

Supporting Information for:

Nanoparticle surface charge influences uptake, translocation, and leaf distribution in vascular plants with contrasting anatomy

Eleanor Spielman-Sun,^a Astrid Avellan,^a Garret D. Bland,^a Ryan V. Tappero,^b Alvin S. Acerbo,^b
Jason M. Unrine,^c Juan Pablo Giraldo,^d Gregory V. Lowry^{*a}

^a Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States

^b National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, United States

^c Department of Plant and Soil Sciences, University of Kentucky, Lexington, Kentucky 40546, United States

^d Department of Botany and Plant Sciences, University of California, Riverside, CA 92521, United States

*Corresponding author:

Address: Carnegie Mellon University, Pittsburgh, PA 15213

Phone: (412) 268-2948

Email: glowry@cmu.edu

Number of Pages: 18

Number of Figures: 14

Number of Tables: 3

Table of Contents

Figure S.1 – NP hydrodynamic diameters	Page S2
Table S.1 – Dissolved Ce in exposure solution post-exposure	Page S3
Table S.2 – Total Ce uptake and root surface area approximations	Page S4
Table S.3 – LCF fitting statistics for XANES of Roots	Page S5
Figure S.2 – XRF maps of corn exposed to CeO ₂ (–)	Page S6
Figure S.3 – XRF maps of corn exposed to CeO ₂ (0)	Page S7
Figure S.4 – XRF maps of rice exposed to CeO ₂ (–)	Page S8
Figure S.5 – XRF maps of rice exposed to CeO ₂ (0)	Page S9
Figure S.6 – XRF maps of lettuce exposed to CeO ₂ (–)	Page S10
Figure S.7 – XRF maps of lettuce exposed to CeO ₂ (0)	Page S11
Figure S.8 – XRF maps of tomato exposed to CeO ₂ (–)	Page S12
Figure S.9 – Large tri-colored XRF map of tomato exposed to CeO ₂ (–)	Page S13
Figure S.10 – XRF maps of tomato exposed to CeO ₂ (0)	Page S14
Figure S.11 – XRF maps of lettuce exposed to CeO ₂ (+)	Page S15
Figure S.12 – XRF maps of lettuce exposed to CeO ₂ (+)	Page S16
Figure S.13 – XRF maps of tomato exposed to CeO ₂ (0)	Page S17
Figure S.14 – XRF map of Ce accumulation in tomato trichomes	Page S18

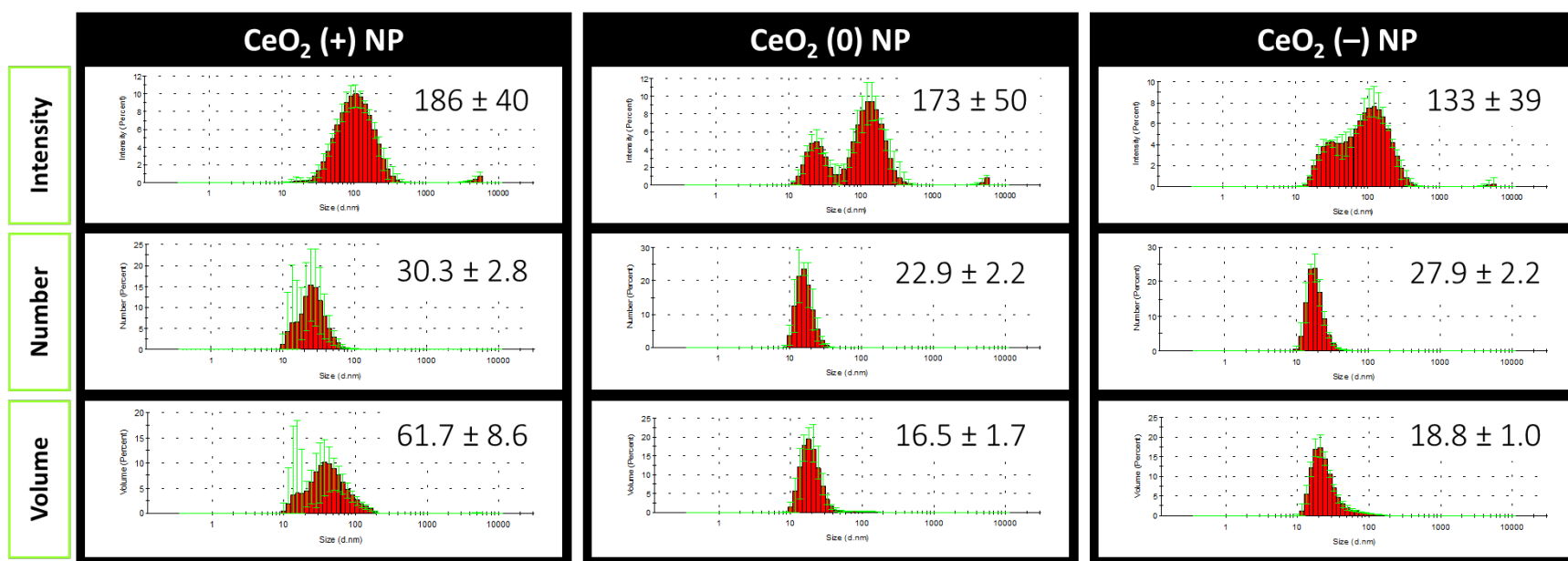


Figure S1. Intensity, number, and volume weighted distributions of the hydrodynamic diameters (nm) of CeO₂(+), CeO₂(0), and CeO₂(-) NPs at 50 mg-Ce/L in exposure medium (basal salt solution, pH=5.6). Values are presented with standard deviation over 5 replicates.

Table S1: Dissolved fraction of Ce remaining in solution after 48 h of hydroponic exposure to 50 mg-Ce/L as CeO₂(+), CeO₂(0) or CeO₂(-) NPs. The dissolved fraction was calculated as a percent of Ce concentration in ultra-filtered (3 kDa cutoff) suspensions divided by the total Ce concentration of the solution. Measurements were made in triplicate. Majority of the remaining Ce is not dissolved.

	Positive	Neutral	Negative
Corn	0.14 ± 0.08 %	0.02 ± 0.01 %	0.01 ± 0.01 %
Rice	0.04 ± 0.01 %	0.00 ± 0.01 %	0.05 ± 0.01 %
Tomato	0.04 ± 0.01 %	0.04 ± 0.01 %	0.02 ± 0.01 %
Lettuce	0.12 ± 0.01 %	0.03 ± 0.01 %	0.01 ± 0.01 %

Table S2: Total Ce concentrations on/in dried plant roots after 48 h of hydroponic exposure to 50 mg-Ce/L as CeO₂(+), CeO₂(0) or CeO₂(-) NPs. The reported values are means averaged from four replicates \pm SD. Plant root surface area (SA) approximations were also averaged over four sets of plant roots per species.

Plant Species	Root SA (cm ²)	NP Surface Charge	Ce association with roots (mg/kg)
Corn	6.6 \pm 1.2	(+)	13,640 \pm 7,200
		(0)	5,730 \pm 2,270
		(-)	3,700 \pm 1,110
Rice	0.6 \pm 0.2	(+)	20,780 \pm 6,380
		(0)	2,230 \pm 500
		(-)	1,470 \pm 670
Tomato	11.3 \pm 3.2	(+)	47,330 \pm 3,100
		(0)	11,640 \pm 1,320
		(-)	2,410 \pm 1,450
Lettuce	1.3 \pm 1.0	(+)	31,530 \pm 4,690
		(0)	1,470 \pm 670
		(-)	1,150 \pm 770

Table S3: Ce L_{III} XANES linear combination fitting (LCF) results of roots after 48 h of hydroponic exposure to 50 mg-Ce/L as CeO₂(+), CeO₂(0) or CeO₂(−) NPs. Roots were rinsed for 30s in Ce-free medium prior to lyophilization and analysis. Spectra are shown in **Figure 4**.

	Positive				Neutral				Negative			
	Corn	Rice	Tomato	Lettuce	Corn	Rice	Tomato	Lettuce	Corn	Rice	Tomato	Lettuce
Ce(III)	-	-	-	-	18.0%	10.5%	18.8%	31.5%	-	7.6%	10.4%	23.9%
Ce(IV)	98.8%	96.9%	100.5%	89.4%	88.5%	89.8%	87.9%	80.6%	105.5%	94.3%	93.7%	85.8%
R Factor	0.0025	0.0008	0.0007	0.0035	0.0018	0.0018	0.0015	0.0094	0.0026	0.0032	0.0024	0.1910
Red. χ^2	0.0011	0.0003	0.0004	0.0017	0.0008	0.0007	0.0084	0.0048	0.0013	0.0013	0.0014	0.0410

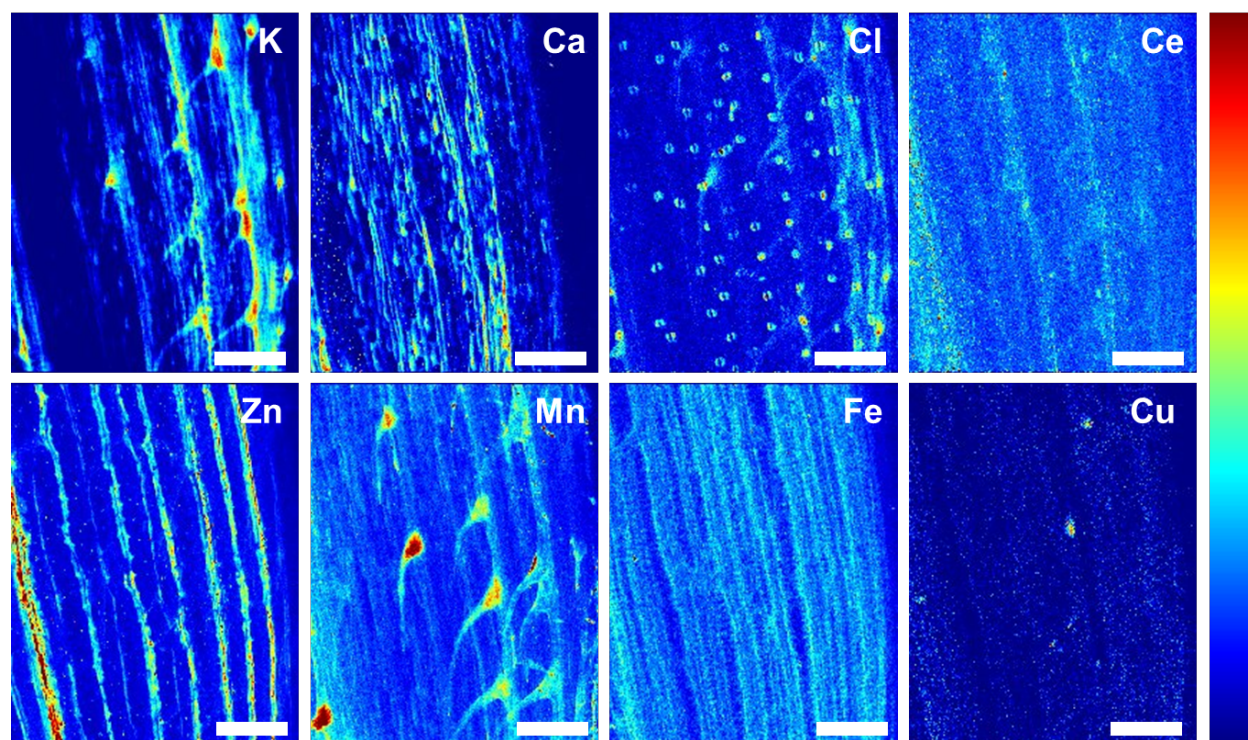


Figure S2. XRF maps showing elemental distribution in a corn leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as $\text{CeO}_2(-)$ NPs. Ce signal was not sufficient to perform μ -XANES. Scale bar=200 μm .

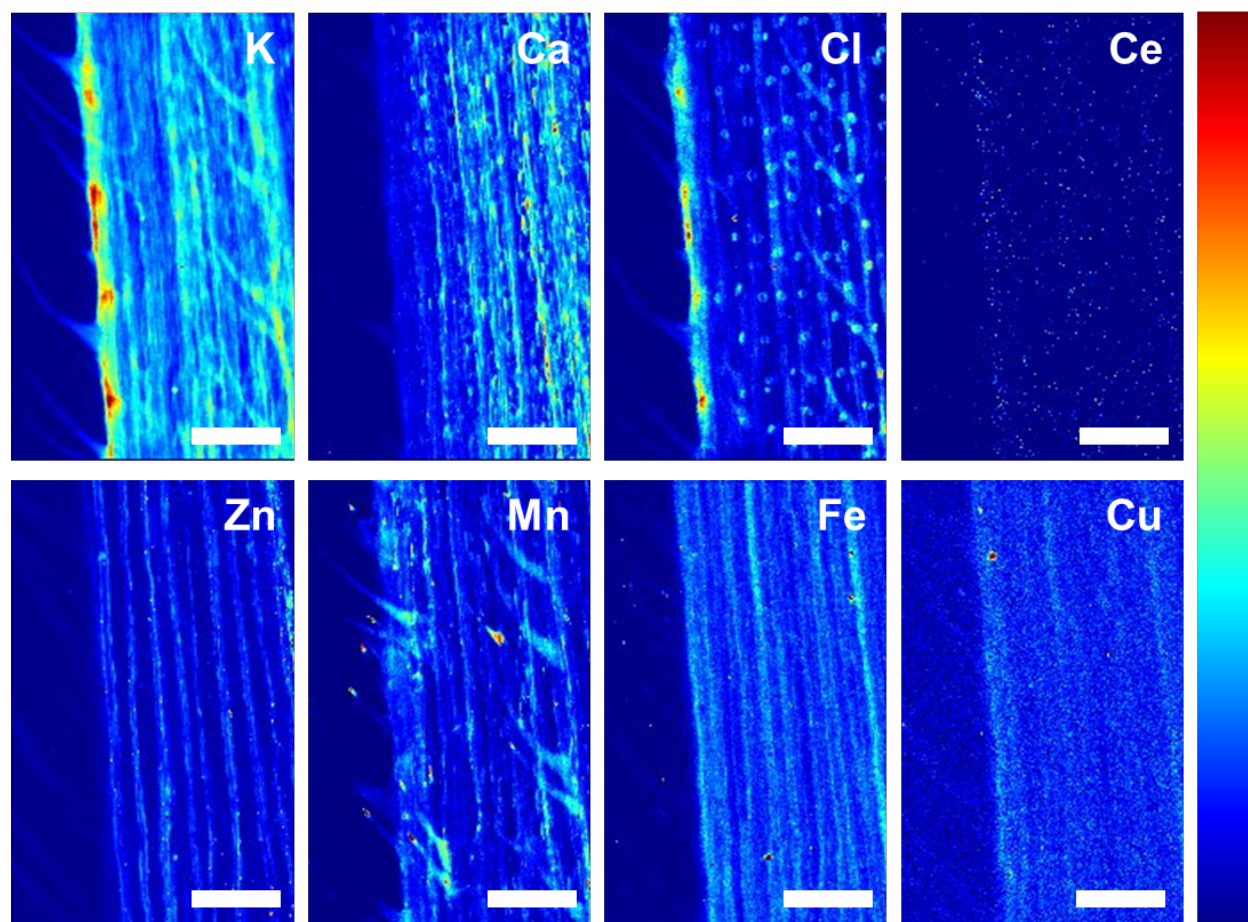


Figure S3. XRF maps showing elemental distributions in a corn leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as $\text{CeO}_2(0)$ NPs. Ce signal was not sufficient to perform μ -XANES. Scale bar=200 μm .

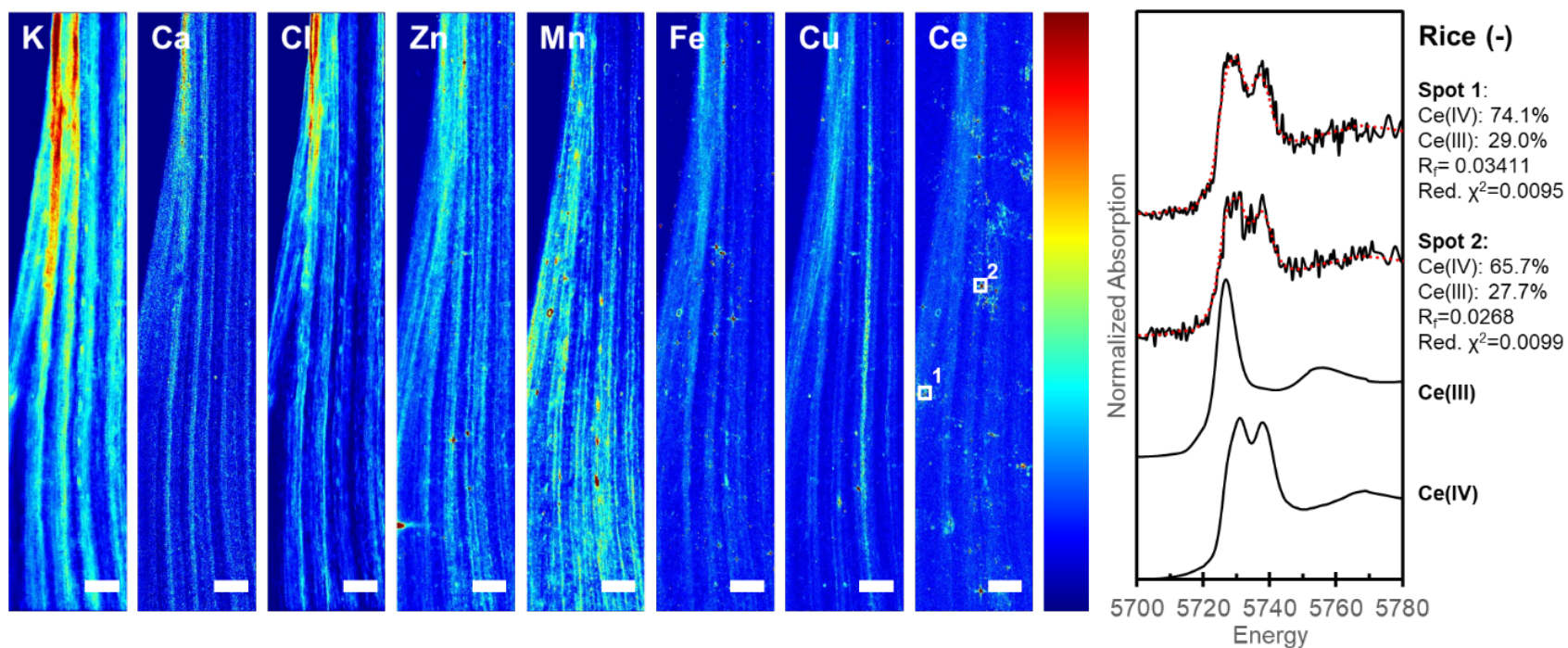


Figure S4. XRF maps showing elemental distributions in a rice leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as CeO₂(-) NPs. Ce L(III) μ -XANES spectra (solid, black) from high intensity spots are indicated with white boxes on the Ce map. LCF results (dotted, red) are presented with fitting statistics and Ce(III) and Ce(IV) model compounds. Scale bar=200 μ m

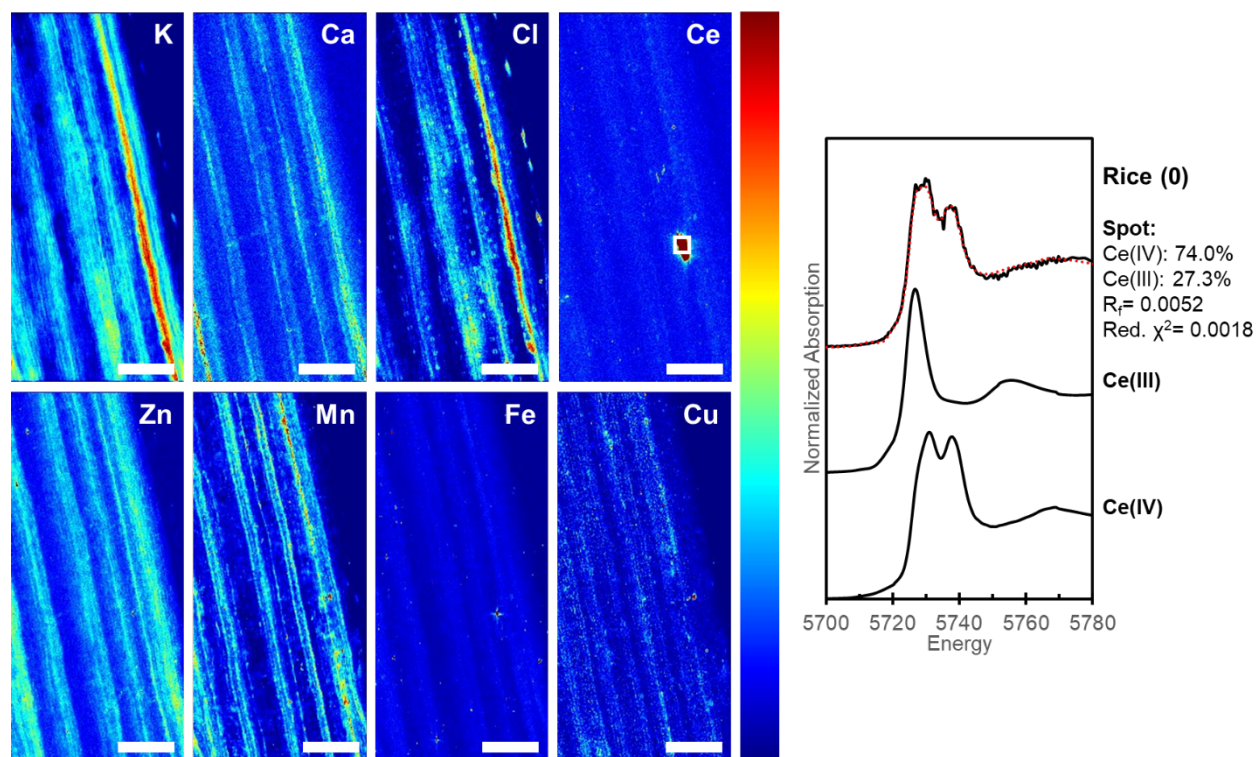


Figure S5. XRF maps showing elemental distributions in a rice leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as $\text{CeO}_2(0)$ NPs. Ce L(III) μ -XANES spectrum (solid, black) from high intensity spot is indicated with a white box on the Ce map. LCF result (dotted, red) is presented with fitting statistics and Ce(III) and Ce(IV) model compounds. Scale bar=200 μ

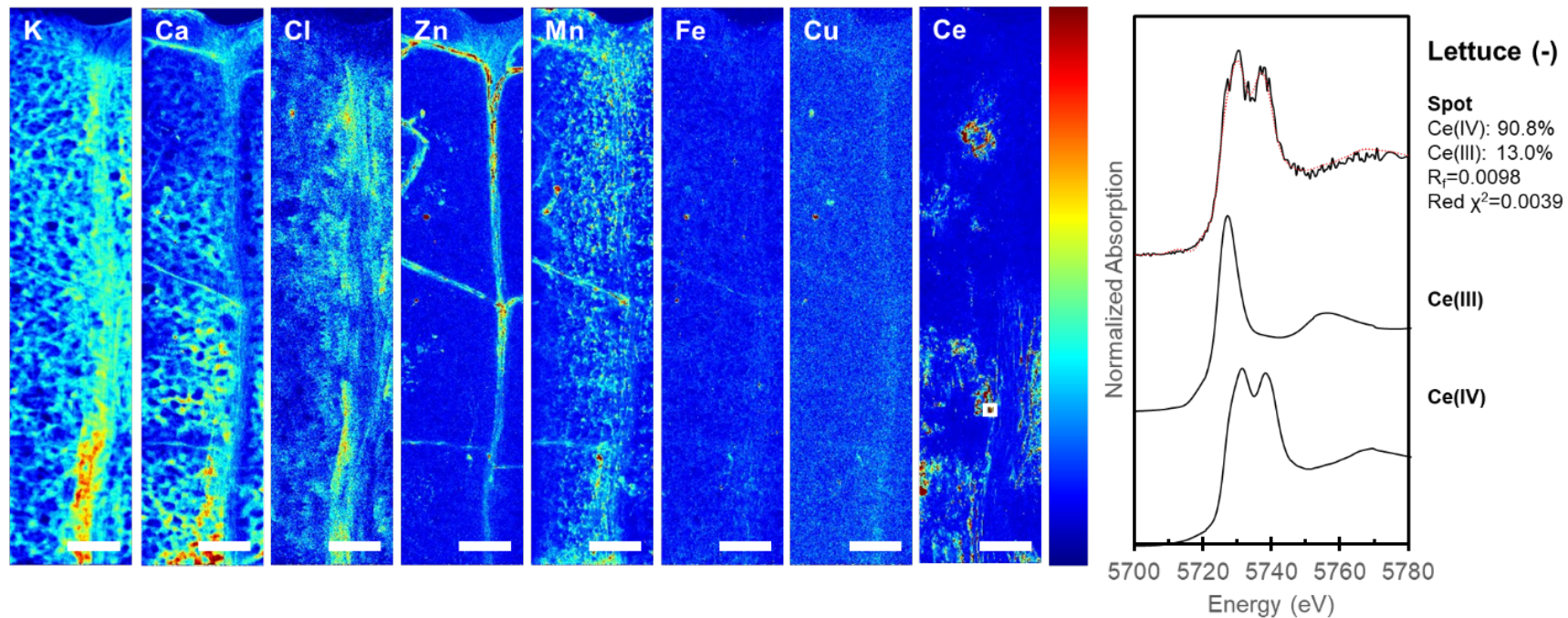


Figure S6. XRF maps showing elemental distribution in a lettuce leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as $\text{CeO}_2(-)$ NPs. Ce L(III) μ -XANES spectrum (solid, black) from high intensity spot is indicated with a white box on the Ce map. LCF result (dotted, red) is presented with fitting statistics and Ce(III) and Ce(IV) model compounds. Scale bar=200 μm .

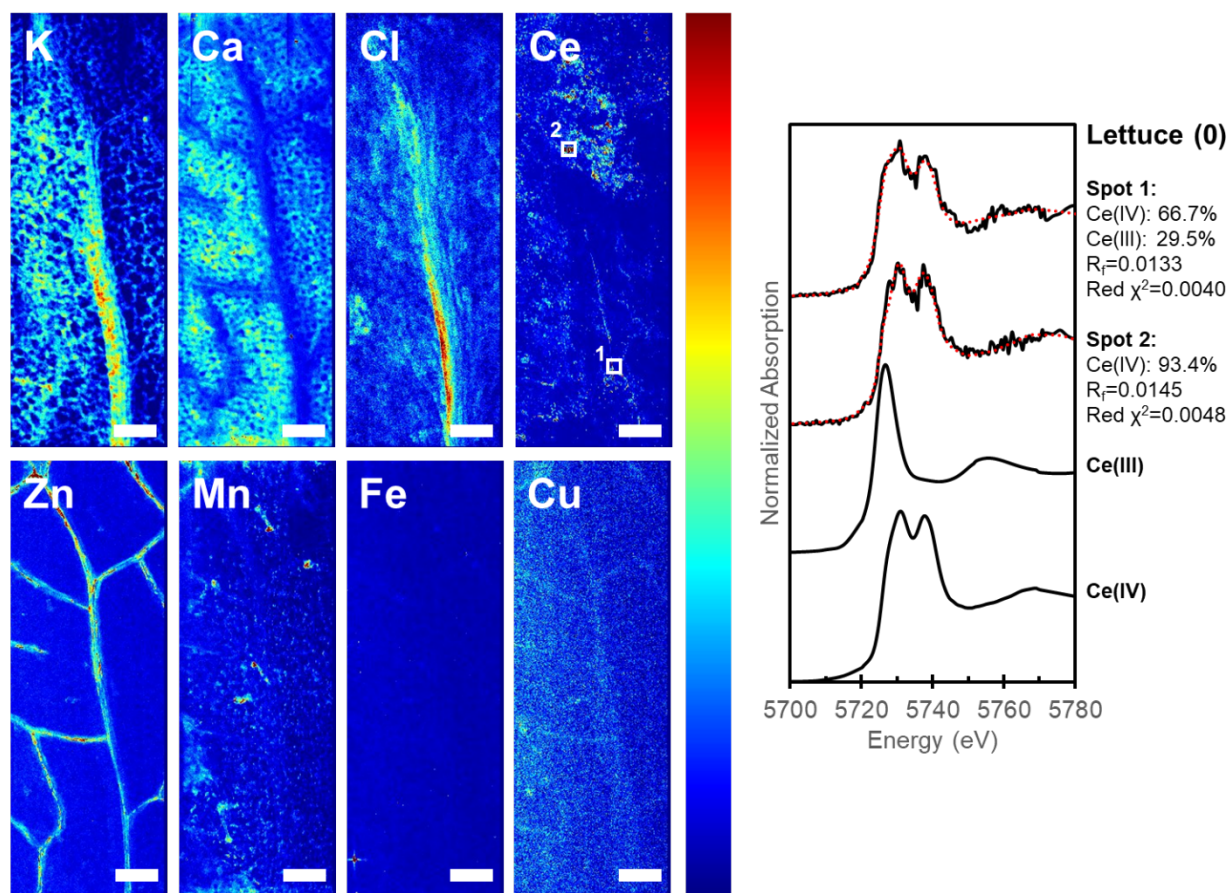


Figure S7. XRF maps showing elemental distribution in a lettuce leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as $\text{CeO}_2(0)$ NPs. Ce L(III) μ -XANES spectra (solid, black) from high intensity spots are indicated with white boxes on the Ce map. LCF results (dotted, red) are presented with fitting statistics and Ce(III) and Ce(IV) model compounds. Scale bar=200 μm .

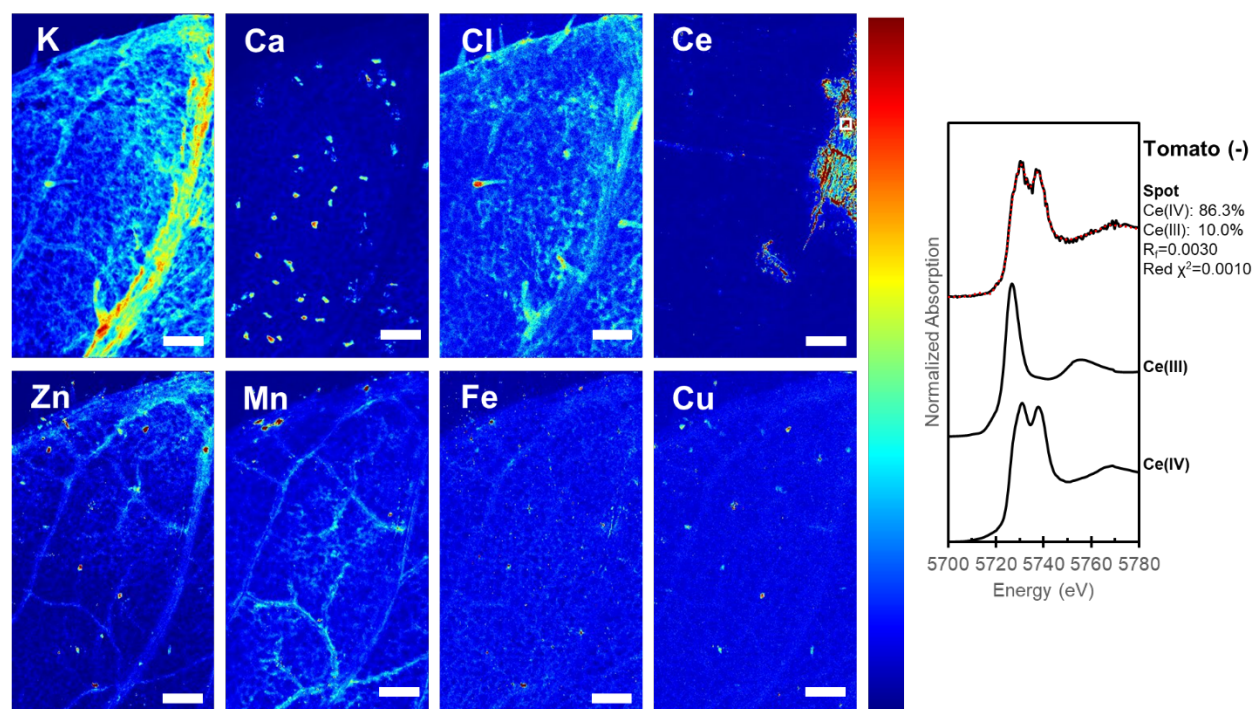


Figure S8. XRF maps showing elemental distributions in a tomato leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as CeO_2 (-) NP. Ce L(III) μ -XANES spectrum (solid, black) from high intensity spot is indicated with a white box on the Ce map. LCF result (dotted, red) is presented with fitting statistics and Ce(III) and Ce(IV) model compounds. Scale bar=200 μm

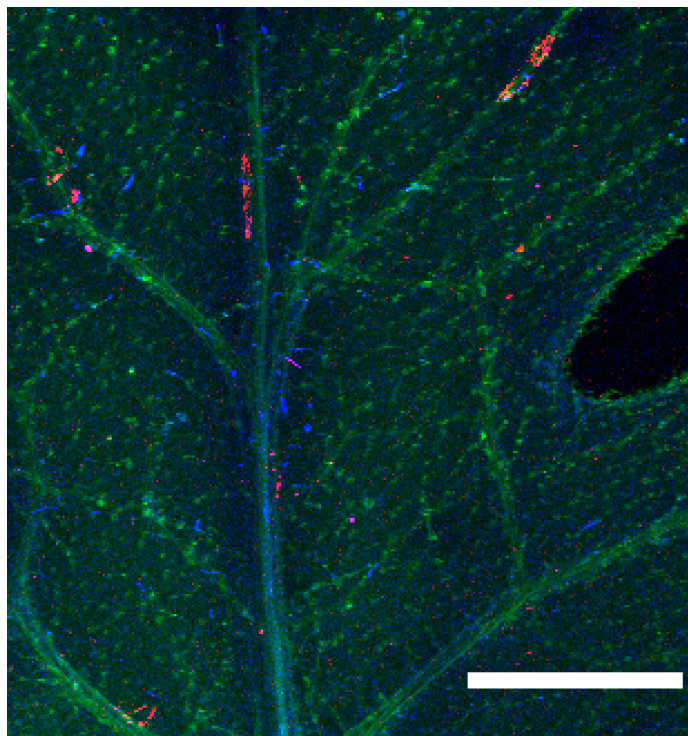


Figure S9. Tri-colored XRF map showing Ce (red), K (green), and Mn (blue) distributions in a tomato leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as CeO₂ (–) NP. Collected at NSLS-II on BL 4-BM. Elemental maps were collected using a step size of 15 μ m and a dwell time of 0.1 s. Scale bar=1 mm

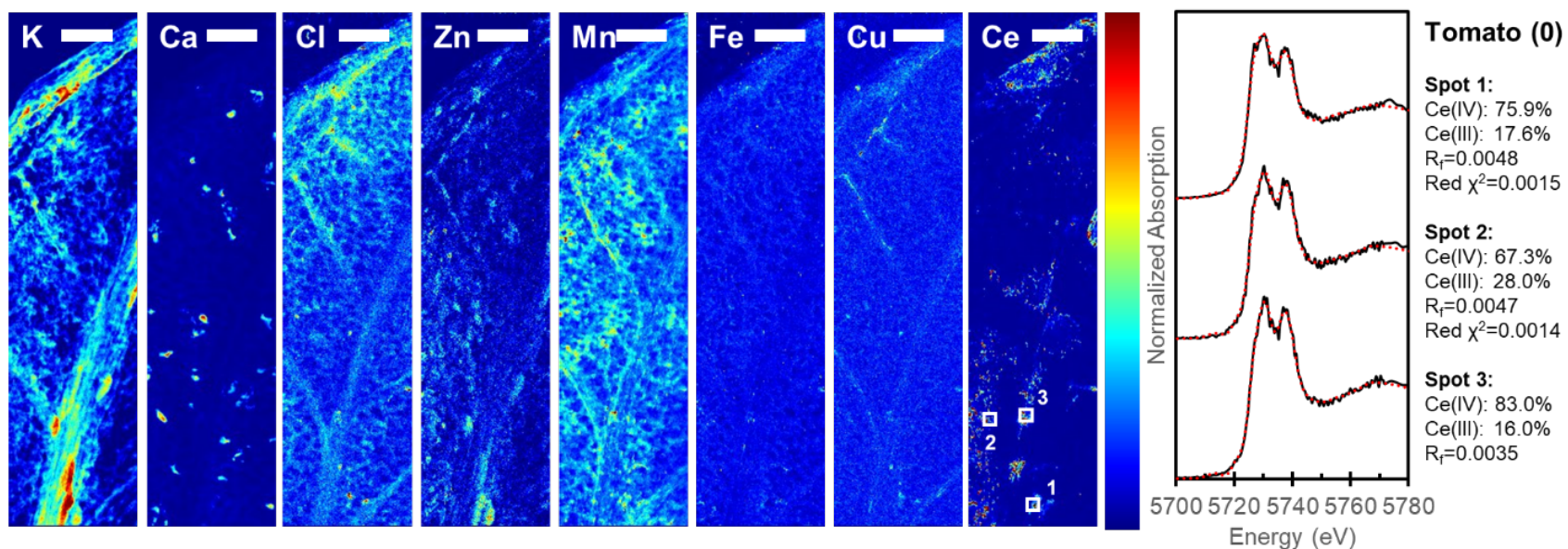
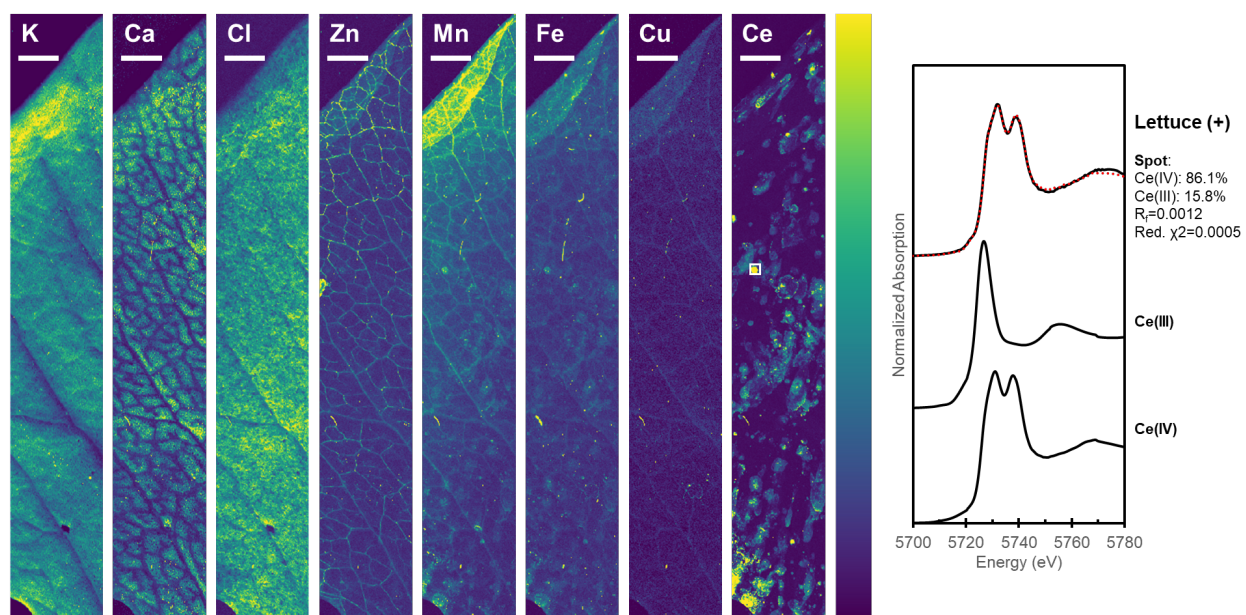


Figure S10. XRF maps showing elemental distributions in a tomato leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as $\text{CeO}_2(0)$. Ce L(III) μ -XANES spectra (solid, black) from high intensity spots are indicated with white boxes on the Ce map. LCF results (dotted, red) are presented with fitting statistics. Scale bar=200 μm .



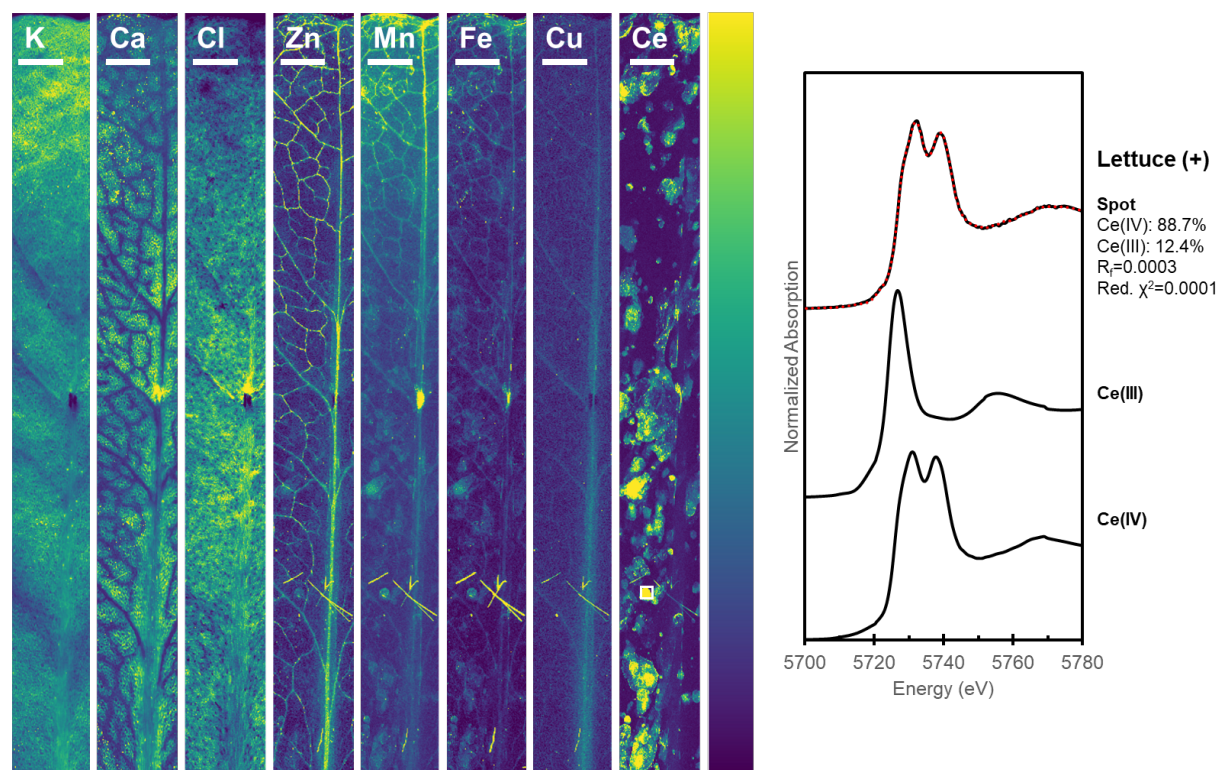


Figure S12. XRF maps showing elemental distributions in the central vein of a lettuce leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as CeO₂ (+). Ce L(III) μ -XANES spectrum (solid, black) from high intensity spot is indicated with a white box on the Ce map. LCF result (dotted, red) is presented with fitting statistics and Ce(III) and Ce(IV) model compounds. Scale bar= 1 mm.

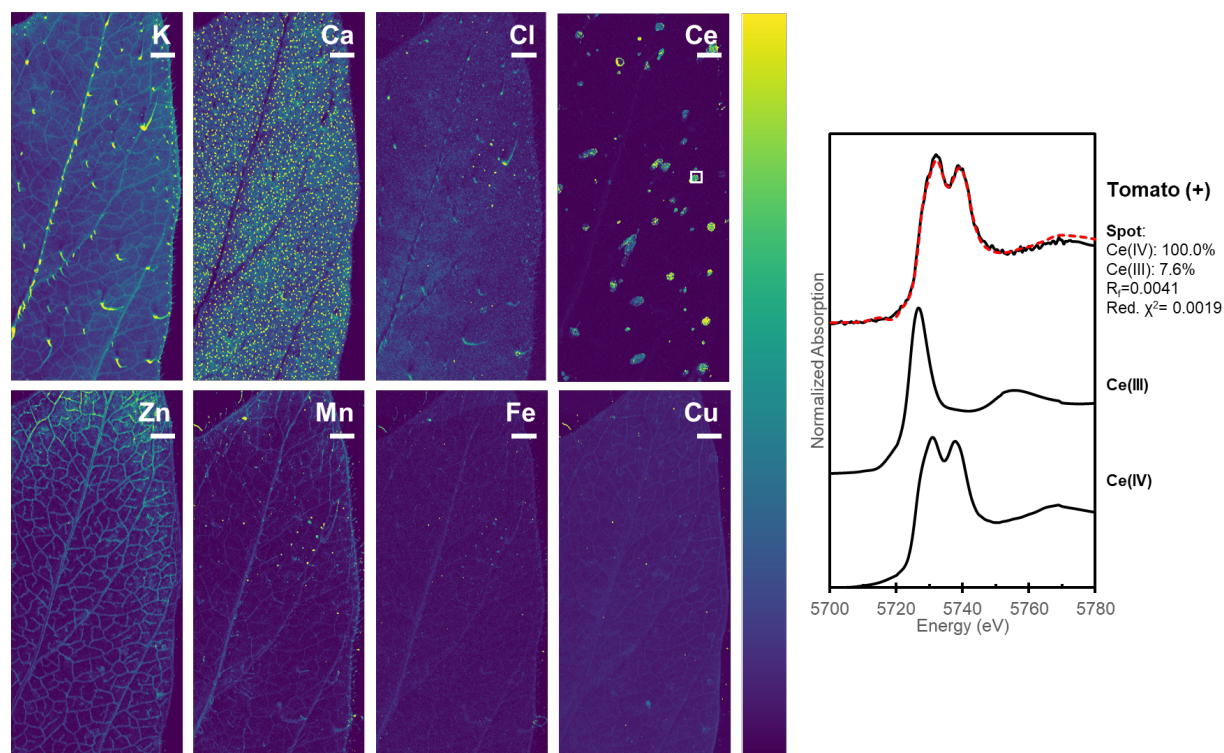


Figure S13. XRF maps showing elemental distributions in a tomato leaf after 48 h of hydroponic exposure to 50 mg-Ce/L as CeO_2 (+). Ce L(III) μ -XANES spectrum (solid, black) from high intensity spot is indicated with a white box on the Ce map. LCF result (dotted, red) is presented with fitting statistics and Ce(III) and Ce(IV) model compounds. Scale bar= 1 mm.

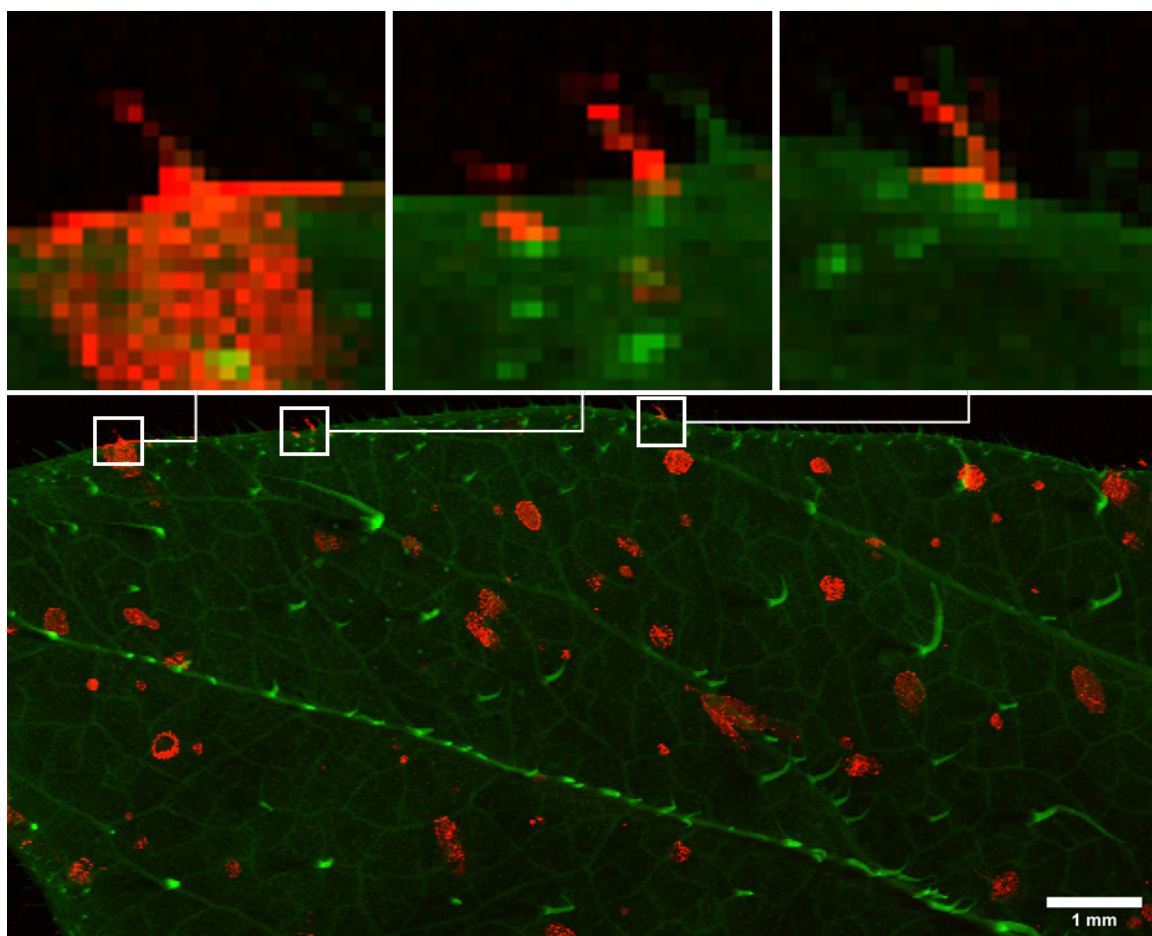


Figure S14. Dual-colored XRF map showing Ce (red) and K (green) distribution in a tomato leaf after 48 h of hydroponic exposure to 50 mg-Ce/L of $\text{CeO}_2(+)$ NPs. White boxes (500 μm x 500 μm) indicate Ce-trichome colocalization.