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

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Figure S1: Soil Sampling Location Map

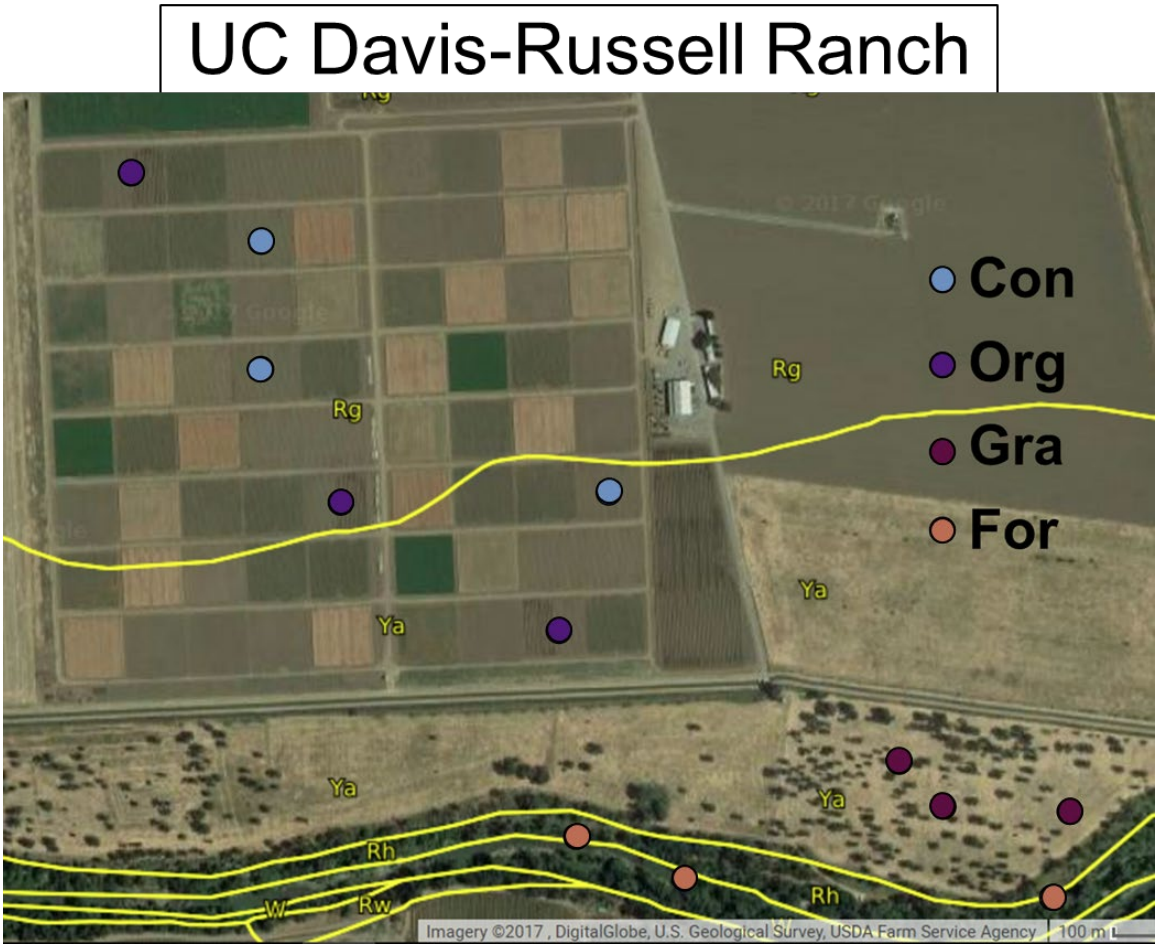

Figure S1) Soil sampling locations at the UC Davis Russell Ranch Long term agricultural experiment station. Soils from the top 10 cm were compiled from three locations representing conventional agricultural management (Con), organic agricultural management (Org), unmanaged grassland (Gra), and unmanaged riparian oak forest (Oak).

Figure S2: Confirmation of nano particulate CuO as tenorite phase CuO by Cu K-edge XANES

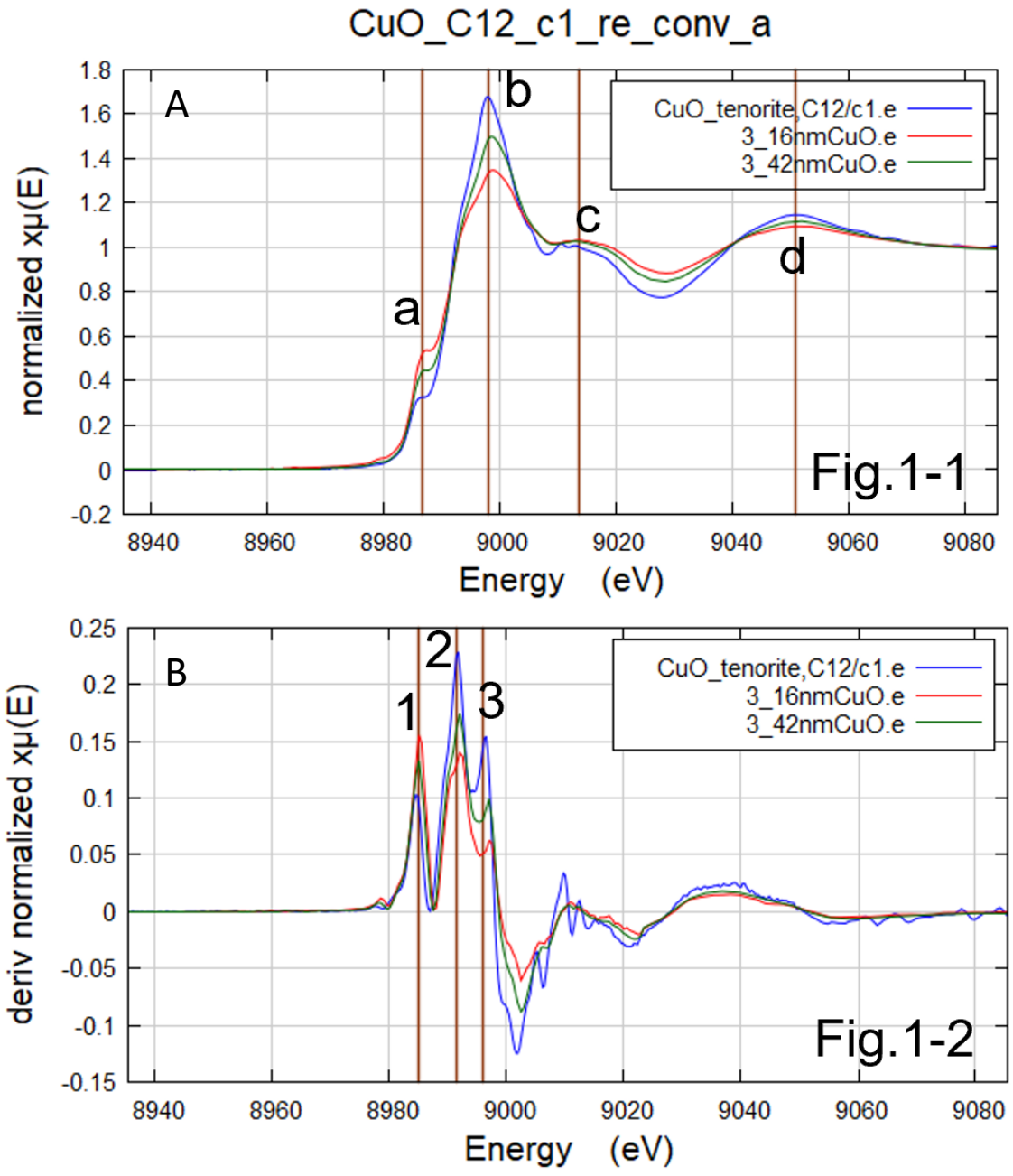

Figure S2) A: Cu K-edge normalized X-ray adsorption near-edge structure (XANES) spectra of 16nm CuO, 42nm CuO, and a reference CuO compound of unknown size (CuO_tenorite,C12/c1) B First derivative of normalized XANES data for 16nCuO, 42nCuO, and CuO_tenorite,C12/c1; data collected at the Canadian Light Source on the HXMA beamline.

Figure S3: Con soil spectra, fit, and residuals after treatment with $CuCl_2$, 16nCuO, 42nCuO, and bCuO

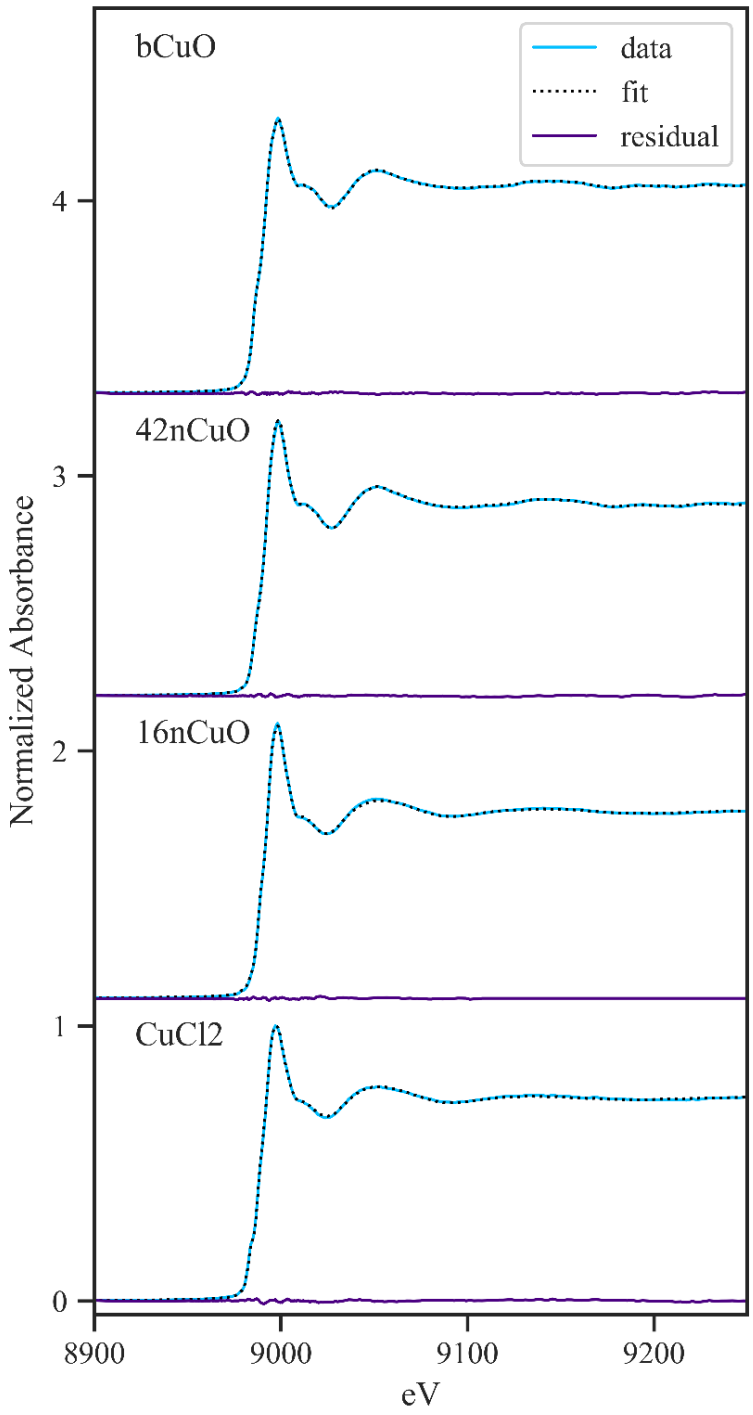

Figure S3) Cu K-edge XANES spectra (blue) of the conventional soil treated with 1000 mg Cu/kg Soil from $CuCl_2$, 16nCuO, 42nCuO, and bCuO. The best fits (dotted black) based on linear combination fitting are overlaid on the soil spectra and the residuals of the fits (purple) are also plotted.

Figure S4: Relationship between total soil organic carbon and microbial biomass with and without copper treatment.

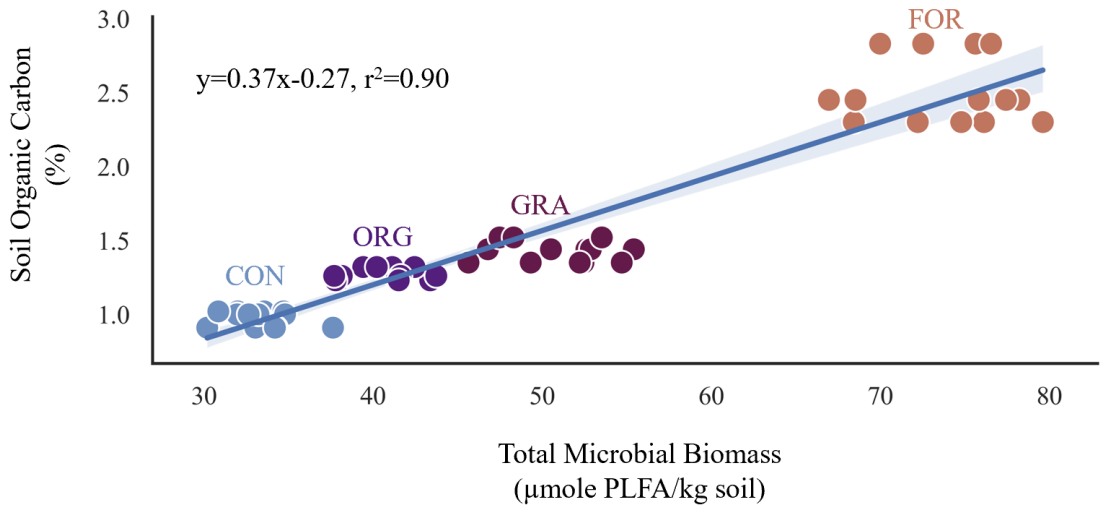

Figure S4) Soil organic carbon content plotted against total microbial biomass (µmole PLFA/kg soil) for Con, Org, Gra, and For soils with and without copper treatment.

Table S1: Table of Cu-bearing XANES standards and notes

Standard	**Notes**
Atacamite	$Cu_2(OH)_3Cl$
Chalcopyrite	$CuFeS_2$
Cu-Acetylacetonate	$Cu(C_5H_7O2)_2$
Cu_2O	Cu_2O
Cufoil_1032	Cu
16nmCuO	CuO
42nmCuO	CuO
Cu_2S	Cu_2S
Cu-Albite	Cu adsorbed to Albite, prepared according to Furnare et al 2005.
$CuCO_3$	$CuCO_3$
Cu-Chlorite	Cu adsorbed to Chlorite, prepared according to Furnare et al 2005.
$CuCl_2$	$CuCl_2$
Cu-FA	Cu complexed by Suwanee River fulvic acid, prepared according to Karlsson et al. 2006.
Cu-HA	Cu complexed by Leonardite humic matter, prepared according to Karlsson et al. 2006.
Cu-Illite	Cu adsorbed to Illite, Furnare et al 2005
Cu-Montmorillonite	Cu adsorbed to Montmorillonite, prepared according to Furnare et al 2005.
Cu-NOM	Cu complexed by Suwanee River natural organic matter, prepared according to Karlsson et al. 2006.
Cu-Orthoclase	Cu adsorbed to Orthoclase, prepared according to Furnare et al 2005.
$Cu_3(PO_4)_2$	$Cu_3(PO_4)_2$
Cu-Phytate	Precipitate from phytic acid using $CuCl_2$ and NaOH in a background of HCl, prepared according to He et al 2006.
Cu-Quartz	Cu adsorbed to Quartz, prepared according to Furnare et al 2005.
CuS	CuS
$CuSO_4$	CuSO4
Cu-Serpentine	Cu adsorbed to Serpentine, prepared according to Furnare et al 2005.
Cu-Vermiculite	Cu adsorbed to Vermiculite, prepared according to Furnare et al 2005.

Table S2: Specific phospholipid fatty acids used in analysis

#	**Phospholipid Fatty Acids**
1	14:0 iso
2	14:1 w8c
3	14:0
4	15:1 iso w6c
5	15:4 w3c
6	15:0 iso
7	15:0 anteiso
8	15:0
9	16:0 iso
10	16:1 w9c
11	16:1 w7c
12	16:1 w5c
13	16:0
14	17:1 iso w9c
15	17:1 anteiso w9c
16	17:0 iso
17	17:0 anteiso
18	17:1 w8c
19	17:0 cyclo w7c
20	17:0
21	17:1 w7c 10-methyl
22	17:0 10-methyl
23	18:2 w6c
24	18:1 w9c
25	18:1 w7c
26	18:1 w5c
27	18:0
28	18:1 w7c 10-methyl
29	18:0 10-methyl
30	19:0 cyclo w7c
31	20:4 w6c
32	20:1 w9c
33	20:0
34	20:0 10-methyl
35	21:1 w3c
36	22:0
37	24:0

Table S3: Available Cu at 1 hr

Available Cu at 1 h in soils from the conventional (Con), organic (Org), grassland (Gra), and forest (For) systems that were untreated (-, 0) or treated with 10 and 1000 mg Cu/kg soil from $CuCl_2$, 16nCuO, 42nCuO, and bCuO.

			1 hr Cu (mg Cu kg^{-1} soil)	
Management	**Cu Conc.**	**Cu Form**	**Mean**	**Std Dev**
CON	0	-	0.015	0.007
	1000	$CuCl_2$	115.966	19.123
		16nCuO	17.870	2.795
		42nCuO	1.775	0.236
		bCuO	0.772	0.055
ORG	0	-	0.183	0.015
	1000	$CuCl_2$	98.118	25.549
		16nCuO	17.300	0.627
		42nCuO	2.593	0.114
		bCuO	1.154	0.029
GRA	0	-	0.098	0.066
	1000	$CuCl_2$	111.434	31.823
		16nCuO	19.114	1.049
		42nCuO	2.559	0.171
		bCuO	1.037	0.046
FOR	0	-	0.081	0.014
	1000	$CuCl_2$	72.689	10.414
		16nCuO	24.093	3.764
		42nCuO	4.352	0.559
		bCuO	1.033	0.058

Table S4: Available Cu at 70 days

Available Cu at 70 days in soils from the conventional (Con), organic (Org), grassland (Gra), and forest (For) systems that were untreated (-, 0) or treated with 10 and 1000 mg Cu/kg soil from $CuCl_2$, 16nCuO, 42nCuO, and bCuO.

			70 day Cu (mg Cu kg^{-1} soil)	
Management	**Cu Conc.**	**Cu Form**	**Mean**	**Std Dev**
CON	0	-	0.02246	0.00434
	1000	$CuCl_2$	0.65351	0.03596
		16nCuO	0.61611	0.18857
		42nCuO	0.70331	0.20096
		bCuO	0.25853	0.06869
ORG	0	-	0.14606	0.00707
	1000	$CuCl_2$	1.06106	0.16419
		16nCuO	1.32679	0.49535
		42nCuO	1.10617	0.11765
		bCuO	0.74221	0.09826
GRA	0	-	0.02248	0.00525
	1000	$CuCl_2$	0.81974	0.08623
		16nCuO	0.80366	0.23659
		42nCuO	1.45831	0.60031
		bCuO	0.42662	0.16117
FOR	0	-	0.03297	0.00263
	1000	$CuCl_2$	1.20088	0.88173
		16nCuO	0.96328	0.18201
		42nCuO	1.83178	0.74722
		bCuO	0.53740	0.03877

Table S5: 1 hr pH

Soil pH at 1 hr in soils from the conventional (Con), organic (Org), grassland (Gra), and forest (For) systems that were untreated (-, 0) or treated with 1000 mg Cu/kg soil for $CuCl_2$, 16nCuO, 42nCuO, and bCuO.

			1 hr soil pH	
Management	**Cu Conc.**	**Cu Form**	**Mean**	**Std Dev**
CON	0	-	7.49	0.02
	1000	$CuCl_2$	6.58	0.01
		16nCuO	7.90	0.01
		42nCuO	8.18	0.01
		bCuO	8.12	0.02
ORG	0	-	7.62	0.05
	1000	$CuCl_2$	6.75	0.08
		16nCuO	7.90	0.01
		42nCuO	8.16	0.02
		bCuO	8.10	0.01
GRA	0	-	7.21	0.01
	1000	$CuCl_2$	6.51	0.06
		16nCuO	7.73	0.03
		42nCuO	7.99	0.01
		bCuO	7.96	0.02
FOR	0	-	7.32	0.03
	1000	$CuCl_2$	6.87	0.01
		16nCuO	7.84	0.01
		42nCuO	8.09	0.02
		bCuO	8.03	0.02

Table S6: 70 day soil pH

Soil pH at 70 days in soils from the conventional (Con), organic (Org), grassland (Gra), and forest (For) systems that were untreated (-, 0) or treated with 10 or 1000 mg Cu/kg soil from $CuCl_2$, 16nCuO, 42nCuO, and bCuO.

			70 day soil pH	
Management	**Cu Conc.**	**Cu Form**	**Mean**	**Std Dev**
CON	0	-	7.29	0.06
	1000	$CuCl_2$	6.33	0.11
		16nCuO	7.61	0.12
		42nCuO	7.48	0.09
		bCuO	7.35	0.07
ORG	0	-	7.79	0.06
	1000	$CuCl_2$	6.56	0.03
		16nCuO	7.68	0.12
		42nCuO	7.67	0.09
		bCuO	7.38	0.13
GRA	0	-	7.40	0.08
	1000	$CuCl_2$	6.20	0.08
		16nCuO	7.55	0.05
		42nCuO	7.46	0.04
		bCuO	7.37	0.10
FOR	0	-	7.68	0.03
	1000	$CuCl_2$	6.64	0.16
		16nCuO	7.38	0.04
		42nCuO	7.48	0.10
		bCuO	7.31	0.12

Table S7: Change in pH over time

Change in soil pH in soils from the conventional (Con), organic (Org), grassland (Gra), and forest (For) systems that were untreated (-, 0) or treated with 1000 mg Cu/kg soil from $CuCl_2$, 16nCuO, 42nCuO, and bCuO.

			Change in pH over time	
Management	**Cu Conc.**	**Cu Form**	**Mean**	**STD**
CON	0	-	-0.19	0.08
	1000	$CuCl_2$	-0.25	0.12
		16nCuO	-0.29	0.12
		42nCuO	-0.70	0.08
		bCuO	-0.77	0.08
ORG	0	-	0.17	0.11
	1000	$CuCl_2$	-0.19	0.05
		16nCuO	-0.23	0.13
		42nCuO	-0.49	0.10
		bCuO	-0.72	0.13
GRA	0	-	0.19	0.09
	1000	$CuCl_2$	-0.31	0.11
		16nCuO	-0.19	0.06
		42nCuO	-0.53	0.04
		bCuO	-0.59	0.08
FOR	0	-	0.36	0.04
	1000	$CuCl_2$	-0.23	0.17
		16nCuO	-0.46	0.03
		42nCuO	-0.61	0.09
		bCuO	-0.72	0.13

Table S8: HXMA Cu K-edge XANES least-square linear combination fitting results

Specific fit components, sum of fit components, and sum of squares XANES data collected on HXMA for Con, Org, Gra, and For soils treated with 1000 mg Cu kg^{-1} soil $CuCl_2$, 16nCuO, 42nCuO, and bCuO. Soil bound Cu components are shaded in gray, CuO in green.

Management	Cu Form	SS	Sum	Cu (II) - Albite	Cu (II) - Montmorillonite	Cu (II) - Serpentine	Cu (II) - Vermiculite	Cu (II) - Orthoclase	Cu (II)- Illite	Cu (II)- HA	Cu (II)- NOM	Cu (II)- (acac)2tey	Cu (II)- phytate	$Cu_3(PO_4)_2$	16nCuO	42nCuO
Con	$CuCl_2$	2.38E-05	.99	0.319	0.404						0.272					
Org	$CuCl_2$	2.11E-05	1.01	0.581						0.303				0.122		
Gra	$CuCl_2$	2.91E-05	1.01	0.433			0.377					0.197				
For	$CuCl_2$	2.46E-05	0.99	0.5							0.265	0.251				
Con	16nCuO	1.82E-05	1.01	0.287		0.582				0.136						
Org	16nCuO	1.83E-05	1.01	0.551						0.437				0.019		
Gra	16nCuO	5.61E-05	0.98	0.512		0.213				0.258						
For	16nCuO	3.00E-05	1.01	0.598							0.100	0.308				
Con	42nCuO	1.58E-05	1.01	0.344						0.182					0.481	
Org	42nCuO	5.93E-05	0.99	.248						.249					0.496	
Gra	42nCuO	3.27E-05	0.98					0.296					0.305		0.387	
For	42nCuO	2.75E-05	0.99					0.212		0.281						0.494
Con	bCuO	1.25E-05	1.01		0.354									0.051	0.601	
For	bCuO	3.73E-05	1.01		0.310							0.1043			0.595	

Table S9: Total microbial biomass

Total biomass as estimated by total phospholipid fatty acid analysis (µmol PLFA kg^{-1} soil**)** in soils from the conventional (Con), organic (Org), grassland (Gra), and forest (For) systems that were untreated (-, 0) or treated with 10 or 1000 mg Cu/kg soil from $CuCl_2$, 16nCuO, 42nCuO, and bCuO.

			Total Biomass (µmol PLFA kg^{-1} soil)	
Management	**Cu Conc.**	**Cu Form**	**Mean**	**Std Dev**
CON	0	-	33.26	0.27
	1000	$CuCl_2$	35.70	1.67
		16nCuO	31.06	1.23
		42nCuO	32.73	1.32
		bCuO	32.55	1.67
ORG	0	-	42.23	1.62
	1000	$CuCl_2$	42.53	1.16
		16nCuO	38.50	0.79
		42nCuO	40.17	2.09
		bCuO	39.80	1.94
GRA	0	-	55.06	0.50
	1000	$CuCl_2$	46.63	0.93
		16nCuO	49.91	0.85
		42nCuO	51.12	2.44
		bCuO	52.87	0.65
FOR	0	-	77.86	1.95
	1000	$CuCl_2$	70.56	3.13
		16nCuO	75.85	0.25
		42nCuO	68.98	0.87
		bCuO	76.25	1.35

Table S10: Total soil respiration

Total soil respiration (µmol CO2-C kg^{-1} soil) in soils from the conventional (Con), organic (Org), grassland (Gra), and forest (For) systems that were untreated (-, 0) or treated with 10 or 1000 mg Cu/kg soil from $CuCl_2$, 16nCuO, 42nCuO, and bCuO.

			Total soil respiration (µmol CO_2-C kg^{-1} soil)	
Management	**Cu Conc.**	**Cu Form**	**Mean**	**Std Dev**
CON	0	-	51833.68	547.30
	1000	$CuCl_2$	28660.11	473.62
		16nCuO	44957.28	1071.75
		42nCuO	48401.10	2224.88
		bCuO	49515.65	1098.53
ORG	0	-	58341.50	2794.15
	1000	$CuCl_2$	35980.91	722.07
		16nCuO	53255.25	3288.04
		42nCuO	61430.95	1122.07
		bCuO	59081.91	3636.63
GRA	0	-	87704.58	1165.69
	1000	$CuCl_2$	43771.86	1298.69
		16nCuO	65874.18	3906.68
		42nCuO	72572.30	5259.54
		bCuO	72365.94	7021.58
FOR	0	-	122172.74	3127.46
	1000	$CuCl_2$	80172.04	4693.65
		16nCuO	112696.86	2737.19
		42nCuO	109093.16	4642.92
		bCuO	118878.87	4099.16

Table S11: Biomass normalized respiration

Biomass Normalized Respiration (µmol CO2-C/ µmol PLFA) in soils from the conventional (Con), organic (Org), grassland (Gra), and forest (For) systems that were untreated (-, 0) or treated with 10 or 1000 mg Cu/kg soil from $CuCl_2$, 16nCuO, 42nCuO, and bCuO.

			Biomass Normalized Respiration (µmol CO2-C/ µmol PLFA)	
Management	**Cu Conc.**	**Cu Form**	**Mean**	**Std Dev**
CON	0	-	1558.20	9.82
	1000	$CuCl_2$	804.03	41.29
		16nCuO	1449.44	92.13
		42nCuO	1482.03	120.42
		bCuO	1523.10	67.97
ORG	0	-	1381.37	13.30
	1000	$CuCl_2$	846.60	35.63
		16nCuO	1384.77	112.57
		42nCuO	1532.54	98.28
		bCuO	1488.40	148.20
GRA	0	-	1592.92	6.57
	1000	$CuCl_2$	938.80	26.61
		16nCuO	1319.26	55.93
		42nCuO	1418.96	53.69
		bCuO	1368.76	132.09
FOR	0	-	1569.24	26.96
	1000	$CuCl_2$	1135.93	33.13
		16nCuO	1485.70	35.37
		42nCuO	1581.59	65.00
		bCuO	1560.05	81.84