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Supplementary Information

Interplay of metal-based nanoparticles with plant rhizosphere microenvironment: Implications for nanosafety and nano-enabled sustainable agriculture

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Table S1 Effect of metal-based nanomaterials on rhizosphere soil chemical properties.

Soil property	NMs types	Concentration	Size	Incubation time	Plant types	Effects	Reference
Soil pH	Ag NPs	0.025, 0.25 and 2.5 mg/kg	20.4±3.2 nm	20 days	*Zea mays* L.	Under the treatment of 2.5 mg/kg Ag NPs, soil pH significantly increased from 8.64 to 8.72.	1
	Ag NPs	10 mg/kg	7–14 nm	72 weeks	Tomato	Ag NPs did not significantly alter soil pH.	2
	Ag NPs	1, 10, and 50 mg/kg	15 nm	7, and 63 days	*Lactuca sativa*	Under short-term exposure (7 days) to Ag NPs, soil pH increased significantly from 7.70 to 7.87. However, soil pH was not changed significantly under Ag NPs at 63 days.	3
	Ag NPs	100 mg/kg	20 nm	60 days	Cucumber (*Cucumis sativa*)	Ag NPs increased soil pH from 5.18 to 5.26.	4
	GSNPs, CSNPs	20, 25, 50, and 100 mg/kg	–	60 days	*P. vulgaris*	CSNPs and CSNPs increased soil pH, and the degree of variation depended on the concentration and type of NPs.	5
	CeO_2 NPs	25 mg/kg	25 nm	150 days	Rice	CeO_2 NPs affected soil pH with negligible regardless	6

					of the presence or absence of Fe^{2+}.	
ZnO NPs	200, 500, and 1000 mg/kg	50 nm	30 days	Pokeweed	Soil pH increased from 7.5 to 8.0 under ZnO NPs exposure.	7
ZnO NPs	1.7 mg Zn/kg	Length: 400 nm; width: 150 nm	After wheat full maturity	Wheat (*Triticum aestivum* L.)	In either arid or non-arid soil, the application of ZnO NPs did not alter the soil pH.	8
ZnO NPs	20, 225, 450, and 900 mg Zn/kg	68±12 nm	35 days	Wheat, maize, radish, bean, lettuce, tomato, pea, cucumber, and beet.	After 24 h of contamination with ZnO NPs, the soil pH increased slightly with increasing Zn concentration. In the subsequent 35-day plant culture test, no significant changes in soil pH occurred regardless of plant type.	9
ZnO NPs	0, and 500 mg/kg	30 nm	9 weeks	Maize	ZnO NP decreased soil pH from 8.36 to 7.99 without additional P, but increased pH from 8.35 to 8.54 of inoculated soil with the addition of 50 mg/kg P.	10
ZnO NPs	0, 50, and 500	30±10	1 month	Maize	ZnO NPs increased soil pH in a dose-dependent	11

		ZnO mg/kg	nm			manner.	
Soil organic matter	Ag NPs	0.025, 0.25 and 2.5 mg/kg	20.4±3.2 nm	20 days	*Zea mays* L.	2.5 mg/kg Ag NPs decreased the content of DOC by 23.42%.	1
	GSNPs, CSNPs	20, 25, 50, and 100 mg/kg	–	60 days	*P. vulgaris*	SNPs significantly increased total organic carton, being greatest for GSNP50 (61.9%).	5
	Ag NPs	1, 10, and 100 mg/kg	–	4 weeks	*Arabidopsis thaliana* Col-0	Ag NPs significantly increased the content of humic substances.	12
	Ag NPs	100 mg/kg	20 nm	60 days	Cucumber (*Cucumis sativa*)	Ag NPs did not alter the content of soil DOC.	4
	CeO_2 NPs	25 mg/kg	25 nm	150 days	Rice	CeO_2 NPs affected DOC content and soil organic matter with negligible regardless of the presence or absence of Fe^{2+}.	6
	ZnO NPs	200, 500, and 1000 mg/kg	50 nm	30 days	Pokeweed	ZnO NPs did not significantly altered the content of soil organic cardon.	7

Soil nutrients	Ag NPs	0.025, 0.25 and 2.5 mg/kg	20.4±3.2 nm	20 days	*Zea mays* L.	2.5 mg/kg Ag NPs decreased the AP content by 4.7%.	1
	Ag NPs	10 mg/kg	7–14 nm	72 weeks	Tomato	Ag NPs decreased the availability of soil N, P and K, significantly.	2
	Ag NPs	100 mg/kg	20 nm	60 days	Cucumber (*Cucumis sativa*)	The bioavailable fraction of the essential elements increased significantly with the presence of Ag NPs.	4
	GSNPs, CSNPs	20, 25, 50, and 100 mg/kg	–	60 days	*P. vulgaris*	SNPs significantly increased N and P availability, and the degree of variation depended on the concentration and type of NPs.	5
	CeO_2 NPs	25 mg/kg	25 nm	150 days	Rice	CeO_2 NPs decreased the content of NO_3^-–N by 70.59%. But, the co-exposure of NPs and Fe^{2+} increased the content of NH_4^+-N by 52%.	6
	ZnO NPs	200, 500, and 1000 mg/kg	50 nm	30 days	Pokeweed	500 mg/kg ZnO NPs decreased soil AP content by 27.27%, but did not alter total N and NH_4^+-N content, significantly.	7
	ZnO NPs	1.7 mg Zn/kg	Length:	After wheat full	Wheat	In either arid or non-arid soil, the addition of ZnO	8

			400 nm; width: 150 nm	maturity	(*Triticum aestivum* L.)	NPs did not alter the content of soil NH_4^+-N, NO_3^--N, and P.	
	ZnO NPs	0, and 500 mg/kg	30 nm	9 weeks	Maize	In soil without additional P addition, ZnO NPs did not alter the soil AP content, significantly. But, ZnO NPs reduced the AP content by 50.36% in the presence of exogenous P (50 mg/kg) and AMF.	10
Toxic metal	Ag NPs	0.025, 0.25 and 2.5 mg/kg	20.4±3.2 nm	20 days	*Zea mays* L.	Soil soluble Ag significantly increased.	1
	Ag NPs	1, 10, and 50 mg/kg	15 nm	7, and 63 days	*Lactuca sativa*	Soil extractable Ag increased significantly, was concentration-dependent, and varied over time	3
	Nano-ZnO, Nano-CuO	300 mg/kg	Nano-ZnO: 50±10 nm; Nano-CuO:	30 days	H. vulgare L. (*cultivar Ella*)	Under ENPs co-exposure, the extractable metal concentrations in soil were lower than under single treatments.	13

		100±25 nm				
CeO_2 NPs	25 mg/kg	25 nm	150 days	Rice	Fe^{2+} promoted the accumulation of residual Ce in soil compared to individual CeO_2 NPs.	6
ZnO NPs	200, 500, and 1000 mg/kg	50 nm	30 days	Pokeweed	ZnO NPs exposure significantly increased soil Zn^{2+} content.	7
ZnO NPs	1.7 mg Zn/kg	Length: 400 nm; width: 150 nm	After wheat full maturity	Wheat (*Triticum aestivum* L.)	Under drought conditions, Zn NPs significantly increased the soil residual Zn content, but in non-arid soils, the effect was not significant.	8
ZnO NPs	3, 20, and 225 mg Zn/kg	57±32 nm	Aging for 1 year; Plant culture: 30 and 60 days (green pea), 60 and 90 days (beet)	Green pea (*Pisum sativum* L.) and beet (*Beta vulgaris* L).	The exposure of high-dose ZnO NPs significantly increased the content of potentially available Zn in both soils, higher in acidic soil than in calcareous soils.	14
ZnO NPs	3, 20, and 225 mg Zn/kg	58.40±3 0.13 nm	30 days (bean), 90 days (tomato)	Bean (*Phaseolus*	The exposure of high-dose ZnO NPs significantly increased the content of potentially available Zn in	15

				vulgaris) and tomato (*Solanum lycopersicon*)	both soils, much higher in acidic soil than in calcareous soils.	
ZnO NPs	20, 225, 450, and 900 mg Zn/kg	68±12 nm	35 days	Wheat, maize, radish, bean, lettuce, tomato, pea, cucumber, and beet.	In acidic soils, ZnO NPs increased the content of bioavailable Zn in a dose-dependent manner, and it varies in the rhizosphere soil of different plant species.	9
ZnO NPs	25, 50, 75, and 100 mg/kg	20–30 nm	125 days	Wheat	ZnO NPs inhibited the toxicity of Cd on plants.	16
ZnO NPs	25, 50, and 100 mg/kg	20–30 nm	125 days	Wheat	With increasing levels of ZnO NPs, the mobility of Cd in soil decreased significantly.	17
ZnO NPs (coated and non-	10, 100, and 1000 mg/kg	100 nm (coated ZnO	30 days	Cucumber	Organic matter and the dose and source of Zn changed the distribution of ZnO among soil five fractions.	18

coated)		NPs), 75 nm (non-coated ZnO NPs)				
ZnO NPs	0, 50, 250, and 500 mg/kg	30 nm	9 weeks	Sweet sorghum	ZnO NPs exhibited synergistic toxicity with Cd at high doses and antagonistic toxicity at low doses.	19
ZnO NPs	0, and 500 mg/kg	30 nm	9 weeks	Maize	ZnO NPs increased the concentration of soil extractable Zn, which is affected by AMF inoculation.	10

Note: GSNPs, green silver nanoparticles; CSNPs, conventionally synthesized silver nanoparticles; SNPs, silver nanoparticles; AMF, arbuscular mycorrhizal fungi; DOC, dissolved organic cardon; AP, available P.

Table S2 Effect of metal-based nanomaterials on rhizosphere microorganism.

Type of microorganism	NMs types	Concentration	Size	Incubation time	Plant types	Effects	Reference
Fungi	Ag NPs	0.025, 0.25 and 2.5 mg/kg	20.4±3.2 nm	20 days	*Zea mays* L.	2.5 mg/kg Ag NPs significantly decreased the diversity of AMF community, changed community structure, and decreased the mycorrhizal colonization of AMF.	[1]
	ZnO NPs	0, 50, 250, and 500 nm	30 nm	9 weeks	Sweet sorghum	Cd and ZnO NPs alone or in combination reduced the root colonization rate of AMF.	[19]
	ZnO NPs	0, and 500 mg/kg	30 nm	9 weeks	Maize	ZnO NPs decreased root colonization rate of AMF.	[10]
	ZnO NPs	0, 50, and 500 ZnO mg/kg	30±10 nm	1 month	Maize	ZnO NPs alone or in combination with MPs affected the structure and diversity of AMF community.	[11]
	TiO_2 NPs	1, 100, and 1000 mg/kg	29±9 nm; 92±31 nm	12 weeks	Wheat	TiO_2 NPs did not affect root colonization rate of AMF.	[20]
Bacteria	GSNPs, CSNPs	20, 25, 50, and 100 mg/kg	–	60 days	*P. vulgaris*	GSNPs significantly increased the counts of total bacteria, nitrogen fixing and phosphate solubilizing bacteria.	[5]

Ag NPs	1 and 3 mg/kg	10–12 nm	14 d	Wheat	Ag NPs or combined treatments with glyphosate reduced rhizosphere soil bacterial Alpha-diversity and richness, and significantly altered the microbial community structure.	21
Ag NPs	1 mg/kg	9–10 nm	0, 2, 7, 21, 35 and 49 days	Wheat	Ag NPs could significantly affect soil bacterial community structure, most prominently during the period of transition from wheat seedling stage to vegetative stage.	22
Ag NPs	1, 10, and 100 mg/kg	–	4 weeks	*Arabidopsis thaliana* Col-0	Altered microbial structure by Ag NPs led to a significant decrease in the functional diversity. And the activities of plant growth-promoting bacteria changed.	12
Ag NPs	1, 10, and 50 mg/kg	15 nm	7, and 63 days	*Lactuca sativa*	Ag NPs altered the structure of bacterial community by regulating bacterial populations associated with elemental cycling and stress tolerance.	3
Ag NPs	1 mg/kg	20 nm	120 days	Rice	1 mg/kg Ag NPs had no significant effect on the bacterial community diversity, but significantly reduced their richness.	23
Ag NPs	100 mg/kg	20 nm	60 days	Cucumber	Ag NPs significantly reduced microbial community	4

				(*Cucumis sativa*)	richness, and altered bacterial community composition.	
CeO_2 NPs	25 mg/kg	25 nm	150 days	Rice	CeO_2 NPs did not affect α-diversity of bacterial community, but the combined exposure of Fe^{2+} and CeO_2 NPs decreased α-diversity of bacterial community. In addition, CeO_2 NPs changed bacterial community composition.	[6]
ZnO NPs	200, 500, and 1000 mg/kg	50 nm	30 days	Pokeweed	The bacterial community structure at the phylum and genus levels was altered upon ZnO NPs exposure. Among them, the relative abundance of bacterial taxa associated with hydrocarbon-degradation was significantly reduced.	[7]
ZnO NPs	0, 1, 10, and 100 mg ZnO/kg	90 nm	7 weeks	Lettuce (*Lactuca sativa* L.)	Despite no change of alpha diversity, 10 mg/kg ZnO NPs altered the soil bacterial community structure.	[24]

Table S3 Effects of metal-based nanomaterials on soil enzyme activities.

NMs types	Concentration	Size	Incubation time	Plant types	Effects	Reference
Ag NPs	0.025, 0.25 and 2.5 mg/kg	20.4±3.2 nm	20 days	*Zea mays* L.	2.5 mg/kg Ag NPs decreased soil alkaline phosphatase activity by 4.24%.	[1]
Ag NPs	0.024, 0.24, 4.80 and 9.6 mg/kg	10–40 nm	28 days	The wetland plants (*I. wilsonii*, *A. donax*, and *T. orientalis*)	4.80 and 9.6 μg/g Ag NPs inhibited the exoenzyme activities, but the effects of 0.024 μg/g Ag NPs on the exoenzyme activities correlated with plant types.	[25]
Ag NPs	10 mg/kg	7–14 nm	72 weeks	Tomato	Ag NPs decreased the activities of urease and phosphatase, significantly.	[2]
GSNPs, CSNPs	20, 25, 50, and 100 mg/kg	–	60 days	*P. vulgaris*	SNPs significantly increased urease activity. Among them, 50 mg/kg GSNP increased its activity by 9.66%.	[5]
Ag NPs	1, 10, and 100 mg/kg	–	4 weeks	*Arabidopsis thaliana*	100 mg/kg Ag NPs significantly altered soil enzyme activities. Among them, the activities of enzymes (cellulase activity, amylase activity, and	[12]

				Col-0	protease activity) responsible for depolymerizing complex organic matter were increased in a dose-dependent manner, but the activities of dehydrogenase activity and keratinase activity were decreased.	
CeO_2 NPs	25 mg/kg	25 nm	150 days	Rice	Compared to control, CeO_2 NPs increased invertase and dehydrogenase activities, but suppressed cellulase activity. However, the presence of Fe^{2+} mitigated the effects of the nanoparticles.	6
ZnO NPs	200, 500, and 1000 mg/kg	50 nm	30 days	Pokeweed	Enzyme activities associated with the carbon cycle (glucosidase activity) were enhanced upon ZnO NPs exposure.	7
ZnO NPs	0, 50, 250, and 500 mg/kg	30 nm	9 weeks	Sweet sorghum	High doses of ZnO NPs inhibited the activities of urease, phosphatase and catalase, but the addition of Cd alleviated the inhibitory impact of ZnO NPs.	19

Table S4 Effects of metal-based nanomaterials on plant root function

NMs types	Concentration	Size	Incubation time	Plant types	Effects	Reference
Ag NPs	0.025, 0.25 and 2.5 mg/kg	20.4±3.2 nm	20 days	*Zea mays* L.	2.5 mg/kg Ag NPs decreased plant root biomass, significantly.	[1]
CuO-NPs, Al_2O_3-NPs	20, 200, and 2000 mg/kg	CuO-NPs: 18 nm; Al_2O_3-NPs: 21 nm	40 days	Tomato	CuO-NPs and Al_2O_3-NPs significantly increased total soluble protein in the root; CuO-NPs inhibited the root/shoot length in a dose-dependent manner except 200 μg/g CuO-NPs in soil significantly increased root length; Al_2O_3-NPs increased fresh weight of roots and shoots in a dose-dependent manner; NPs caused mass production of the roots ROS, and activated the antioxidant system.	[26]
Ag NPs, Fe NPs	1.53×10^{13} NPs/m^2 Ag NPs, 2.35×10^{11} NPs/m^2 Fe NPs	Ag NPs: 81.84±0.67 nm; Fe NPs: 207.30±2.	25 days	Soybean (*Glycine max*)	Ag NPs decreased the dry biomass of plant root, and induced oxidative stress of plant roots, but Ag NPs did not cause root length changes and the upregulation of genes related to lignification in soybean seedlings; Fe NPs triggered upregulation of POD2 and POD7 genes, but no changes in	[27]

		0 nm.			root biochemical marker levels were observed.	
Ag NPs	833 mg Ag/kg dry soil	48.8±12.6 nm	14 days (*T. pratense)*, and 21 days (*E. lanceolatus)*	*T. pratense,* and *E. lanceolatus*	Ag NPs exposure inhibited plant growth, and roots exhibited severe dysplasia and dark discoloration.	28
Nano-ZnO, Nano-CuO	300 mg/kg	Nano-ZnO: 50±10 nm; Nano-CuO: 100±25 nm	30 days	*H. vulgare* L. (cultivar Ella)	Under nano-Zn exposure, the accumulation of Zn in the roots was lower than that in the leaves, while under nano-Cu exposure, the accumulation of Cu in the roots was higher than in the leaves.	13
Cu NPs, Ni NPs, and Zn NPs	100, 1000, and 10000 mg/kg	Cu NPs:50 nm; Ni NPs: 70–80 nm; Zn NPs:	7 days	Radish (*Raphanus sativus* L.)	NPs decreased the length of plants roots. Among them, the order of phytotoxicity was Cu NPs, Zn NPs, and Ni NPs.	29

		90–150 nm				
Cu/Fe based nanoparticles	0.2, 0.1, 0.05, and 0.025 µg ai/gr soil	36 nm	40 days	Tomato	Cu/Fe based NPs evidently increased root weight of tomato plants.	30
Ag NPs	Ag concentration: 10.4±2.1 mg.kg (exposed treatments)	22.6±7.8 nm	Lettuce: 52 days; Radish: 71 days; Chili: 67 days.	Chili (*Capsicum annuum* L.), lettuce (*Lactuca sativa*), and radish (*Raphanus sativus* L.)	Ag NPs significantly reduced the fresh weight of radish roots. Moreover, it had minimal impacts on the contents of essential elements in the radish roots.	31
Ag NPs	1 mg/kg	9–10 nm	0, 2, 7, 21, 35 and 49 days	Wheat	Ag NPs did not significantly affect wheat root growth.	22
Ag NPs	25 mg/kg	25 nm	150 days	Rice	Under the treatment of CeO_2 NPs, the SOD activity was decreased, and the CAT activity was increased in roots. In addition, the co-exposure of CeO_2 NPs and Fe^{2+} decreased MDA content.	6
Ag NPs	1, 10, and 50	15 nm	7, and 63	*Lactuca sativa*	Ag NPs did not alter root biomass, and Ag contents in plant	3

	mg/kg		days		roots increased before 15 days and subsequently decreased.	
Ag NPs	20, 200, and 2000 mg/kg	5.6 nm	3 months	Wheat (*Triticum aestivum* L.)	Compared with the control, length and fresh weight of root decreased with increasing dose of Ag NPs.	32
Ag NPs	100 mg/kg	20 nm	60 days	Cucumber (*Cucumis sativa*)	Ag NPs decreased the biomass of cucumber roots, significantly.	4
ZnO NPs	200, 500, and 1000 mg/kg	50 nm	30 days	Pokeweed	Root length was inhibited under ZnO NPs exposure, but the biomass of root was not affected, significantly.	7
ZnO NPs, CuO NPs	50, 500, 1000 and 2000 mg/kg	ZnO NPs: 34±10 nm; CuO NPs: 18.4±5.5 nm.	20 days, 40 days	Maize (*Zea mays*)	ZnO NPs significantly promoted root length of maize at low concentrations (0.05 and 0.5 mg/g), but ZnO and CuO NPs significantly inhibited it at high concentrations (2 mg/g). And, similar trends were shown for root dry weight. In addition, NPs could induce oxidative stress in roots.	33
ZnO NPs, CuO NPs, Al_2O_3 NPs, and TiO_2 NPs	50, 500, 1000, 2000, and 4000 mg/kg	3.9–34 nm	30 days	Cucumber (*Cucumis sativus*)	High concentration of NPs significantly inhibited plant root growth, and induced membrane damage in root tissue and improved the activities of antioxidant enzymes.	34
ZnO NPs	300, 600, and	Average	90 days	Tomato (*Solanum*	ZnO NPs increased H_2O_2 and MDA content, and decreased	35

	1000 mg/kg	length: 148 nm		*lycopersicum*)	APX and SOD in the root, significantly.	
ZnO NPs	3, 20, and 225 mg Zn/kg	55±27 nm	3 months	Cherry tomato (*Solanum lycopersicum* L var. cerasiforme)	ZnO NPs changed the content of micronutrients and macronutrients in plant roots, and the effect was related to soil type.	36
CuO NPs	100, and 300 mg Cu/kg	–	7 days	Wheat (*Triticum aestivum*)	In alkaline calcareous soil (pH 8.3), CuO NPs did not alter the length of wheat root, but 300 mg/kg CuO NPs significantly reduced it in acidic soil.	37
ZnO NPs	1, 3, and 5 mg Zn/kg	18 nm	After sorghum full maturity	Sorghum (*Sorghum bicolor* var. 251)	Under drought stress, ZnO NPs increased the dry weight of plant root, and promoted the uptake of N, P, and K by sorghum roots.	38
ZnO NPs	20, 225, 450, and 900 mg Zn/kg	68±12 nm	35 days	Wheat, maize, radish, bean, lettuce, tomato, pea, cucumber, and beet.	Both in acidic soil and calcareous soil, the plant root Zn content increased with the increase of Zn dose in the soil, and the root Zn content varied significantly between different plant species.	9
ZnO NPs	25, 50, 75, and	20–30 nm	125 days	Wheat	ZnO NPs increased the dry weight of wheat root.	16

	100 mg/kg					
ZnO NPs	25, 50, and 100 mg/kg	20–30 nm	125 days	Wheat	ZnO NPs promoted the growth of root, and decreased the Cd concentration in a dose-dependent manner whether in the absence of drought or drought conditions.	17
CuO NPs, and ZnO NPs	300 mg Cu/kg, 500 mg Zn/kg	50 nm (CuO NPs), 70 nm (ZnO NPs)	13 days	Wheat	CuO NPs caused the growth of root hairs near the root tip, while ZnO NPs promoted lateral root development.	39
Uncoated (Z-COTE®) and coated (Z-COTE-HP1®) ZnO nanomaterials (NMs)	62.5, 125, 250, and 500 mg/kg	–	45 days	Common bean (*Phaseolus vulgaris* L. var. red hawk kidney)	Z-COTE-HP1® increased the root length at all concentrations. At the treatment of 125 mg/kg Z-COTE-HP1®, the content of Zn, S and Mg in roots increased by 140%, 65%, and 44%, respectively.	40
ZnO NPs	10, 100, and	100 nm	30 days	Cucumber	Root showed an inverse U-shape response to ZnO NPs dose,	18

(coated and non-coated)	1000 mg/kg	(coated ZnO NPs), 75 nm (non-coated ZnO NPs)			namely, low concentration promotion and high concentration inhibition. In addition, under 1000 mg/kg ZnO NPs treatment, the root tip deformation was observed, which depended on the soil organic matter.	
ZnO NPs	0, 50, 250, and 500 mg/kg	30 nm	9 weeks	Sweet sorghum	The coexistence of high-dose ZnO NPs and Cd had synergistic toxicity and inhibited plant growth.	19
ZnO NPs	0, and 500 mg/kg	30 nm	9 weeks	Maize	500 mg/kg ZnO NPs increased the absorption of Mg and Cu by AMF inoculated plants, and decreased the P absorption of AMF uninoculated plants.	10
ZnO NPs	0, 50, and 500 ZnO mg/kg	30±10 nm	1 month	Maize	ZnO NPs did not change root dry biomass, significantly. But, microplastics increased Zn content in roots under the treatment of ZnO NPs.	11

Note: POD, peroxidase; MDA, malondialdehyde; APX, ascorbate peroxidase; SOD, superoxide dismutase; CAT, catalase.

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