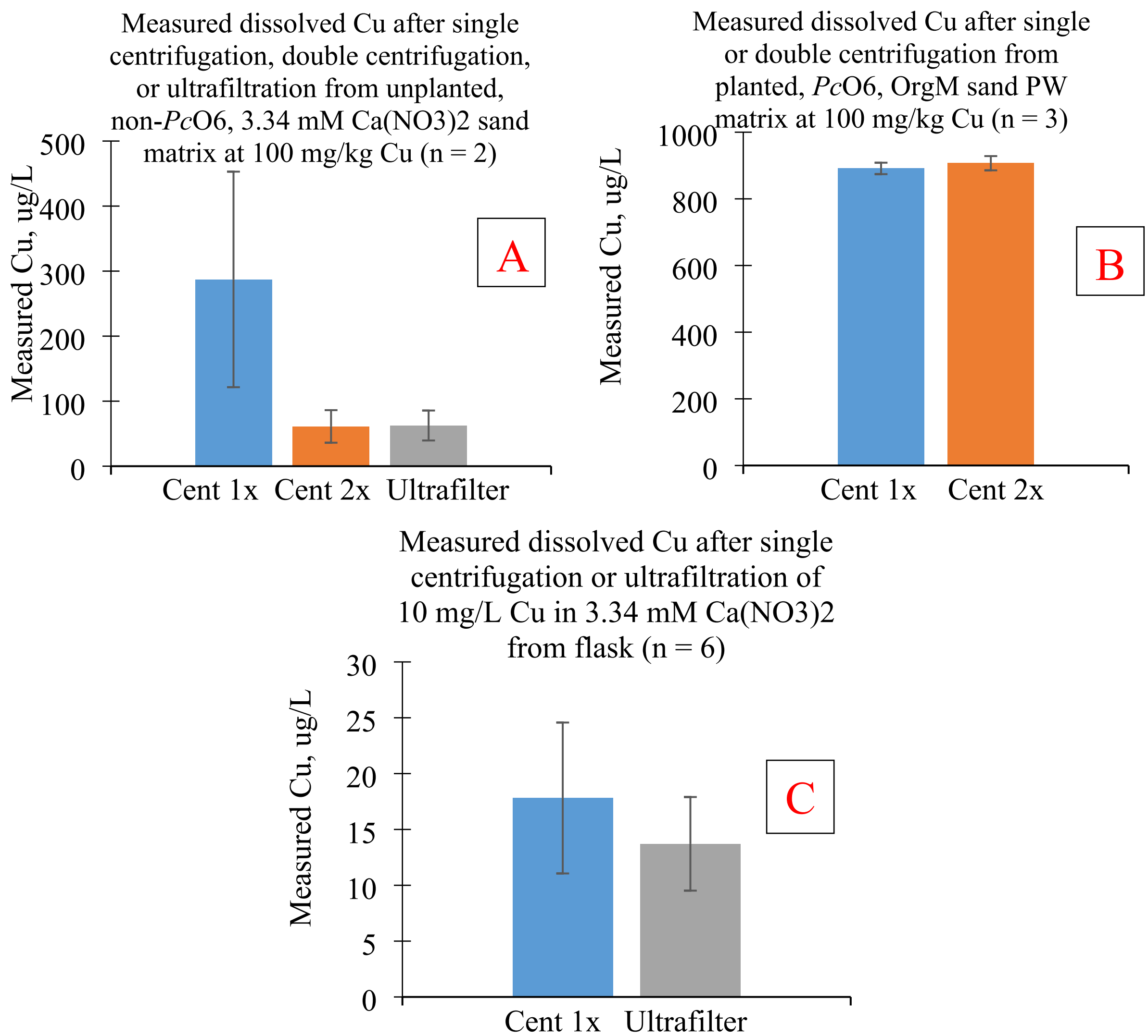

Fig. S2: NP removal comparisons of single or double centrifugation and/or ultrafiltration of: A) Pore water (PW) from CuO NPs at 100 mg/kg Cu/sand in the unplanted electrolyte sand at 10 days, B) CuO NPs at 100 mg/kg Cu/sand in the planted OrgM sand PW with *Pc*O6 at 10 days, and C) CuO NPs at 10 mg/L Cu in the electrolyte in a flask at 10 days. Error bars show standard deviation of the measurements.

Explanation of Fig. S2: NPs were not efficiently removed by single centrifugation of the sand PW from the unplanted 3.34 mM $Ca(NO_3)_2$ sand PW at harvest (Fig. S2A); in these centrifugation tubes, there was visible but inconsistent pelleting of the NPs after centrifugation and suspended NPs were seen. A second centrifugation removed more Cu from suspension (Fig. S2A). The Cu measured after a double centrifugation matched Cu measured after ultrafiltration, as expected (Fig. S2A); ultrafilters are highly efficient at removing NPs and complexes > 3 kDa, of which no > 3 kDa complexes should exist in this unplanted, non-SPE matrix. By contrast, double centrifugation of a planted, *Pc*O6, OrgM sand PW removed no additional Cu from suspension and clear pellets formed on the first centrifugation (Fig. S2B). The DOC present in this sand PW allowed NP removal in a single centrifugation. Finally, a lower dose of NPs, 10 mg/L Cu, in 3.34 mM $Ca(NO_3)_2$ with no root or *Pc*O6 exposure was as efficiently removed by single centrifugation as ultrafiltration (Fig S2C). The higher NP dose from a sand matrix raises the risk of resuspension during removal of the supernatant, but that risk is avoided with a lower NP dose.

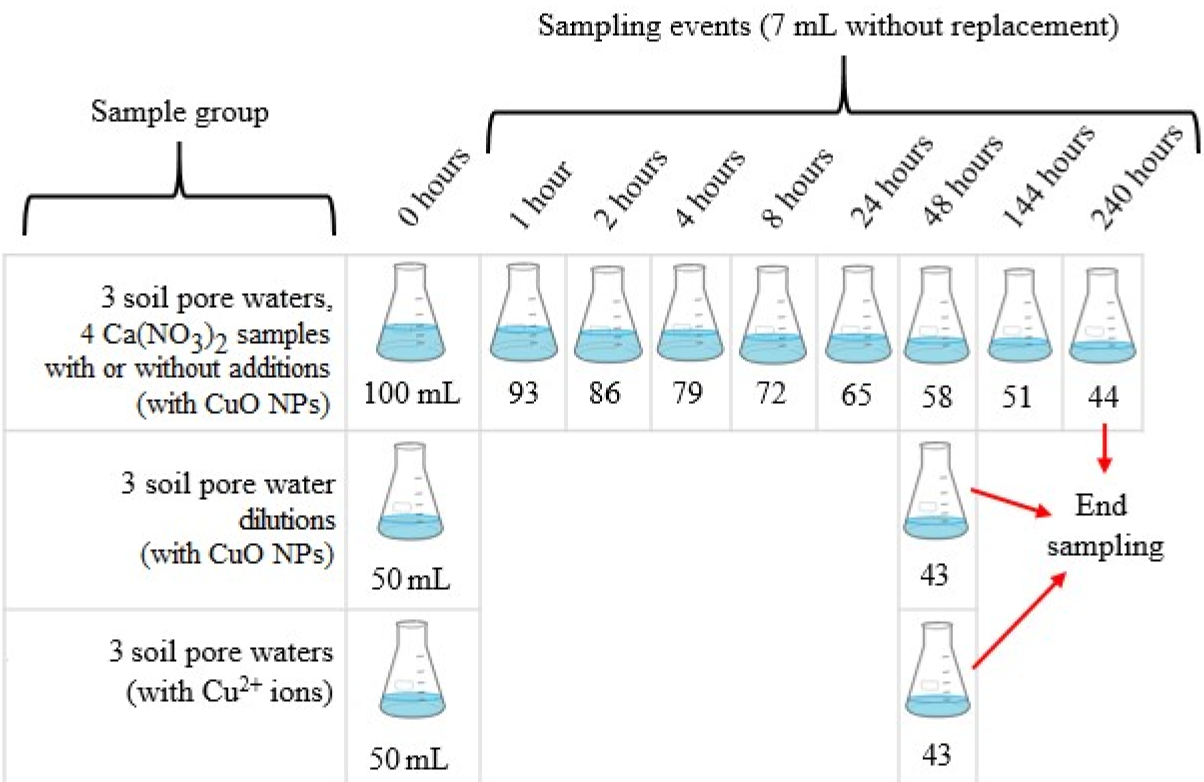

Fig. S3: Schematic of sampling schedule for 240-hour batch solubility study in flask (top row) and 48-hour solubility studies in flasks (bottom rows).

Table S5. Conditional stability constants (K^c) and activity based constants (K^o) included in the modified geochemical database as calculated by the Davies equation.

Complex	log K_c	log K_0	Reference
HGluconate	3.66	3.87	Bechtold et al. 2002
CuGluconate	2.51	2.94	Gajda et al. 1998
CuGluconate$(OH)_3$	-20.96	-20.53	Gajda et al. 1998
CuGluconate$_2$	4.59	5.13	Gajda et al. 1998
CuGluconate$_2$(OH)	-0.6	-0.06	Gajda et al. 1998
CuGluconate$_2(OH)_2$	-8.28	-7.96	Gajda et al. 1998
Cu_2Gluconate$_2(OH)_3$	-7.25	-6.07	Gajda et al. 1998
Cu_2Gluconate$_2(OH)_4$	-15.46	-14.50	Gajda et al. 1998
FeGluconate	10.51	11.15	Bechtold et al. 2002
FeGluconate(OH)	9.03	10.10	Bechtold et al. 2002
FeGluconate$(OH)_2$	6.35	7.63	Bechtold et al. 2002
FeGluconate$(OH)_3$	1.78	3.06	Bechtold et al. 2002
FeGluconate$(OH)_4$	-8.4	-7.33	Bechtold et al. 2002
FeGluconate$_2$	22.23	23.30	Bechtold et al. 2002
FeGluconate$_2$(OH)	18.22	19.50	Bechtold et al. 2002
FeGluconate$_2(OH)_2$	15.3	16.58	Bechtold et al. 2002
FeGluconate$_2(OH)_3$	9.84	10.91	Bechtold et al. 2002
FeGluconate$_2(OH)_4$	-1.15	-0.51	Bechtold et al. 2002
FeGluconate$_2(OH)_5$	-20	-20.01	Bechtold et al. 2002
Fe_2Gluconate$_2(OH)_7$	-1.42	0.50	Bechtold et al. 2002
CaFeGluconate$_2$	20.96	21.60	Bechtold et al. 2002
CaFeGluconate$_2$(OH)	22.47	23.75	Bechtold et al. 2002
CaFeGluconate$_2(OH)_2$	19.06	20.77	Bechtold et al. 2002
CaFeGluconate$_2(OH)_3$	14.82	16.74	Bechtold et al. 2002
CaFeGluconate$_2(OH)_4$	6.65	8.57	Bechtold et al. 2002
CaFeGluconate$_2(OH)_5$	-2.63	-0.92	Bechtold et al. 2002
CaFeGluconate	16.26	16.04	Bechtold et al. 2002
CaFeGluconate(OH)	13.89	14.53	Bechtold et al. 2002
CaFeGluconate$(OH)_2$	11.21	12.49	Bechtold et al. 2002
CaFeGluconate$(OH)_3$	7.13	8.84	Bechtold et al. 2002
CaFeGluconate$(OH)_4$	-0.99	0.93	Bechtold et al. 2002
CaFeGluconate$(OH)_5$	-11.01	-9.09	Bechtold et al. 2002
MgGluconate	0.7	1.21	Cannan and Kibrick 1938

BaGluconate	0.95	1.46	Cannan and Kibrick 1938
ZnGluconate	1.7	2.21	Cannan and Kibrick 1938
CaGluconate	1.8	1.80	Pallagi et al. 2010
Cu-DMA	18.7	19.98	Murakami et al. 1989
Fe-DMA	18.38	20.31	Murakami et al. 1989
Fe-DMA-OH	16.25	18.18	Murakami et al. 1989
Ca-DMA	3.34	4.62	Murakami et al. 1989
Mn-DMA	8.29	9.68	Murakami et al. 1989
Ni-DMA	14.78	16.06	Murakami et al. 1989
Zn-DMA	12.84	14.12	Murakami et al. 1989
H-DMA	9.55	10.19	Murakami et al. 1989
H2-DMA	17.33	18.40	Murakami et al. 1989
H3-DMA	20.73	22.01	Murakami et al. 1989
H4-DMA	23.45	24.73	Murakami et al. 1989
H5-DMA	25.38	26.45	Murakami et al. 1989

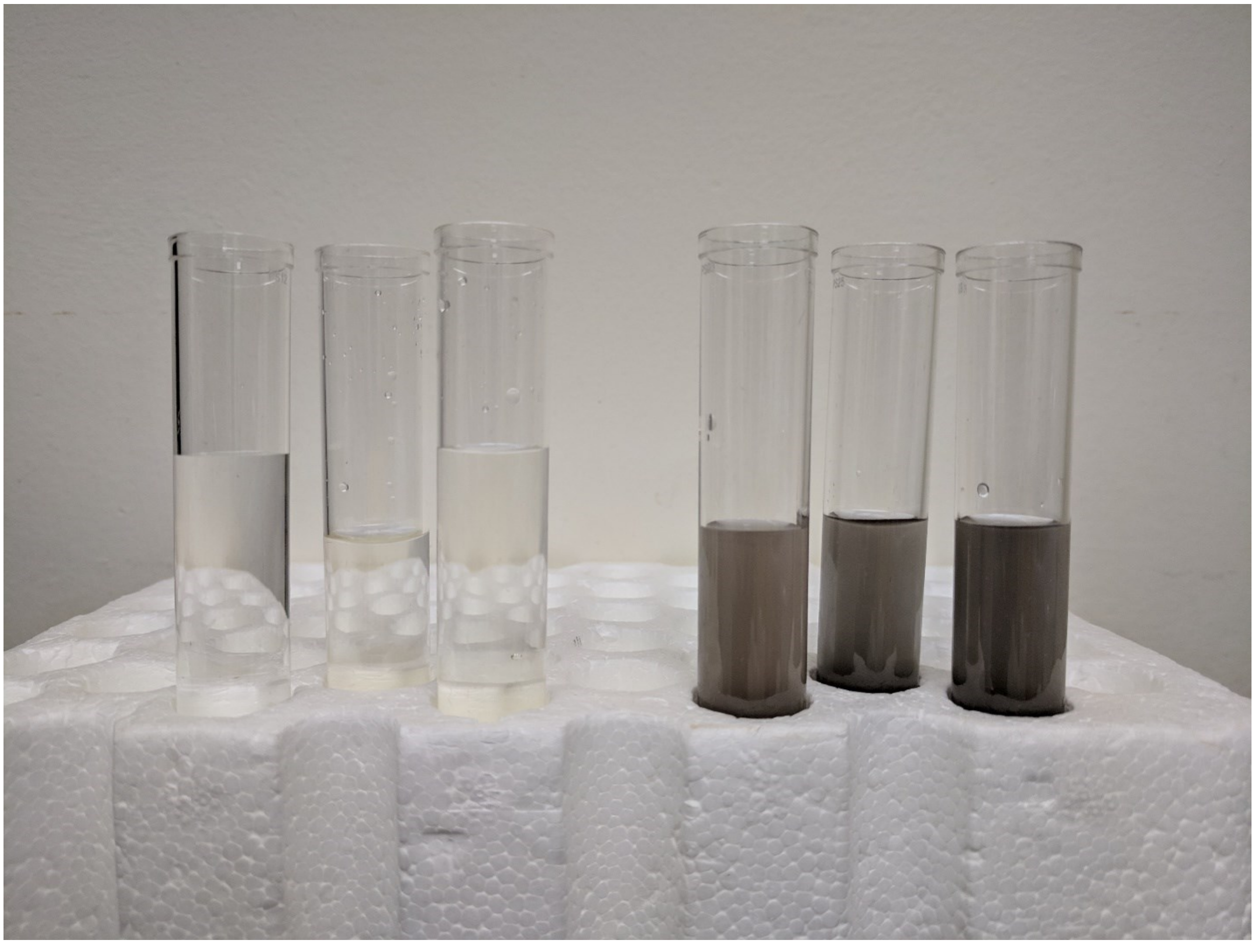

Fig. S4: Particles from CuO NPs treatments are visible in the planted sand PWs from systems with electrolyte or SPEs and CuO NPs immediately after extraction (right hand side). The sand PWs from systems with planted sand PWs of electrolyte and SPEs but no NPs are clear in comparison (left hand side). After time settling was observed.

Table S6: Correlations of PCA components in samples with CuO NPs. Bolded correlations are significant ($p < 0.05$) and bolded, red correlations are R > |0.5|. Correlations with an asterisk indicate correlations formed by two distinct groups of samples rather than a continuous relationship (see Fig. S5).

	Dissolved Cu	EC	pH	DMA	DOC	Sulfate	Nitrate	Nitrite
Gluconate	**0.719**	-0.035	**0.326**	**-0.452**	**0.666**	**0.250***	0.005	**-0.474**
Nitrite	**-0.379**	0.193	-0.028	**0.508**	**-0.493**	-0.094*	0.177	
Nitrate	**0.399***	**0.971**	**0.267***	-0.189	**0.442**	**0.820***		
Sulfate	**0.808***	**0.826***	**0.402***	0.043*	**0.742***			
DOC	**0.916**	**0.397**	**0.305**	-0.268				
DMA	**-0.313**	-0.005	-0.114					
pH	**0.292**	**0.415***						
EC	**0.323***							

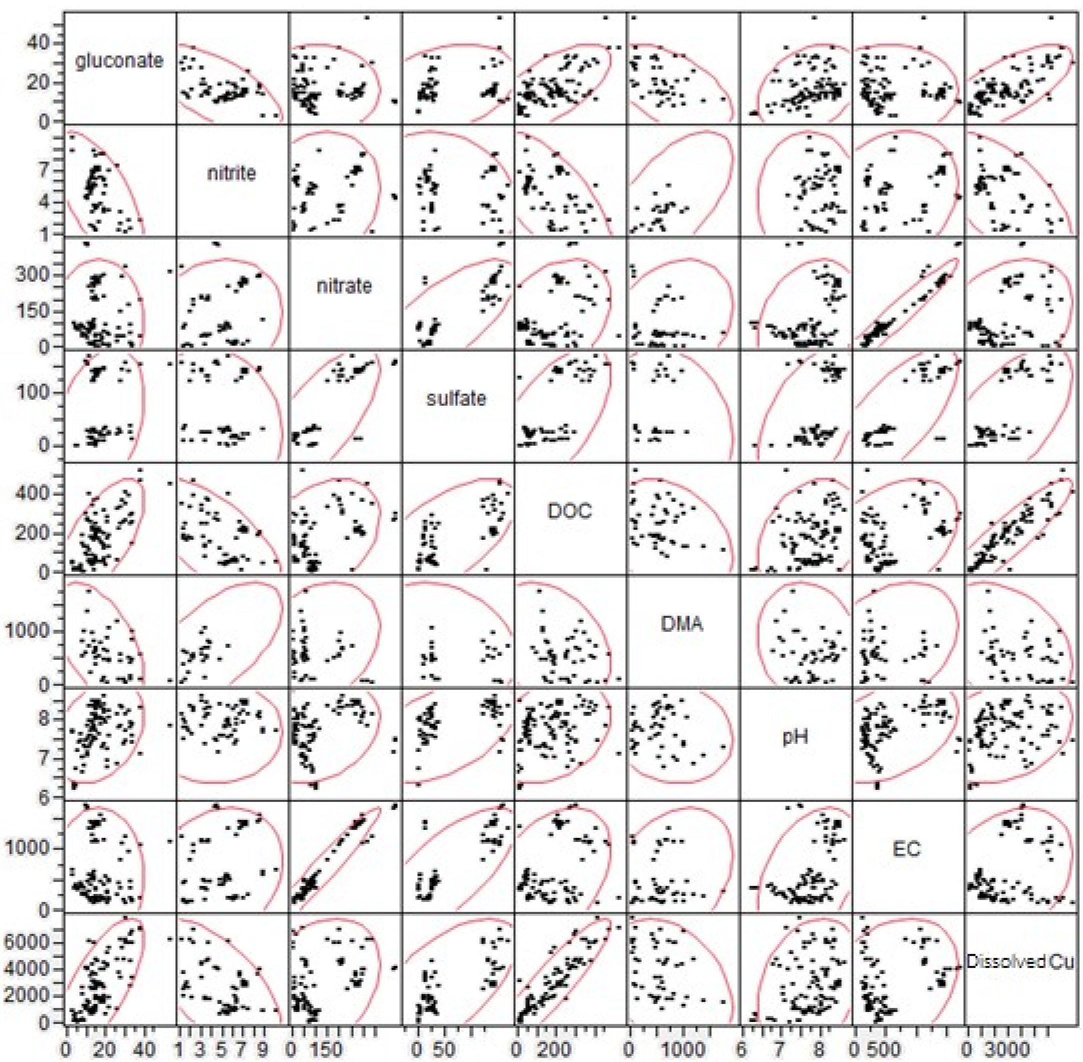

Fig. S5: Correlations of PCA components in samples with CuO NPs. Fig. S5 corresponds with Table S6. Note that some correlations (i.e. the correlation of dissolved Cu and sulfate) are due to two distinct groups of samples rather than a continuous relationship.

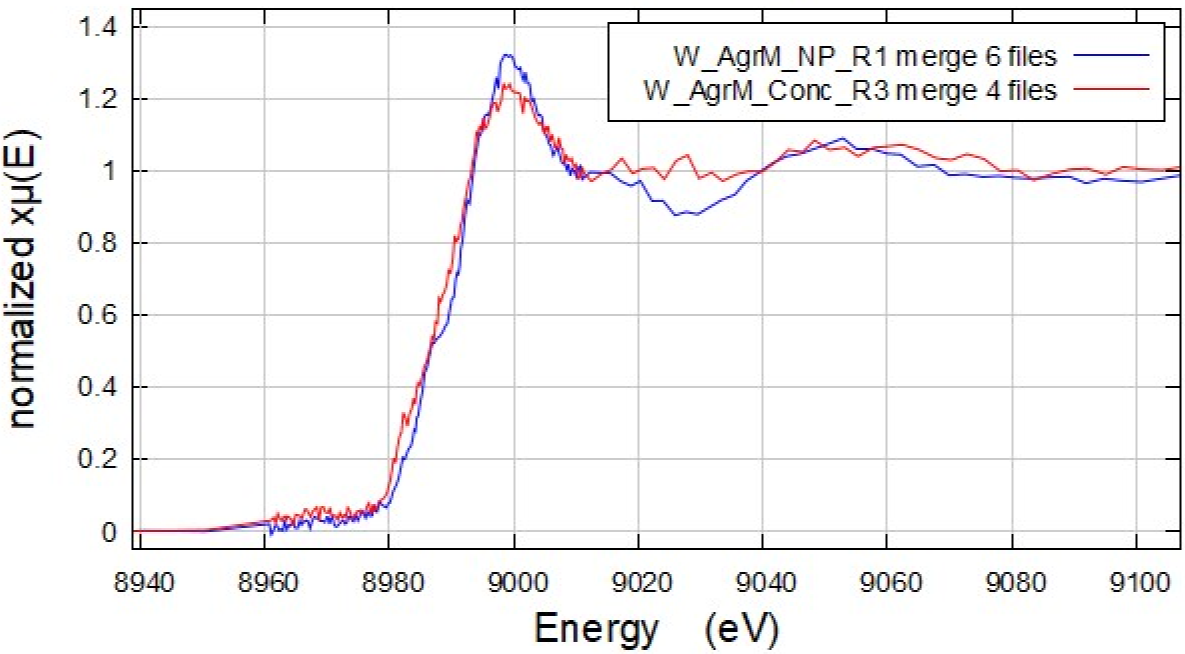

Fig. S6: XANES spectra of AgrM sand PW from wheat growth without *Pc*O6 colonization before removal of CuO NPs (blue line) and after (red line). The lack of the characteristic pre-white line shoulder in the red spectrum indicates that the CuO NPs were successfully removed by centrifugation, and the absence of shift in the edges indicates that the Cu was in the oxidized form.

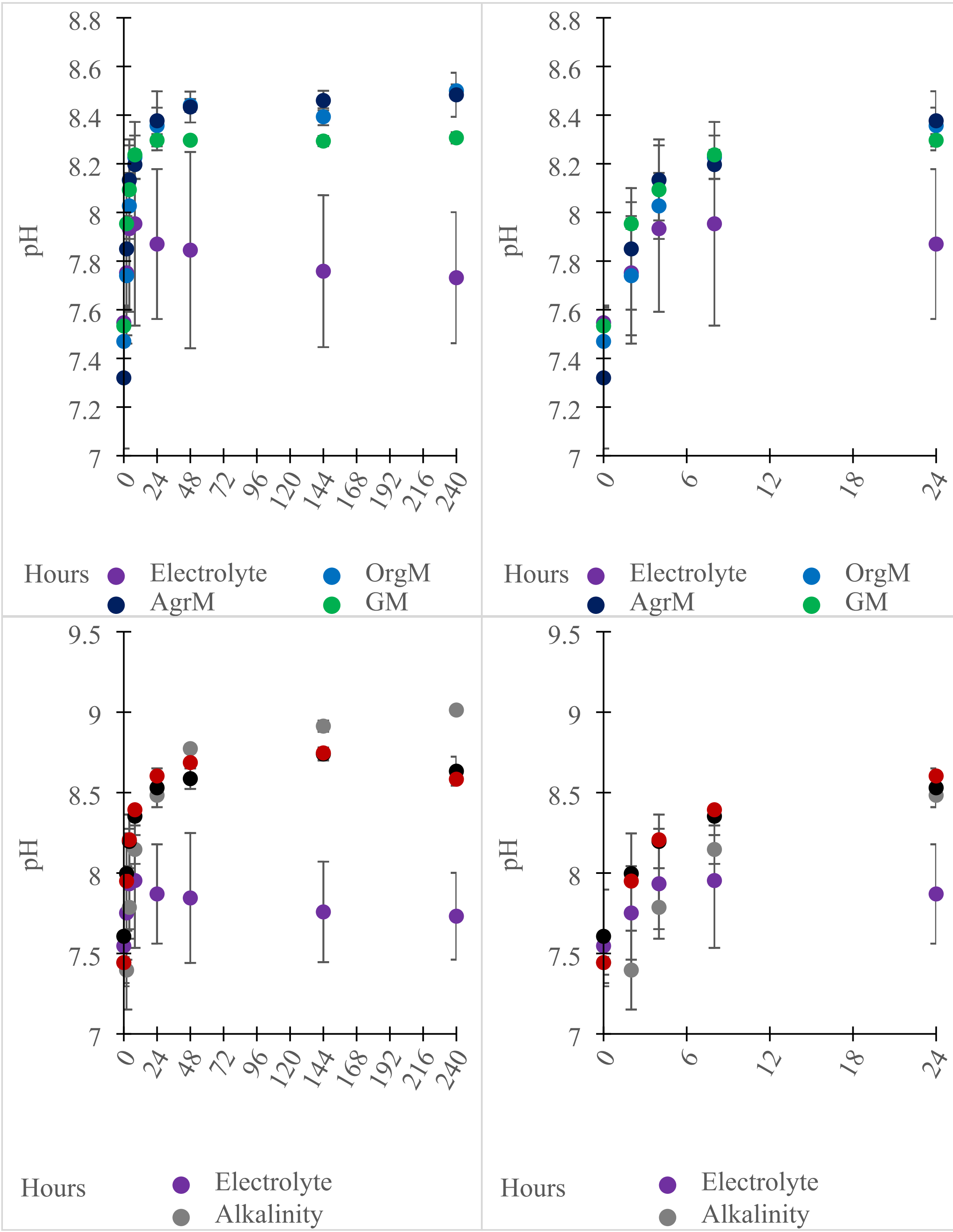

Fig. S7. pH in all SPEs (top) and electrolyte, alkalinity, phosphate, and fulvic acid treatments (bottom) with CuO NPs in flasks as a function of time. Points are average of independent sample measurements (n = 3, except n = 6 in electrolyte and n = 2 in AgrM after 8 hours due to bacterial contamination of one sample). Dunnett's test showed no differences from the electrolyte in any treatment during hours 0-8, and that every treatment was different from the electrolyte during hours 24-240.

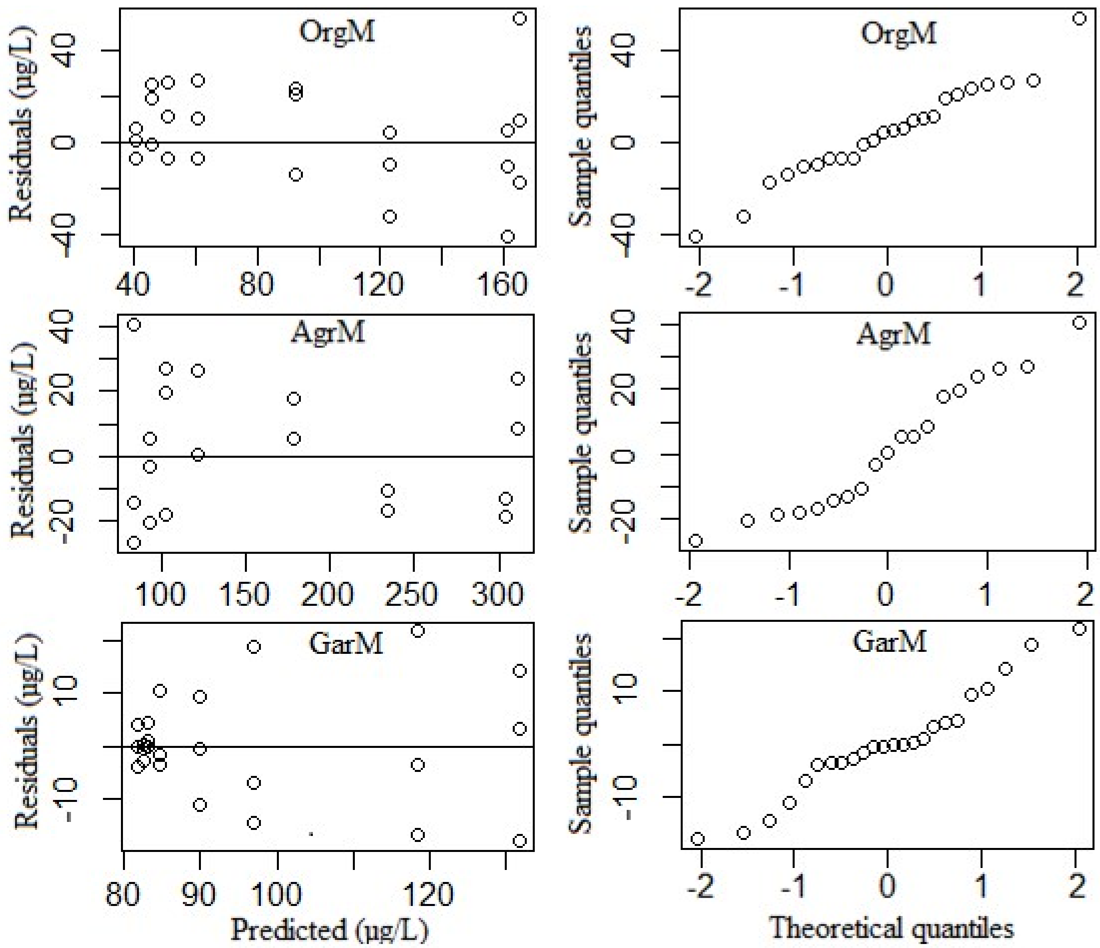

Fig. S8: Residuals (left) and normal quantile plots (right) from first order kinetics models for the SPEs. Valid models have residuals that average 0, and are identically, independently, normally distributed. The normal quantile plot should follow a straight diagonal line.

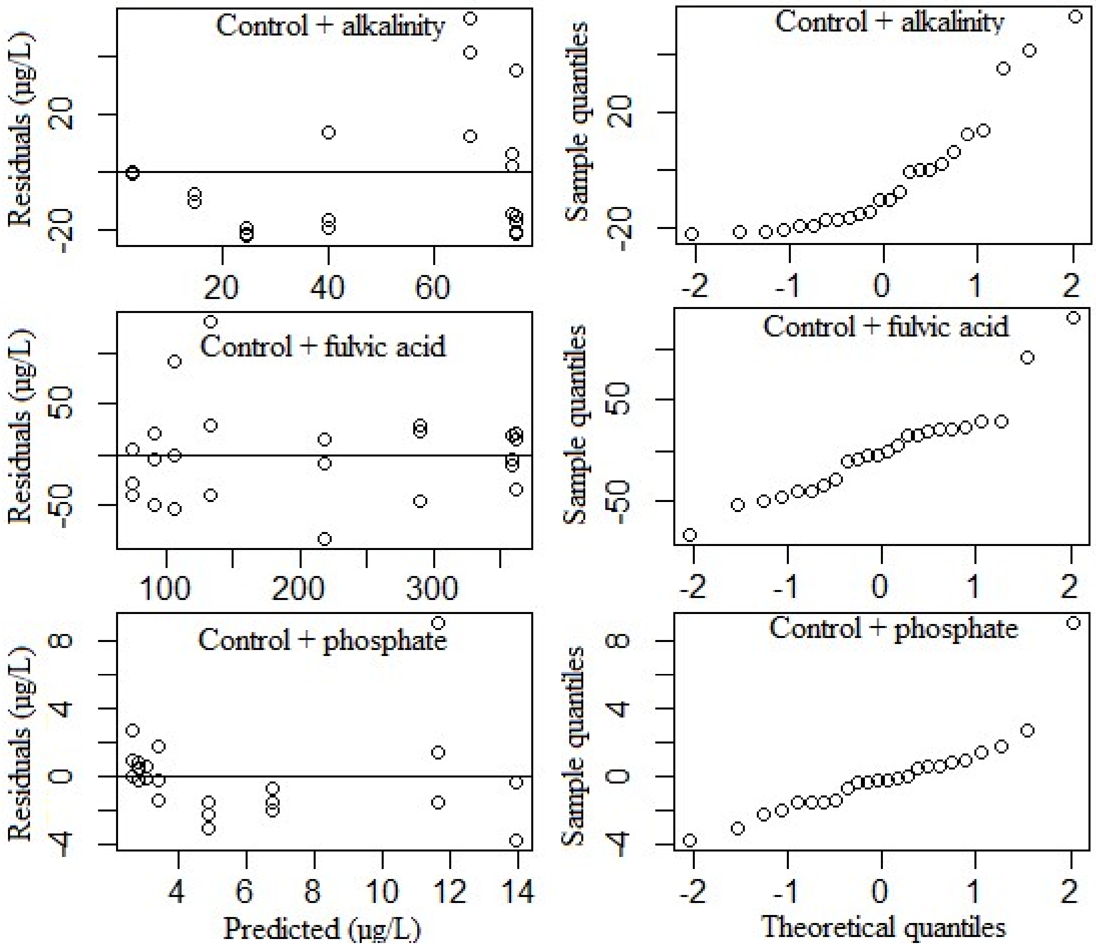

Fig. S9: Residuals (left) and normal quantile plots (right) from first order kinetics models for the calcium nitrate treatments. Valid models have residuals that average 0, and are identically, independently, normally distributed. The normal quantile plot should follow a straight diagonal line.

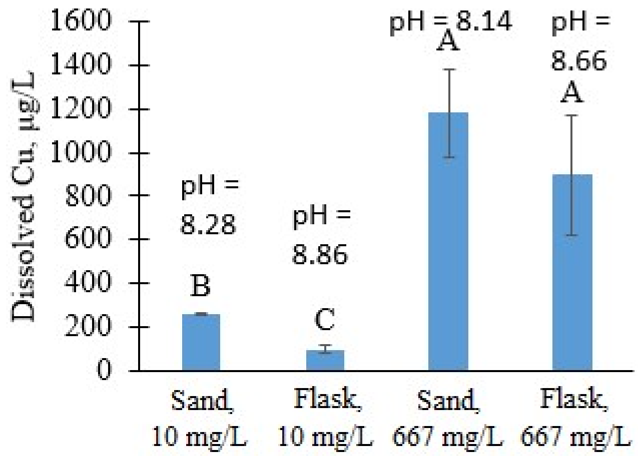

Fig. S10: Dissolved Cu measured in a Millville series soil SPE (similar to GarM SPE) after 10 days in a flask or sand Magenta box at 10 mg/L Cu or 667 mg/L Cu as CuO NPs. N = 3, error bars = standard deviation. Differing letters indicate significant differences by Tukey HSD test after two-way ANOVA.

Table S7: Comparison of dissolved Cu immediately after addition of Cu^{2+} ions to SPEs or electrolyte to dissolved Cu measured in all SPEs 48 hours later from flasks. The amount of Cu ions added to each treatment was approximately equivalent to the 240 h steady state solubility of CuO NPs previously observed. Numbers are average of independent triplicates ± standard deviation. Sorption of Cu ions to colloidal organic matter in the pore waters is negligible. In the electrolyte, a small pH rise (7.50 to ~7.85) by 48 h limited solubility of Cu^{2+}.

Soil pore water	Initial dissolved Cu concentration (µg/L)	Cu ions added (µg/L)	Initial dissolved Cu concentration immediately after ion addition (µg/L)	Dissolved Cu concentration at 48 h (µg/L)
Electrolyte	0	~25	26.2 ± 2.0	16.1 ± 2.2
OrgM	13.4	~230	243 ± 4.7	240 ± 3.3
AgrM	23.8	~270	314 ± 20	299 ± 7.2
GarM	48.4	~60	109 ± 2.2	128 ± 14

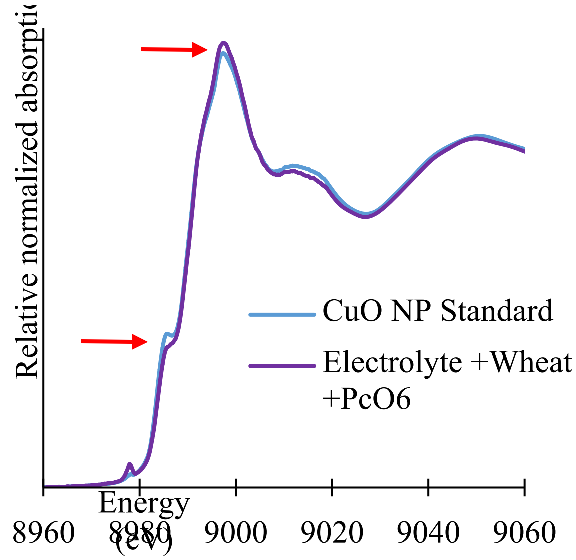

Fig. S11: Overlaid XAFS spectra of the CuO NP standard and a sample (Electrolyte + wheat + *Pc*O6), showing subtle differences in the area of the pre-white line shoulder and white line.

Table S8: Linear combination fit results for all treatments of normalized spectra.

				CuO NPs		Cu acetate		Cu sulfate	
Data	**rfactor**	**chinu**	**chisqr**	**weight**	**error**	**weight**	**error**	**weight**	**error**
Electrolyte	Not enough NPs collected for measurement.								
Electrolyte + PcO6	4.49E-04	1.08E-04	2.26E-02	79.21%	0.97%	15.53%	1.32%	5.26%	1.64%
Electrolyte + Wheat	4.32E-04	1.03E-04	2.16E-02	82.27%	0.95%	14.29%	1.29%	3.44%	1.60%
Electrolyte + Wheat + PcO6	4.23E-04	1.02E-04	2.12E-02	80.37%	0.94%	14.00%	1.28%	5.63%	1.59%
OrgM	3.91E-04	9.30E-05	1.94E-02	84.82%	0.90%	12.51%	1.23%	2.67%	1.52%
OrgM + PcO6	3.86E-04	9.21E-05	1.93E-02	83.77%	0.89%	14.55%	1.22%	1.68%	1.51%
OrgM + Wheat	3.93E-04	9.36E-05	1.96E-02	85.14%	0.90%	13.11%	1.23%	1.76%	1.53%
OrgM + Wheat + PcO6	4.29E-04	1.03E-04	2.16E-02	82.83%	0.95%	15.36%	1.29%	1.81%	1.60%
AgrM	3.16E-04	7.57E-05	1.58E-02	84.53%	0.81%	13.65%	1.11%	1.82%	1.37%
AgrM + PcO6	1.45E-04	3.45E-05	7.22E-03	88.34%	0.55%	8.27%	0.75%	3.39%	0.93%
AgrM + Wheat	2.16E-04	5.19E-05	1.09E-02	86.92%	0.67%	12.17%	0.92%	0.90%	1.14%
AgrM + Wheat + PcO6	4.10E-04	9.84E-05	2.06E-02	81.94%	0.92%	15.23%	1.26%	2.82%	1.56%
GarM	3.25E-04	7.80E-05	1.63E-02	84.25%	0.82%	14.15%	1.12%	1.60%	1.39%
GarM + PcO6	4.67E-04	1.10E-04	2.30E-02	86.29%	0.98%	10.39%	1.33%	3.32%	1.65%
GarM + Wheat	4.80E-04	1.15E-04	2.39E-02	82.85%	1.00%	13.72%	1.36%	3.43%	1.69%
GarM + Wheat + PcO6	4.80E-04	1.15E-04	2.39E-02	82.85%	1.00%	13.72%	1.36%	3.43%	1.69%

Table S9: Linear combination fit results for all treatments of first derivative spectra.

				CuO NP		Cu acetate		Cu sulfate	
Data	**rfactor**	**chinu**	**chisqr**	**weight**	**error**	**weight**	**error**	**weight**	**error**
Electrolyte	Not enough NPs collected for measurement.								
Electrolyte + Wheat	1.40E-02	3.40E-05	7.10E-03	86.62%	1.89%	10.40%	2.07%	2.98%	2.80%
Electrolyte + PcO6	1.43E-02	3.48E-05	7.27E-03	85.03%	1.91%	10.74%	2.09%	4.23%	2.84%
Electrolyte + Wheat + PcO6	1.93E-02	4.65E-05	9.73E-03	84.85%	2.21%	10.37%	2.42%	4.78%	3.28%
OrgM	8.33E-03	1.97E-05	4.11E-03	89.29%	1.44%	8.00%	1.57%	2.71%	2.13%
OrgM + Wheat	1.03E-02	2.45E-05	5.12E-03	88.82%	1.61%	8.62%	1.76%	2.57%	2.38%
OrgM + PcO6	1.33E-02	3.19E-05	6.66E-03	87.65%	1.83%	10.24%	2.00%	2.11%	2.72%
OrgM + Wheat + PcO6	1.14E-02	2.76E-05	5.77E-03	87.59%	1.71%	10.42%	1.86%	1.99%	2.53%
AgrM	9.01E-03	2.16E-05	4.51E-03	88.91%	1.51%	8.59%	1.65%	2.50%	2.23%
AgrM + Wheat	5.85E-03	1.41E-05	2.94E-03	91.26%	1.22%	7.18%	1.33%	1.56%	1.80%
AgrM + PcO6	6.28E-03	1.46E-05	3.06E-03	92.92%	1.24%	3.75%	1.36%	3.33%	1.84%
AgrM + Wheat + PcO6	1.13E-02	2.73E-05	5.71E-03	87.44%	1.70%	9.65%	1.85%	2.91%	2.51%
GarM	7.90E-03	1.90E-05	3.97E-03	90.52%	1.42%	7.53%	1.55%	1.94%	2.10%
GarM + Wheat	1.36E-02	3.26E-05	6.82E-03	87.52%	1.85%	9.25%	2.03%	3.23%	2.75%
GarM + PcO6	1.09E-02	2.56E-05	5.36E-03	89.26%	1.64%	8.03%	1.80%	2.72%	2.44%
GarM + Wheat + PcO6	1.36E-02	3.26E-05	6.82E-03	87.52%	1.85%	9.25%	2.03%	3.23%	2.75%

Table S10: Linear combination fit results for all treatments of $\chi(k)$ space.

				CuO NP		Cu acetate		Cu sulfate	
Data	**rfactor**	**chinu**	**chisqr**	**weight**	**error**	**weight**	**error**	**weight**	**error**
Electrolyte	Not enough NPs collected for measurement.								
Electrolyte + Wheat	3.32E-02	1.35E-02	1.34E+00	85.60%	4.27%	0.00%	6.70%	22.79%	5.17%
Electrolyte + PcO6	4.43E-02	1.79E-02	1.77E+00	91.50%	4.93%	0.00%	7.73%	13.88%	5.95%
Electrolyte + Wheat + PcO6	4.00E-02	1.66E-02	1.65E+00	87.28%	4.75%	0.00%	7.44%	21.64%	5.74%
OrgM	4.24E-02	1.76E-02	1.74E+00	88.48%	4.88%	0.00%	7.65%	19.69%	5.90%
OrgM + Wheat	4.01E-02	1.70E-02	1.68E+00	87.16%	4.80%	0.00%	7.53%	23.04%	5.80%
OrgM + PcO6	4.67E-02	1.85E-02	1.83E+00	84.99%	5.01%	0.00%	7.85%	20.99%	6.05%
OrgM + Wheat + PcO6	4.80E-02	2.04E-02	2.01E+00	89.12%	5.25%	0.00%	8.23%	19.94%	6.34%
AgrM	4.45E-02	1.91E-02	1.89E+00	85.15%	5.08%	0.00%	7.97%	25.99%	6.14%
AgrM + Wheat	2.83E-02	1.19E-02	1.18E+00	100.00%	0.00%	0.00%	0.00%	7.60%	0.00%
AgrM + PcO6	3.66E-02	1.50E-02	1.48E+00	86.71%	4.50%	0.00%	7.07%	21.56%	5.44%
AgrM + Wheat + PcO6	2.66E-02	1.15E-02	1.14E+00	90.55%	3.95%	0.00%	6.20%	21.18%	4.78%
GarM	4.01E-02	1.65E-02	1.63E+00	93.97%	4.73%	0.00%	7.42%	12.20%	5.71%
GarM + Wheat	3.28E-02	1.40E-02	1.39E+00	87.27%	4.35%	0.00%	6.83%	23.76%	5.26%
GarM + PcO6	3.94E-02	1.62E-02	1.60E+00	85.65%	4.68%	0.00%	7.35%	22.96%	5.66%
GarM + Wheat + PcO6	3.28E-02	1.40E-02	1.39E+00	87.27%	4.35%	0.00%	6.83%	23.76%	5.26%

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