UNIVERSITY OF CALIFORNIA
UC CEIN Center for Environmental Implications of Nanotechnology
NSF: DBI-0830117

Entry into and Potential Impacts of Manufactured Nanomaterials in Terrestrial Ecosystems

CalRecycle Used Oil/HHW 2015

April 7-10, 2015

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University of California, Santa Barbara

UNIVERSITY OF CALIFORNIA
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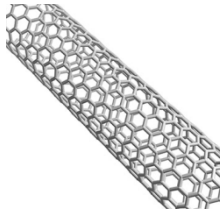
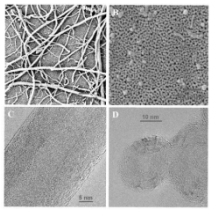
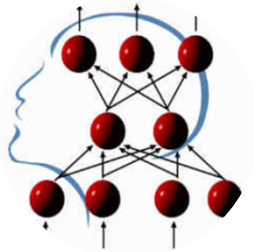
UC CEIN Predictive and Multi-disciplinary Environmental Nanoscience

MNM libraries

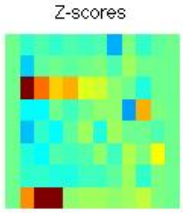


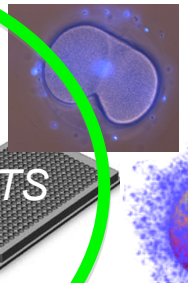


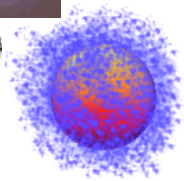
Nanoparticle structural & physicochemical information



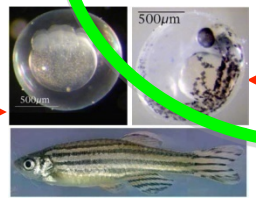
- Data integration
- Pattern Recognition (heatmaps, self –organizing etc)
- Machine Learning
-







Cell, embryo, biomolecules



In vivo toxicity

Predictive toxicology

- Hazard ranking
- Risk profiling
- Exposure modeling
- Property-activity relationships

Fate & transport

Multimedia Analysis

Main Points of this Presentation

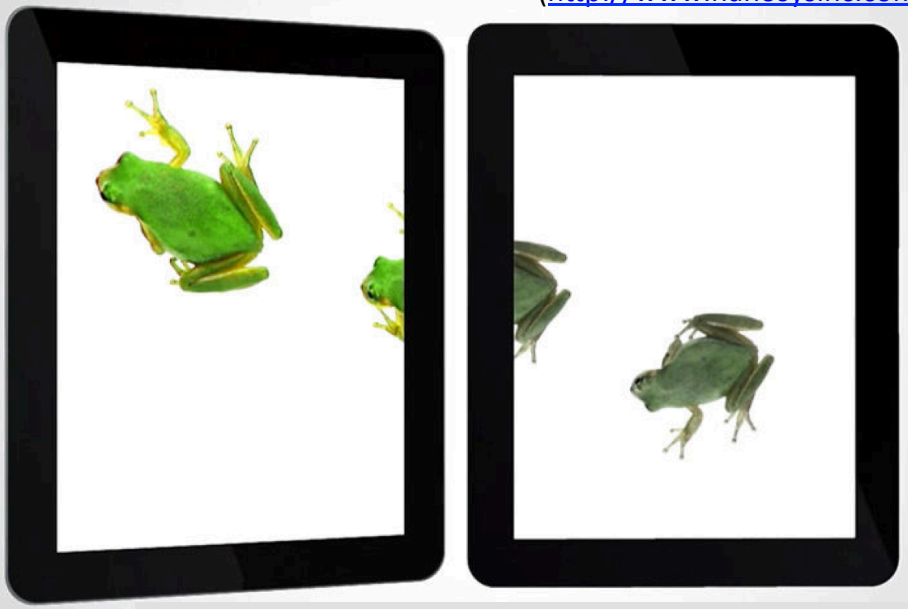
- Nanotechnology is here
- Nanomaterials transport / distribute / transform
  - Terrestrial exposures possible
- Potential outcomes:
  - changed ecosystem services
  - trophic transfer
  - effects on food supply
- Moving forward: rapid screening for the environment

Manufactured nanomaterials are used

Nanosilver in textiles

Nano-carbon in parts

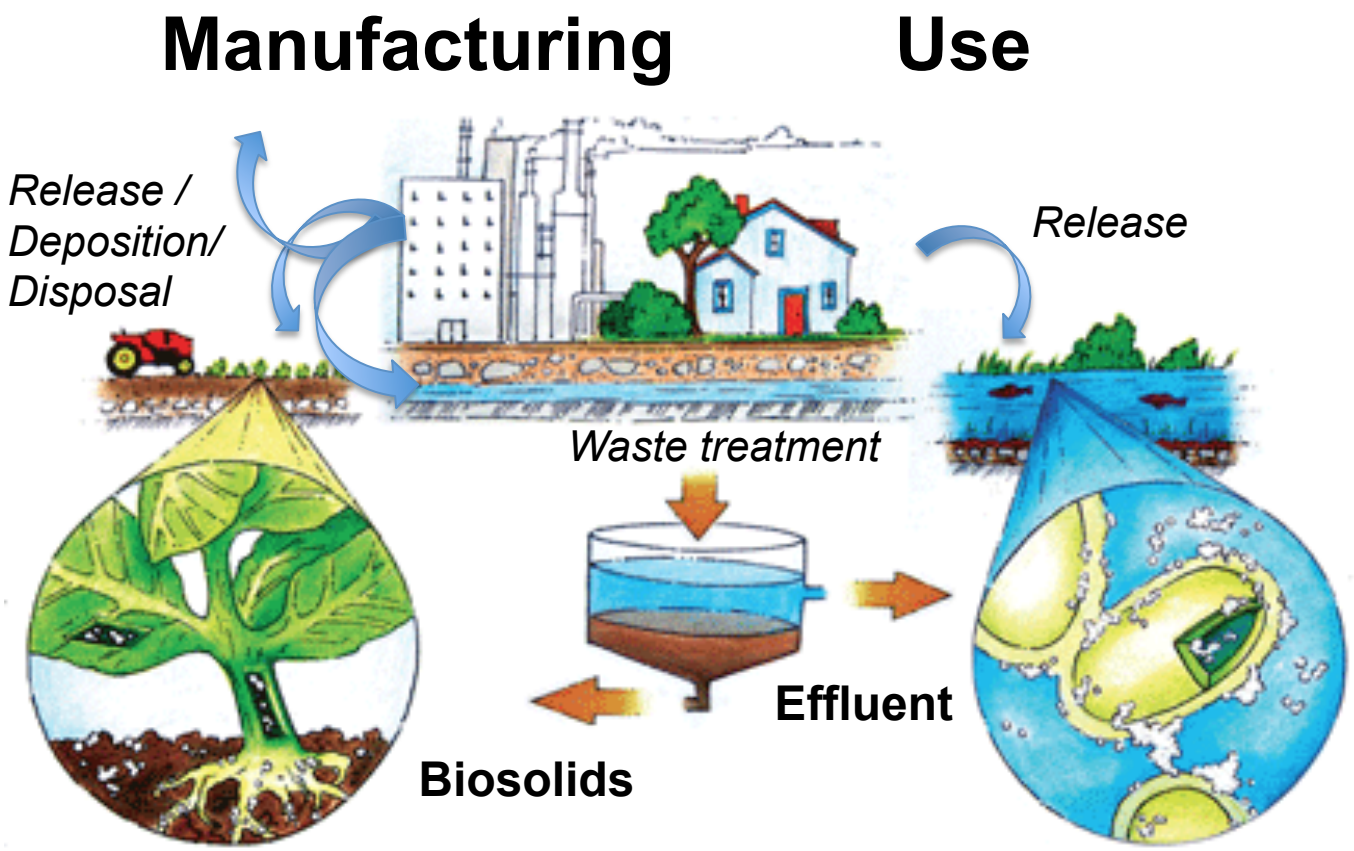
(http://www.nanosysinc.com/#lcd-revolution)



Quantum dots in displays

Metal oxides in coatings

Environmental Exposure Pathways



Agriculture

Water Resources

Art by Allison Horst, CEIN Ph.D., as published in *Chemical & Engineering News*, March 14, 2011

WWTP effluent and biosolids

(Keller and Lazareva, 2014. ES&T Letters)

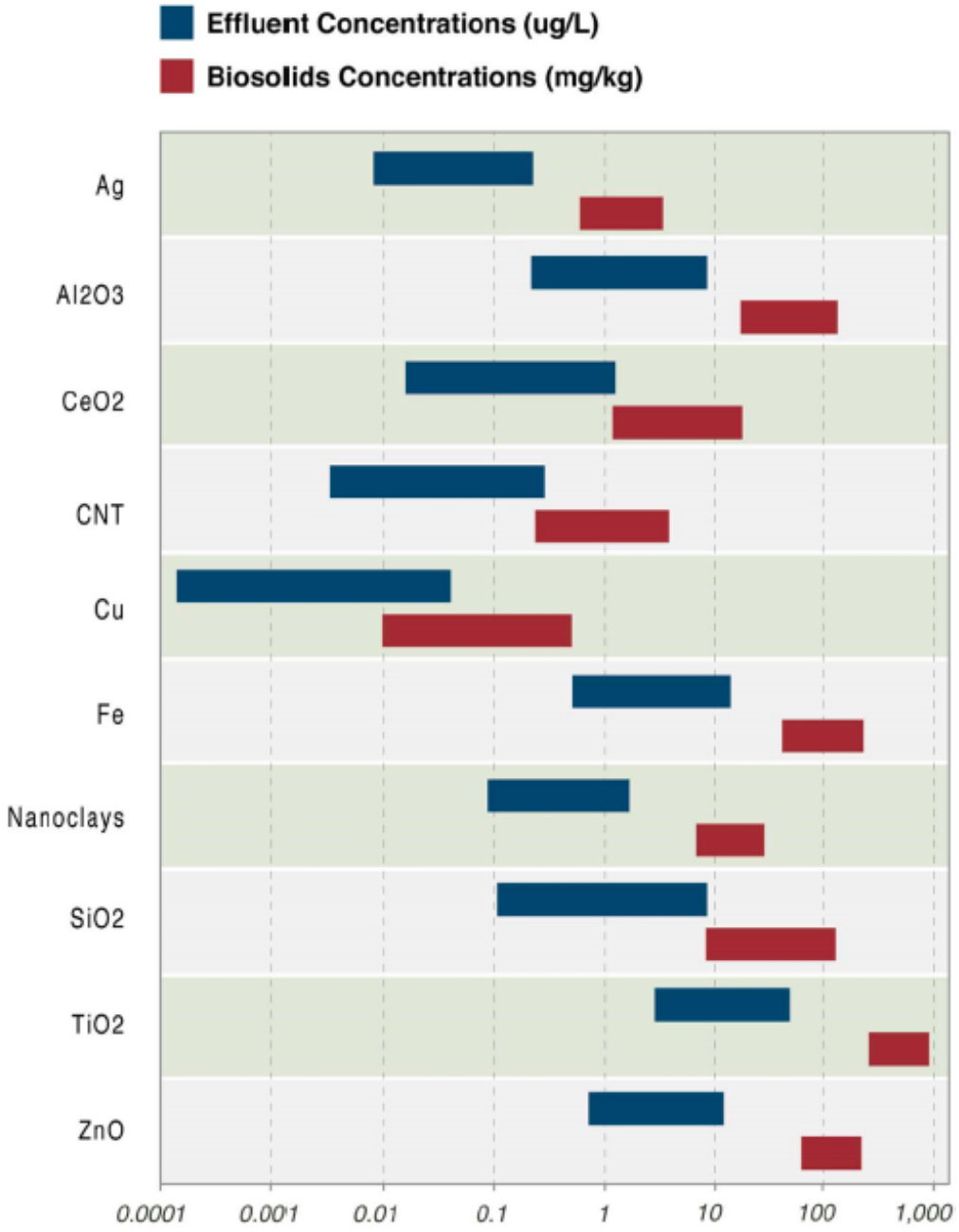
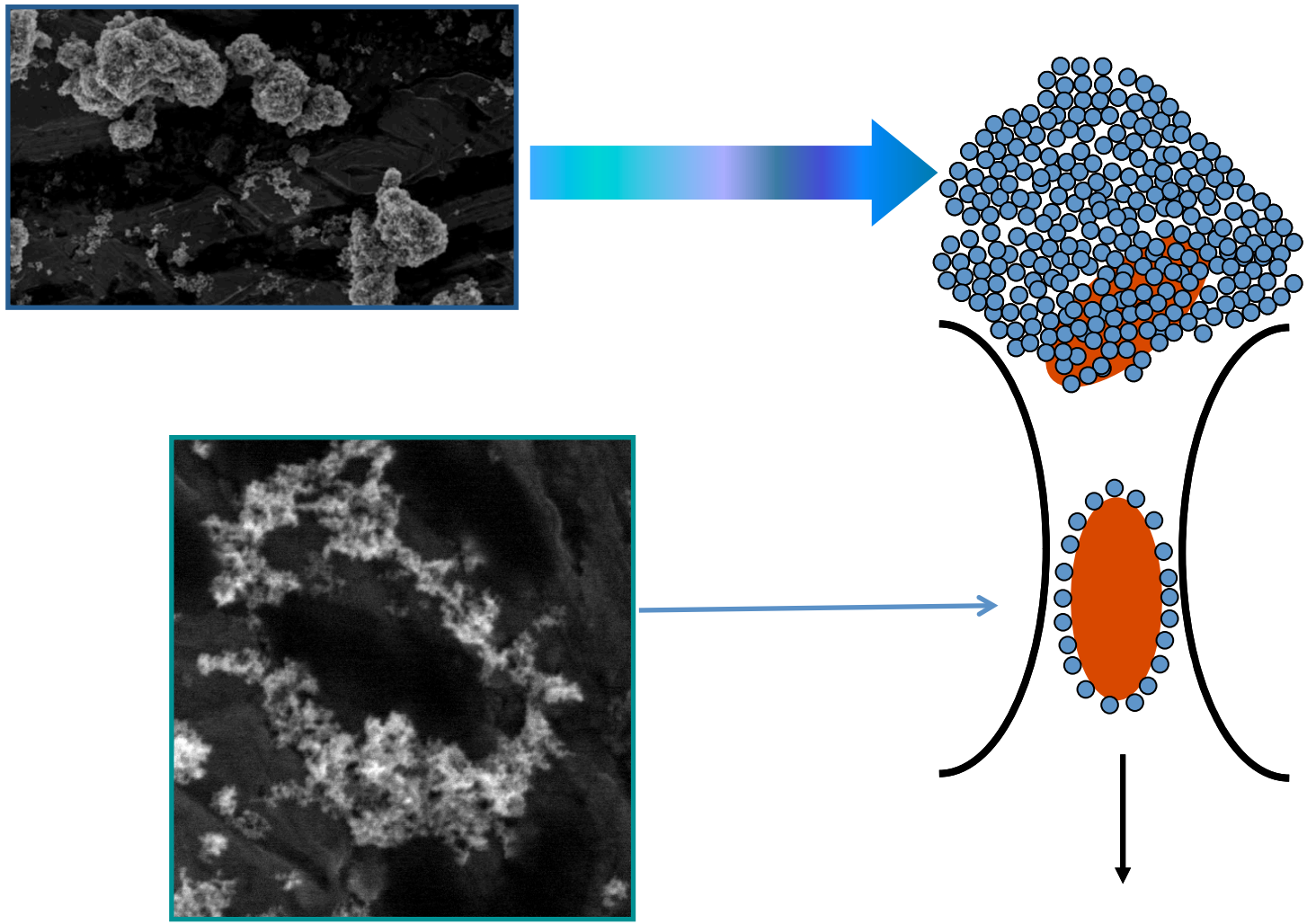


Figure 4. Predicted ENM concentrations in San Francisco Bay WWTP effluent and biosolids.

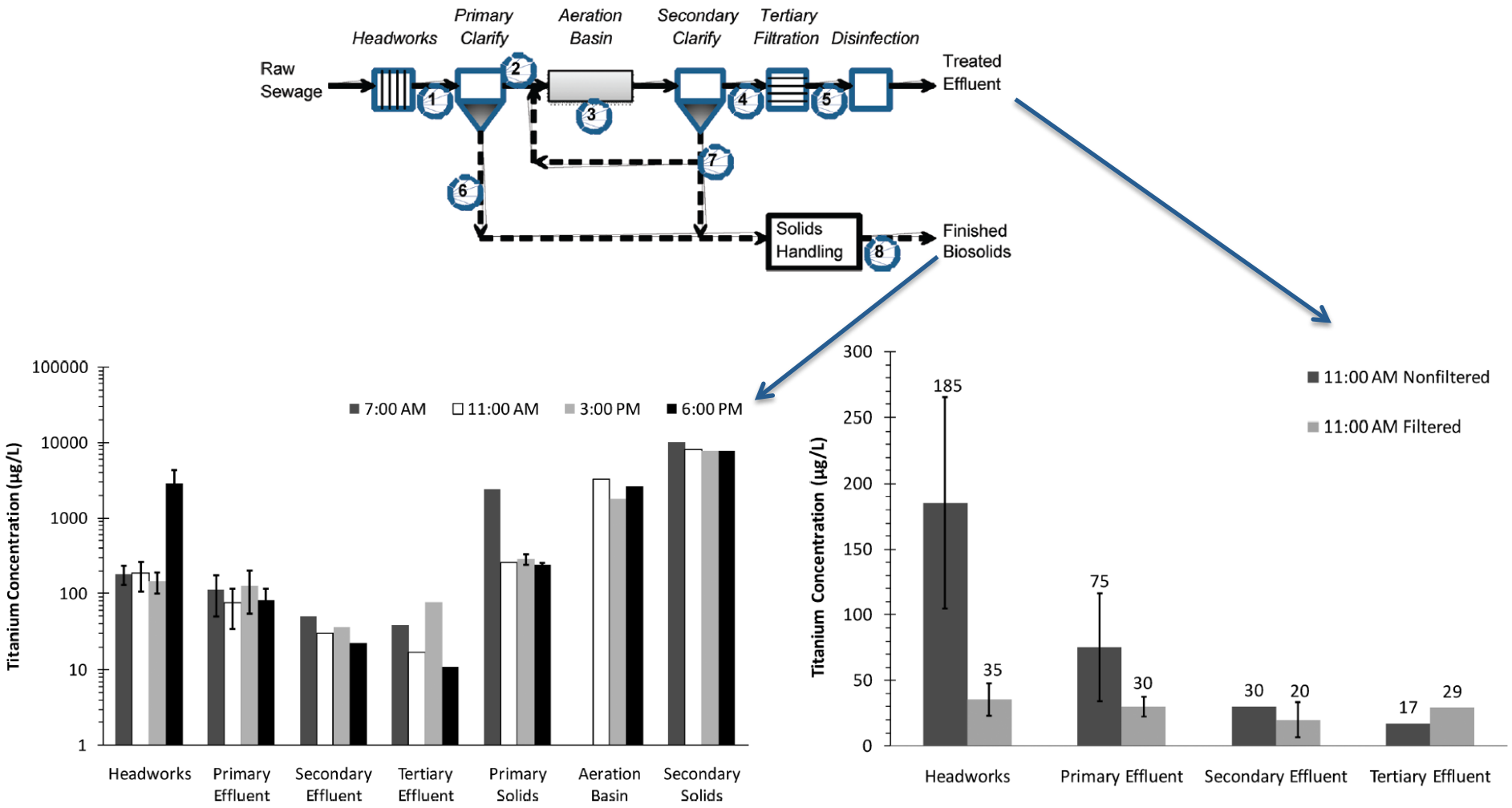
activated sludge in an aeration basin

NMs sorb to bacteria



(Horst *et* al. 2010. AEM)

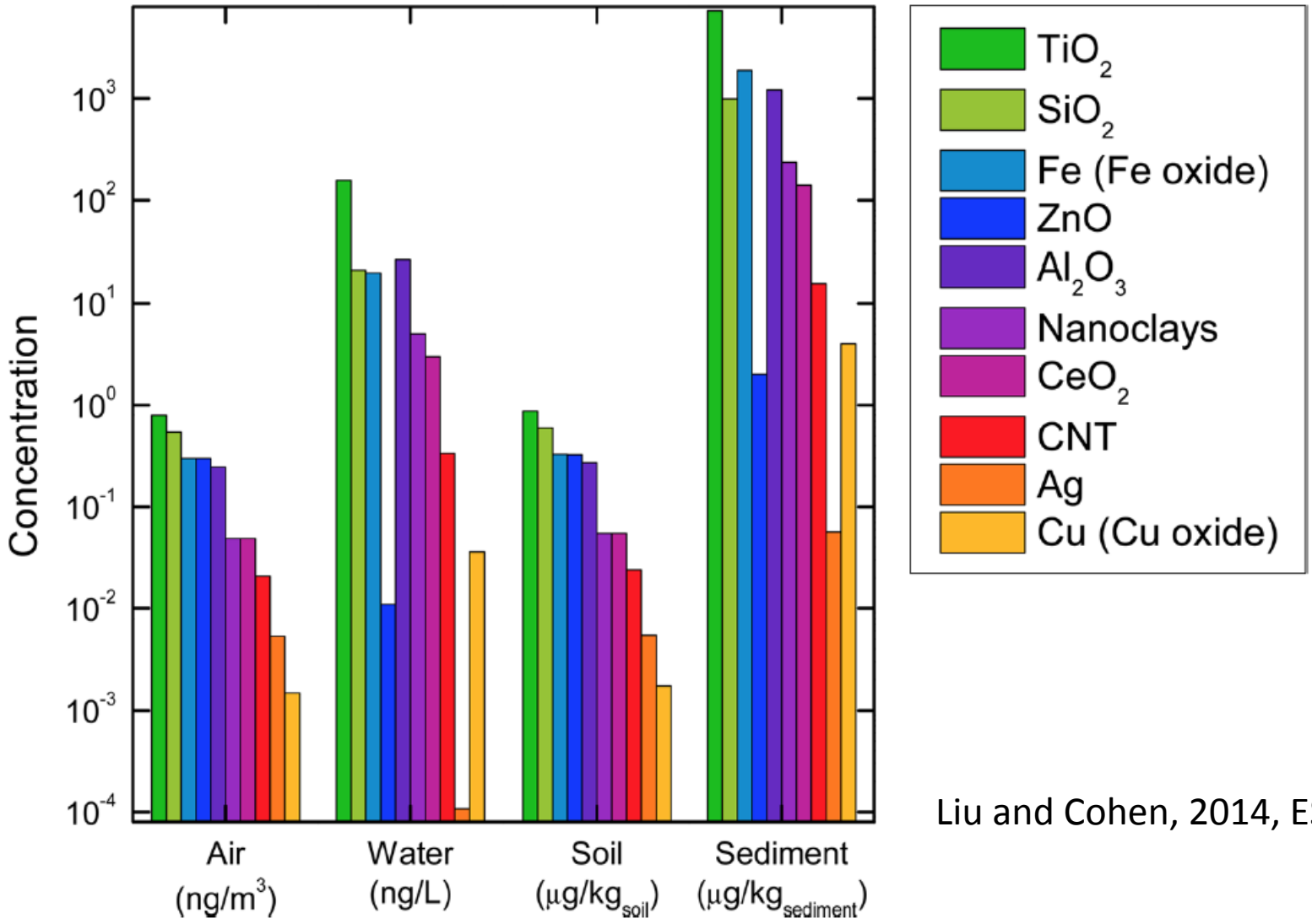
Nanomaterials in Biosolids



(Kiser et al., ES&T, 2009)

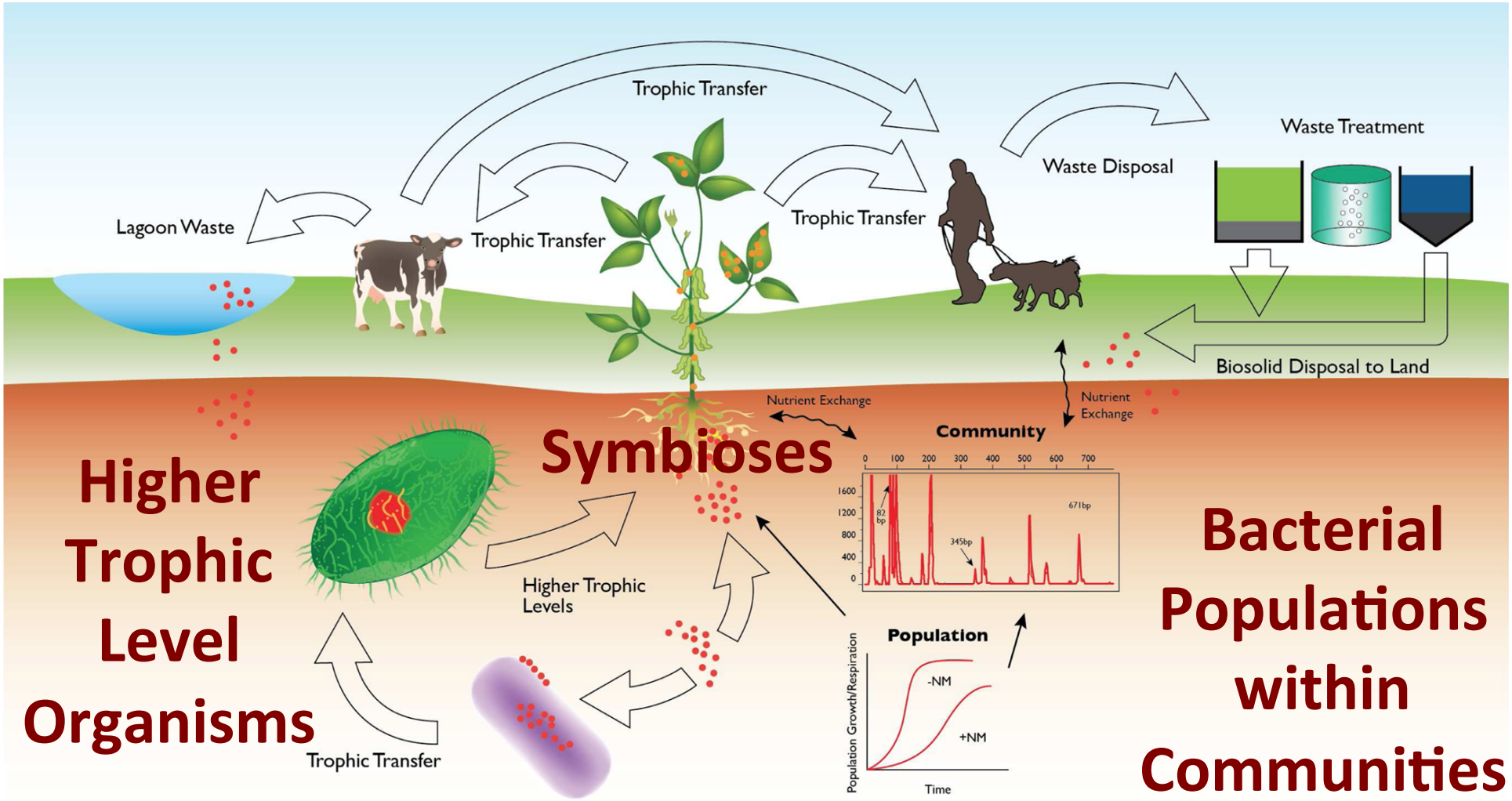
land application of biosolids

Multimedia Model for Los Angeles (http://nanoinfo.org/mendnano/)



Liu and Cohen, 2014, ES&T

complex terrestrial interactions w/ MNMs



(*from* Holden, Nisbet, Lenihan, Miller, Cherr, Schimel, Gardea-Torresdey. 2013. ACR)

Predictive Terrestrial Ecological Nanotoxicology

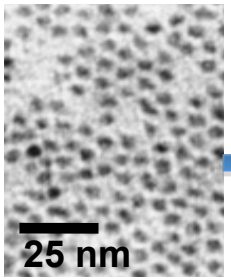
Holden et al. 2013. Acc. Chem. Res.; Holden et al. 2014. Curr. Opin. Biotechnol.

Hydroponic Plants

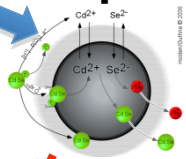
Ecosystem

Soil Bacterial Communities

NMs



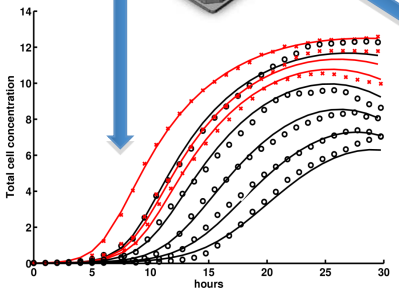
Microbial Populations

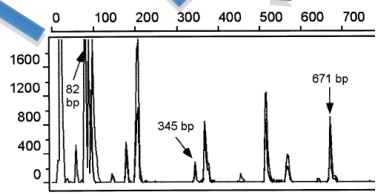


SCREENING

Trophic Transfer

Sentinel Bacteria



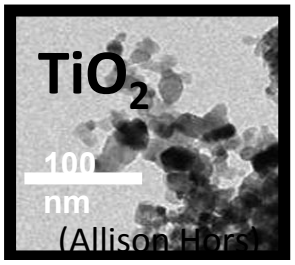


PREDICTIONS

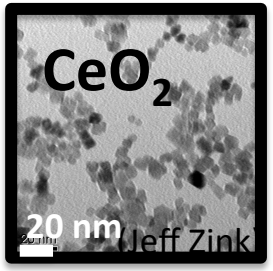
Klanjscek et al. 2012 PLoS One
Klanjscek et al. 2013 Ecotoxicology

http://www.nsf.gov/news/news_images.jsp?cntn_id=104178&org=NS

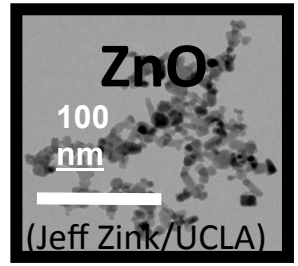
Industrial Metal Oxide Nanomaterials



(Allison Hors)



(Jeff Zink)



(Jeff Zink/UCLA)

Keller et al. 2010. Environ. Sci. Technol.

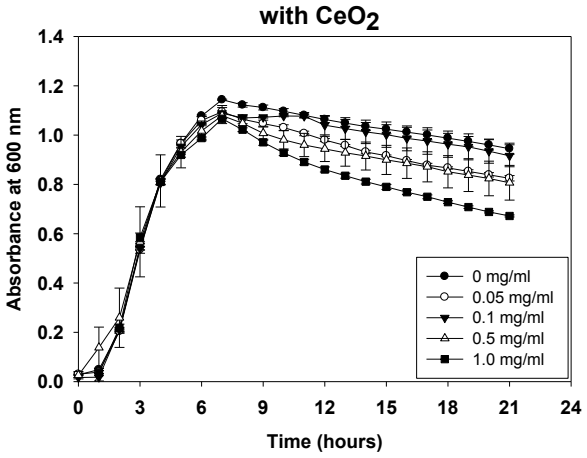
properties	technique	unit	TiO_2 Evonik 4168063098	CeO_2 Meliorum 121008	ZnO Meliorum 121008
primary size	TEM[a]	nm	27 ± 4	rods: (67 ± 8) × (8 ± 1) (≤10% polyhedra: 8 ± 1 nm)	24 ± 3
particle size in DI water	DLS[a]	nm	194 ± 7	231 ± 16	205 ± 14
phase and structure	XRD[a]		82% anatase and 18% rutile	100% ceria cubic	100% zincite hexagonal
shape/morphology	TEM[a]		semispherical	rods (≤10% Polyhedra)	spheroid
surface area	BET[2]	$m^2\ g^{-1}$	51.5	93.8	42.1
IEP	zetaPALS[a]		6.2	7.5	9.2
EPM in 1 mM KCl	zetaPALS[a]	$10^{-8}\ m^2\ V^{-1}\ s^{-1}$	2.37 ± 0.06	2.19 ± 0.04	1.83 ± 0.11
purity	TGA[a]	wt.%	98.03	95.14	97.27
moisture content	TGA[a]	wt.%	1.97	4.01	1.61

[a] Transmission and scanning electron microscopy (TEM), dynamic light scattering (DLS), X-ray powder diffraction (XRD), isoelectric point (IEP), electrophoretic mobility (EPM), and thermogravimetric analysis (TGA) were done by the UC-CEIN at UCLA . [2] Brunauer–Emmett–Teller analysis (BET) was conducted by Dr. Ponisseril Somasundaran's lab at Columbia University.

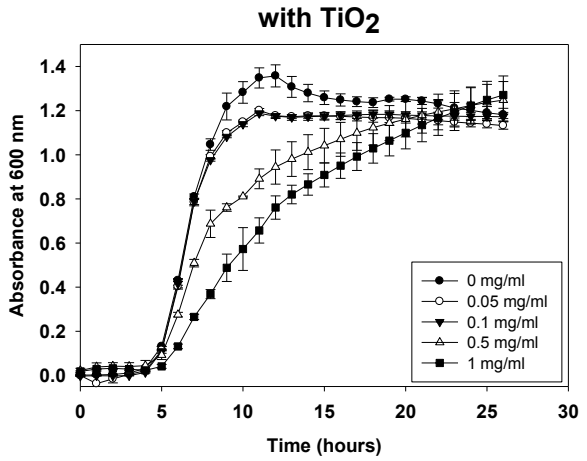
Bacterial Population Growth Impacted in Environmentally-Representative Media

LB (rich)

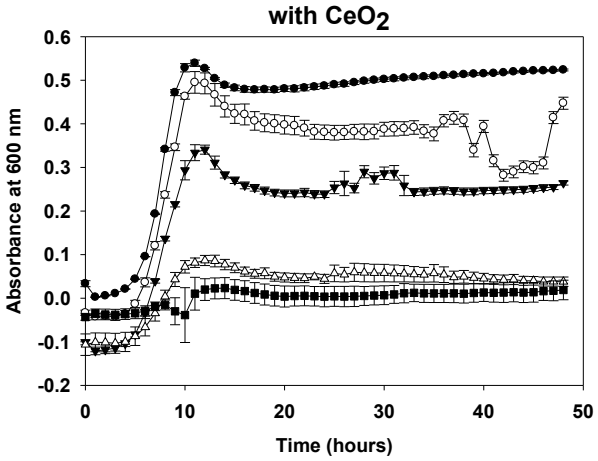
CeO_2



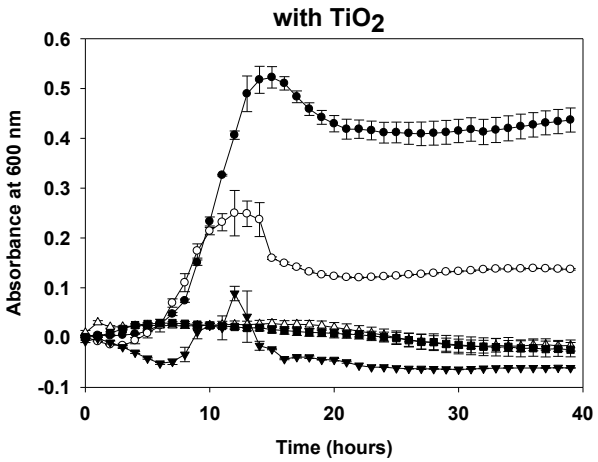
TiO_2



MD (minimal)



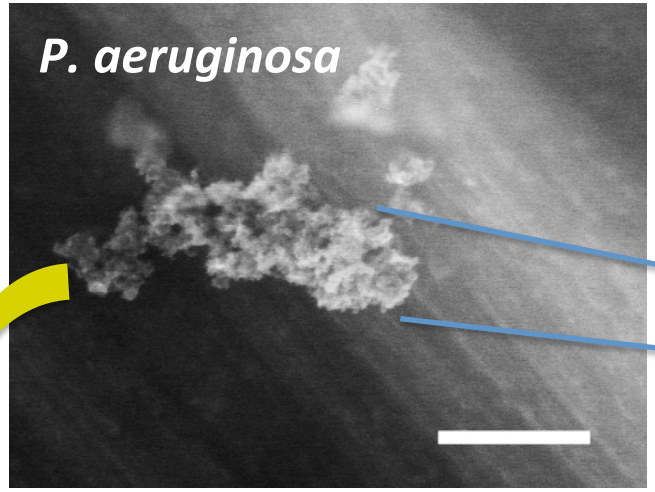
CeO_2

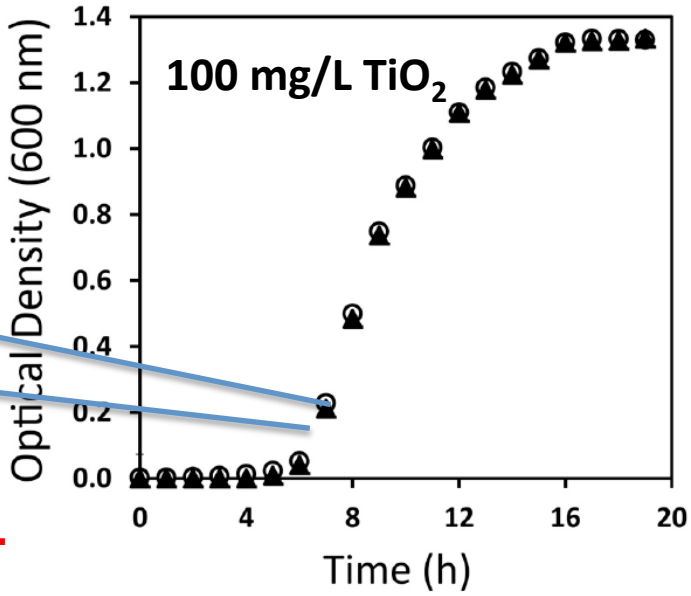


TiO_2

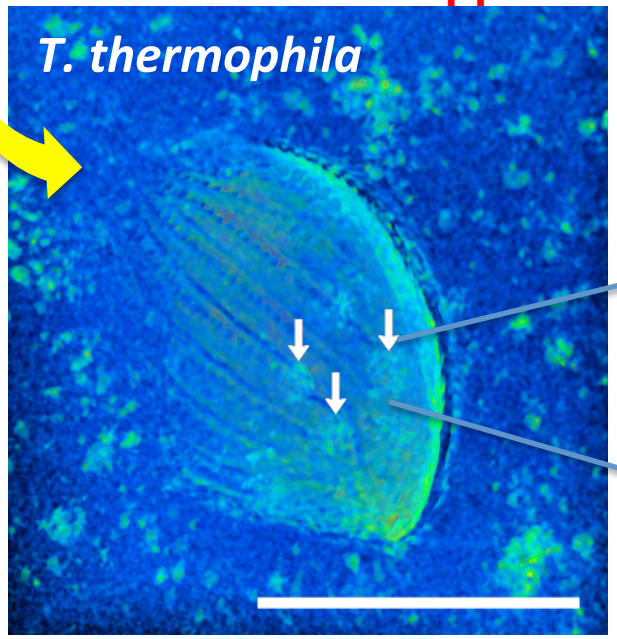
R. Vukanti

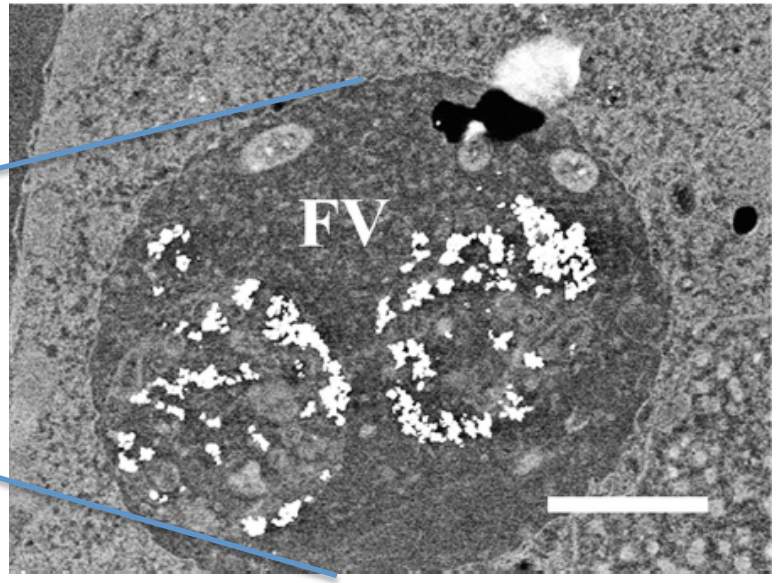
Microbial Population Growth and Trophic Transfer



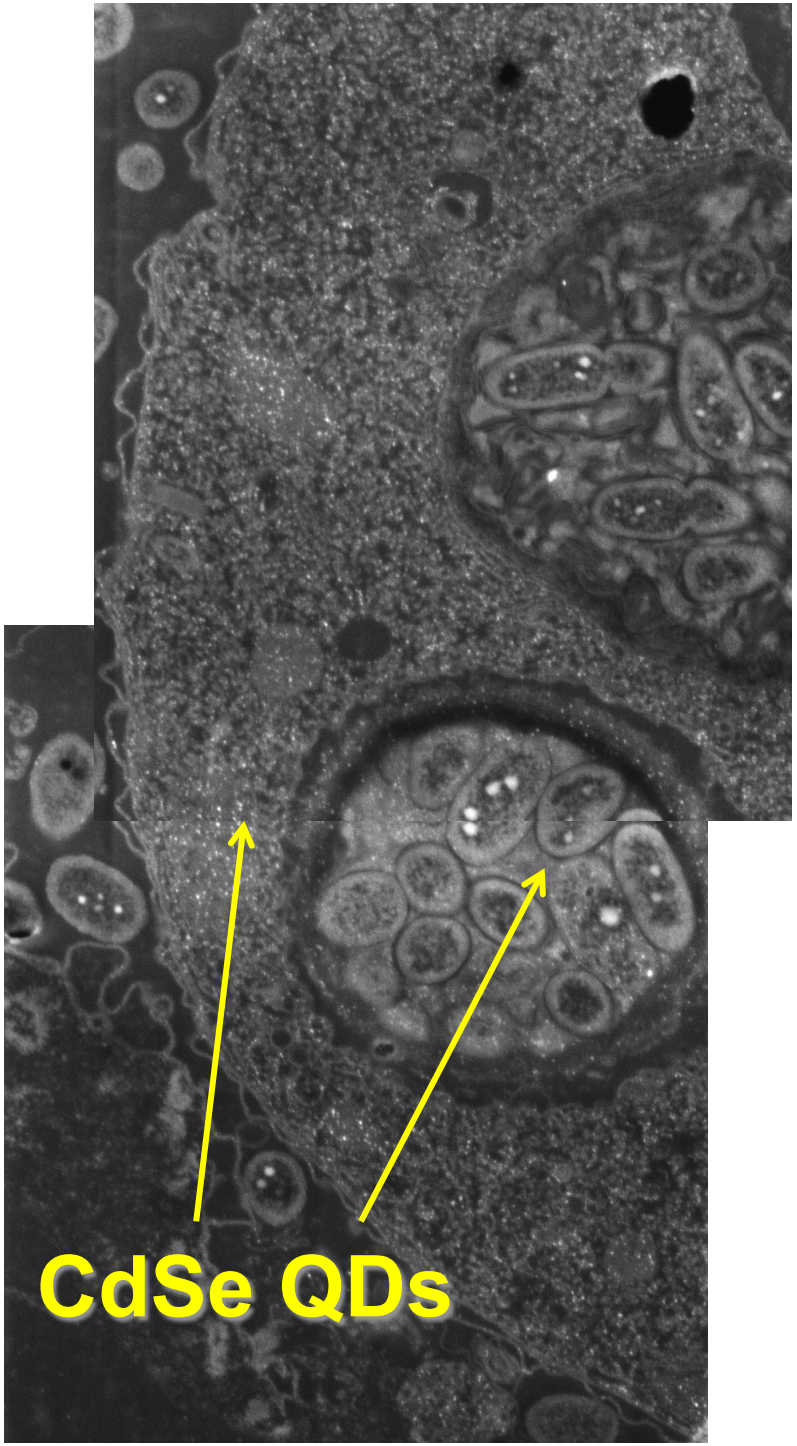


Horst *et* al. 2010. Appl. Environ. Microbiol.

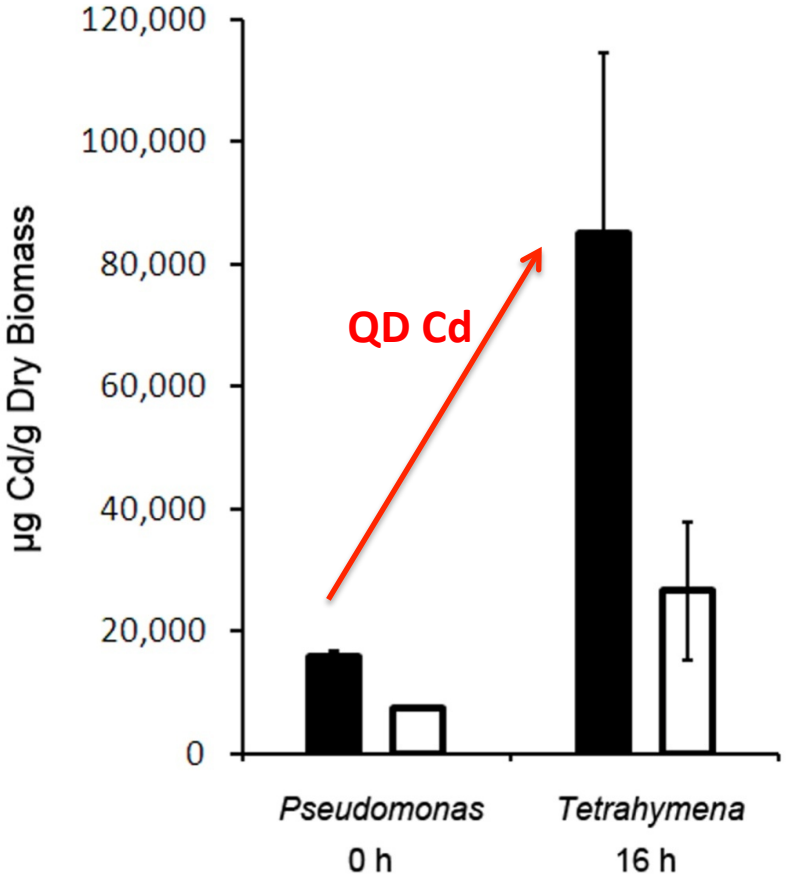




Mielke et al. 2013. Appl. Environ. Microbiol.



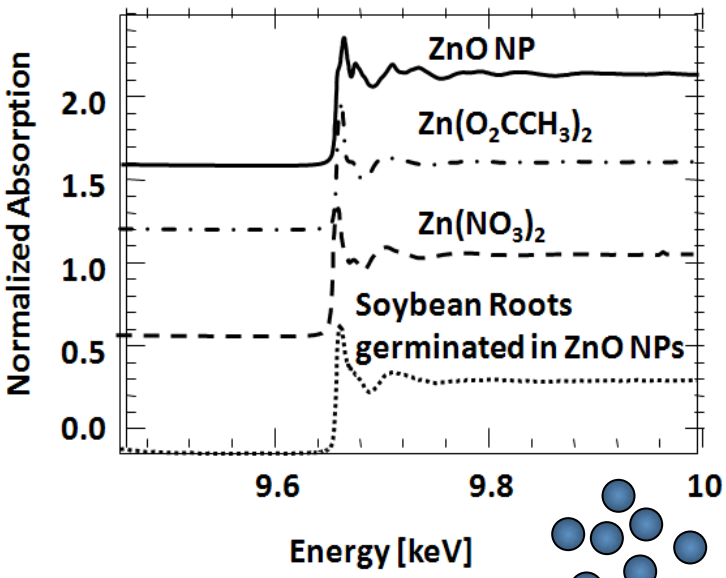
CdSe QDs: Biomagnification from Bacterial Prey into Protozoan Predator



Werlin et al. 2011. Nat. Nano.

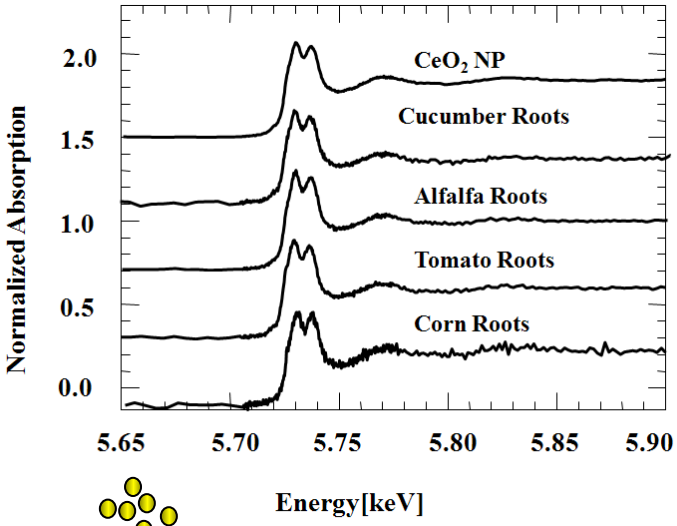
Hydroponic soybean: ZnO and CeO_2 uptake

ZnO XAS results



Gardea-Torresdey
(Univ. Texas- El Paso)

CeO_2 XAS results

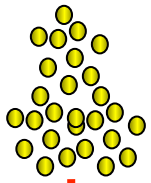


ZnO NPs were biotransformed

??

$Zn(OH)_2$?
Zn^{2+} ?
ZnO

Photo: G. de la Rosa



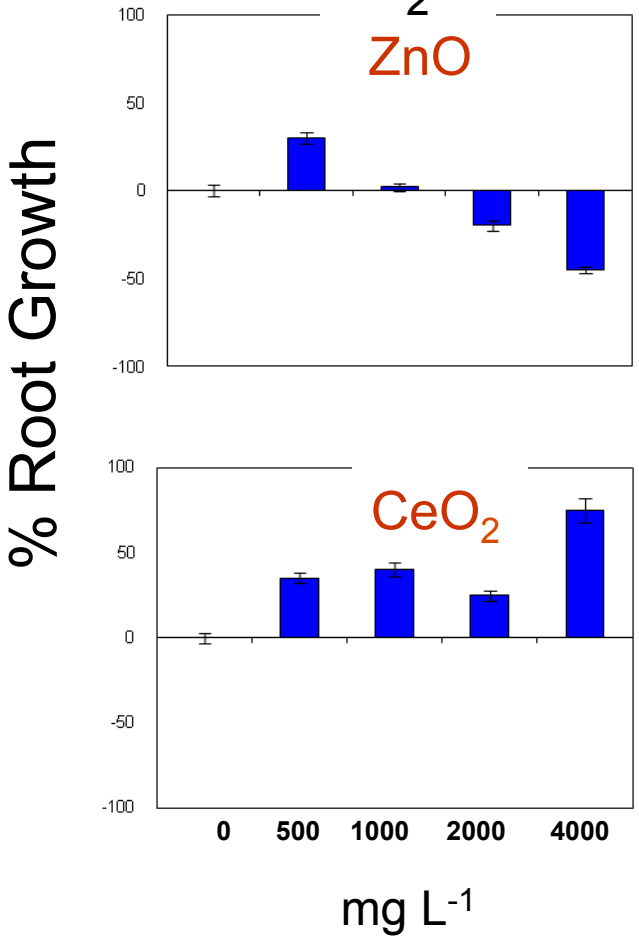
CeO_2 remained unchanged and taken up in roots

Lopez-Moreno et al. 2010. ES&T.
Lopez-Moreno et al. 2010. J. Ag. & Food Chem.

Hydroponic soybean: nZnO impacts growth; $nCeO_2$ is genotoxic

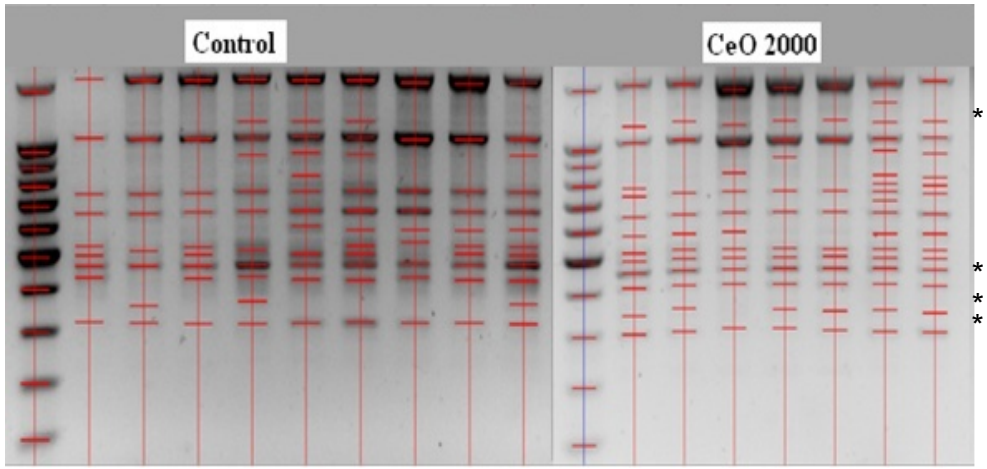
ZnO NPs *reduce* root growth

CeO_2 NPs *increase* root growth



CeO_2 is genotoxic to soybean.

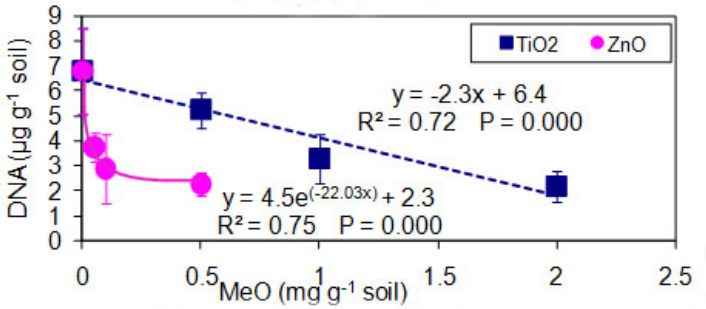
➔four new DNA bands in plants w/ 2000 mg CeO_2 L^{-1}



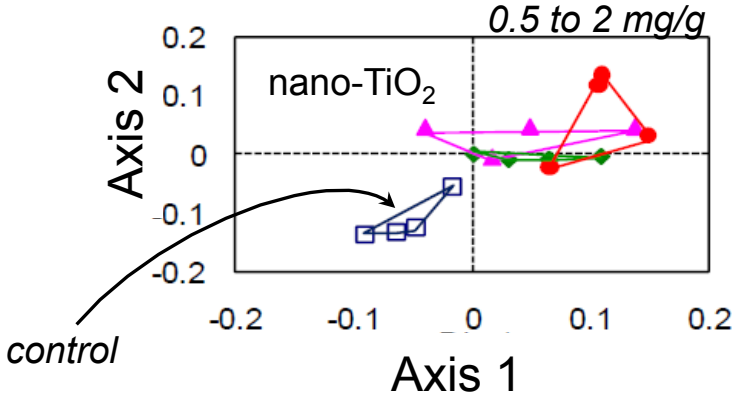
Lopez-Moreno et al. 2010. ES&T.

ZnO and TiO_2 Impact Soil Microbial Communities:

Decrease Soil DNA

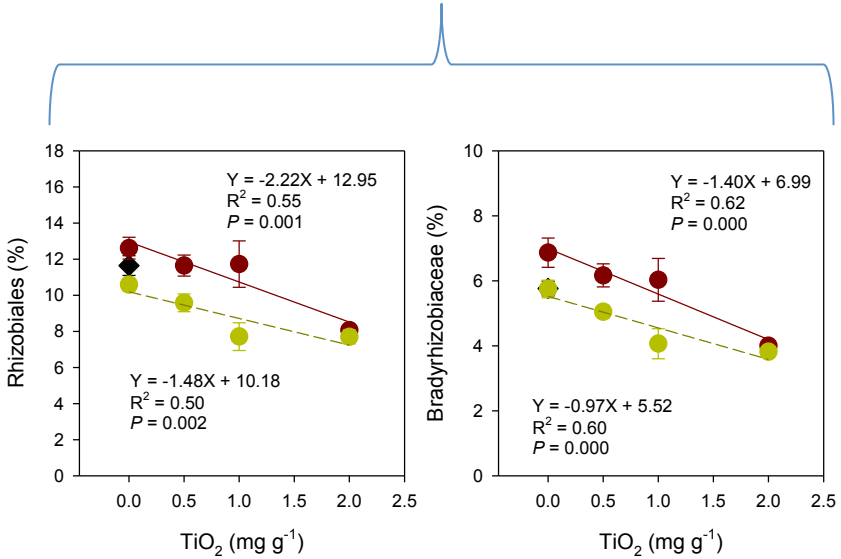


Change bacterial community



Ge et al. 2011. ES&T.

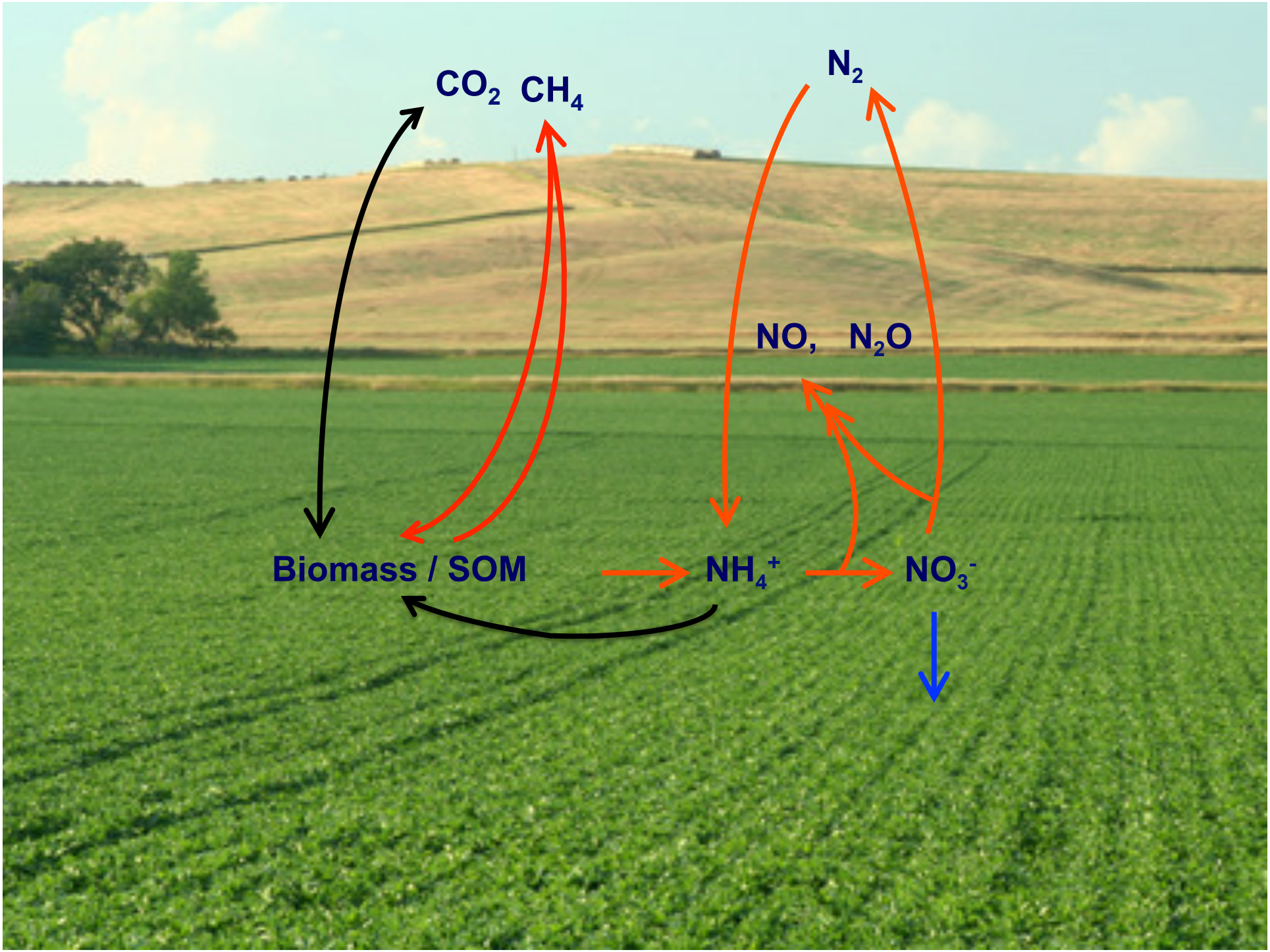
Alter select taxa abundance



Incl.: N_2 fixation, C cycling, CH_4 oxidation

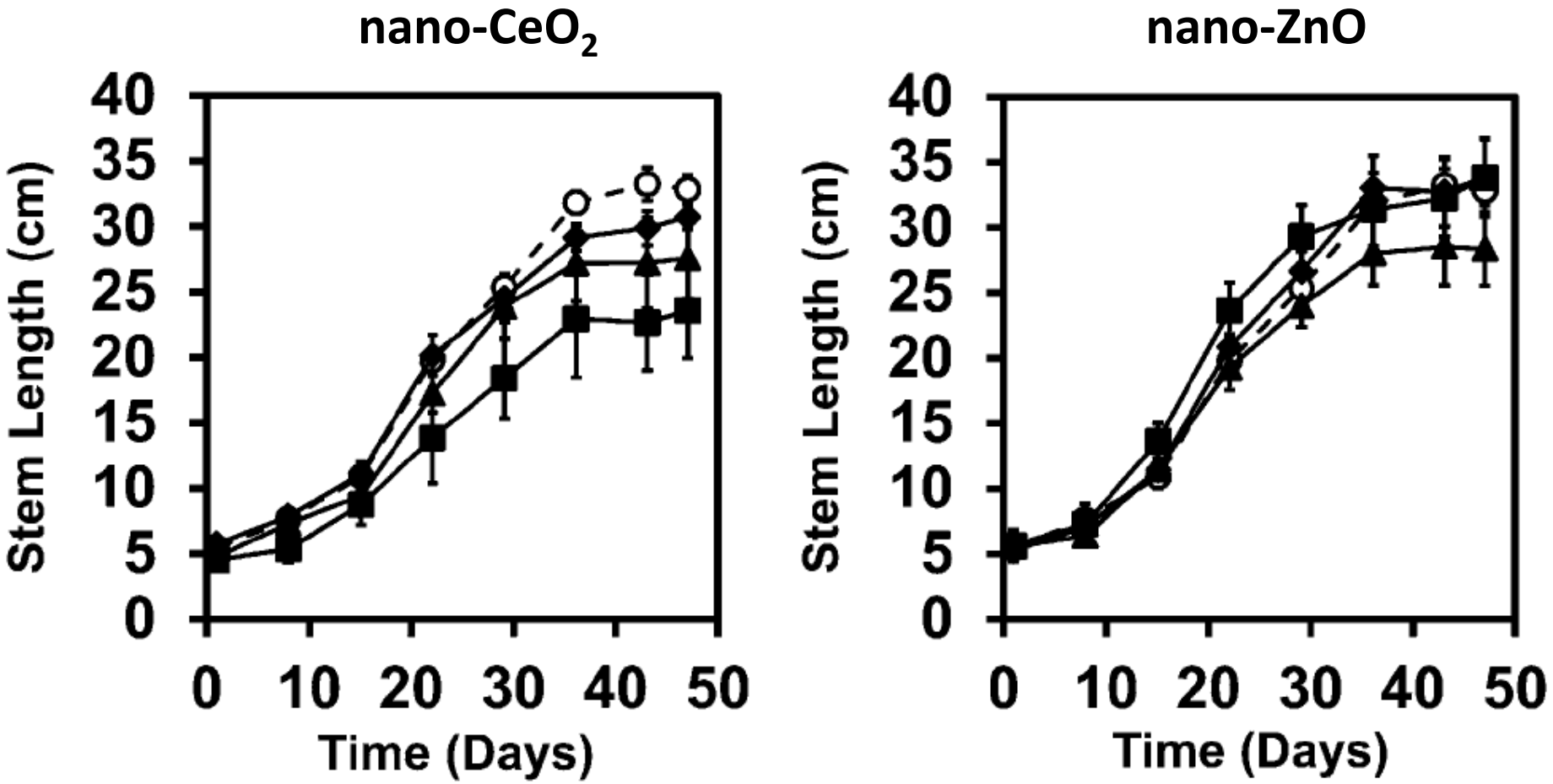
Potential Ecosystem Effects

Ge et al. 2012. Appl. Environ. Microbiol.


CO_2 CH_4
N_2
NO, N_2O
Biomass / SOM
NH_4^+
NO_3^-

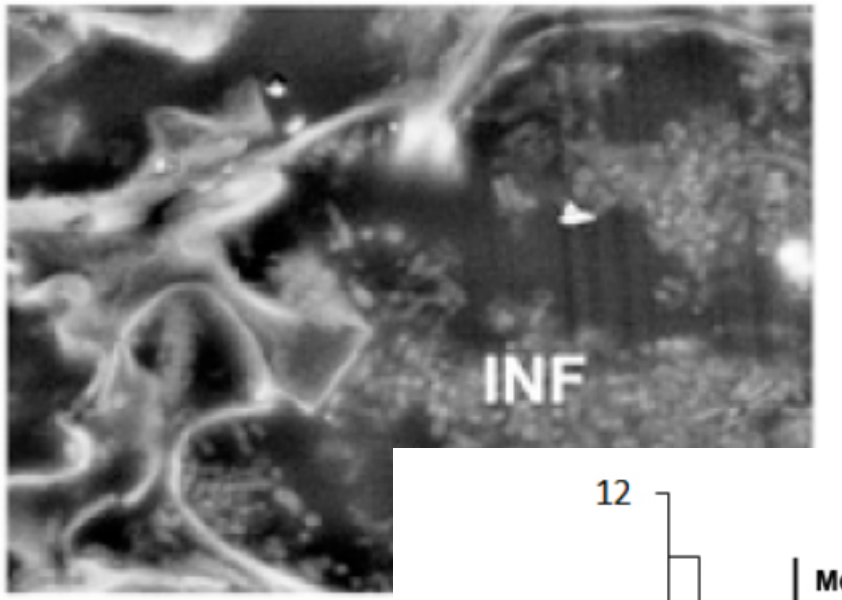

CONTACTOR PANEL

Results: Plant Growth

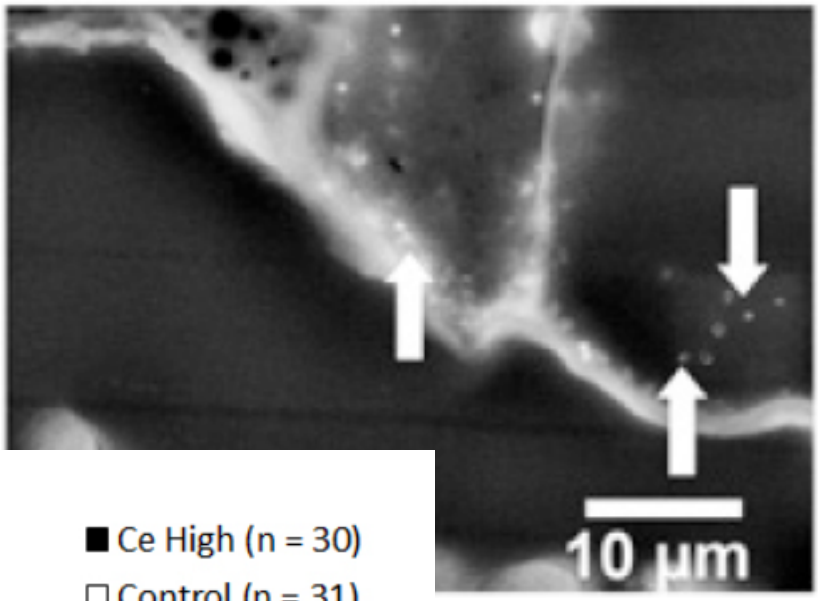


Priester et al. 2012. PNAS.

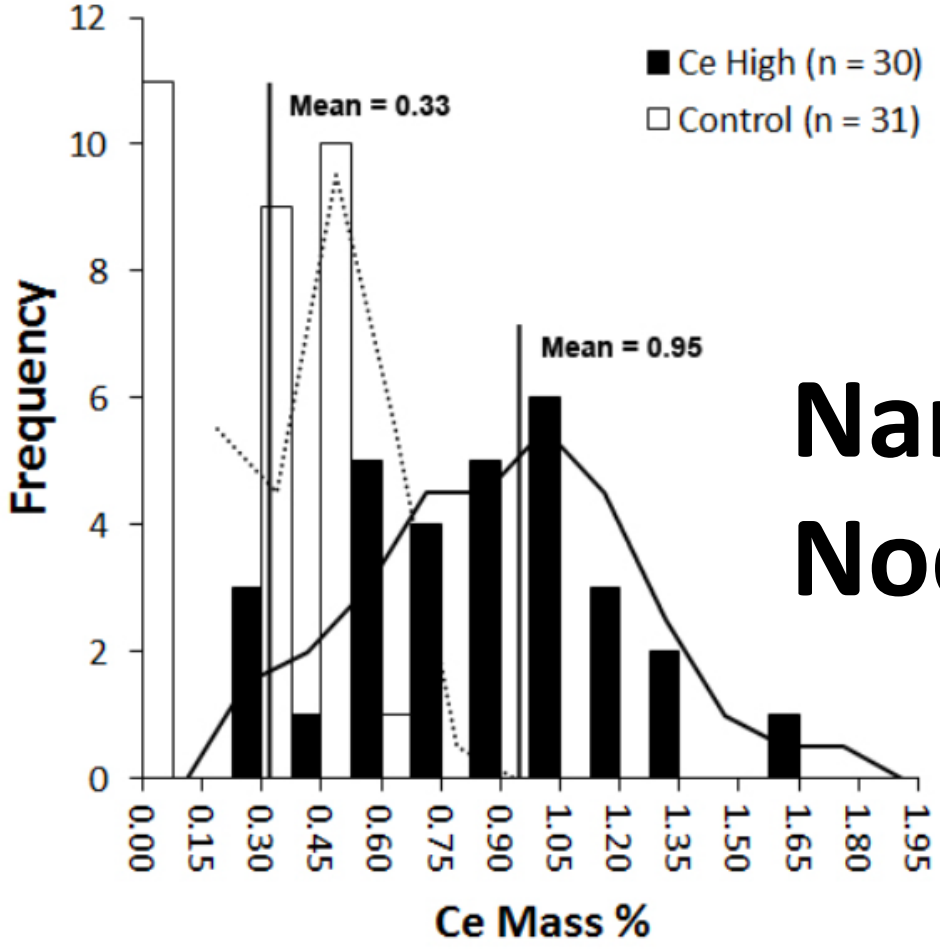
NSF: EF-0830117



Control



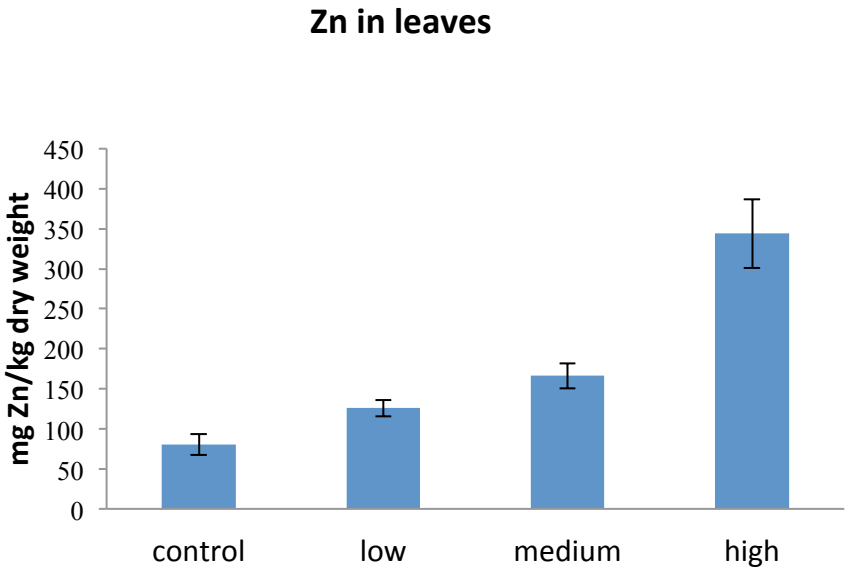
nano-CeO_2

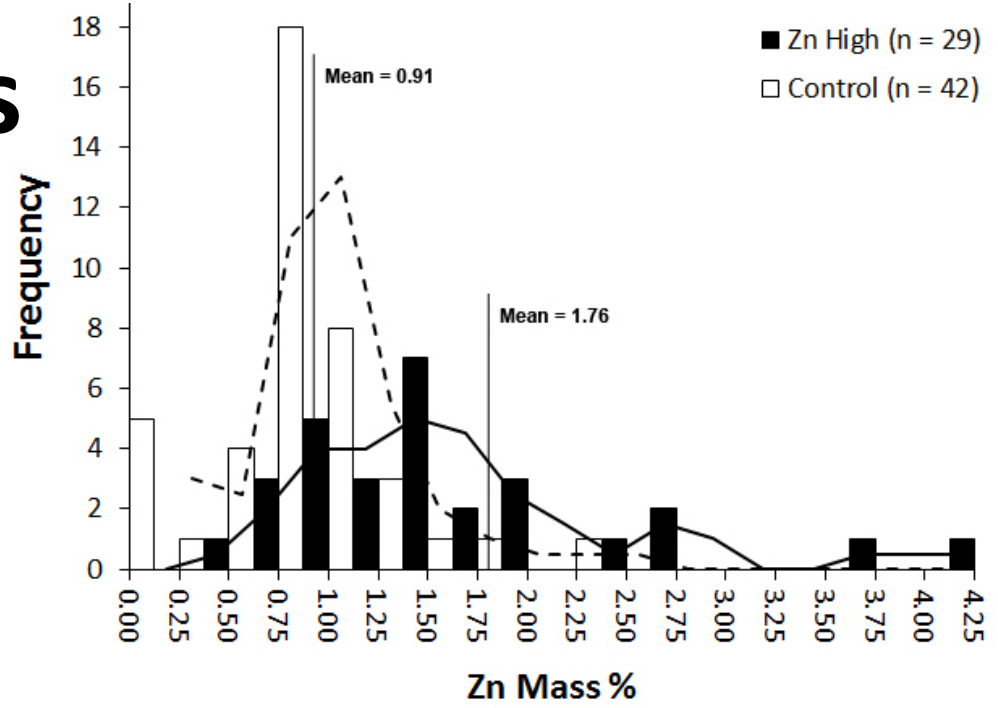


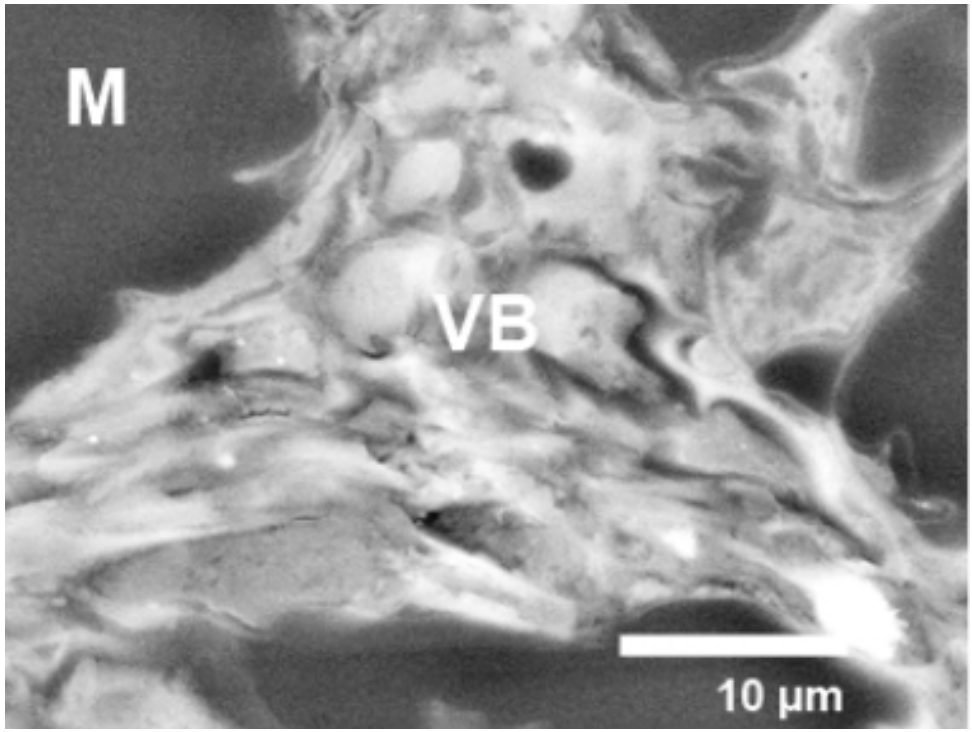
Nano-CeO_2: Nodules

Priester et al. 2012. PNAS.

Nano-ZnO: Leaves

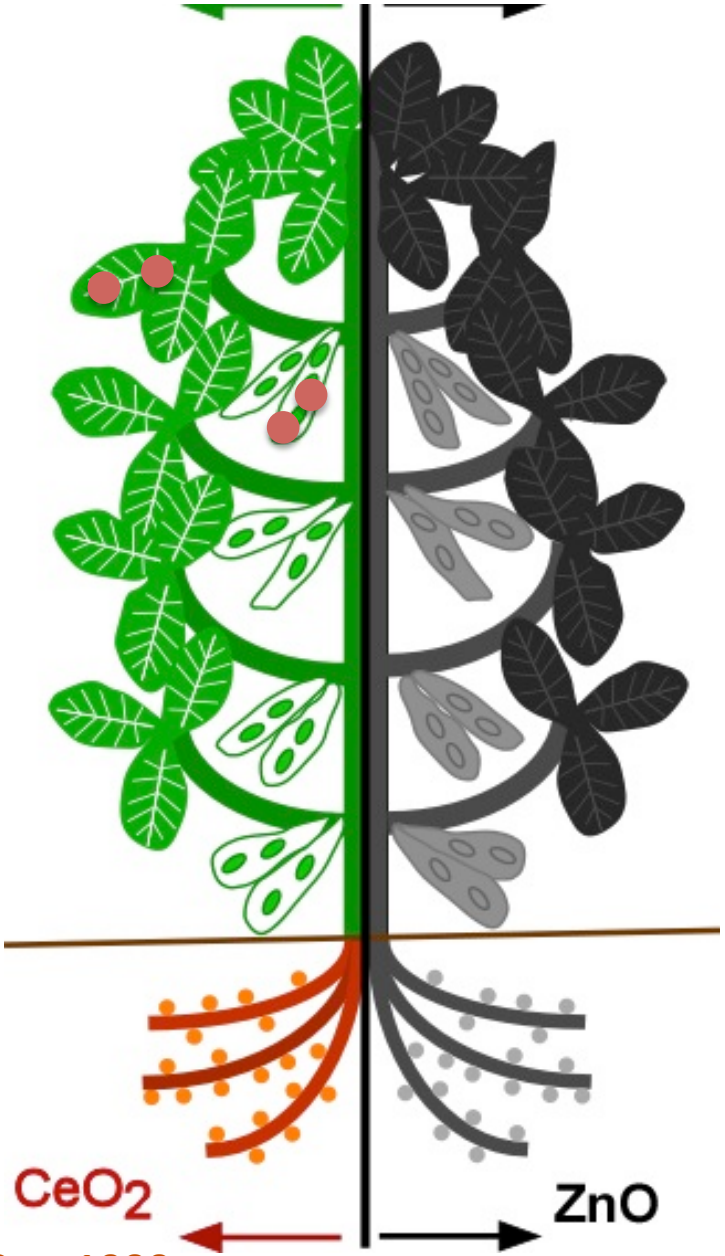






Priester et al. 2012. PNAS.

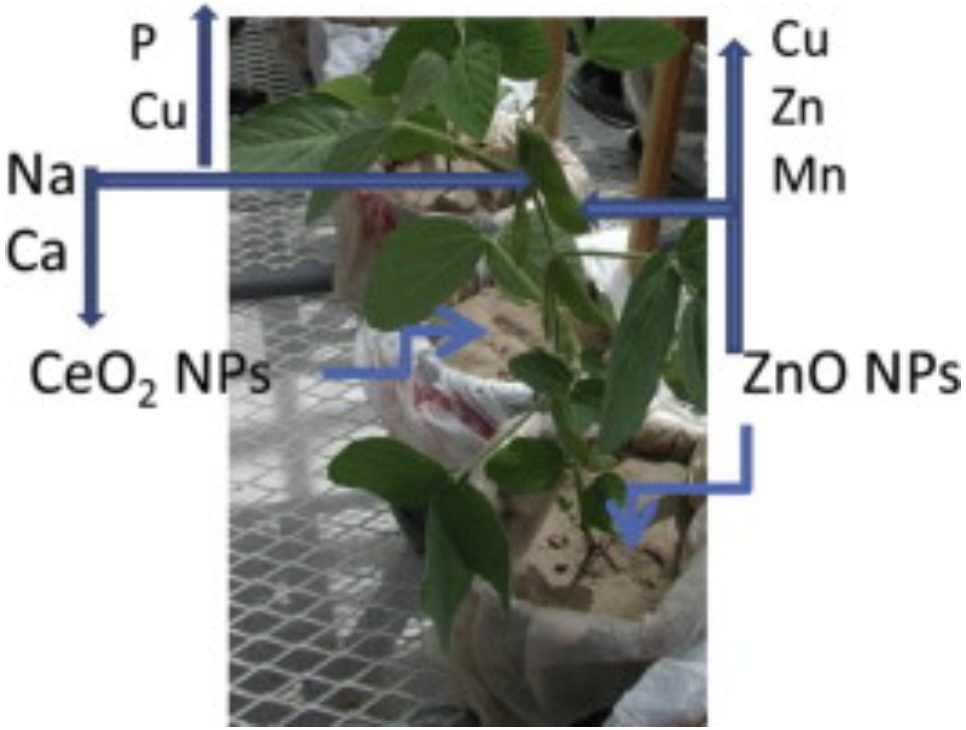
Hernandez-Viezcas et al. 2013. ACS Nano.



Priester et al. 2012. PNAS.

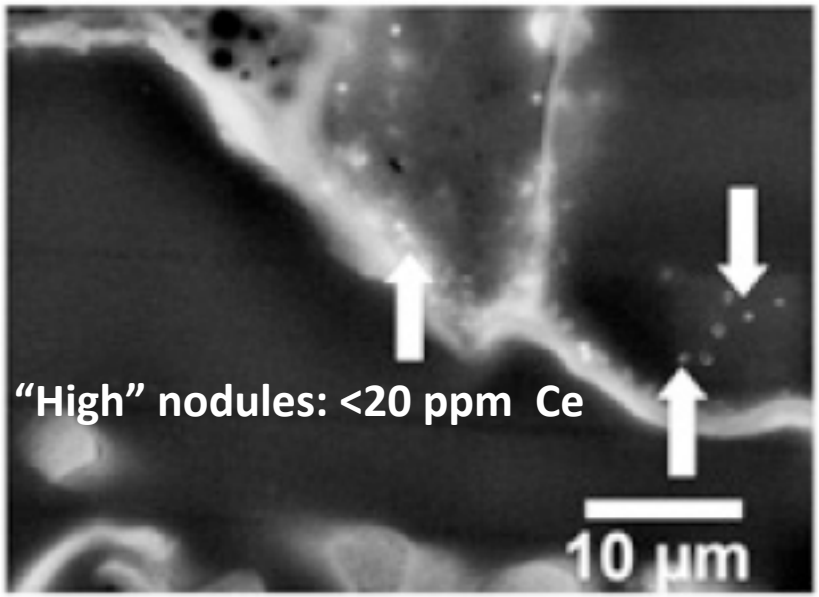
SOYBEAN response to MOx:

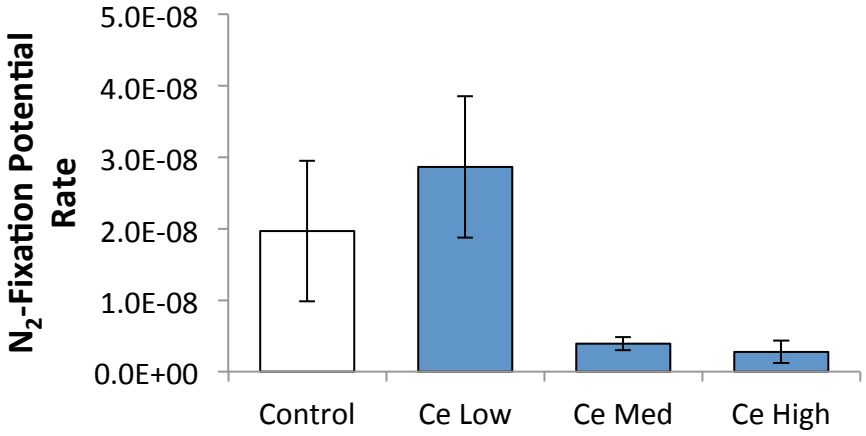
- metal uptake
- CeO_2 NPs in beans and leaves
- plant growth affected
- nutritional quality altered



Peralta-Videa et al. 2014.
Plant Physiol. Biochem.

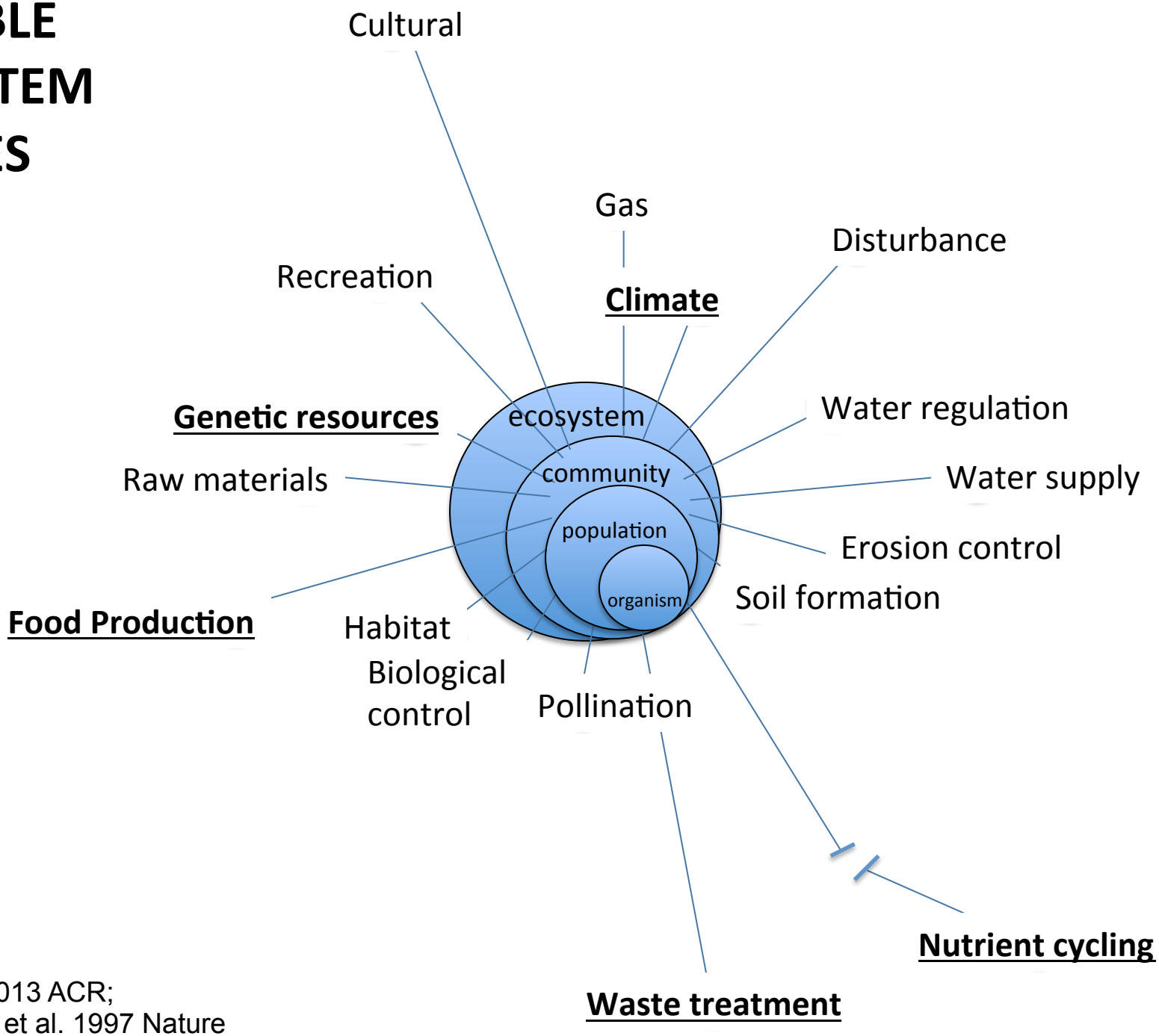
Empty nodules w/o N_2 fixation potential





Priester et al. 2012. PNAS.

VALUABLE ECOSYSTEM SERVICES



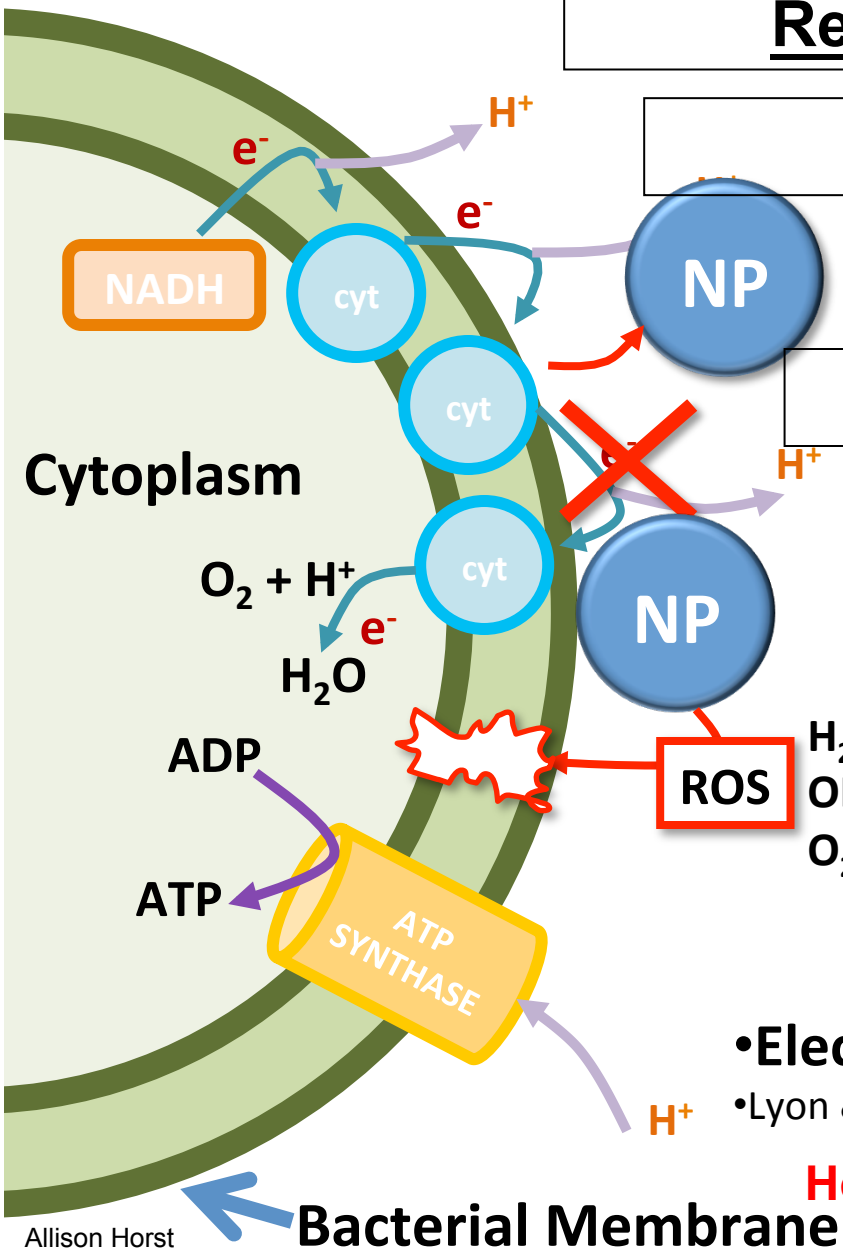
Holden et al. 2013 ACR;
after Costanza et al. 1997 Nature

Bacterial Interactions with MNMs

- C*ommunity* biomass & diversity (Ge et al. EST, 2011;AEM, 2012)
  - could impact ecosystem function (de Vries et al., 2013, PNAS)
- Nutrient cycling reactions catalyzed by bacteria (as above)
  - valuable ecosystem service (Costanza et al., 1997, Nature)
- Transport (Horst et al., 2006, AEM)
- Trophic transfer into food webs (Werlin et al, 2011, Nat. Nanotech.; Mielke et al. 2013, AEM)
- Transformation
  - e.g. if as e^- acceptors (Gralnick and Newman, 2007, Mol. Microbiol.)

(Holden, Schimel and Godwin, 2014, Curr. Opin. Biotechnol.)

Bacterial HTS System



Relevant bacterial strain

Oligotrophic media

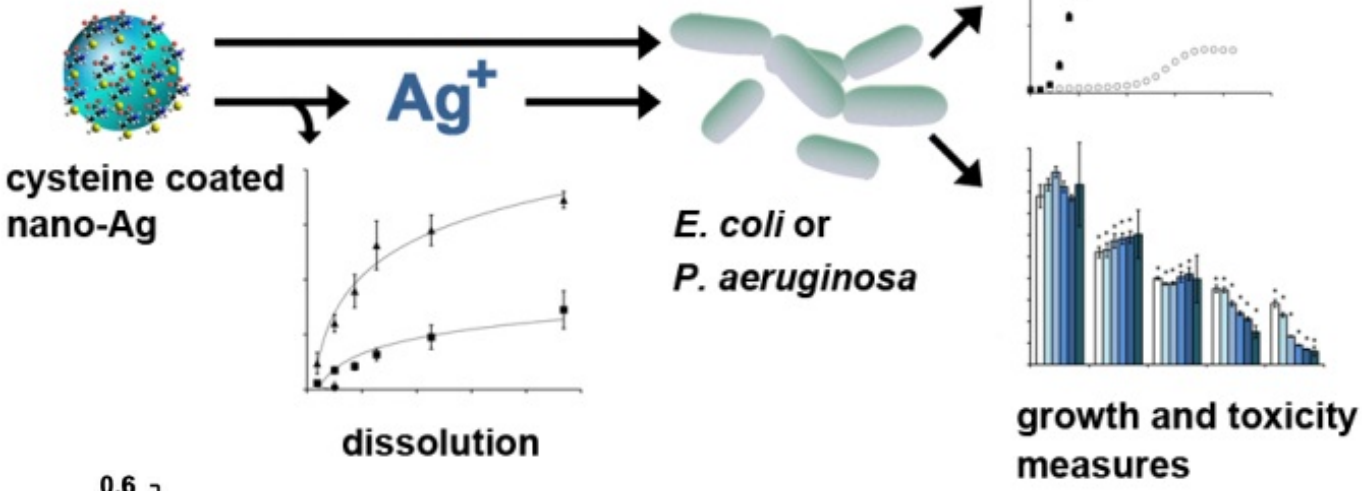
Dispersion protocols

Assays: stress/damage

- **Membrane Potential (MP)**
  Lyon & Alvarez. ES&T (2008)
- **Membrane Integrity (MI)**
  Priester *et al.* ES&T (2009),
  Su *et al.* Biomaterials (2009)
- **Reactive Oxygen Species (ROS)**
  Nel *et al.* Science (2006)
  Priester *et al.* ES&T (2009)
- **Electron Transport Chain (ETC)**
  - Lyon & Alvarez. ES&T (2008)

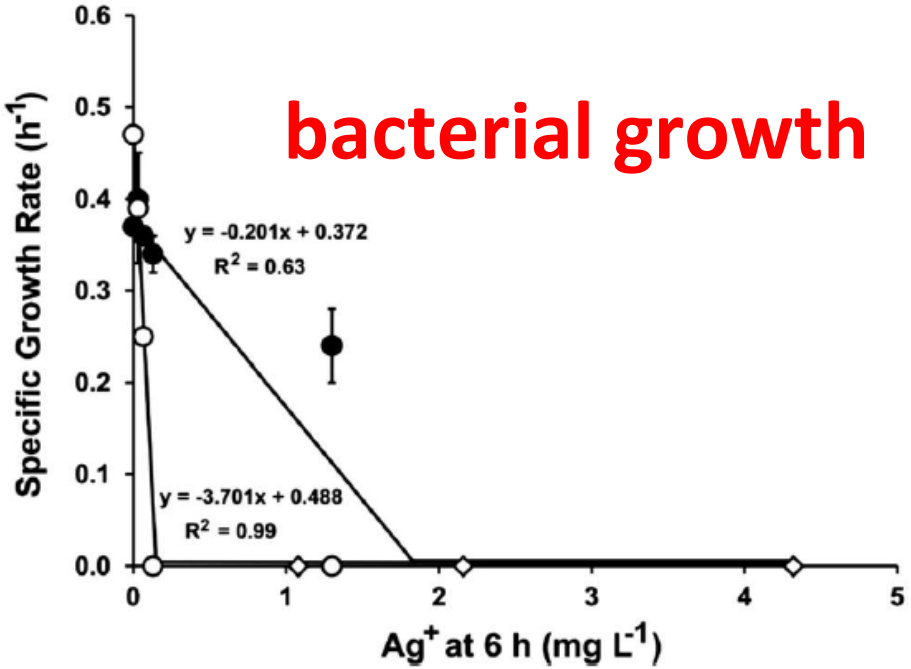
Priester et al., Analyst, 2014
Horst, et al. J. Nanopart. Res. 2012,; Small. 2013
Holden et al. Curr. Opin. Biotechnol. 2014

cysteine-capped nano-Ag dissolution



ROS and membrane integrity

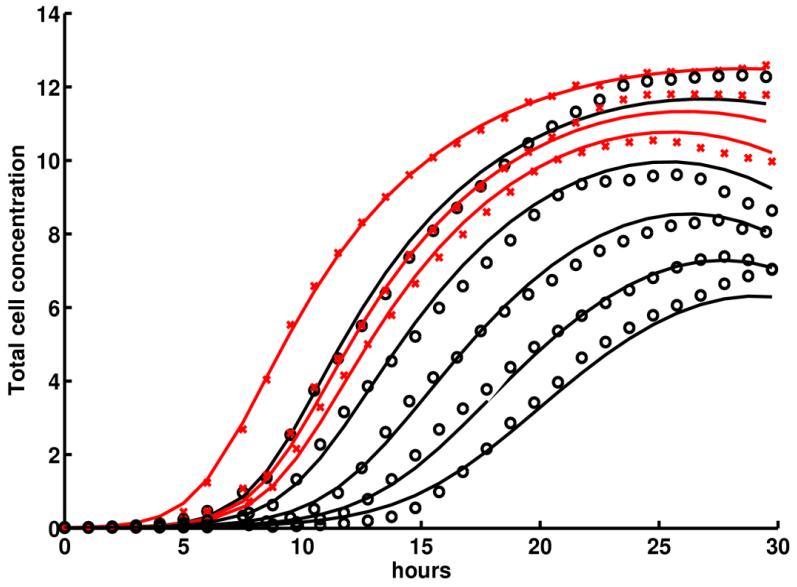
bacterial growth



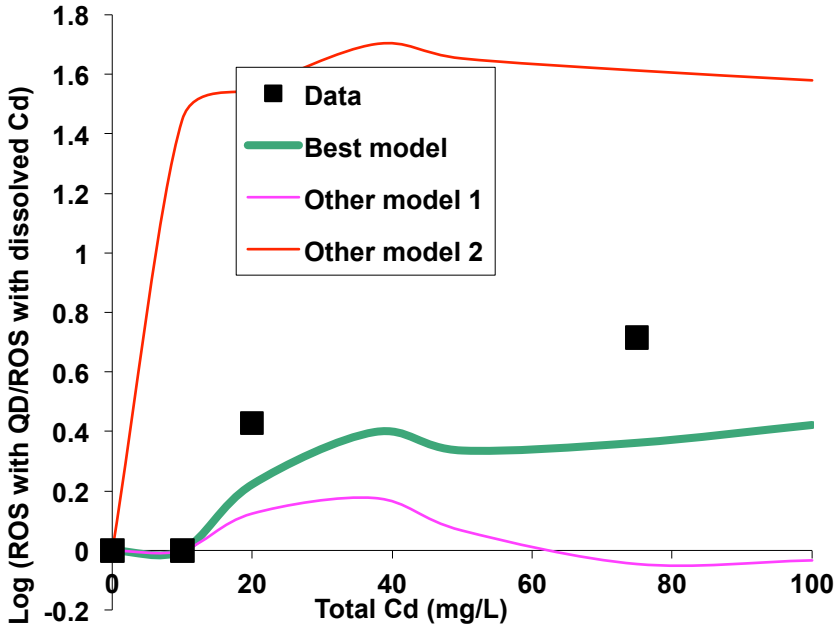
Ag ions from nano-Ag impair growth by ROS-mediated membrane damage

(Priester et al., Analyst, 2014)

Bacterial Population Growth and Toxicity Mechanism Modeling By Dynamic Energy Budget (DEB)



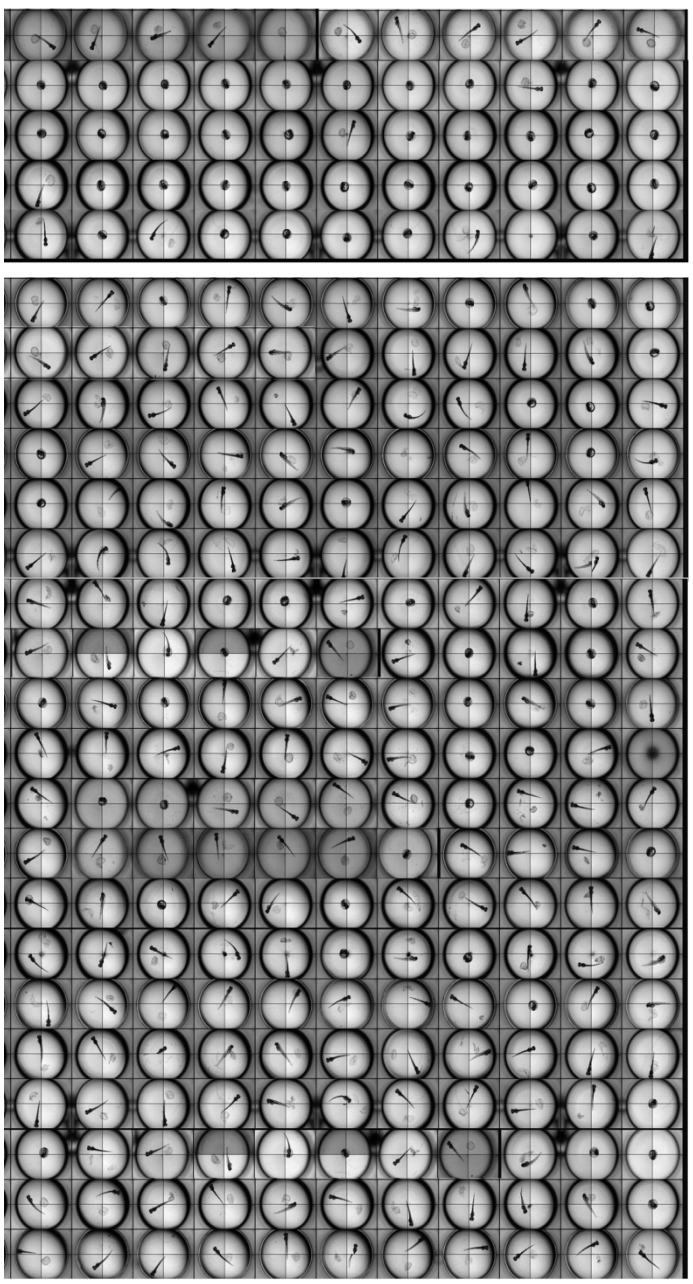
Klanjscek et al. 2012, PLoS ONE



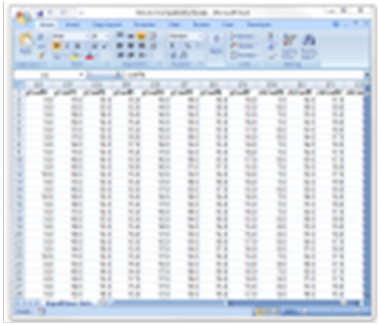
Klanjscek et al. 2013, Ecotoxicology

(*also* Holden, Nisbet, Lenihan, Miller, Cherr, Schimel, Gardea-Torresdey. 2013. ACR)

Zebrafish HTS → hazard ranking on 24 MOx's



Automated machine-learning based on phenotype

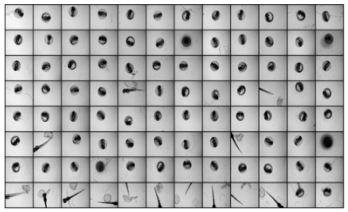


~0.3 M pixels

~70 Features

Feature Extraction → Model Development → Prediction

Y=f(x)



Feature Extraction → Prediction

Phenotype

Active center homology

HELNHALGFYH	*Danio rerio*
HE HALGF H	*Oncorhynchus mykiss*
HE+ HALGF H	*Takifugu rubripes*
HELNHALGF H	*Oryzias latipes*
HEL HALGFYH	*Oreochromis niloticus*
HEL HALGFYH	*Salmo salar*

>500 species

Lin et al. Small. 2013.

Band Gap and Hydration Energy Explain Bacterial Toxicity Across 24 MOx MNMs

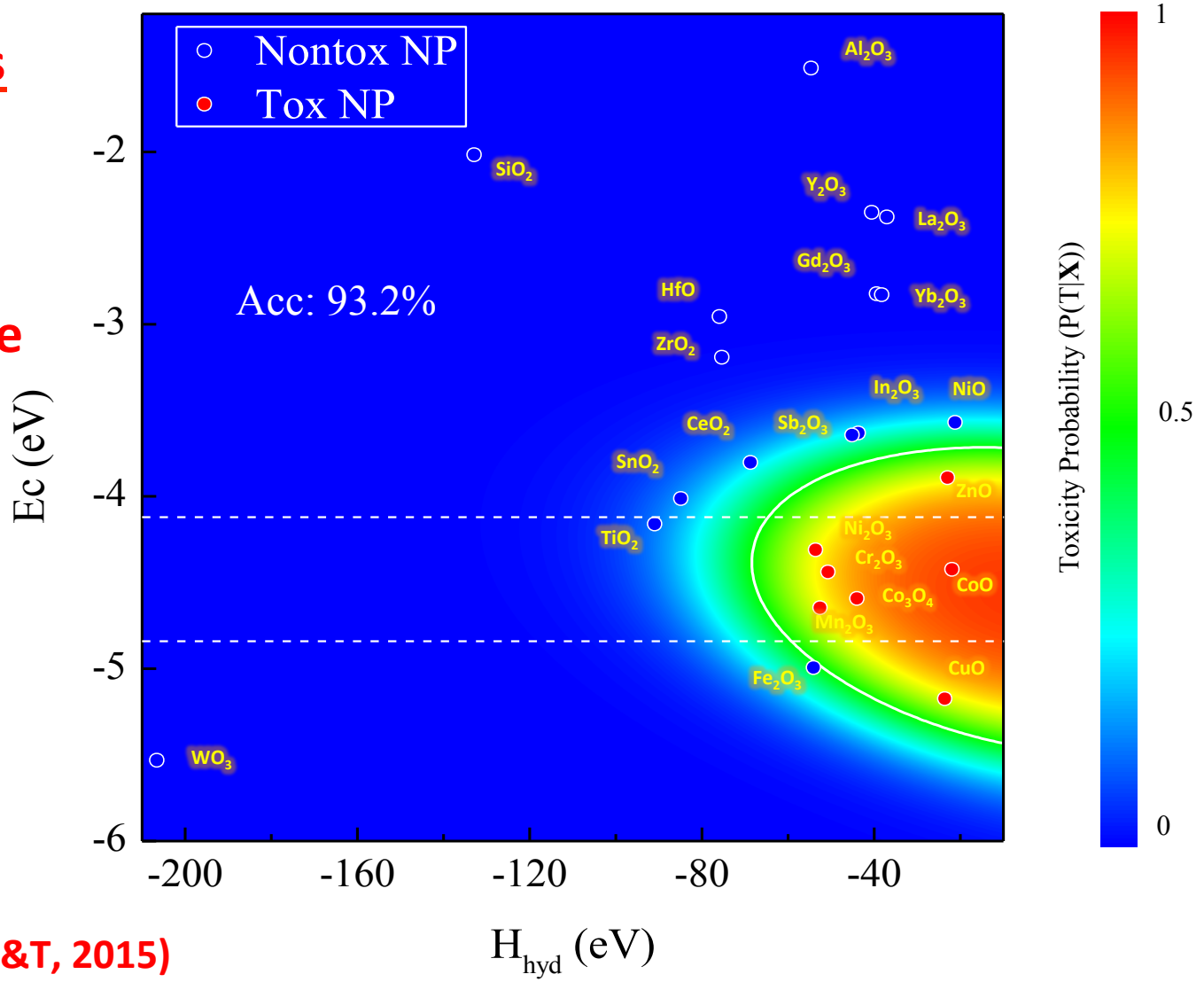
Toxicity indicators

% Growth

Abiotic ROS

Cellular ROS

Membrane damage



(Kaweeteerawat et al. ES&T, 2015)

Moving Forward in Predictive Eco-Nanotox

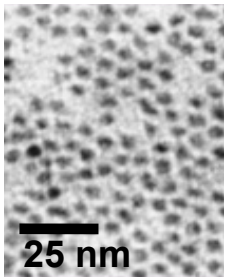
Holden et al. 2013. Acc. Chem. Res.; Holden et al. 2014. Curr. Opin. Biotechnol.

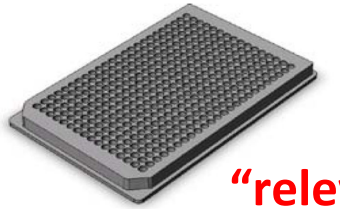
Effects SCREENING

Microcosms

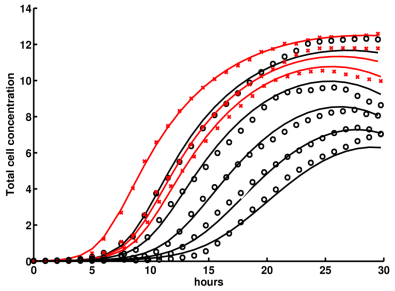
Mesocosm

MNMs





"relevant" Bacteria



Hazard PREDICTIONS

Summary

- Manufactured nanomaterials widely used
- Environmental exposures predicted
- Terrestrial compartments are destinations
- Plants, soil microbes, food, and biogeochemical cycling may be impacted
- Trophic transfer may be initiated
- Tiered approach for screening advocated, with more complex systems tested infrequently
- Predicting desirable
- Efforts are multidisciplinary

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