Electronic Supplementary Material (ESI) for Metallomics.

Supporting Information

Dissolved Cerium contributes to uptake of Ce in presence of differently sized CeO_2-nanoparticles by three crop plants

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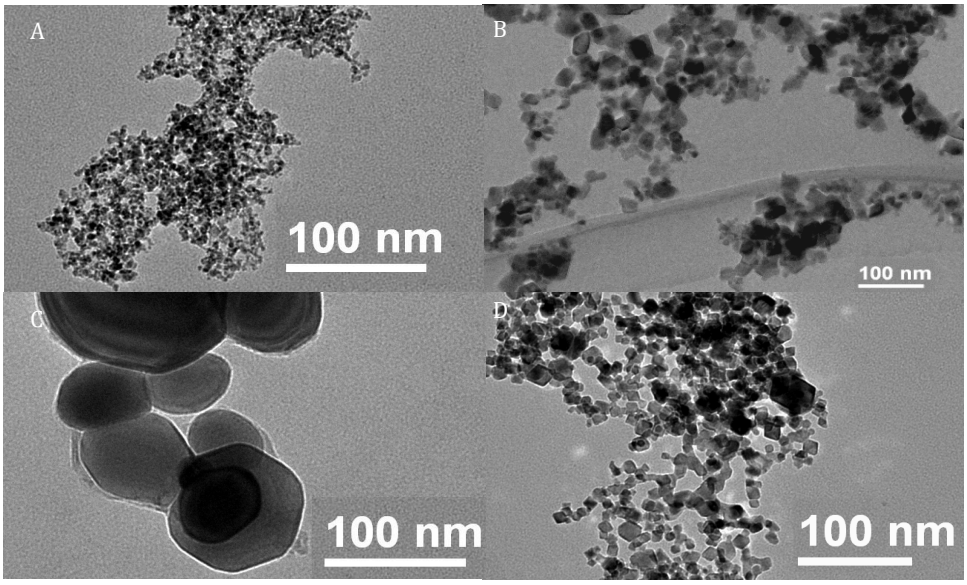
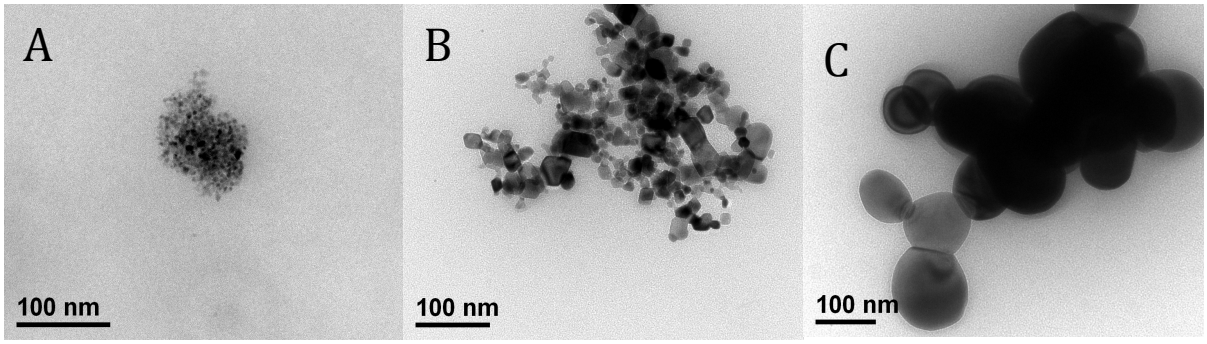


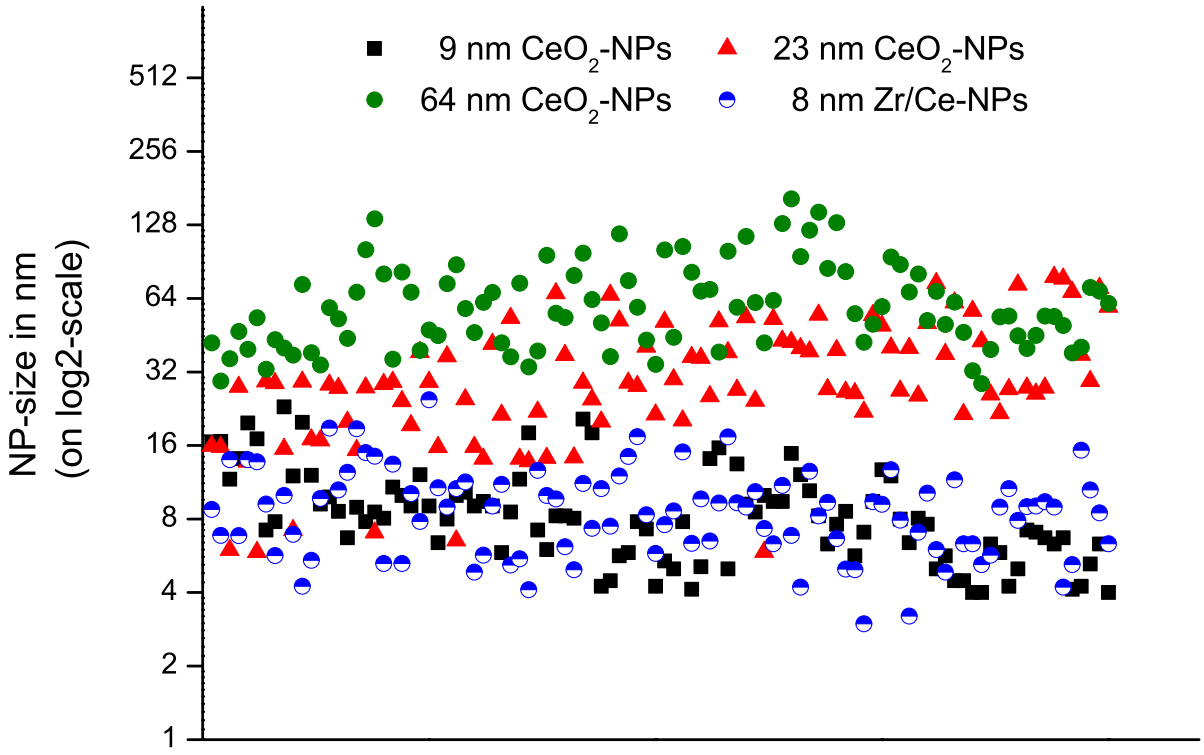
SI Fig. 1 TEM images of CeO_2 and Zr/CeO_x NPs in Millipore water; suspended with polyacrylamide. A) 9 nm CeO_2 NPs, B) 23 nm CeO_2 NPs, C) 64 nm CeO_2 NPs, D) 9 nm Zr/CeO_x NPs



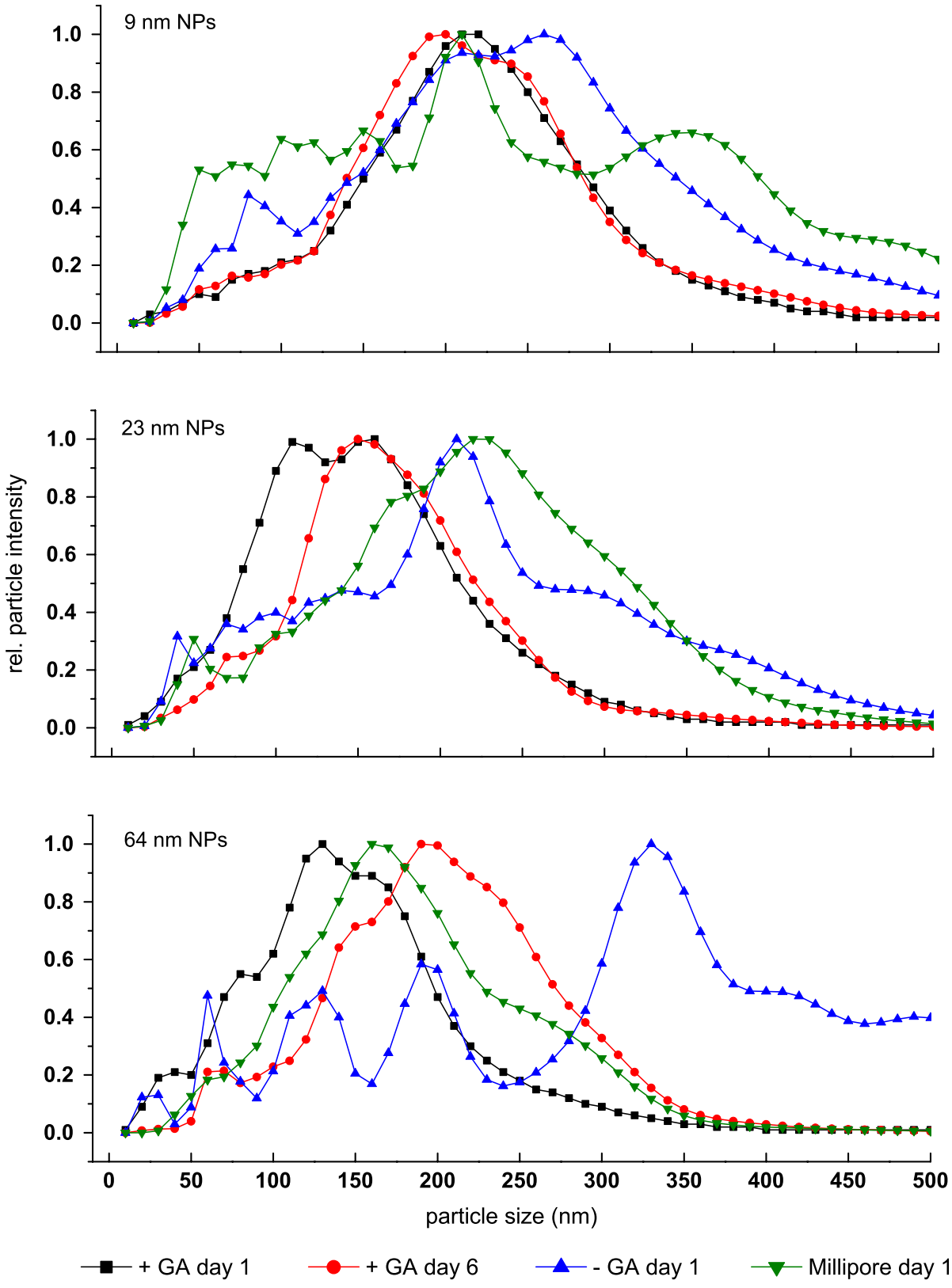
SI Fig 2. TEM images of CeO_2 dispersed in Hoagland medium after 7 d. A) 9 nm CeO_2-NPs, B) 23 nm CeO_2-NPs, C) 64 nm CeO_2-NPs

SI Table 1 XRF analysis of NP-groups. All detected elements are listed.

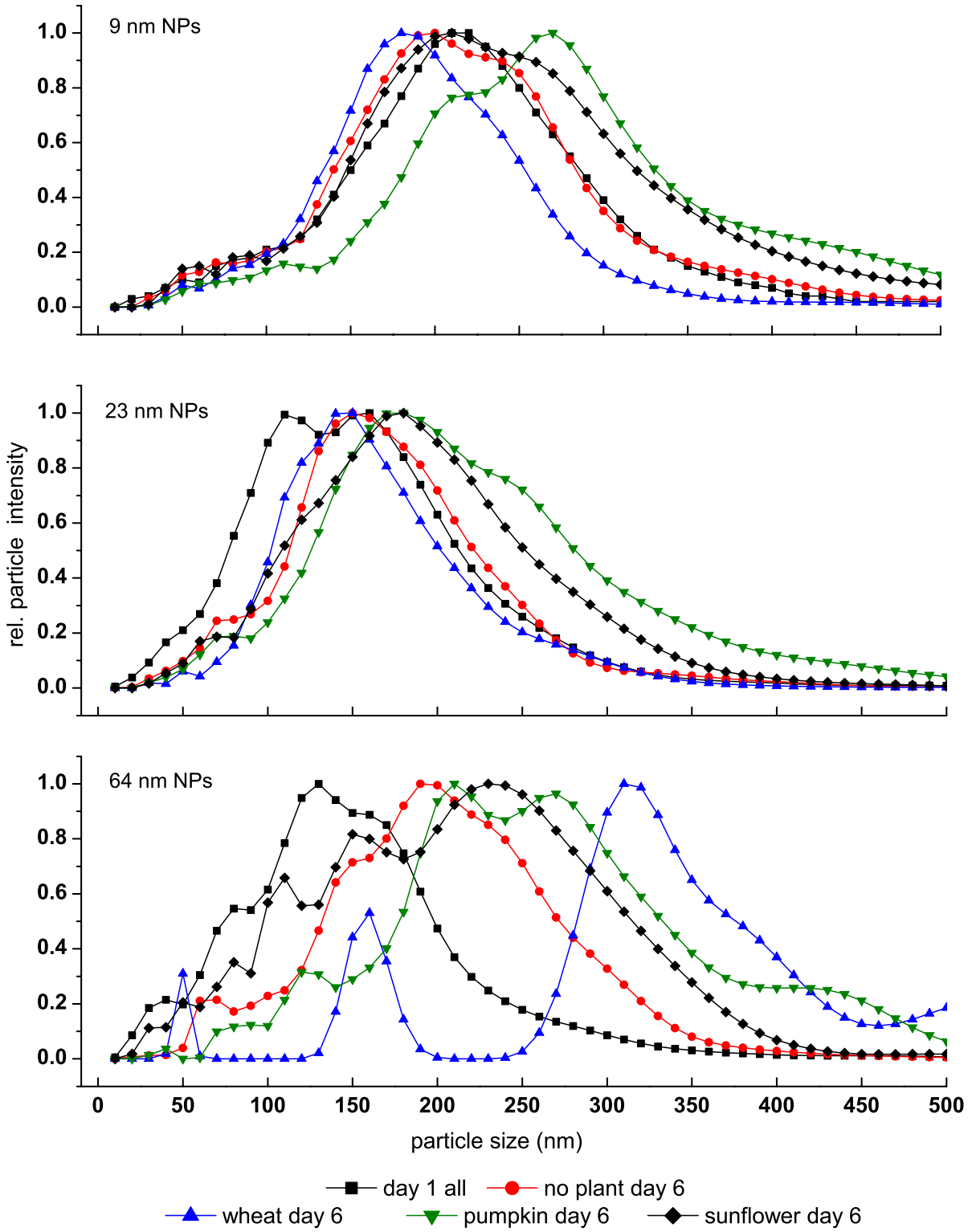
Element in %	**NP-group**			
	CeO_2 9 nm	**CeO_2 23 nm**	**CeO_2 64 nm**	**Zr/CeO_x 8 nm**
Cerium	77.22	81.36	85.18	25.26
Zirconium	< 0.01	< 0.01	< 0.01	23.25
Carbon (total)	1.24	0.21	0.05	0.28
Niobium	< 0.01	< 0.01	< 0.01	0.06
Molybdenum	< 0.01	< 0.01	< 0.01	0.09
Cesium	0.46	0.36	0.24	0.09
Barium	0.45	0.41	0.19	0.03
Lanthanum	0.56	0.60	0.47	0.15
Praseodymium	0.42	0.46	0.47	0.15
Neptunium	0.41	0.47	0.32	< 0.01
Hafnium	< 0.01	< 0.01	< 0.01	0.22
Sulfur	< 0.01	< 0.01	0.05	< 0.01
Chlorine	< 0.01	0.05	0.30	< 0.01
Vanadium	0.08	0.09	0.08	< 0.01



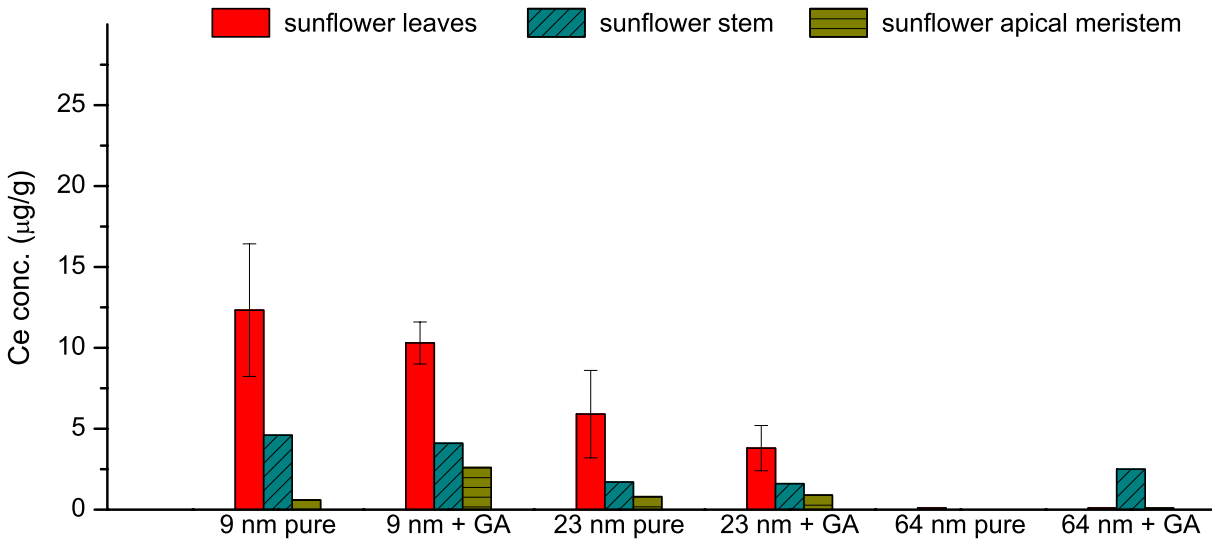
SI Fig. 3 Scatter plot of the size of 100 primary particles in each NP group, measured via TEM-image-recognition.



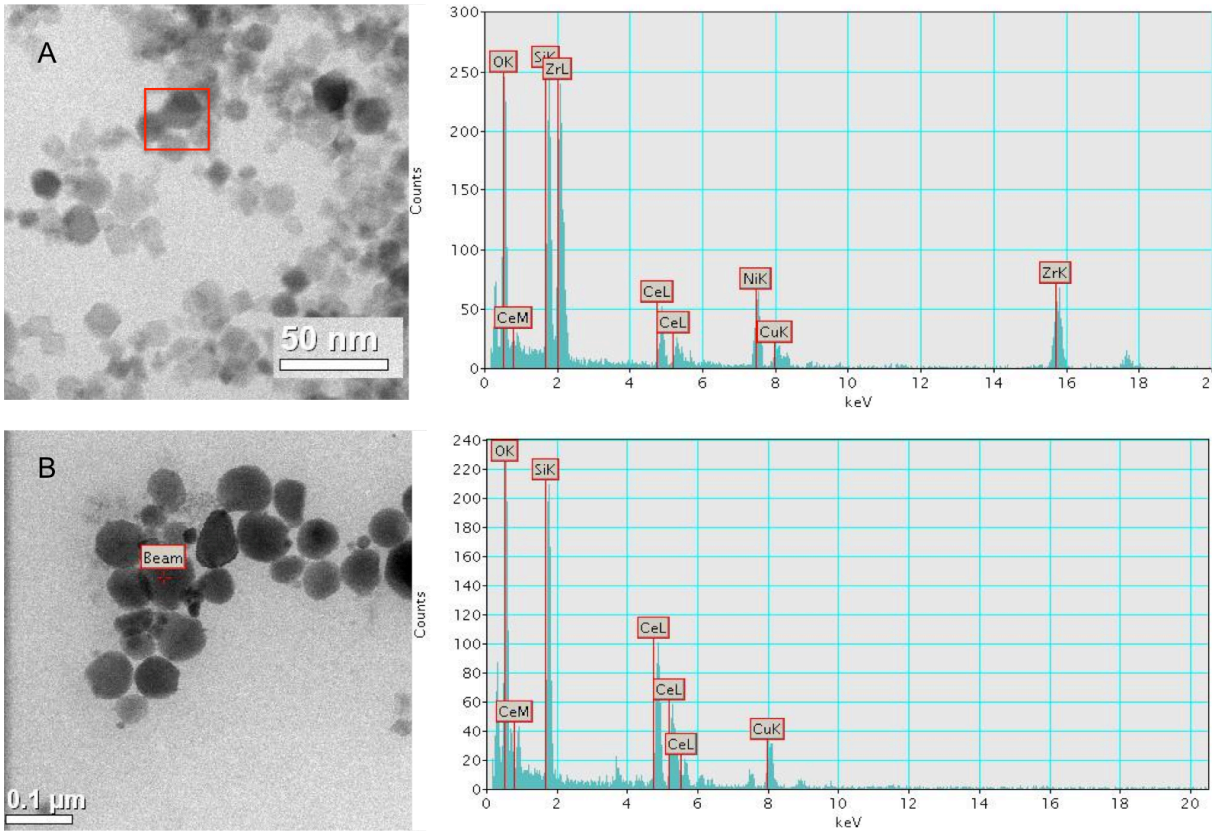
SI Fig. 4 Particle size distribution obtained via NTA (nanosight LM 20) in Hoagland medium without plants. Lines show difference in behavior of NPs in respect to NP-treatment, the legend is the same in all 3 sections



SI Fig. 5 Particle size distribution obtained via NTA (nanosight LM 20). Lines show difference in behavior of NPs in respect to plant species grown on the medium dispersion, the legend is the same in all 3 sections



SI Fig.6 Ce-concentration in µg/g in the specific parts of sunflower shoots after treatment with the different NP-size-groups (x-axis).



SI Fig. 7 Control STEM-EDX images of Zr/Ce-NP. A) Image (left side) and EXD-Spectrum (right side) of Zr/CeO_x-NPs centrifuged on grids right after dispersion in Millipore water. B) Images of particles found in control-leaves mixed with $Ce_2(SO_4)_3$-powder before ashing, right side EDX-spectrum of indicated spot.

*SI Table 2 Plant parameters of pumpkin plants, giving pH of medium dispersion at the time of harvest (d 6), dry weight (DW) of green part (shoot) and the DW of roots per plant, relative chlorophyll content was measured on d 1 and d 6 of treatment and values (d 1) were deduced, negative values indicate decrease of chlorophyll content over time of treatment, whereas positive values indicate an increase. * indicates p< 0.05 and ** p <0.01 for significant changes in relative chlorophyll content. Brackets around plant ID indicate that plant died before treatment started.*

pumpkin plant ID	pH	green DW	root DW	Δ rel. Chlorophyll content = d6 - d1						*/**
				I	II	III	IV	V	VI	
Control 1	5.2	1.53	0.39	-0.3	-7.7	-4.8	-3.6	9	6.5	
Control 2	5.1	1.41	0.56	-3.8	-0.5	-18	-16.7	16.3	16.9	
Control 3	5.3	2.01	0.69	-2.9	-5.2	-5.3	-1.6	3.7	-5.1	
(Control 4)										
Control + GA 1	4.6	2.60	0.81	0.5	-5.6	4.9	-3.1	-1.5	-0.7	
Control + GA 2	4.6	2.06	0.55	0.9	-0.9	-4	0.8	3.2	6.2	
Control + GA 3	5.8	3.57	0.78	-2	-14	-6.5	-9.8	-2.2	-4.4	*
(Control + GA 4)										
9 nm pure 1	5.9	4.76	0.59	-15.2	-15.6	0.9	-2.6	1.4	2	
9 nm pure 2	5.9	*wilted*	0.43	0.7	-8.6	-3.1	-4.9	-6.8	-1.6	*
9 nm pure 3	5.5	2.58	0.54	3.8	0	-2.3	2.3	2.3	0.2	
9 nm pure 4	5.3	1.95	0.37	-1.2	-6.8	0.5	-4.3	-0.8	6.3	
9 nm + GA 1	5.2	2.65	0.70	-5.5	1	-1.1	-0.9	3.8	-1	
9 nm + GA 2	4.8	3.03	1.17	-4.1	-1	2.4	0.3	-4.3	-3.7	
9 nm + GA 3	5.6	2.67	0.58	1.9	5.3	0.8	3.4	5.5	-0.7	*
9 nm + GA 4	5.8	4.63	0.46	0.9	-4.5	5.1	1.7	3.7	-1.3	
23 nm pure 1	5.3	2.97	0.55	0	2.7	-2.7	4.4	-4	5.5	
23 nm pure 2	5.5	4.84	0.68	-1.8	-12.9	-6.9	2.1	2.1	8.5	
23 nm pure 3	5.9	3.02	0.54	-1	-3.1	-0.2	-3.2	1.3	0.4	
23 nm pure 4	5.3	2.71	0.43	1.3	-0.8	-3.4	2.5	0.6	7.3	
23 nm + GA 1	5.6	2.96	0.66	-8.5	-3.1	-2.9	-4	-4.5	-0.4	*
23 nm + GA 2	6.1	2.47	0.31	-5.1	4.6	-0.7	3.4	17.4	12.9	
23 nm + GA 3	6.1	3.07	0.53	-13.9	-10.1	-6.5	-5.3	3.4	1.8	
23 nm + GA 4	6.0	2.82	0.41	-0.2	-2.8	-2.4	6.6	0.1	0.7	
64 nm pure 1	5.6	3.15	0.73	-12	-9.8	0.7	2.6	1.6	1.6	
64 nm pure 2	4.4	2.06	0.68	-2.6	-6.1	1.5	-7.2	2.4	3.6	
64 nm pure 3	4.5	2.38	0.67	0	-0.9	-2.1	-7.8	-3.6	-6.4	*
64 nm pure 4	5.8	2.07	0.33	-7.2	-8.1	4	-5.5	7.6	4.6	
64 nm + GA 1	5.8	2.45	0.37	-2.8	-0.8	2.1	-1.1	-3	1.4	
64 nm + GA 2	5.6	2.66	0.66	-6.1	-13.2	-5.2	-5.8	3	9.6	
64 nm + GA 3	5.5	2.94	0.73	-0.9	-5.5	3.3	2	1.3	-2.4	
64 nm + GA 4	4.7	3.01	0.78	0	-4.1	-0.1	-6.3	1.7	-1.6	

*SI Table 3 Plant parameters of sunflower plants, giving pH of medium dispersion at the time of harvest (d 6), dry weight (DW) of green part (shoot) and the DW of roots per plant, relative chlorophyll content was measured on d 1 and d 6 of treatment and values (d 1) were deduced, negative values indicate decrease of chlorophyll content over time of treatment, whereas positive values indicate an increase. * indicates p< 0.05 and ** p <0.01 for significant changes in relative chlorophyll content. Brackets around plant ID indicate that plant died before treatment started.*

sunflower plant ID	pH	green-DW	root-DW	Δ rel. Chlorophyll content = d6 - d1						*/**
				I	II	III	IV	V	VI	
Control 1	5.4	2.04	0.85	-0.3	3.7	1.5	0.8	2.7	3.6	*
Control 2	5.7	0.49	0.13	8.8	11.9	7.6	2.3	6.7	14.2	**
(Control 3)										
(Control 4)										
Control + GA 1	5.3	2.66	1.19	-3.8	3.7	2.6	3.2	4.2	0.5	
Control + GA 2	5.8	0.96	0.27	-6.6	-2.8	9.5	5.4	2.7	-4.3	
(Control + GA 3)										
(Control + GA 4)										
9 nm pure 1	5.5	2.24	0.63	4.8	4.5	7.7	6.5	1.6	6.1	**
9 nm pure 2	5.6	2.82	1.43	2.4	0.6	3.3	1.4	-1.3	3.3	
9 nm pure 3	5.7	0.83	0.30	9.1	14.3	3.4	5.1	5.3	8.3	**
9 nm pure 4	5.7	0.77	0.25	11.8	10.9	2.7	3.6	8.2	7.5	**
9 nm + GA 1	5.8	1.23	0.37	8.5	5	7.1	5.6	7.1	9.3	**
9 nm + GA 2	5.9	0.70	0.30	7.3	7.8	-0.5	3	9.2	7.5	**
9 nm + GA 3	5.4	2.54	1.43	-1.9	-0.3	2.1	-2.2	3.1	2.8	
9 nm + GA 4	5.8	1.40	0.42	3.9	6.7	3.7	4.1	6	4.5	**
23 nm pure 1	5.5	1.91	0.68	6.5	6	0.3	6.9	5.6	5.4	**
23 nm pure 2	5.7	1.05	0.40	4.4	10.2	2.2	3.3	6.4	7.2	**
23 nm pure 3	5.7	0.84	0.31	13.7	18.9	4	5.5	16.1	15.1	**
23 nm pure 4	5.7	0.82	0.37	6	9.3	2.2	1.8	9.2	8.9	**
23 nm + GA 1	5.5	2.15	0.78	5.3	3.8	3	9.4	3.1	3.7	**
23 nm + GA 2	5.4	1.30	0.58	10.1	9.4	7.6	2	11.2	11	**
23 nm + GA 3	5.7	0.82	0.28	19.8	5.9	2.5	0.4	9.4	7.2	*
(23 nm + GA 4)										
64 nm pure 1	5.7	2.08	0.93	9.2	3.6	7.2	1.2	7	7.2	**
64 nm pure 2	5.3	2.17	0.92	0	3	5.1	3.9	-1.2	-1.8	
64 nm pure 3	5.7	0.52	0.21	4.3	5.5	7	4.6	4.2	2.9	**
64 nm pure 4	5.7	1.19	0.32	10.1	10	3.5	4.6	6.3	4.9	**
64 nm + GA 1	5.7	1.51	0.61	1.4	5.2	0.8	2.6	4.9	5.7	**
64 nm + GA 2	5.9	0.80	0.37	-0.2	2.4	3.2	8.2	4.4	4.1	*
64 nm + GA 3	5.7	1.13	0.48	10.9	8.8	5.1	-3.6	4.4	7.9	*
64 nm + GA 4	5.5	3.66	1.39	-0.3	3.9	7.9	1.2	0	9.7	

*SI Table 4 Plant parameters of wheat plants, giving pH of medium dispersion at the time of harvest (d 6), dry weight (DW) of green part (shoot) and the DW of roots per plant, relative chlorophyll content was measured on d 1 and d 6 of treatment and values (d 1) were deduced, negative values indicate decrease of chlorophyll content over time of treatment, whereas positive values indicate an increase. * indicates p< 0.05 and ** p <0.01 for significant changes in relative chlorophyll content. Brackets around plant ID indicate that plant died before treatment started.*

wheat plant ID	pH	green DW	root DW	Δ rel. Chlorophyll content = d6 - d1						*/**
				I	II	III	IV	V	VI	
Control 1	6.4	0.96	0.31	-10.4	-4.8	11.8	14.9	-2.9	5.3	
Control 2	6.2	1.48	0.55	-5.3	2	-12.2	-11.6	7.1	7	
Control 3	6.2	0.97	0.36	10.5	-3.5	-4.4	1.7	-4	-1.7	
(Control 4)										
Control + GA 1	6.3	1.12	0.37	0.8	-0.6	4.7	2.9	2.1	-5.4	
Control + GA 2	6.3	1.42	0.48	2.8	-1.1	-2.3	1.6	-11.4	-0.1	
Control + GA 3	6.3	1.29	0.34	-6	-2.3	-6.9	-0.9	-7.2	-2.8	**
(Control + GA 4)										
9 nm pure 1	6.3	1.46	0.57	-3.6	5.3	12.3	21.5	14.2	23.4	*
9 nm pure 2	6.4	1.33	0.49	2.1	4.7	9.3	17.2	14.5	13.4	**
9 nm pure 3	6.2	1.17	0.56	-6.5	11.5	4.2	7.5	7.7	14.7	
9 nm pure 4	6.4	0.84	0.46	3.3	2.8	17.9	25.4	1.7	1.4	
9 nm + GA 1	6.3	1.00	0.38	-2.6	5.7	3.2	7	18.6	18.9	
9 nm + GA 2	6.3	1.04	0.34	6.4	9.8	11.3	11.7	13	13	**
9 nm + GA 3	6.3	1.19	0.44	-1.9	5.3	21.2	24.4	-5.9	6.6	
9 nm + GA 4	6.2	1.67	0.63	4.1	7.7	12.8	14.4	4.8	3.9	**
23 nm pure 1	6.2	1.44	0.48	2.1	7.4	10.9	11.9	14.4	6.7	**
23 nm pure 2	6.3	1.34	0.61	4.2	8.2	4.7	9.9	5.8	10.8	**
23 nm pure 3	6.3	1.17	0.60	9.6	21	11.3	21.8	5	7.7	**
(23 nm pure 4)										
23 nm + GA 1	6.3	1.43	0.53	-2.3	6.6	19.6	19.2	4.1	4	
23 nm + GA 2	6.3	1.01	0.33	7.7	13.1	5.6	10.1	-6.4	5.1	
23 nm + GA 3	6.1	0.55	0.26	7.3	12.3	7.4	6.1	5.8	7.4	**
(23 nm + GA 4)										
64 nm pure 1	6.3	1.04	0.47	2.7	6.5	6.6	13.5	22.9	23.8	*
64 nm pure 2	6.4	1.23	0.48	3.5	7.4	10.3	11.4	8.5	12.3	**
64 nm pure 3	6.3	1.26	0.53	-0.6	1.6	5.4	1.8	18.3	10.3	
64 nm pure 4	6.3	1.47	0.55	4.7	5.8	8	7.2	5.2	14	**
64 nm + GA 1	6.3	1.00	0.45	7.2	8.8	8.1	10.1	7.2	12	**
64 nm + GA 2	6.3	1.12	0.77	5.6	5.3	5.9	8.1	5.4	6.3	**
64 nm + GA 3	6.2	1.35	0.59	9.2	10.8	9	8.5	12.7	23.8	**
64 nm + GA 4	6.3	0.92	0.37	2.3	5.3	17	18.8	-3.7	7.9	

SI Table 5 Amounts of available P (free) in mg/L in the growth medium of plants over time of treatments and the corresponding changes in pH.

	d 1	d3	d6	d6	d 1	d3	d6
Plant and treatment	P (free)	P (free)	P (free)	P(total)	pH	pH	pH
Pumpkin control	6.25	2.2	0	0	6	5.41	5
Pumpkin 9 nm NPs	3.68	0.1	0	5	5.63	5.21	4.62
Pumpkin Ce-Citrate	0	0	0	3.75	5.44	5.7	6.14
Sunflower control	6.4	2.4	0	0.1	6	5.58	5.01
Sunflower 9 nm NPs	3.75	1.5	0	5	5.63	5.32	4.92
Sunflower Ce-Citrate	0	0	0	4.5	5.44	5.88	6.4
Wheat control	6.35	6.35	5.3	5	6	5.94	6.11
Wheat 9 nm NPs	3.8	2.15	1.1	6.1	5.63	5.79	5.88
Wheat Ce-Citrate	0	0	0	4.2	5.44	5.78	6.6