Supplementary Materials

Nanoscale hydroxyapatite coated Cu-based nanopesticides exhibited promising benefits: Enhanced application efficiency and plants elements homeostasis

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Table S1 Limit of detection, precision and recovery data of ICP-MS for the selected elements. Al, B, Ca, Co, Cu, Fe, K, Mg, Mn, Mo, Ni, P, S, Sr, Ti, and Zn

Elements	**Limits of detection**	**recovery**	**RSD**
Al	0.059	96.5%	1.2
B	0.044	95.3%	2.8
Ca	0.049	103.5%	1.4
K	0.054	93.5%	1.9
P	0.042	97.8%	2.8
Mo	0.015	92.6%	3.2
Mg	0.038	102.8%	1.9
S	0.061	103.1%	2.6
Co	0.028	96.6%	3.6
Cu	0.068	98.8%	2.1
Fe	0.062	97.6%	1.7
Ti	0.072	92.8%	3.1
Mn	0.035	97.6%	2.6
Sr	0.038	98.2%	1.8
Ni	0.065	102.1%	2.9
Zn	0.048	97.9%	2.2

Table S2 Changed Metabolite Pathway of Microbial Communities between the K60 and CK Treatment.

Pathway	Description	logFC	SE	Pvalues
VALDEG-PWY	L-valine degradation I	1.638	0.5513	0.00296
PWY-3941	β-alanine biosynthesis II	1.569	0.5199	0.002544
PWY-7456	mannan degradation	1.539	0.2762	2.52E-08
PWY-7391	isoprene biosynthesis II (engineered)	1.37	0.2312	3.07E-09
PWY-6174	mevalonate pathway II (archaea)	1.37	0.2186	3.66E-10
ARGDEG-PWY	superpathway of L-arginine, putrescine, and 4-aminobutanoate degradation	1.342	0.2719	7.96E-07
ORNARGDEG-PWY	superpathway of L-arginine and L-ornithine degradation	1.342	0.2719	7.96E-07
PWY-3801	sucrose degradation II (sucrose synthase)	1.184	0.4659	0.01106
PWY-7002	4-hydroxyacetophenone degradation	1.128	0.3195	0.000415
PWY-1422	vitamin E biosynthesis (tocopherols)	1.126	0.515	0.02873
GLCMANNANAUT-PWY	superpathway of N-acetylglucosamine, N-acetylmannosamine and N-acetylneuraminate degradation	1.122	0.2896	0.000107
PWY-6892	thiazole biosynthesis I (E. coli)	1.089	0.2086	1.80E-07
FUCCAT-PWY	fucose degradation	1.057	0.277	0.000135
PWY-922	mevalonate pathway I	1.038	0.3126	0.000896
PWY-5910	superpathway of geranylgeranyldiphosphate biosynthesis I (via mevalonate)	1.034	0.3105	0.000867
P381-PWY	adenosylcobalamin biosynthesis II (late cobalt	1.02	0.4668	0.02891

	incorporation)			
METH-ACETATE-PWY	methanogenesis from acetate	1.008	0.4177	0.01584
PWY-6713	L-rhamnose degradation II	0.9959	0.3123	0.001428
PWY-7210	pyrimidine deoxyribonucleotides biosynthesis from CTP	0.9909	0.3474	0.004341
PWY-7198	pyrimidine deoxyribonucleotides de novo biosynthesis IV	0.9904	0.3476	0.00438
PWY-7347	sucrose biosynthesis III	0.9613	0.2734	0.000437
PWY-7371	1,4-dihydroxy-6-naphthoate biosynthesis II	0.9526	0.1833	2.03E-07
P441-PWY	superpathway of N-acetylneuraminate degradation	0.9498	0.2374	6.31E-05
SUCSYN-PWY	sucrose biosynthesis I (from photosynthesis)	0.9461	0.2693	0.000444
THISYN-PWY	superpathway of thiamin diphosphate biosynthesis I	0.9326	0.1782	1.65E-07
PWY490-3	nitrate reduction VI (assimilatory)	0.9188	0.089	0
PWY-5656	mannosylglycerate biosynthesis I	0.8829	0.1985	8.65E-06
PWY-7274	D-cycloserine biosynthesis	-0.878	0.2394	0.000244
PWY-5183	superpathway of aerobic toluene degradation	-0.9565	0.3721	0.01016
CRNFORCAT-PWY	creatinine degradation I	-0.9716	0.3352	0.00375
PWY-7616	methanol oxidation to carbon dioxide	-1.003	0.09815	0
PWY-6185	4-methylcatechol degradation (ortho cleavage)	-1.122	0.1102	0
PWY-7254	TCA cycle VII (acetate-producers)	-1.128	0.1091	0
PWY-6182	superpathway of salicylate degradation	-1.187	0.1947	1.09E-09
PWY-5417	catechol degradation III (ortho-cleavage pathway)	-1.332	0.1993	2.32E-11
PWY-5431	aromatic compounds degradation via β-ketoadipate	-1.332	0.1993	2.32E-11
PWY-5430	meta cleavage pathway of aromatic compounds	-1.335	0.2405	2.82E-08

PWY0-845	superpathway of pyridoxal 5'-phosphate biosynthesis and salvage	-1.391	0.2219	3.62E-10
PWY-5184	toluene degradation VI (anaerobic)	-1.455	0.5572	0.009018
PWY-6562	norspermidine biosynthesis	-1.513	0.1937	5.55E-15
CATECHOL-ORTHO-CLEAVAGE-PWY	catechol degradation to β-ketoadipate	-1.582	0.2533	4.24E-10
3-HYDROXYPHENYLACETATE-DEGRADATION-PWY	4-hydroxyphenylacetate degradation	-1.618	0.2224	3.44E-13
PWY-7401	crotonate fermentation (to acetate and cyclohexane carboxylate)	-1.647	0.7094	0.02023
CENTBENZCOA-PWY	benzoyl-CoA degradation II (anaerobic)	-1.759	0.4526	0.000102
DHGLUCONATE-PYR-CAT-PWY	glucose degradation (oxidative)	-1.791	0.173	0
BENZCOA-PWY	anaerobic aromatic compound degradation (Thauera aromatica)	-1.815	0.6463	0.004986
P125-PWY	superpathway of (R,R)-butanediol biosynthesis	-2.007	0.1917	0
AST-PWY	L-arginine degradation II (AST pathway)	-2.04	0.1713	0
PYRIDNUCSYN-PWY	NAD biosynthesis I (from aspartate)	0.5459	0.121	6.49E-06

Table S3 Changed Metabolite Pathway of Microbial Communities between the K and CK Treatment.

Pathway	Description	logFC	SE	Pvalues
AST-PWY	L-arginine degradation II (AST pathway)	1.638	0.1066	0
P125-PWY	superpathway of (R,R)-butanediol biosynthesis	1.427	0.186	1.67E-14
PYRIDOXSYN-PWY	pyridoxal 5'-phosphate biosynthesis I	1.299	0.2761	2.55E-06
3-HYDROXYPHENYLACETATE-DEGRADATION-PWY	4-hydroxyphenylacetate degradation	1.209	0.1397	0
CATECHOL-ORTHO-CLEAVAGE-PWY	catechol degradation to β-ketoadipate	1.131	0.1294	0
PWY0-1338	polymyxin resistance	1.02	0.3903	0.008983
PWY-5417	catechol degradation III (ortho-cleavage pathway)	0.9815	0.102	0
PWY-5431	aromatic compounds degradation via β-ketoadipate	0.9815	0.102	0
PWY-6562	norspermidine biosynthesis	0.8813	0.1208	2.92E-13
DHGLUCONATE-PYR-CAT-PWY	glucose degradation (oxidative)	0.8683	0.1744	6.35E-07
PWY-1361	benzoyl-CoA degradation I (aerobic)	0.8683	0.2299	0.000159
PWY-7254	TCA cycle VII (acetate-producers)	0.8582	0.06876	0
PWY-6182	superpathway of salicylate degradation	0.8506	0.09559	0
PWY-6185	4-methylcatechol degradation (ortho cleavage)	0.8506	0.08292	0
CENTBENZCOA-PWY	benzoyl-CoA degradation II (anaerobic)	0.8308	0.3812	0.02929
PWY-7616	methanol oxidation to carbon dioxide	0.7782	0.1634	1.91E-06
PWY-7274	D-cycloserine biosynthesis	0.776	0.5499	0.1582
PWY0-845	superpathway of pyridoxal 5'-phosphate biosynthesis and salvage	0.769	0.1752	1.14E-05

PWY-6731	starch degradation III	0.691	0.1349	2.99E-07
PWY-5181	toluene degradation III (aerobic) (via p-cresol)	0.6652	0.06603	0
P221-PWY	octane oxidation	0.6287	0.08935	1.97E-12
PWY-5705	allantoin degradation to glyoxylate III	0.623	0.07231	0
PWY-5676	acetyl-CoA fermentation to butanoate II	0.6224	0.0902	5.18E-12
PWY-5430	meta cleavage pathway of aromatic compounds	0.6185	0.1901	0.001136
GALLATE-DEGRADATION-II-PWY	gallate degradation I	-0.7	0.1636	1.88E-05
PWY-7377	cob(II)yrinate a,c-diamide biosynthesis I (early cobalt insertion)	-0.7514	0.2803	0.007335
PWY-6507	4-deoxy-L-threo-hex-4-enopyranuronate degradation	-0.767	0.09586	1.33E-15
PWY-7003	glycerol degradation to butanol	-0.7801	0.2413	0.001227
PWY-5531	chlorophyllide a biosynthesis II (anaerobic)	-0.7827	0.09261	0
PWY-7159	chlorophyllide a biosynthesis III (aerobic, light independent)	-0.7827	0.09261	0
PWY-1622	formaldehyde assimilation I (serine pathway)	-0.8043	0.1354	2.88E-09
PWY-6892	thiazole biosynthesis I (E. coli)	-0.8045	0.1339	1.86E-09
PWY-5532	adenosine nucleotides degradation IV	-0.81	0.3416	0.01772
PWY490-3	nitrate reduction VI (assimilatory)	-0.8157	0.1178	4.44E-12
PWY-7084	nitrifier denitrification	-0.8205	0.2342	0.000461
PWY-7002	4-hydroxyacetophenone degradation	-0.8283	0.3172	0.009026
PWY-5941	glycogen degradation II (eukaryotic)	-0.8568	0.3307	0.009575
PWY-5910	superpathway of geranylgeranyldiphosphate biosynthesis I (via mevalonate)	-0.8643	0.3251	0.007852
PWY-922	mevalonate pathway I	-0.8683	0.3271	0.007937
FUCCAT-PWY	fucose degradation	-0.9117	0.2826	0.001256
PWY-1422	vitamin E biosynthesis (tocopherols)	-0.934	0.4591	0.04192

RUMP-PWY	formaldehyde oxidation I	-0.9724	0.1868	1.95E-07
PWY-1861	formaldehyde assimilation II (RuMP Cycle)	-0.9744	0.1867	1.8E-07
CHLOROPHYLL-SYN	chlorophyllide a biosynthesis I (aerobic, light-dependent)	-0.9746	0.3566	0.00627
PWY-5198	factor 420 biosynthesis	-1.003	0.4746	0.03462
PWY-5529	superpathway of bacteriochlorophyll a biosynthesis	-1.003	0.2857	0.000444
PWY-3941	β-alanine biosynthesis II	-1.006	0.4096	0.01406
VALDEG-PWY	L-valine degradation I	-1.027	0.425	0.01571
PWY-622	starch biosynthesis	-1.033	0.547	0.059
PWY-6174	mevalonate pathway II (archaea)	-1.044	0.2619	6.75E-05
P441-PWY	superpathway of N-acetylneuraminate degradation	-1.053	0.1069	0
PWY-7391	isoprene biosynthesis II (engineered)	-1.054	0.2746	0.000125
METHGLYUT-PWY	superpathway of methylglyoxal degradation	-1.083	0.31	0.000478
PWY-3801	sucrose degradation II (sucrose synthase)	-1.139	0.3448	0.00095
P381-PWY	adenosylcobalamin biosynthesis II (late cobalt incorporation)	-1.14	0.1437	2E-15
PWY-7398	coumarins biosynthesis (engineered)	-1.172	0.968	0.2259
GLCMANNANAUT-PWY	superpathway of N-acetylglucosamine, N-acetylmannosamine and N-acetylneuraminate degradation	-1.256	0.1154	0
PWY-7456	mannan degradation	-1.373	0.2546	6.91E-08
SUCSYN-PWY	sucrose biosynthesis I (from photosynthesis)	-1.525	0.2112	5.08E-13
PWY-7347	sucrose biosynthesis III	-1.557	0.2151	4.56E-13

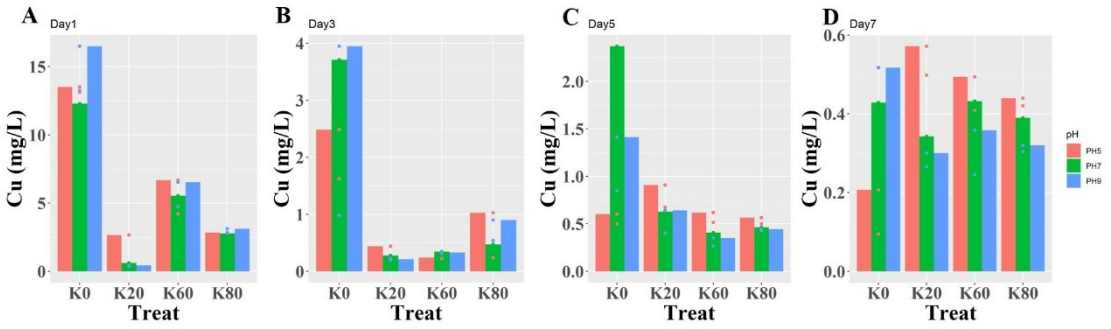

Figure S1 The Cu content release into solution under different pH

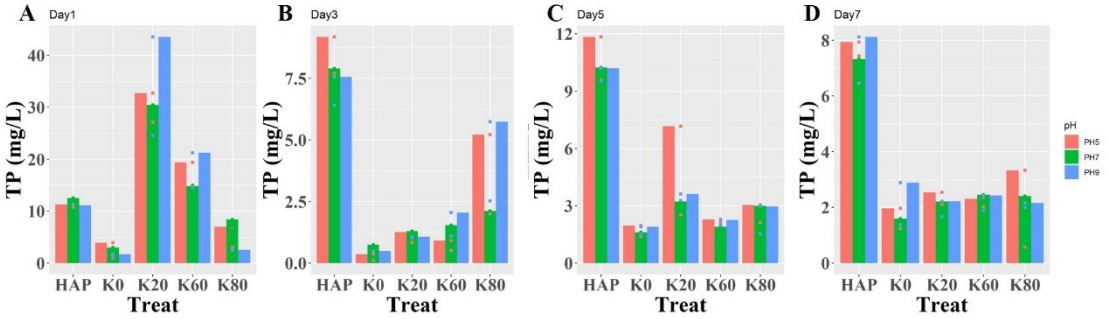

Figure S2 The total P content release into solution under different pH

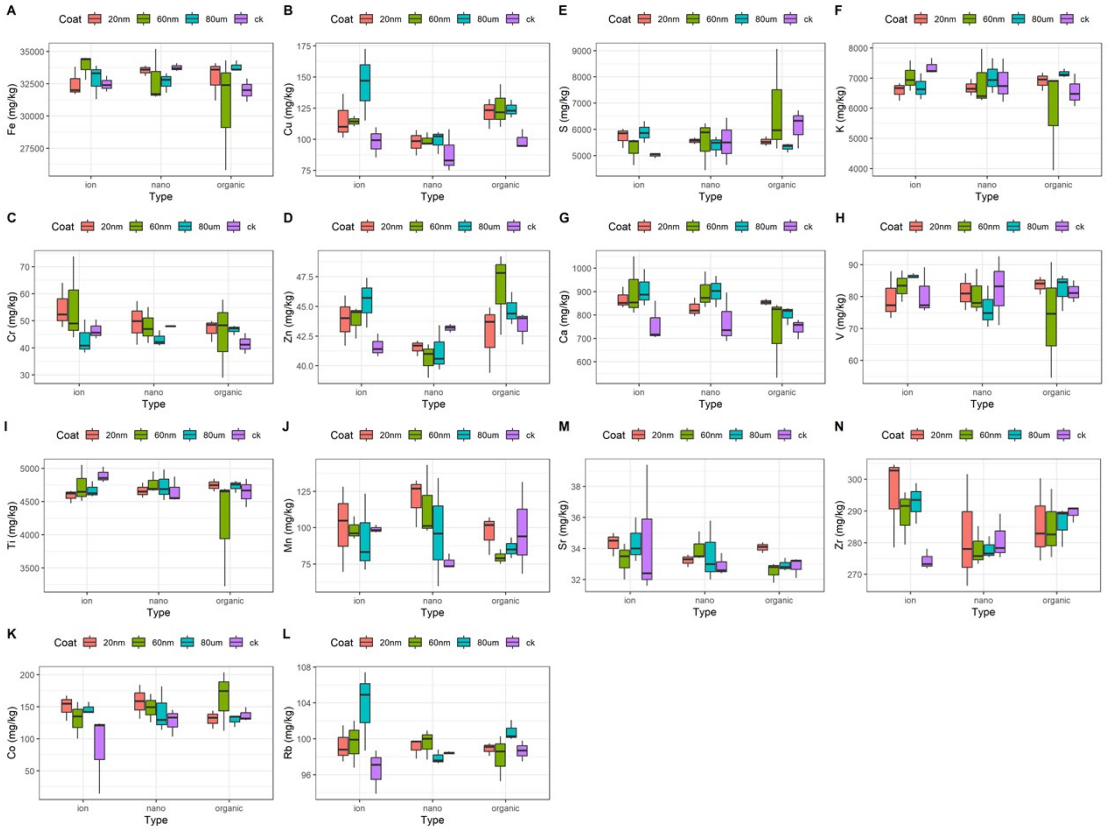

Figure S3 Elements content in upper soil of soil column after leaching experiment

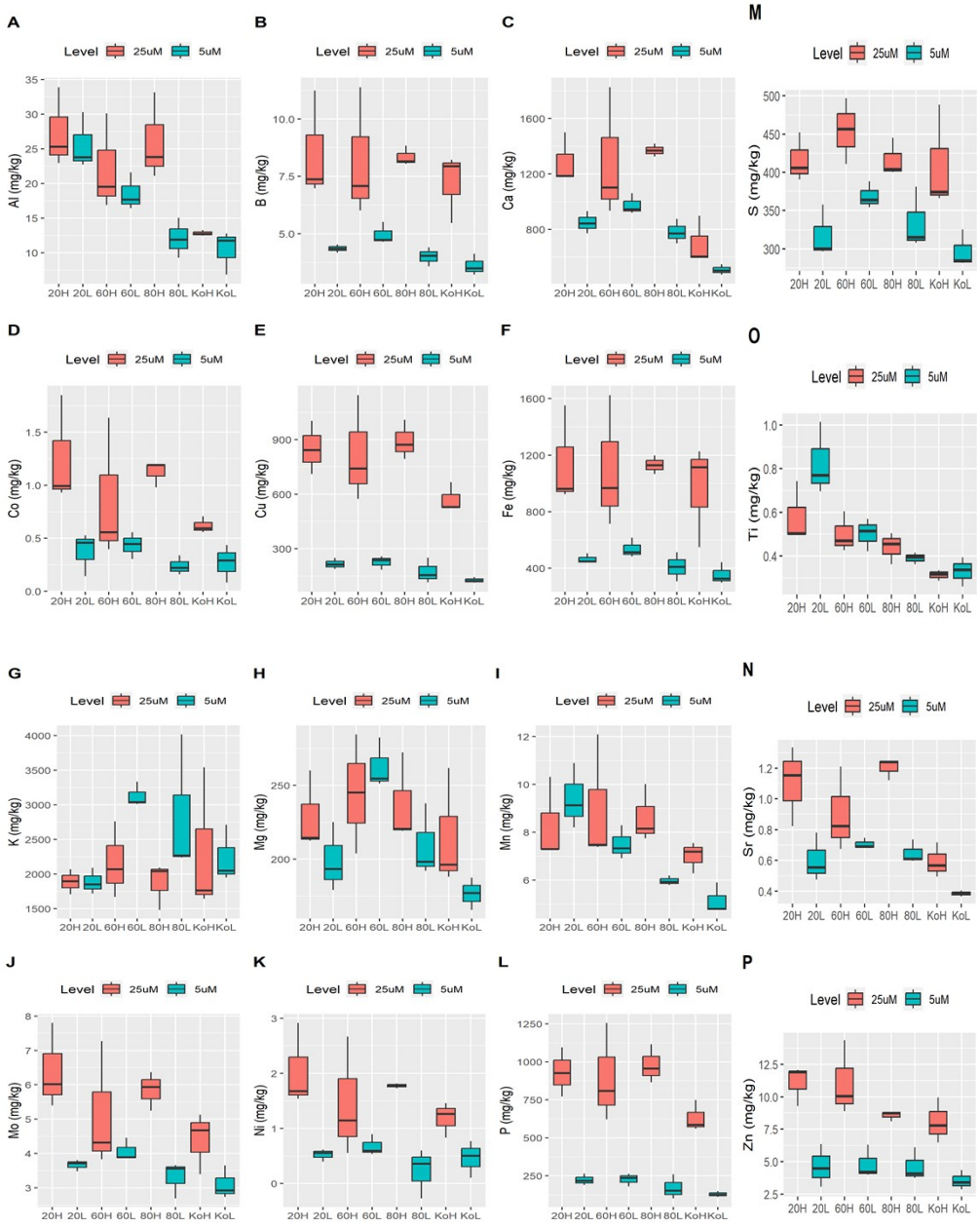

Figure S4 Root ionome variation for elements content in lettuce exposed for three types NanoCu pesticides and original Cu pesticides for a month.

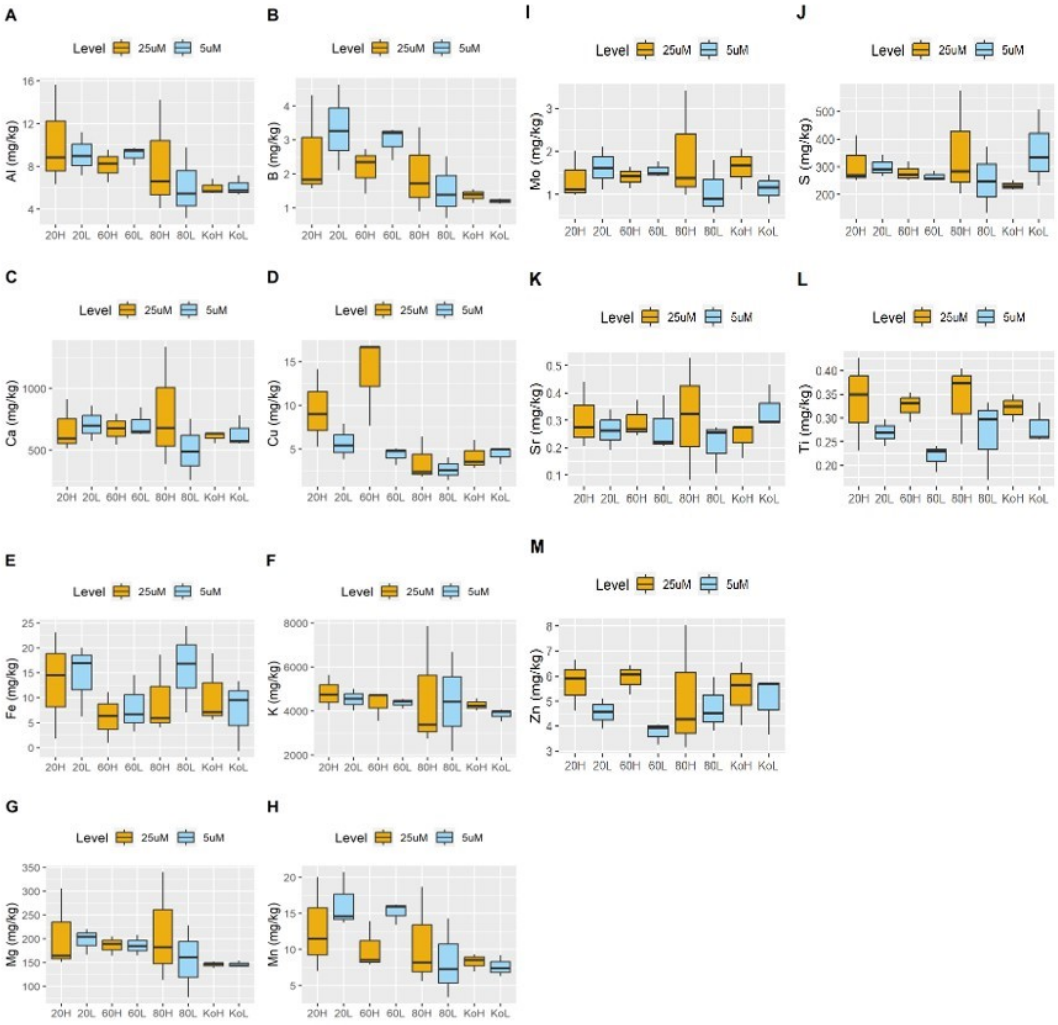

Figure S5 Shoot ionome variation for nutrients elements content in lettuce exposed for three types NanoCu pesticides and original Cu pesticides for a month.