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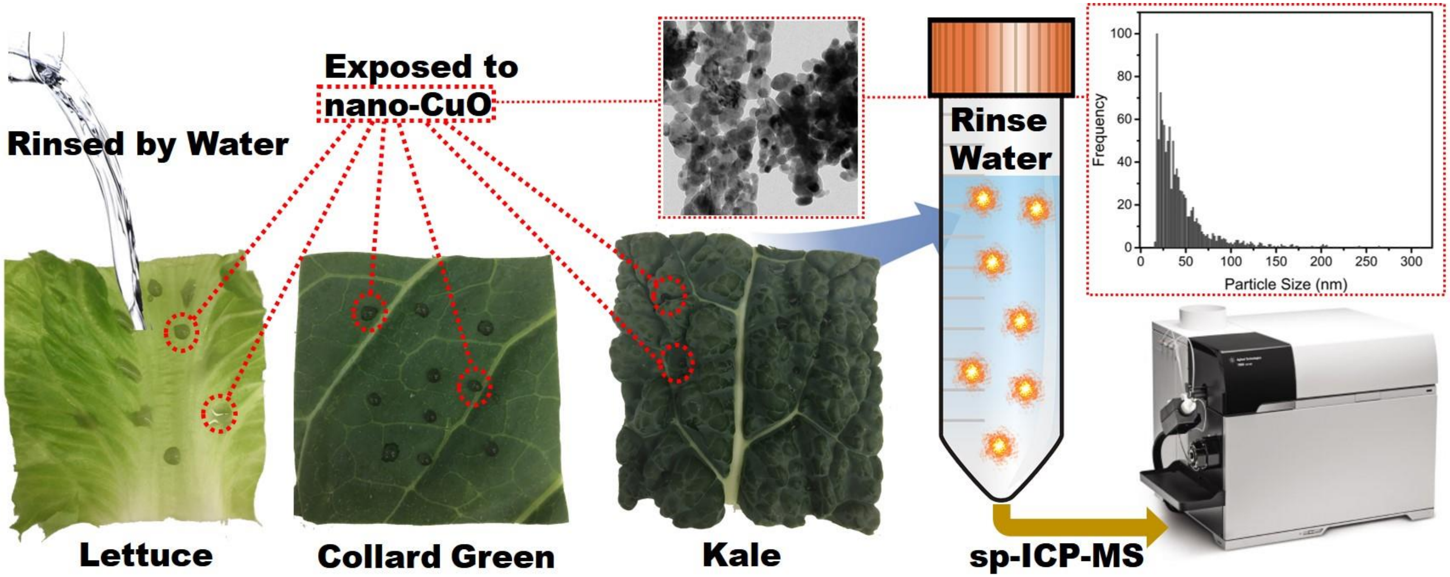
Detection of nanoparticles on plant tissues using sp-ICP-MS



Yuxiong Huang

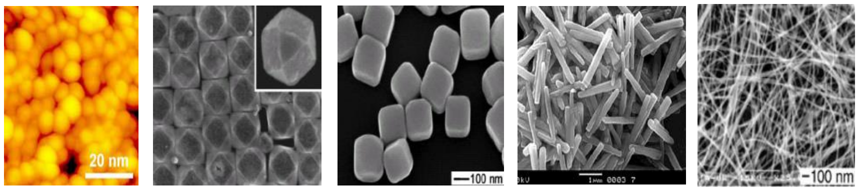
Arturo A. Keller

August, 6, 2018

BREN SCHOOL
UC SANTA BARBARA

Where do nanomaterials come from?

Particles with at least one dimension in the nano-scale (1~100 nm)

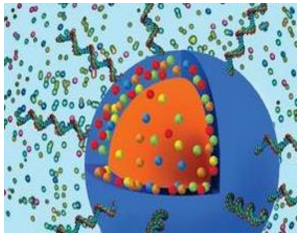


Natural Sources

Produced by redox reactions, weathering, mining, volcanos, dust storms

Unintentionally produced NPs

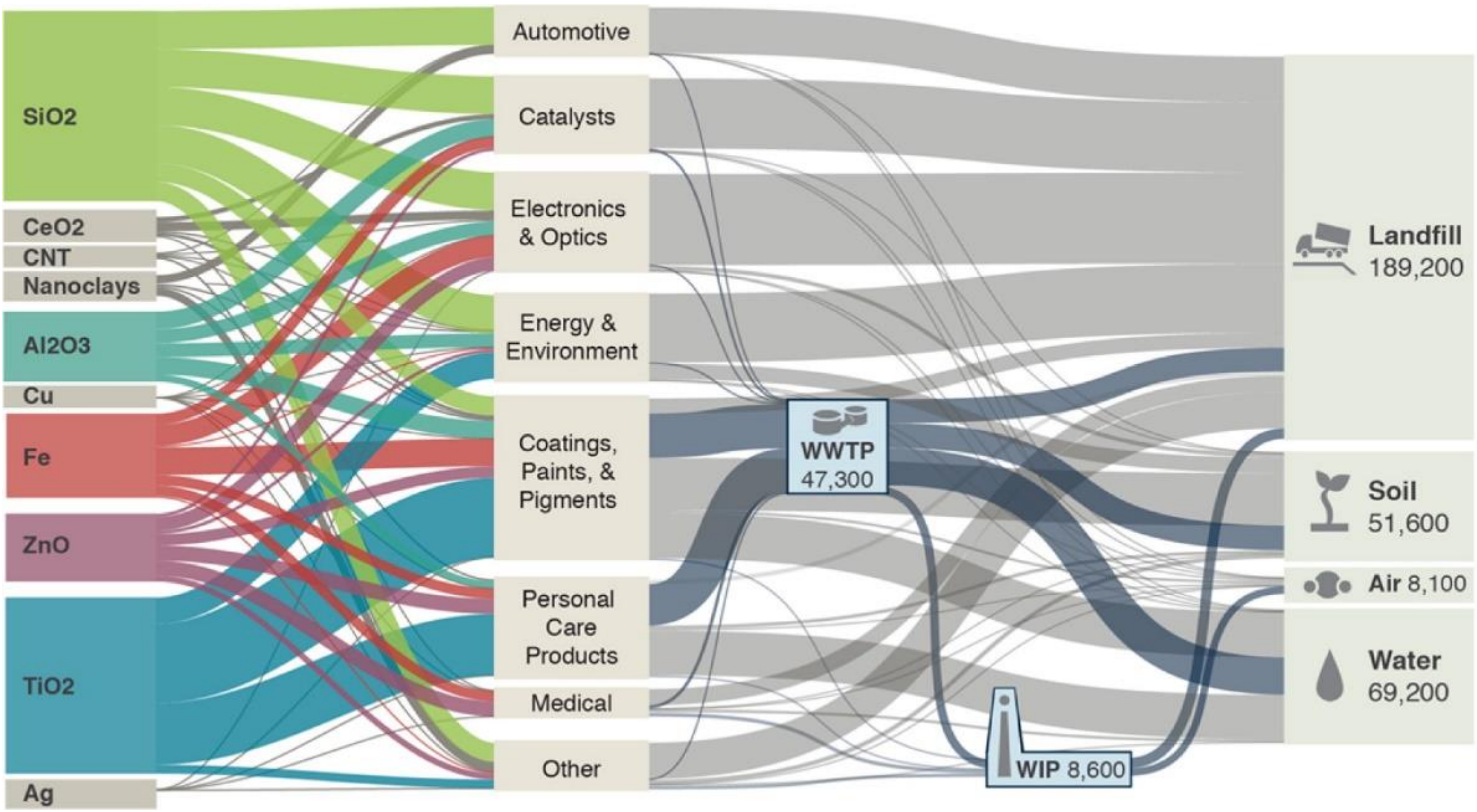
Emitted to air, water and soil from combustion, wear, metal polishing and metal working, electric motors etc.



Engineered NPs

Synthesized for a specific purpose. Usually embedded in other products

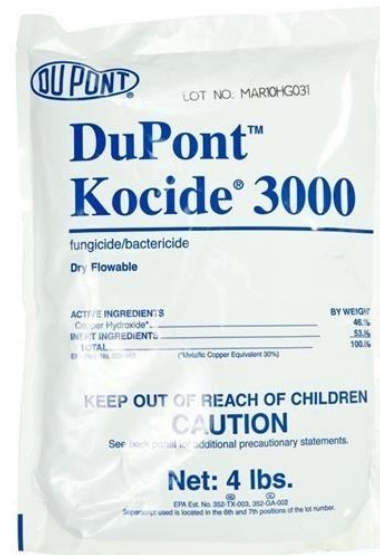
Engineered Nano-Materials(ENMs)



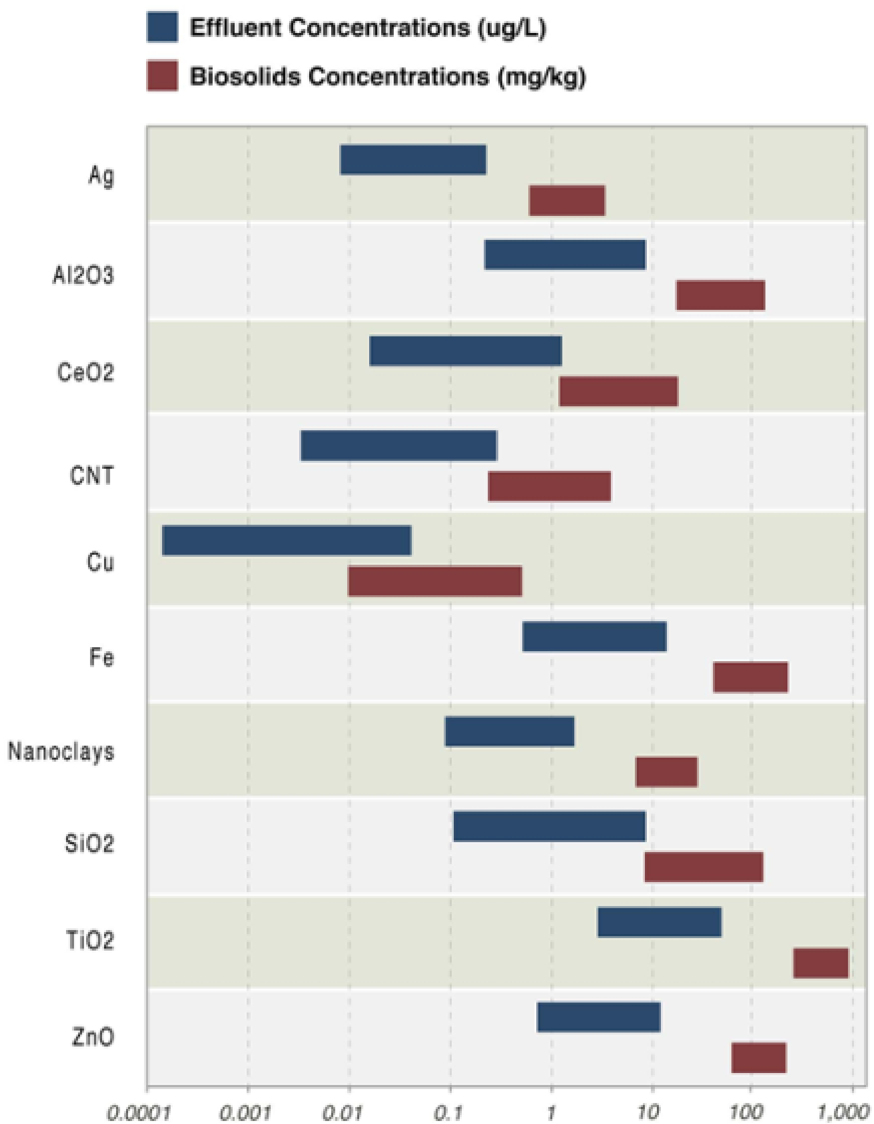
A. A. Keller and A. Lazareva, *Environ Sci Tech Let*, 2014.

Application of ENMs in Agriculture

- Nano-pesticide/fungicide/bactericide
- Nano-fertilizer



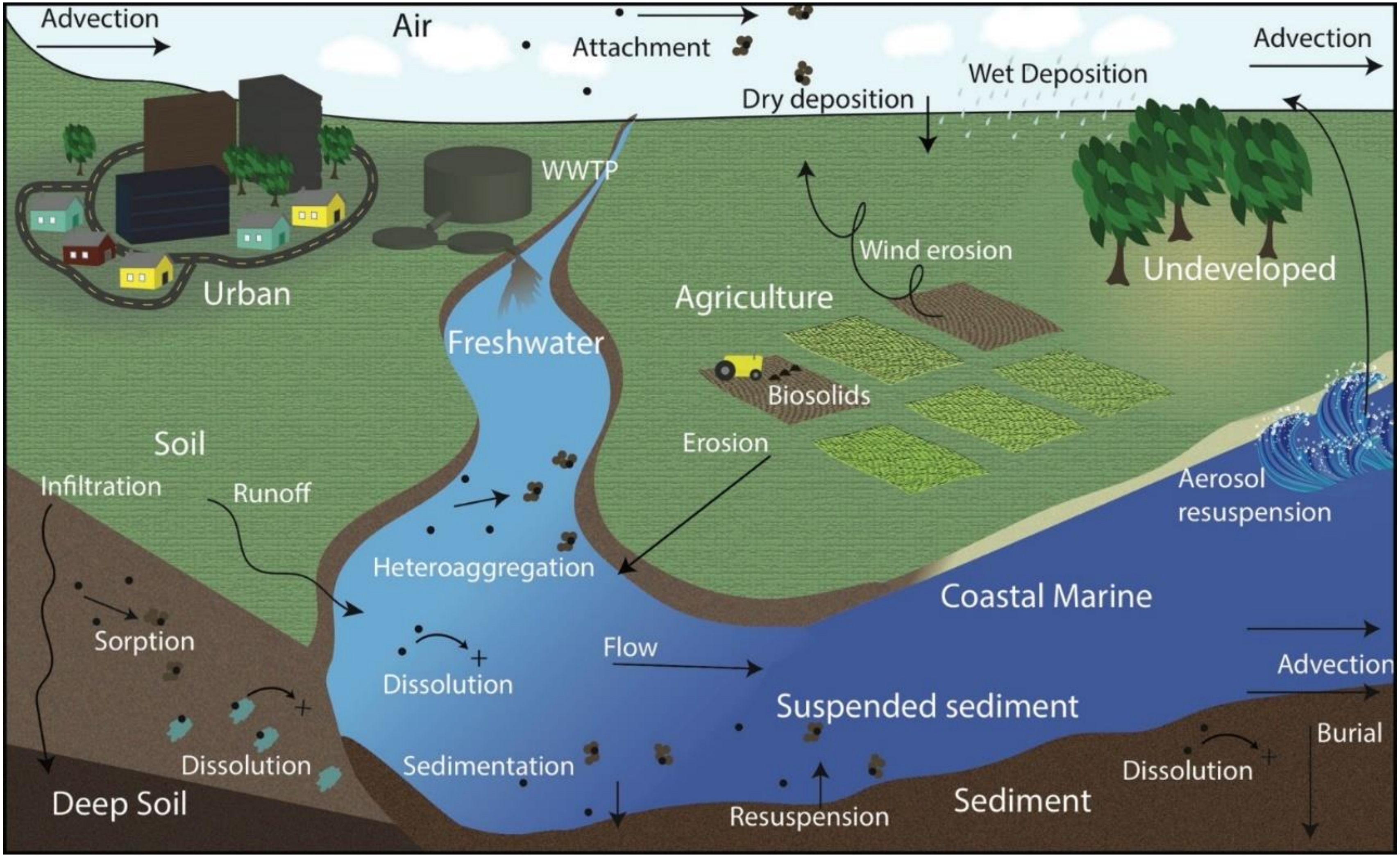
ENMs in Environment



ENM concentrations expected to be at ng/L to ug/L levels at point of release

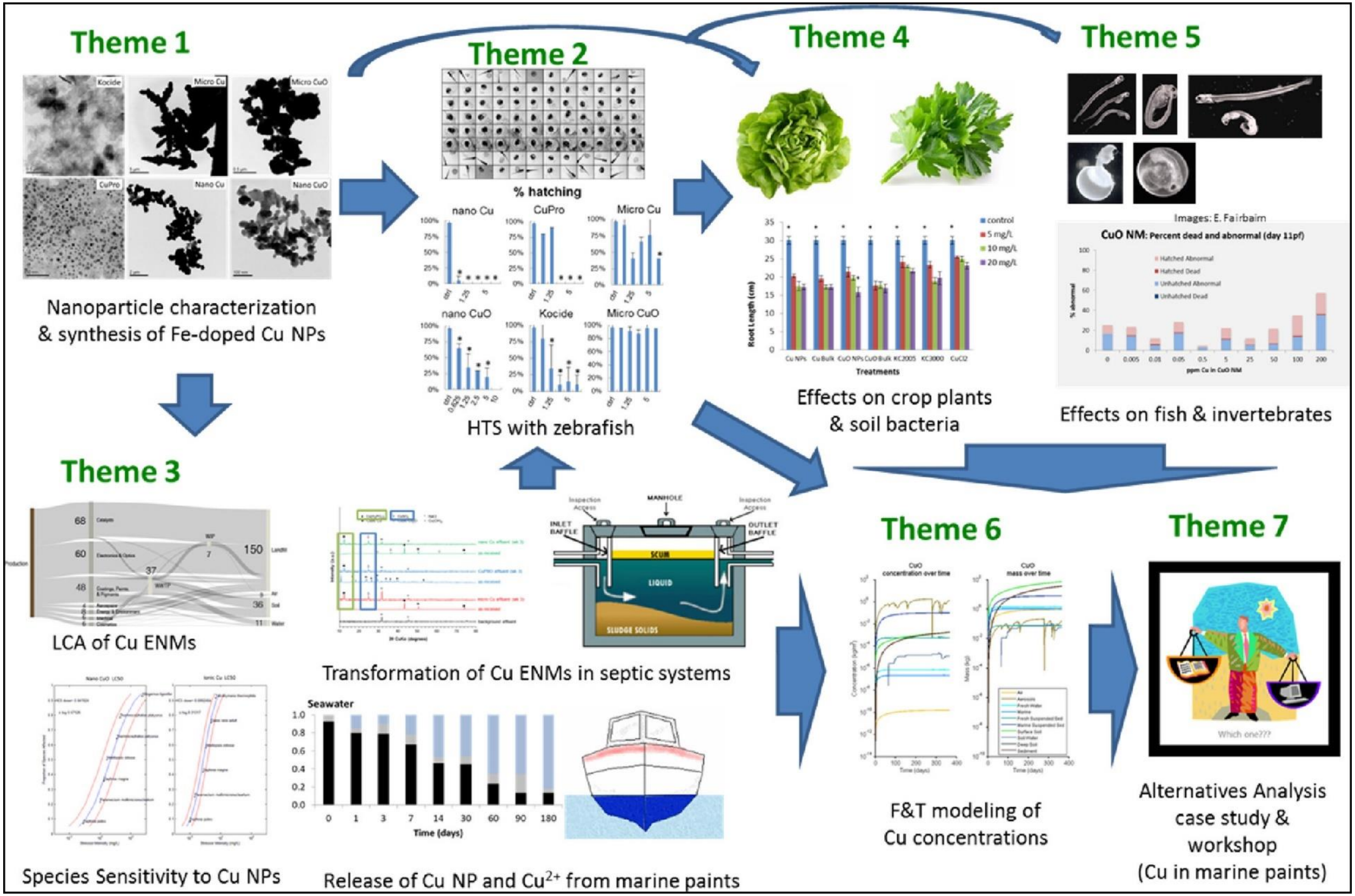
Lazareva and Keller, ACS Sus Chem, 2014

ENMs in Environment



K. L. Garner, S. Suh and A. A. Keller, *Environmental Science & Technology*, 2017

Environmental Implications of Cu Based ENMs



Keller, A. A. and et. al. *NanoImpact* **2017**, *7*, 28-40.

How can we “see” ENMs?

Analytical Challenge

- Can we detect ENMs in water and other environmental matrices?
- Composition?
- Size?
- Quantity?
- Other characteristics?

No EPA methods available to date…

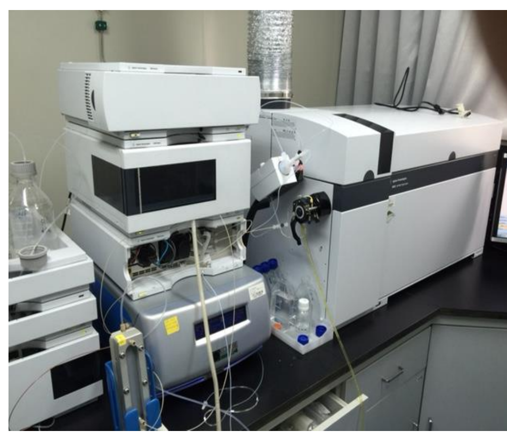
Methods for ENMs Characterization

- **Imaging** methods (TEM, SEM, AFM) are often definitive for detection, shape and size determination. Not quantitative or representative. Labor-intensive.
- **Spectroscopic/optical** methods (UV-Vis, dynamic light scattering) simple, but subject to interferences. No elemental information. DLS needs sharp size distribution.
- **Hyphenated techniques** (Chromatographic (or other online) separation coupled with ICP-MS detection). Allow representative samples, provide good particle size resolution, high elemental sensitivity but no information on individual particles

FFF-ICP-MS

CE -ICP-MS

HPLC-ICP-MS

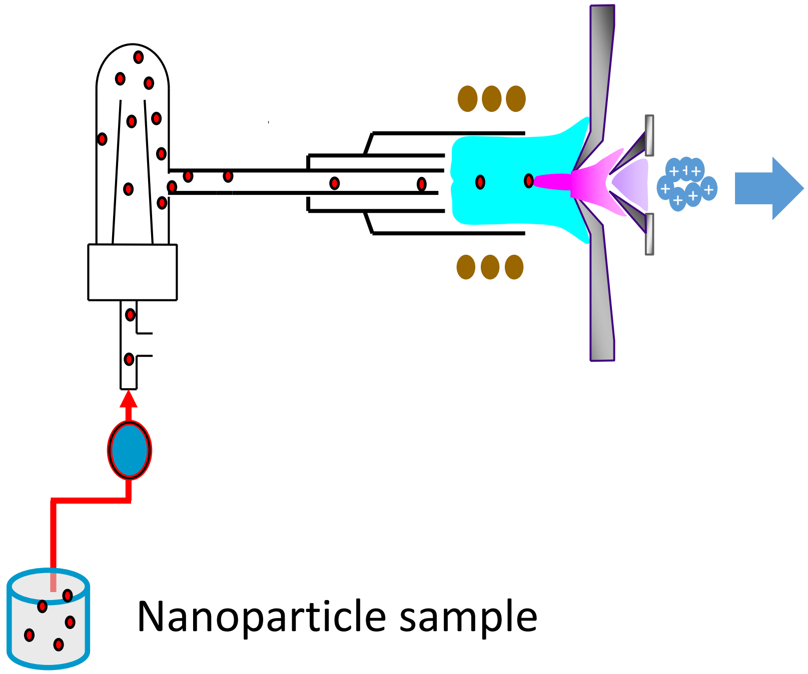


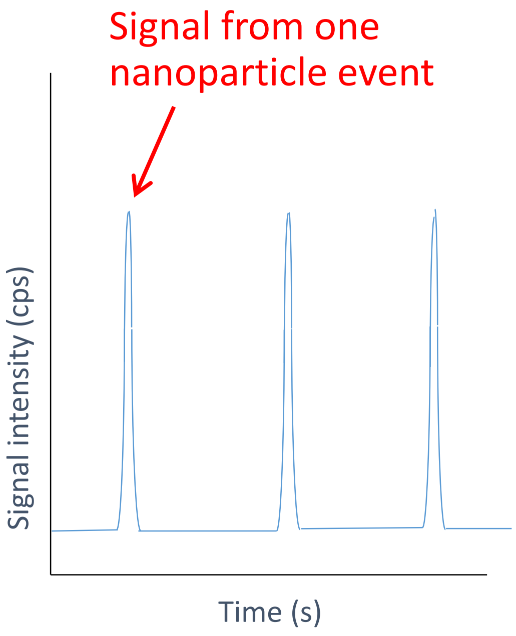
- **Single particle ICP-MS**

Methods for ENMs Characterization

Single Particle ICP-MS (spICP-MS)

- Each nanoparticle gives a transient signal (a plume of ions generated from the particle)
- Use time resolved data acquisition and analysis
- Measure particle concentration, particle effective diameter and composition





Single particle ICP-MS

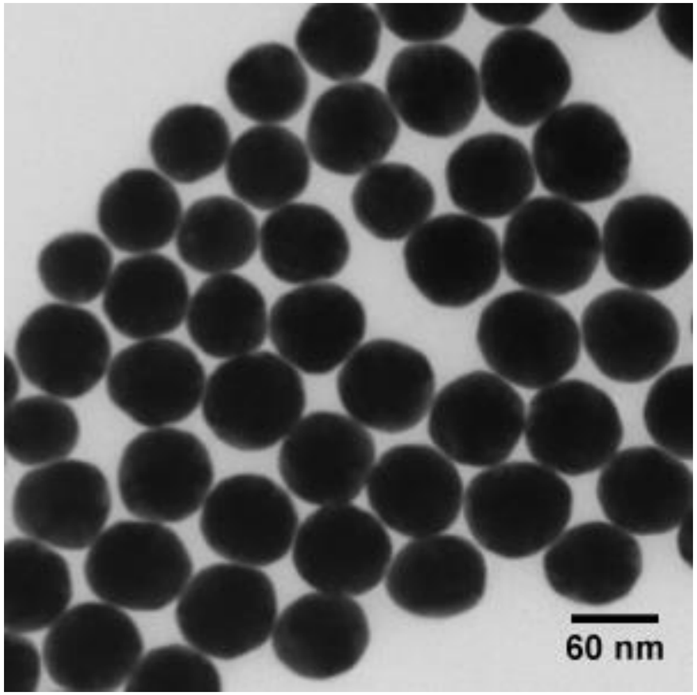
Reference Materials

60 nm Gold Nanospheres

•Unagglomerated and monodisperse

•Mean diameter: 60 nm ± 4 nm

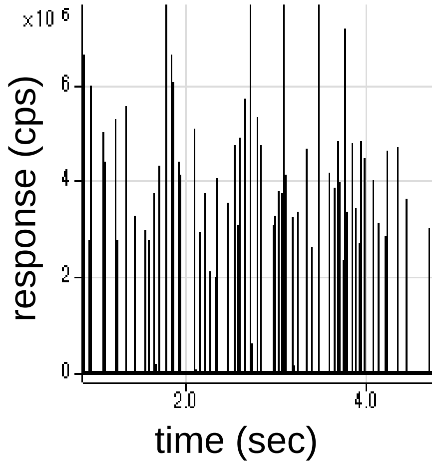
NIST
National Institute of Standards and Technology
U.S. Department of Commerce



nanoComposix

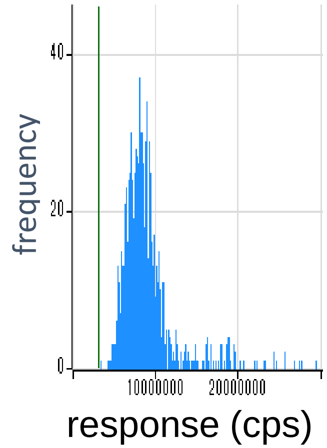
spICP-MS workflow

ICP-MS TRA data



convert

Response vs frequency

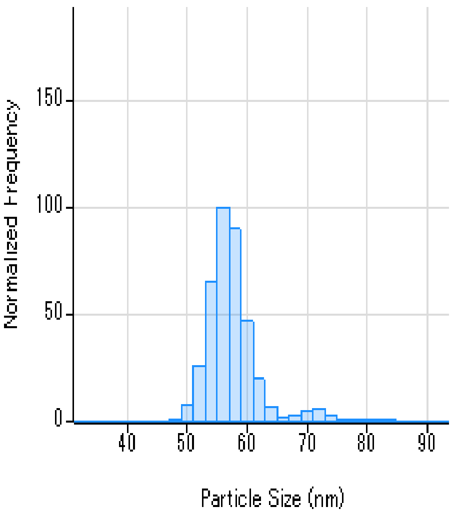


input

- Analyte response factor > Mass of analyte in particle
- Nebulization efficiency (calculated from reference material)
- Analyte density
- Analyte mass fraction in sample particle

calculate

Size distribution

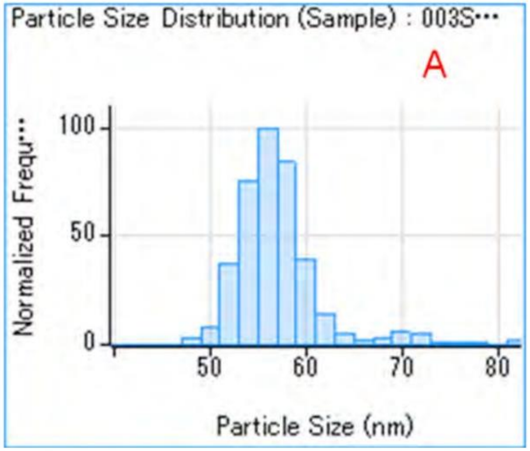


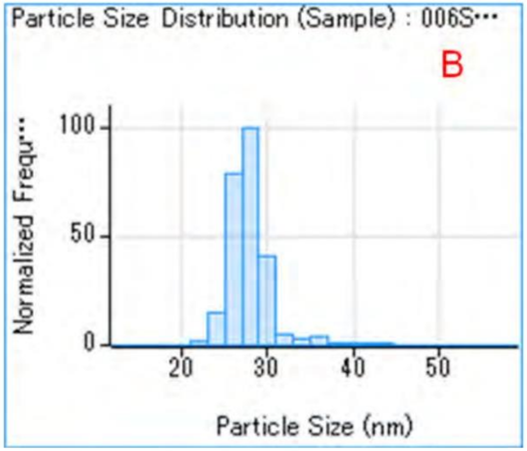
Tabulate and Report

Sample				197 Au						
Data File	Acq. Date-Time	Type	Sample Name	Nebulization Efficiency	# of Particles	Conc. (particles/l)	Conc. (ng/l)	Ionic Conc. (ppb)	BED (nm)	Particle Size (nm)
001IONB.d	5/13/2015 3:10:19 AM	IonicBlk	blank							
002IONS.d	5/13/2015 3:13:07 AM	IonicStd	1ppb							
003_RM.d	5/13/2015 3:15:21 AM	RM	30nm 5ppt	0.071	619	2.5E+7	5.0	0.0178	4.21	27
004SMPL.d	5/13/2015 3:18:20 AM	Sample	60nm 50ppt	0.071	617	2.5E+7	48.6	0.0260	4.73	55
005SMPL.d	5/13/2015 3:20:27 AM	Sample	60nm 50ppt	0.071	681	2.8E+7	51.8	0.0266	4.76	55
006SMPL.d	5/13/2015 3:22:35 AM	Sample	60nm 50ppt	0.071	635	2.6E+7	48.8	0.0258	4.72	55
007SMPL.d	5/13/2015 3:24:26 AM	Sample	60nm 50ppt	0.071	656	2.7E+7	50.4	0.0272	4.80	55
008SMPL.d	5/13/2015 3:28:22 AM	Sample	60nm 50ppt	0.071	649	2.6E+7	48.9	0.0240	4.60	55
009SMPL.d	5/13/2015 3:30:54 AM	Sample	30nm 5ppt	0.071	579	2.3E+7	4.5	0.0083	3.23	26
010SMPL.d	5/13/2015 3:33:29 AM	Sample	30nm 5ppt	0.071	589	2.4E+7	4.8	0.0078	3.16	26
011SMPL.d	5/13/2015 3:37:10 AM	Sample	30nm 5ppt	0.071	568	2.3E+7	4.5	0.0078	3.16	26
012SMPL.d	5/13/2015 3:39:03 AM	Sample	30nm 5ppt	0.071	558	2.3E+7	4.5	0.0076	3.13	26
013SMPL.d	5/13/2015 3:43:05 AM	Sample	30nm 5ppt	0.071	600	2.4E+7	4.7	0.0075	3.12	26

Precision and Accuracy

Sample (Prepared concentration)	Observed Concentration (particles/L)	Observed Concentration (ng/L)	Observed Particle Size (nm)	Reference Particle Size obtained by TEM (nm)
NIST 8013 Nominal 60nm (100 ng/L)	5.59×10^7	103	55	56.0 ± 0.5
NIST 8012 Nominal 30nm (10 ng/L)	4.27×10^7	10.5	28	27.6 ± 2.1





Applications?

Case study: ENMs pathway into plants

- Foliar application
- Delivery to soil surface as slow-release NPs
- Delivery below ground in fertigation suspensions
- Application with biosolids

- Pathway matters in terms of delivered [ENM] and bioavailability

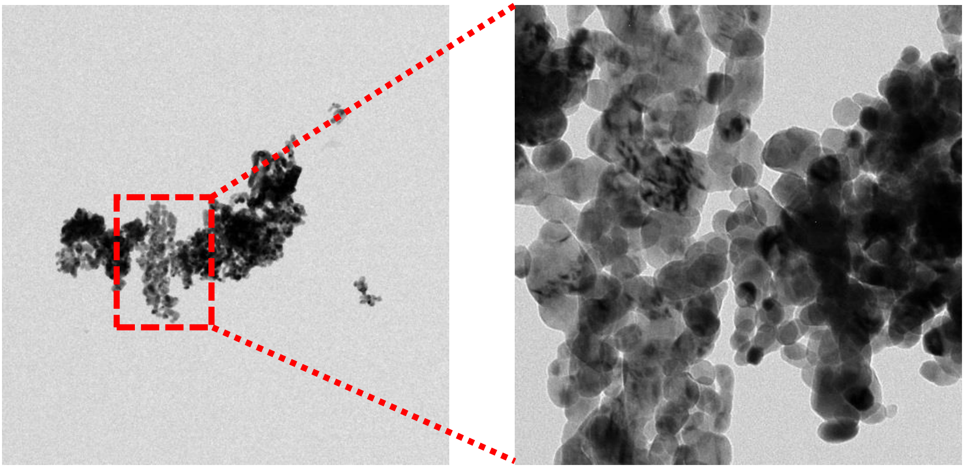
Can we detect ENMs in Edible Plant Tissues with spICP-MS?

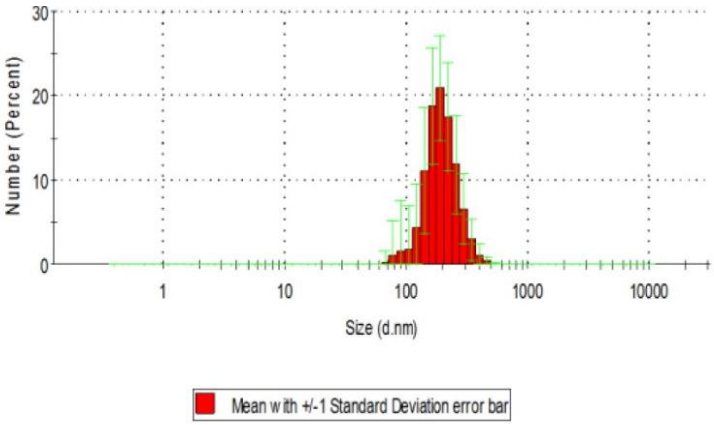
Copper Oxide Nanoparticles (nano-CuO)

Property	nano-CuO
primary particle size (nm)	50[a]
hydrodynamic diameter[b] (nm)	280 ± 15
copper content (wt %)	74.3 ± 1.2
main copper phase	monoclinic CuO
density (g/cm^3)	6.349
BET surface area (m^2/g)	12.31 ± 0.05
isoelectric point (IEP)	6.3
CCC at pH 7 (mM NaCl)	40
water content (wt %)	0.23

[a]As provided by the manufacturer.
[b]Measurement was done in DI water at pH 7.

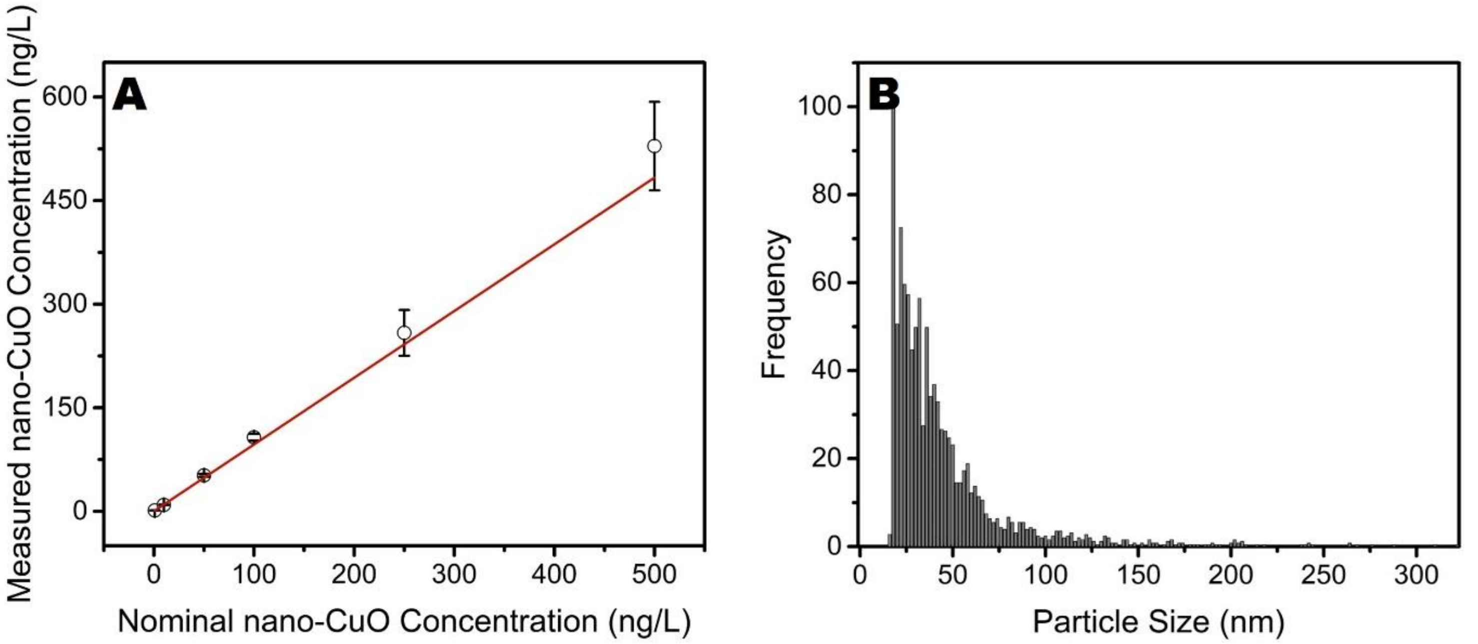
TEM Image of nano-CuO





Size distribution of nano-CuO in DI at pH 7 (via DLS)

Analyze nano-CuO with spICP-MS



Nominal nano-CuO concentration (ng/L)	Ionic Cu concentration (ng/L)			Median size (nm)			Mean size (nm)		
	Avg.	Std.	RSD (%)	Avg.	Std.	RSD (%)	Avg.	Std.	RSD (%)
1	0.11	0.01	9.3	16.48	0.81	4.9	18.51	1.56	8.4
10	0.39	0.04	10.8	15.99	0.00	0.0	23.62	0.54	2.3
50	2.33	0.06	2.5	24.84	4.40	17.7	36.73	3.62	9.9
100	2.78	0.20	7.3	25.26	2.36	9.3	37.15	2.24	6.0
250	32.12	3.36	10.4	31.76	0.11	0.3	34.01	0.60	1.8
500	35.10	2.47	7.0	31.63	0.10	0.3	34.01	0.72	2.1

A. A. Keller, Y. Huang, J. Nelson; *J. Nanoparticle Res.* **2018,** *20* (4), 101.

Detect ENMs in leaf tissues via spICP-MS

Organic Vegetables

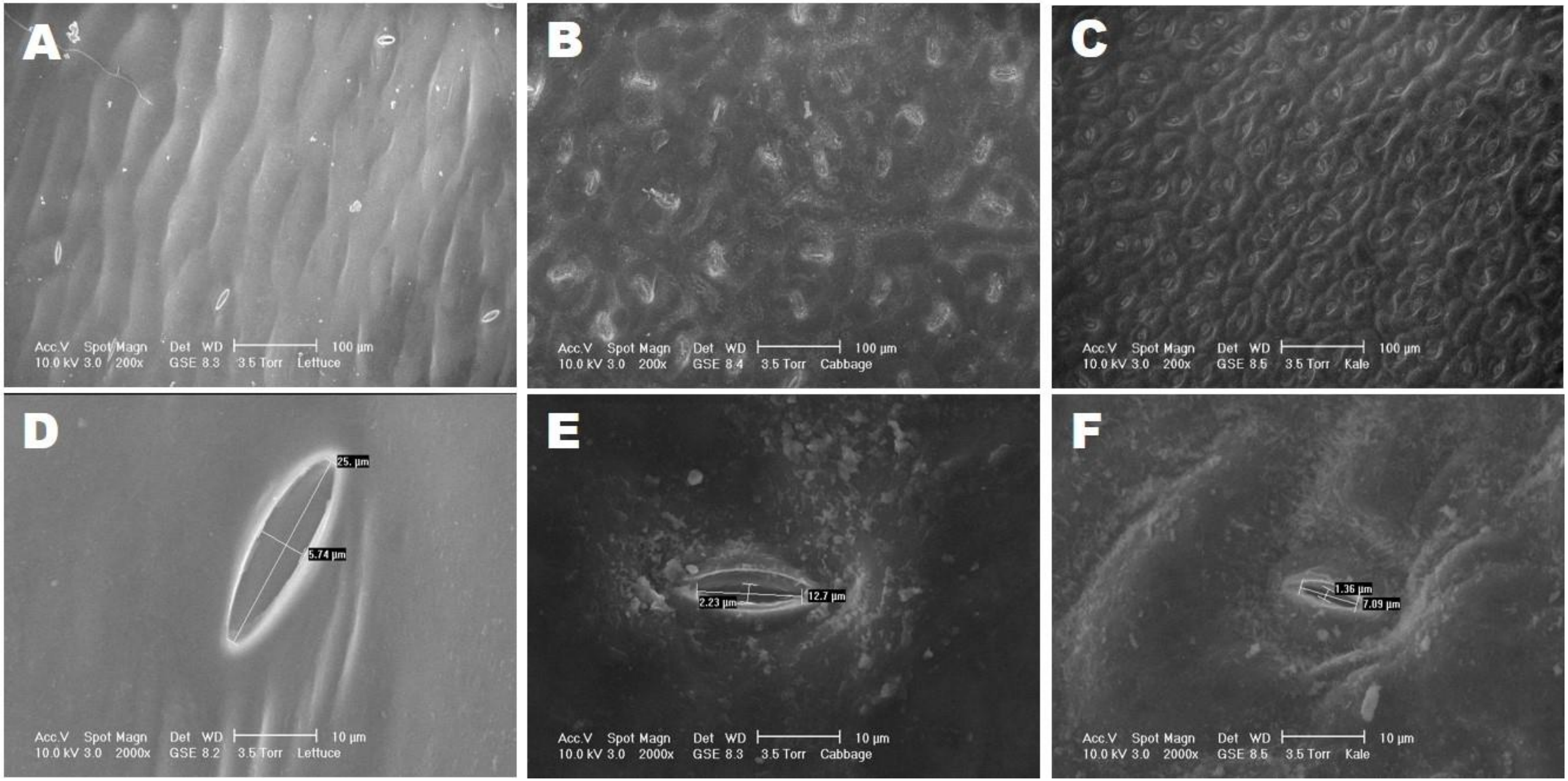
Kale
(Brassica oleracea, var. Acephala Lacinato)

Lettuce
(Lactuca sativa var. green leaf cultivar)

Collard Green
(Lactuca sativa var. green leaf cultivar)

Leaf surface roughness

ESEM

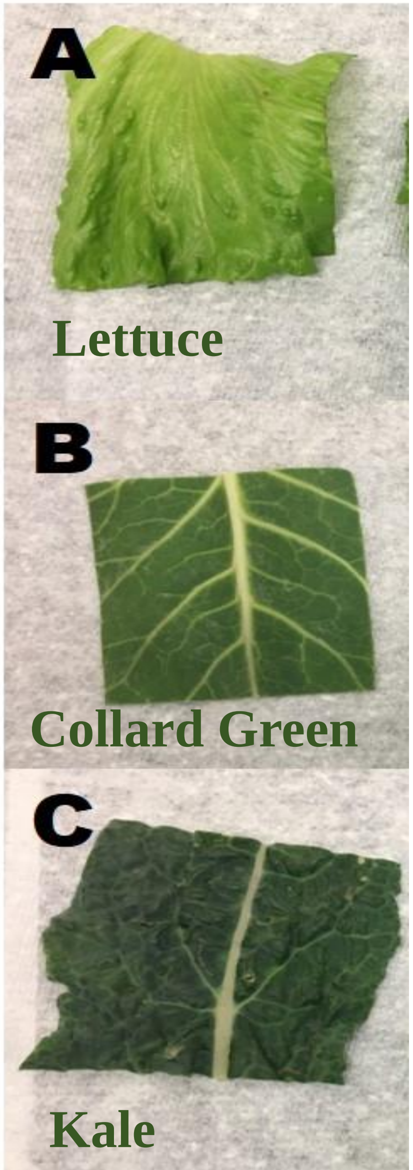


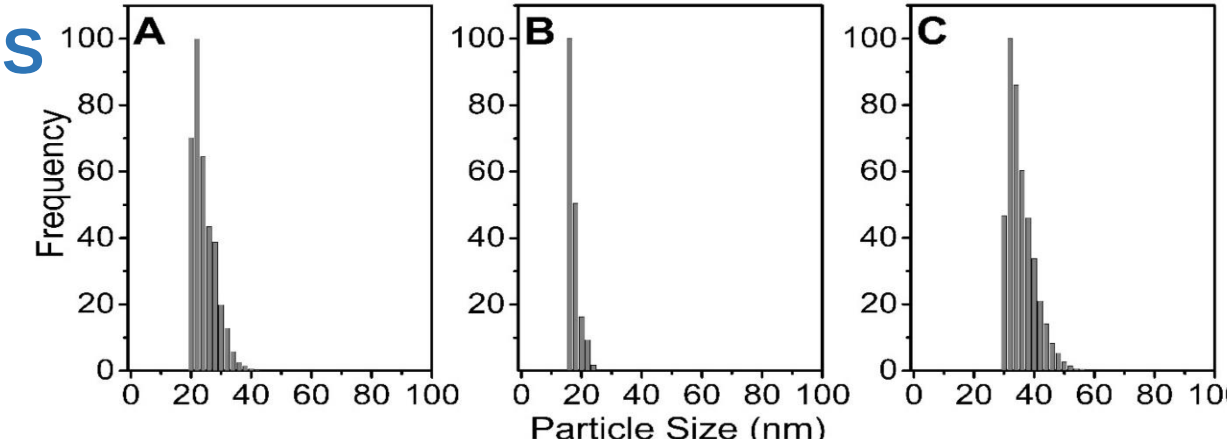
Lettuce **Collard Green** **Kale**

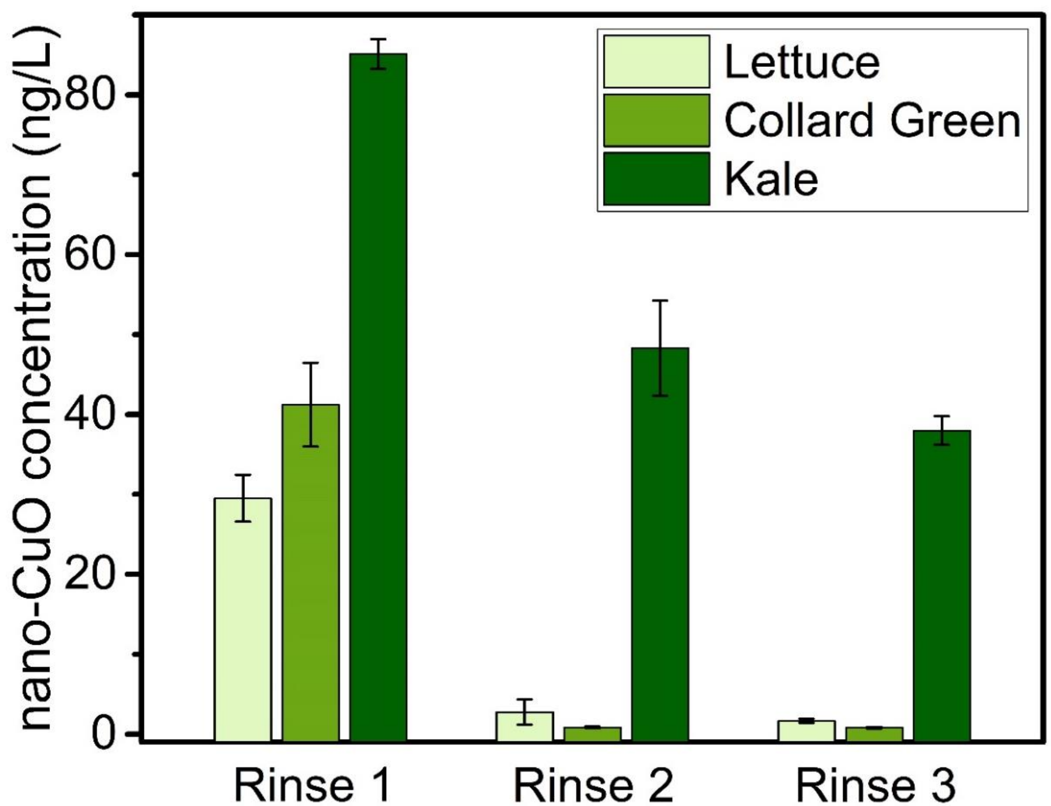
A. A. Keller, Y. Huang, J. Nelson; *J. Nanoparticle Res.* **2018,** *20* (4), 101.

Rinse Leaf with DI water

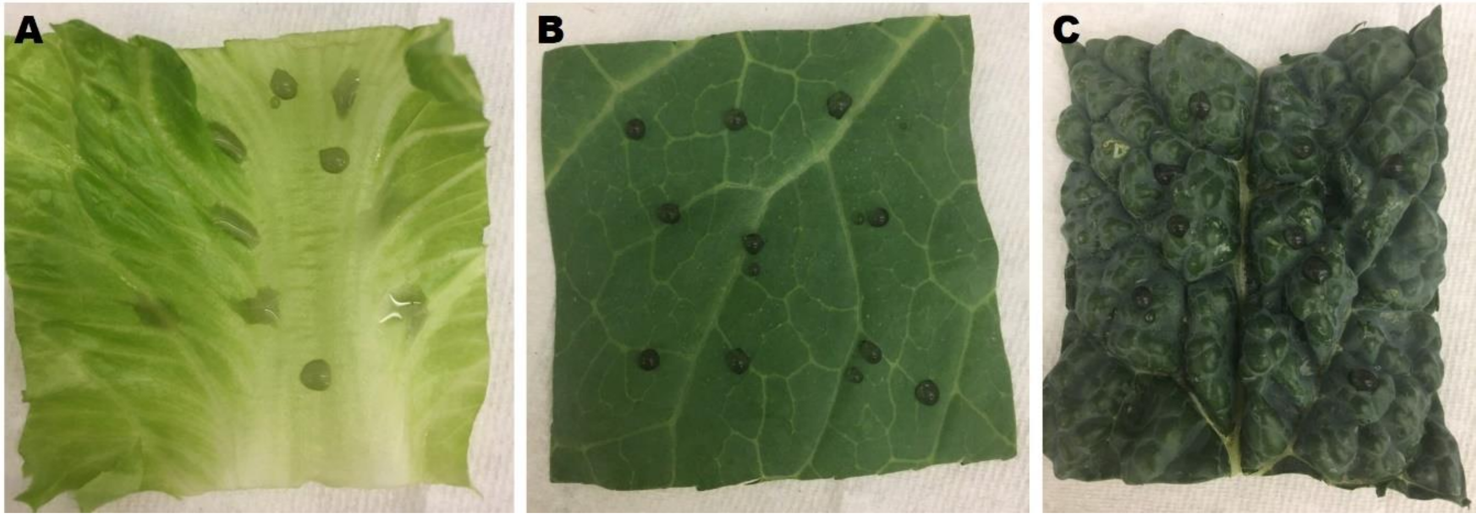
Detect with spICP-MS





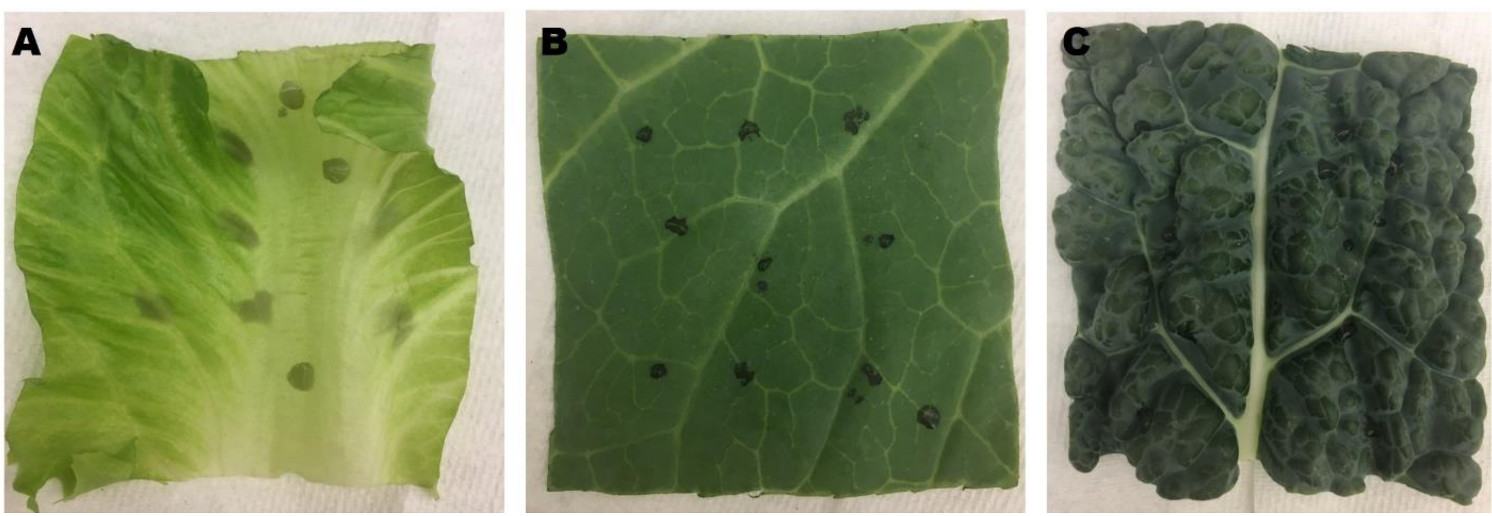


Expose Leaf to nano-CuO



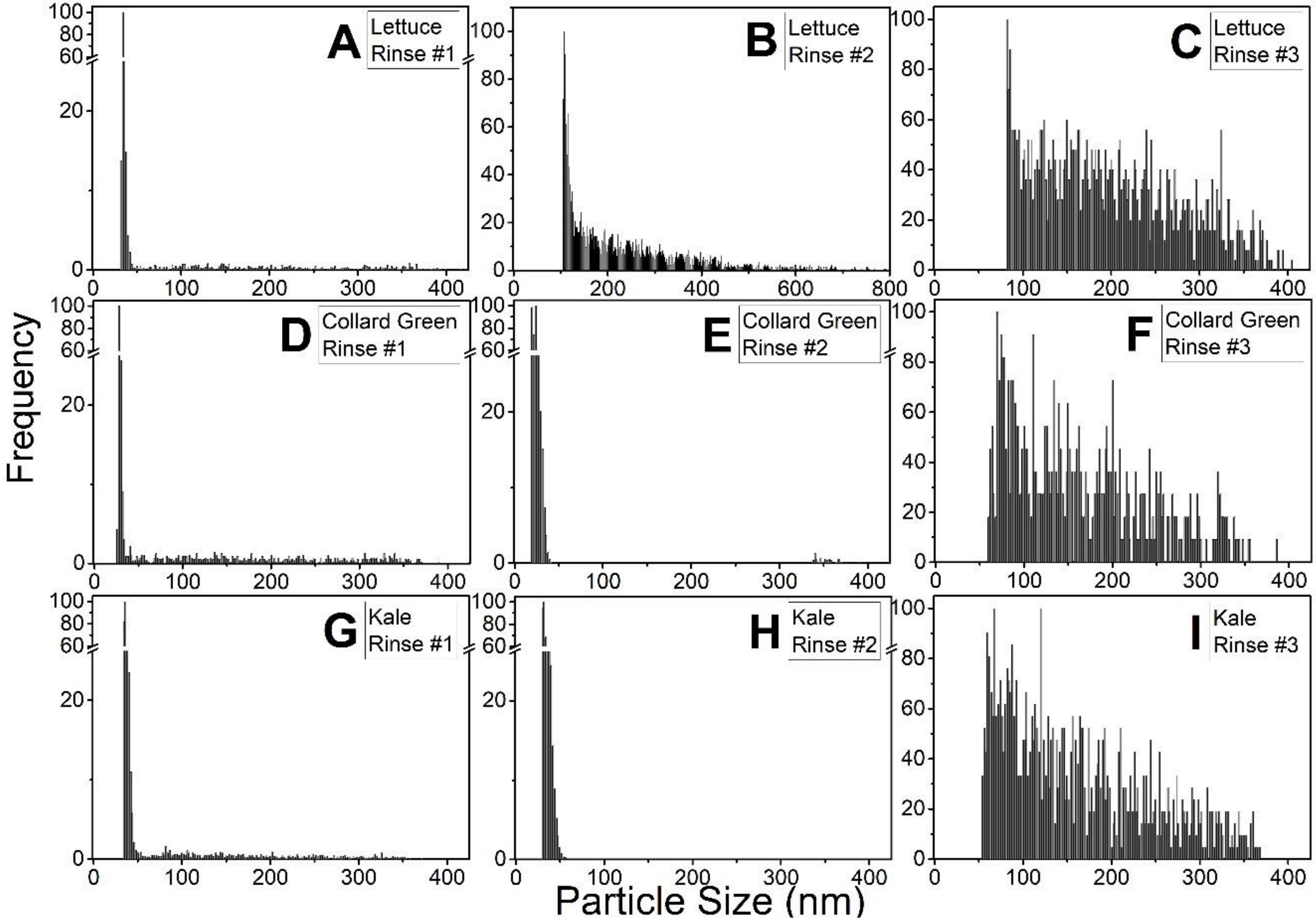
Lettuce Collard Green Kale

2-hour air dry



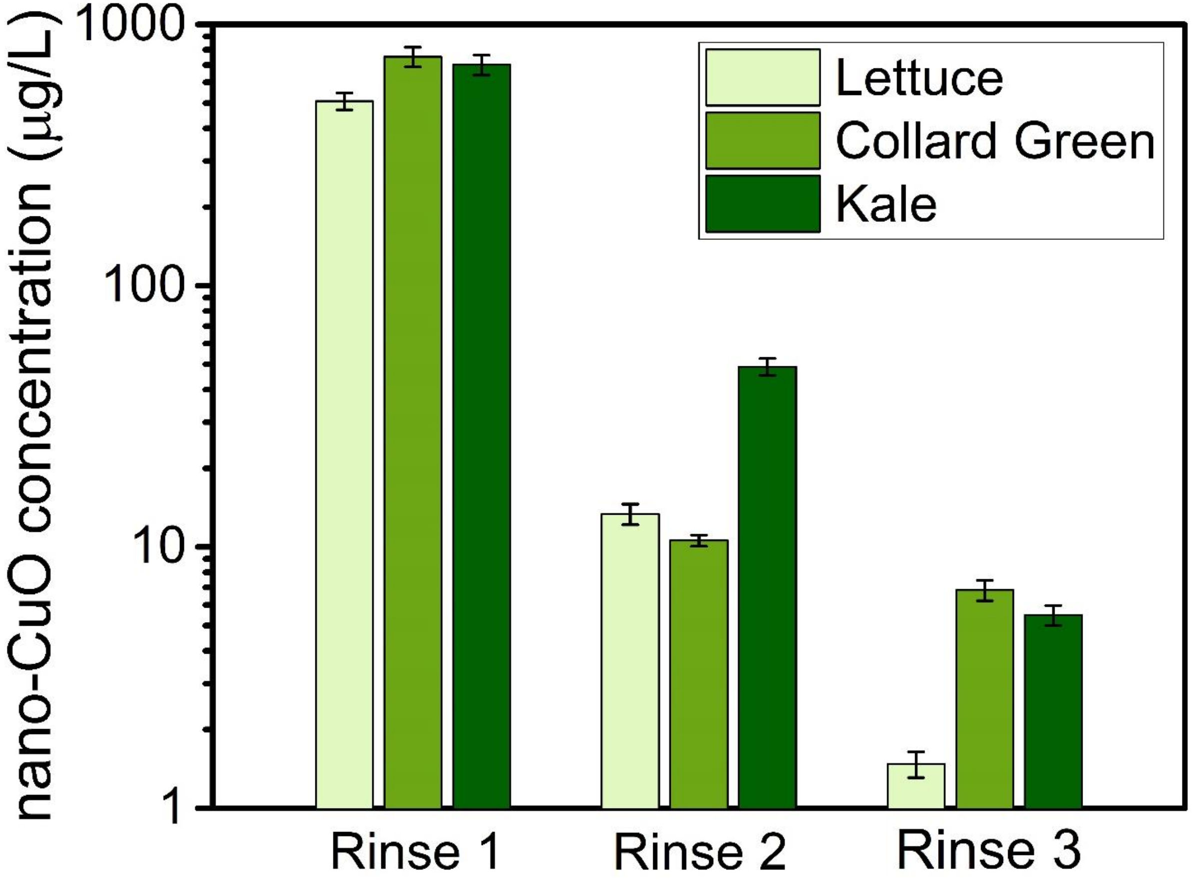
Rinse Leaf with DI after nano-CuO exposure

Detect with spICP-MS



Rinse Leaf with DI after nano-CuO exposure

Detect with spICP-MS



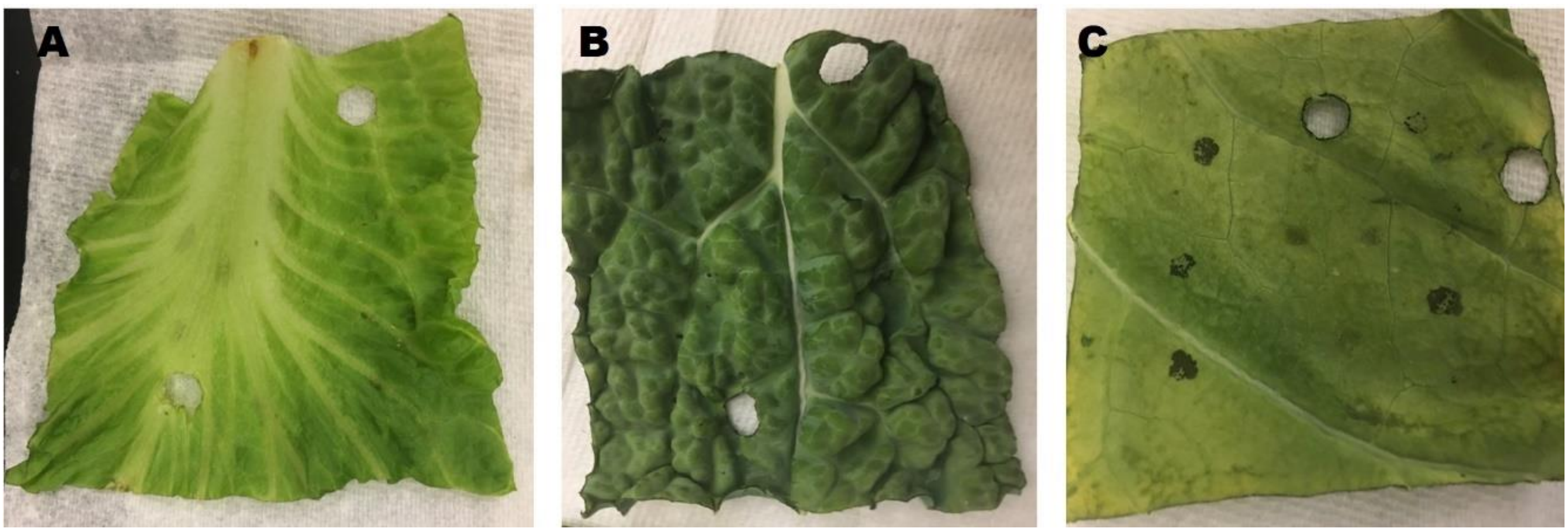
- Concentrations in first rinse around 500-750 µg/L
- Residual washable concentration after 2 rinses is less than 10 µg/L
- Leaf surface roughness may influence residual

Any nano-CuO within the leaf tissues?

Enzymatic digestion

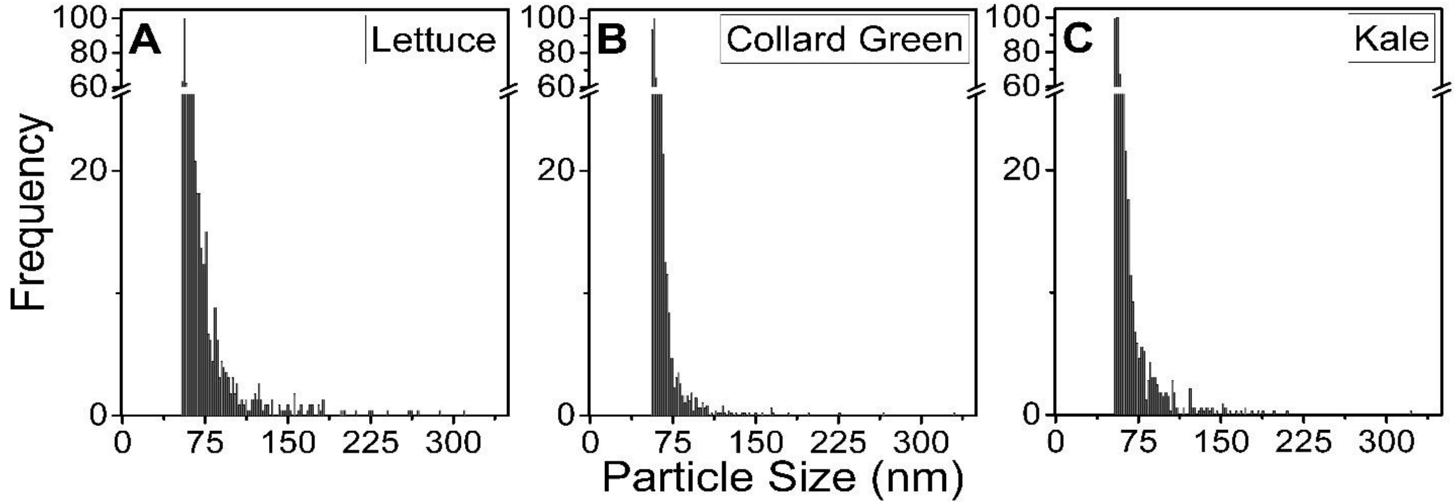
Macerozyme R-10 enzyme

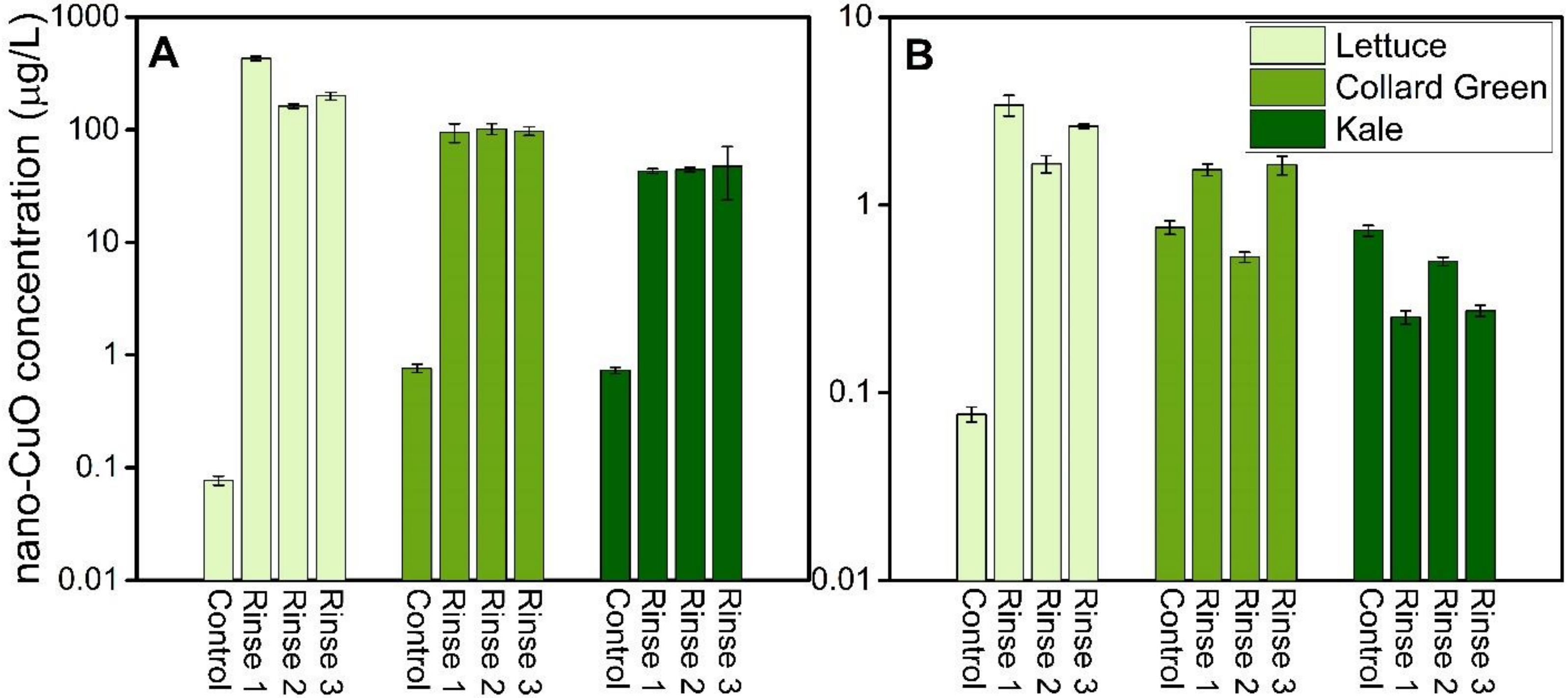
- Mixed with plant tissue samples to digest tissues and release nano-CuO
- 24 hr digestion
- Neutral pH to avoid digesting nano-CuO
- Filtration
- Analyze with spICP-MS



Lettuce | Collard Green | Kale

Yes! Leaf tissues retain ENMs





Conclusions

- ✓spICP-MS offers a great approach for quantitative analysis of nanoparticles
- ✓Provides concentration, size distribution, composition, dissolved ion concentration
- ✓Can be applied to water and some biological tissues
- ✓NPs were found in all rinse water samples, as individual nanoparticles as well as aggregates
- ✓The concentration of nano-CuO in rinse water was highly related to leaf surface characteristics
- ✓Substantial fraction of the nano-CuO can remain on the leaf surface or perhaps even enter via the stomata.
- ✓After three cycles of rinse, the residual Cu concentration were below any toxicity concern for humans

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Acknowledgments

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

NSF

Agilent Technologies

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