NACK NETWORK
Building College-University Partnerships for Nanotechnology Workforce Development

NCI Southwest

Occurrence, Removal and Regulation of Nanomaterials at Publicly Owned Sewage Treatment Works

Thursday, May 26, 2016

CLICK HERE FOR THE WEBINAR RECORDING

Occurrence, Removal and Regulation of Nanomaterials at Publicly Owned Sewage Treatment Works

Begin Recording

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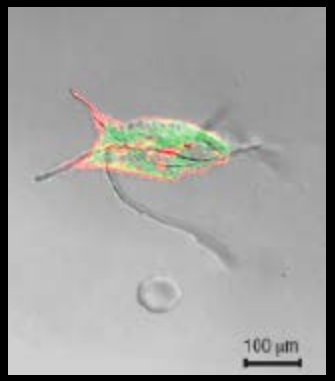
Benefits & Risks of Nanotechnology

GOOD nano

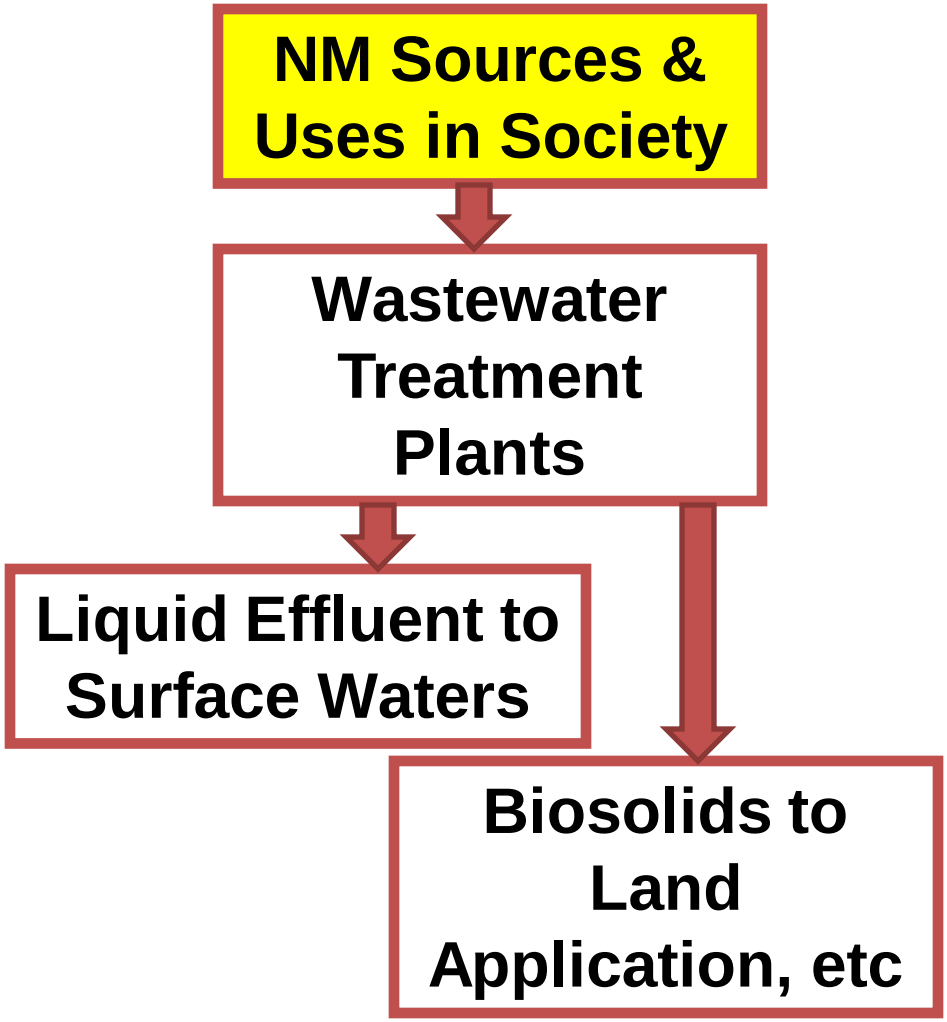
Quantum size effects result in unique mechanical, electronic, photonic, and magnetic properties

BAD nano

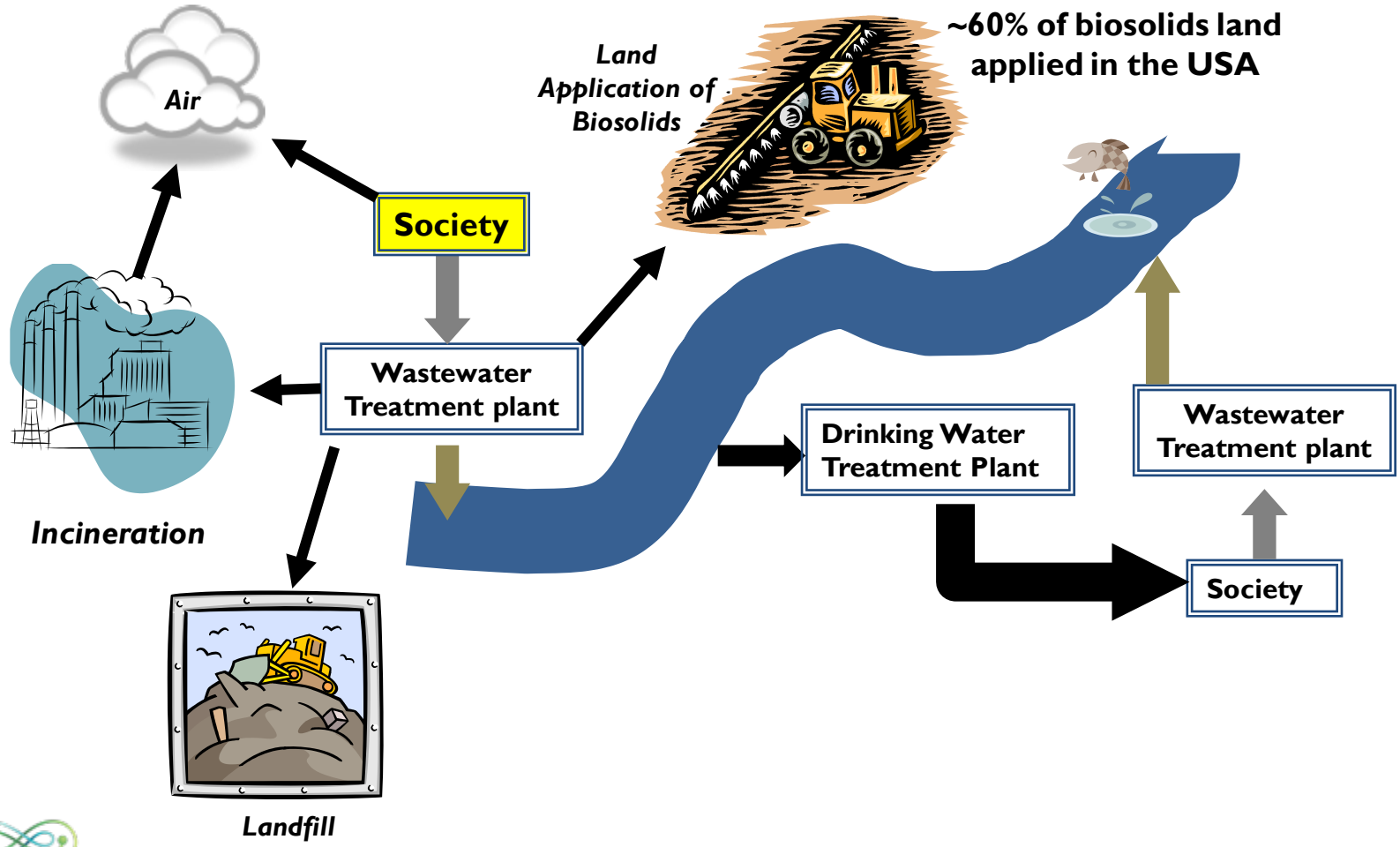


Nanoparticles operationally defined as < 100 nm in at least one-dimension

Presentation Outline

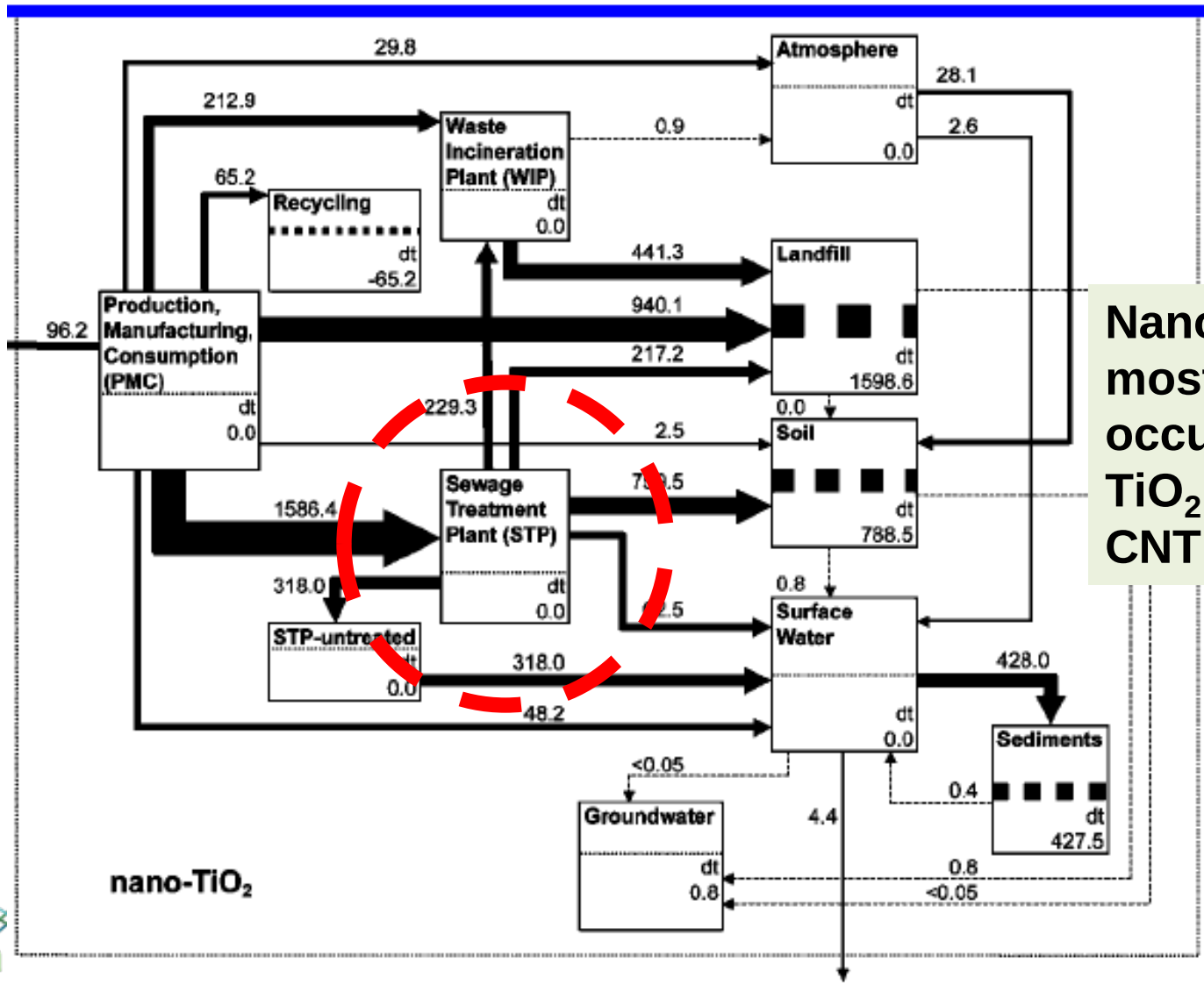


Society is a source of incidental & engineered Nanomaterials



Projections indicate high NM loadings to Sewers & WWTPs

Environ. Sci. Technol. 2009 43, 9216–9222



Nanomaterials most likely to occur:
TiO_2 > ZnO > Ag > CNT > fullerene

LCnano Product Lines include

NM Functionality & Application

Reactive NMs

Ag^0 clothing

CeO_2 in Polishing Agents

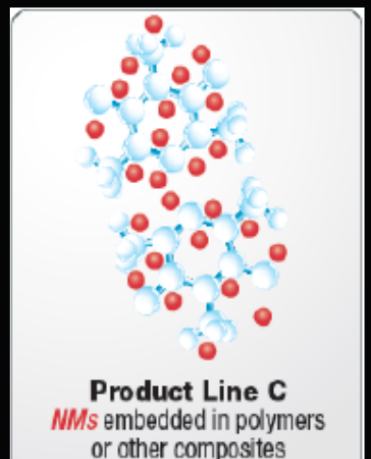
TiO_2 in Foods

"Free" NMs

Embedded NMs

SiO_2 in Foods

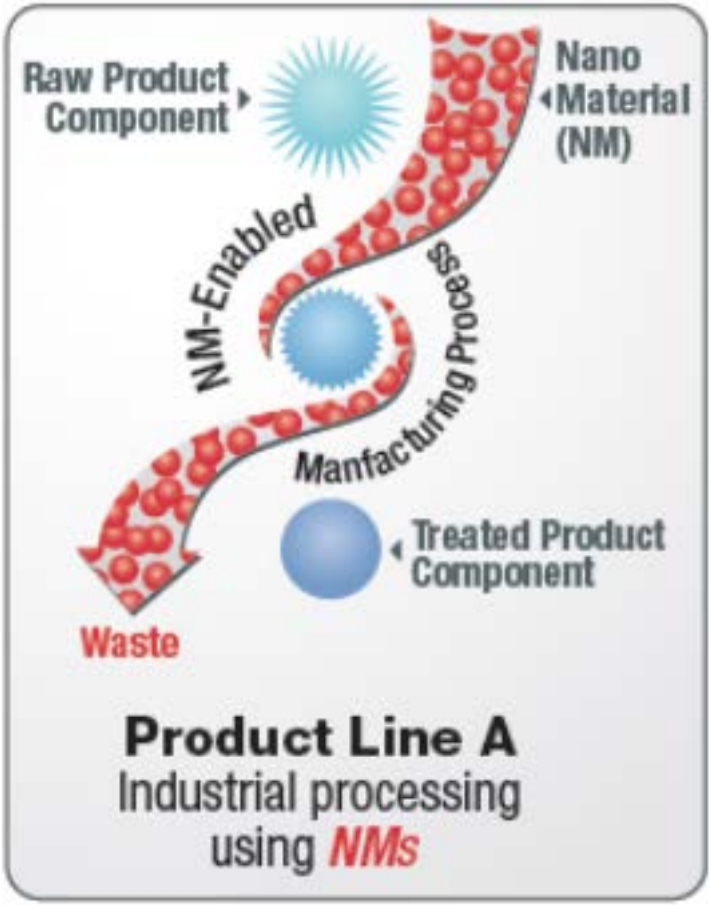
Passive NMs



SiO_2 in flor coatings

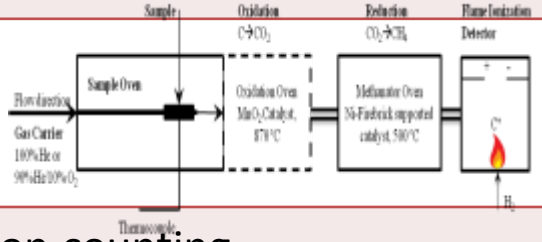
Product Line A
Polishing Agents

- Industrial processes for electronics, optics etc use polishing agents in fluids
- >>$1B industry
- SiO_2, Al_2O_3, CeO_2 are common polishing agents
- Polishing agents end up in sewers – not consumer products
- No direct regulation exists for their discharge to sewers



Common Direct NM Detection

Method	NM Type	Generalized Detection Limit Comments
Light scattering (UV/VIS)	any	**> 1 mg/L** in water **0.05 mg/L** with HPLC of NM extract
ICP-MS (better than ICP-AES) TOF-MS (emerging)	metals	**> 10 ppt** in water (total metal conc) Ability to get size, # and concentration dosimetry (sp- , FFF-, centrifugal – ICP-MS)
LC-MS	C60	**~ 1 ppt**
Thermal combustion or Microwave thermal analysis	MWCNT SWCNT	**~ 1 ppb**
Isotopes	^{14}C Metal isotopes	**< 1 ppb** by Scintillation counting Isotopic ratios



Environ. Sci.: Nano, 2015, 2, 227–244

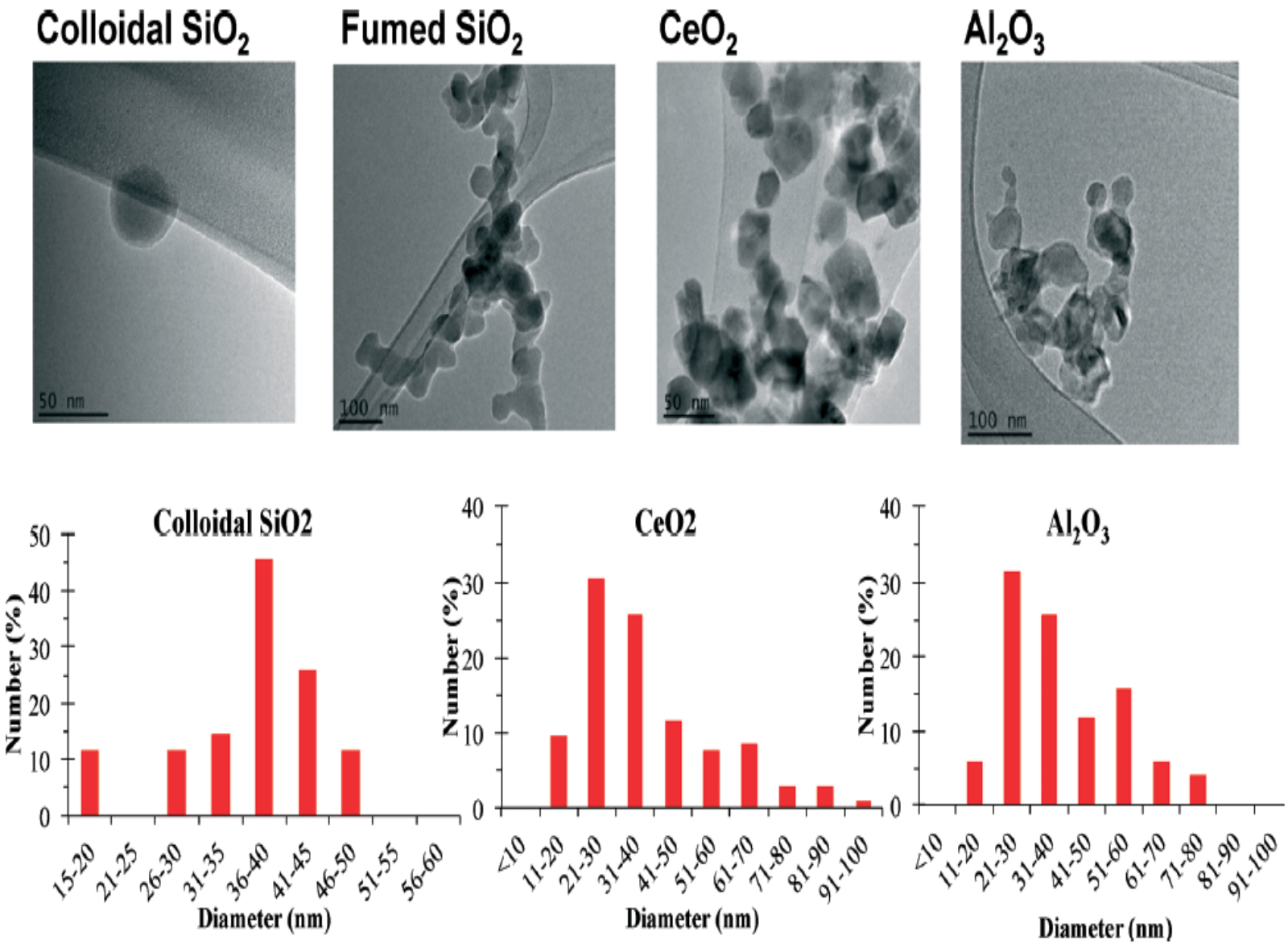
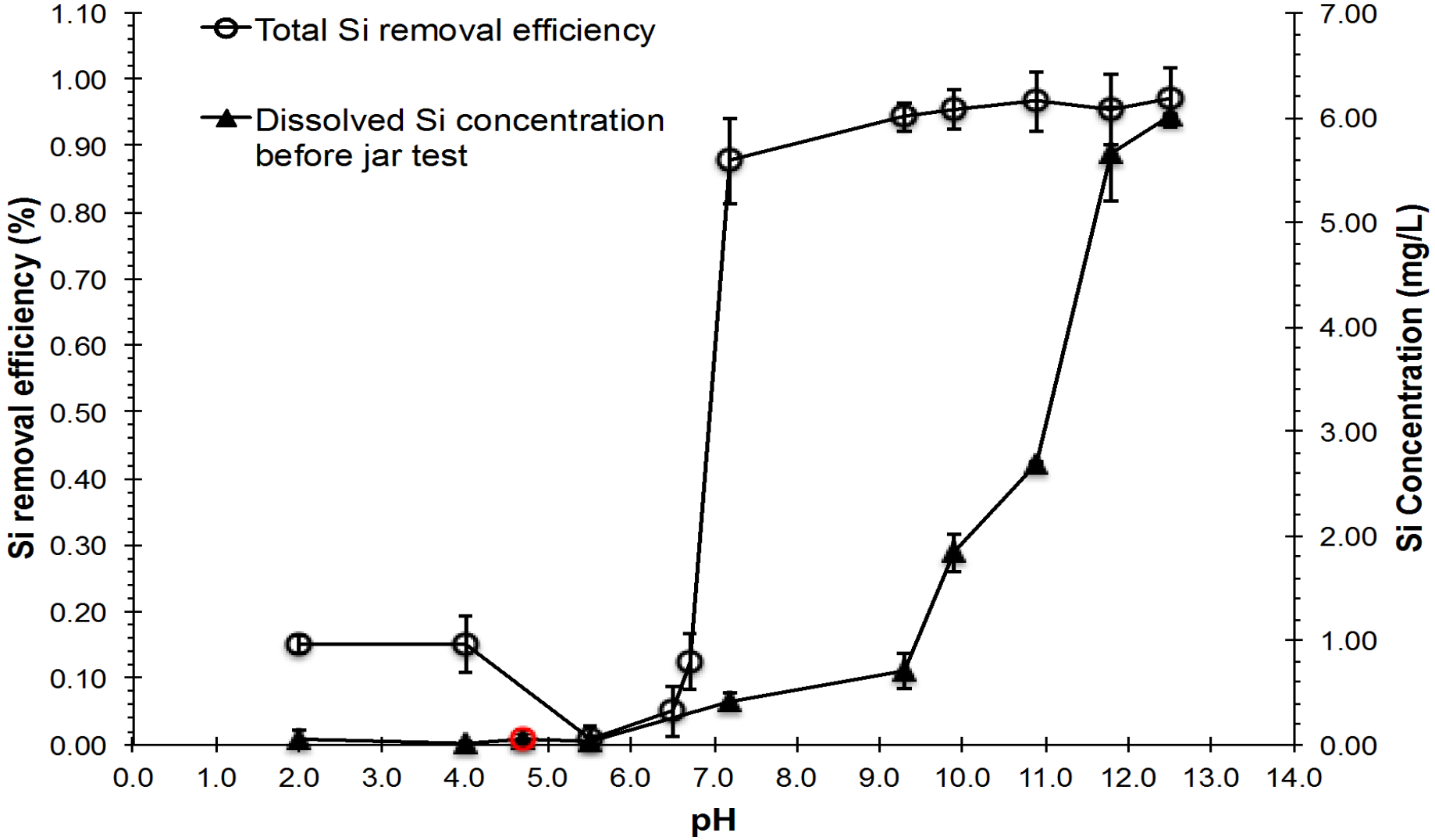
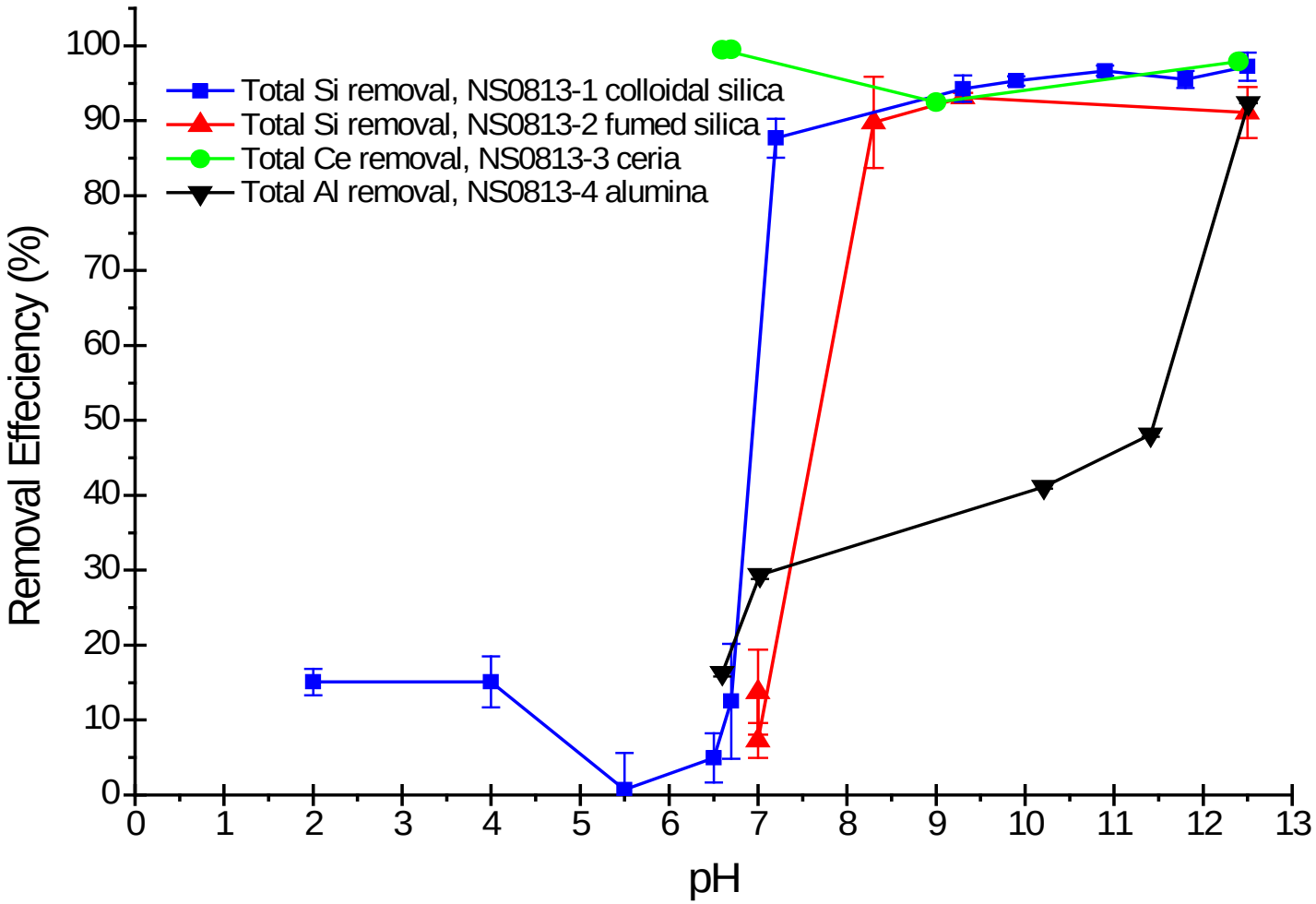


Fig. 6 TEM images and TEM based particle size distributions for CMP nanoparticles. The size distribution histogram for colloidal silica, ceria, or alumina is obtained by sizing >50 particles under the corresponding TEM images. Fumed silica particles were not sized because of their coalesced state.

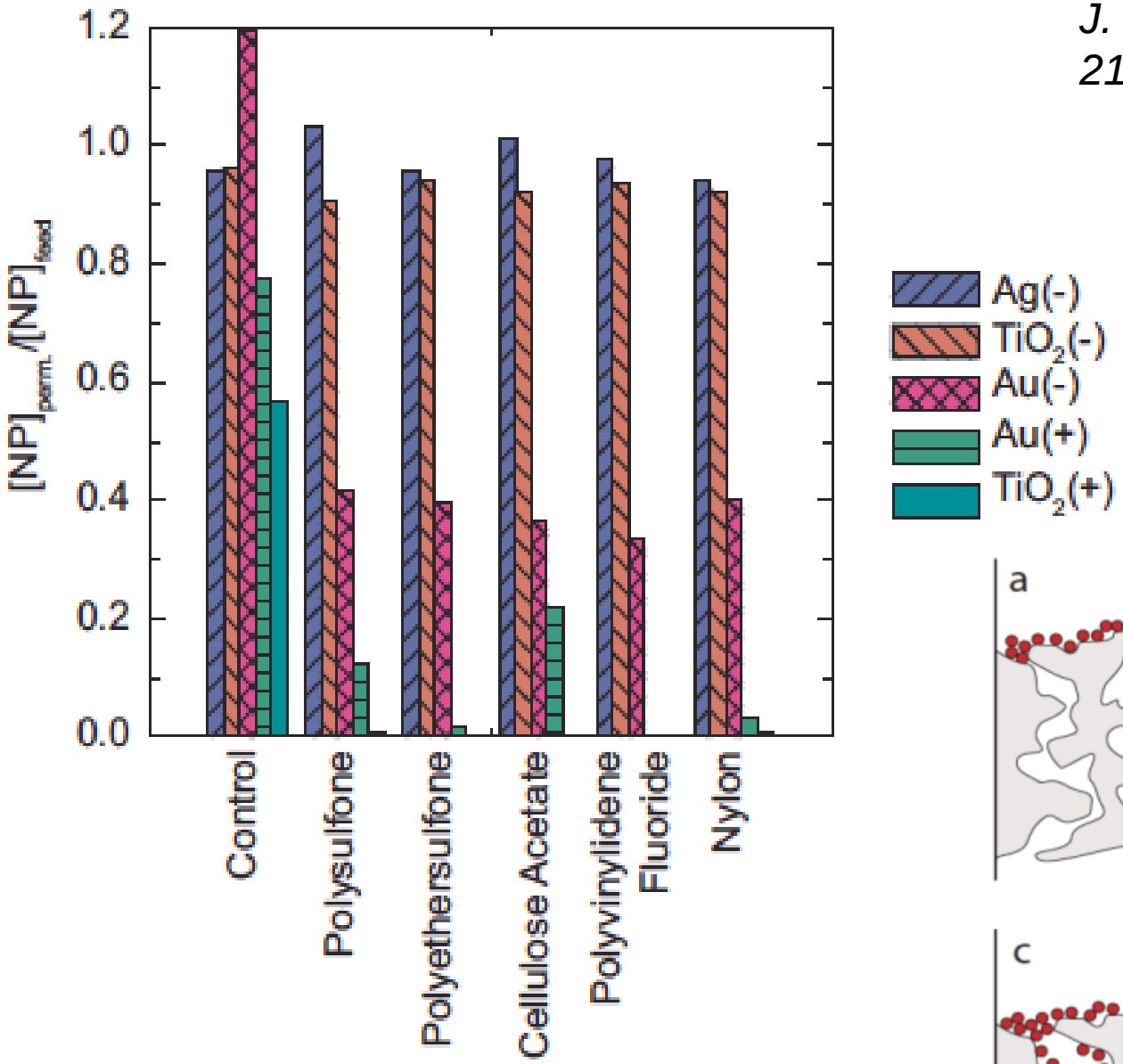
On-site Chemical Lime Softening Tr
of CMP wastestreams





Removal efficiencies of Si, Ce and Al for 4 CMP slurries under different pH conditions. Ca dosage was 2mM in all cases. Started concentrations: $C_{0Si,slurry\ 1}$=24 mg/L, $C_{0Si,slurry\ 2}$=20mg/L, $C_{0Ce,slurry\ 3}$=19.5mg/L, $C_{0Al,slurry\ 4}$=31mg/L. pH values are obtained after jar test when reactions are considered in equilibrium.

J. of Hazardous Materials
211-212, 285-295 (2012)



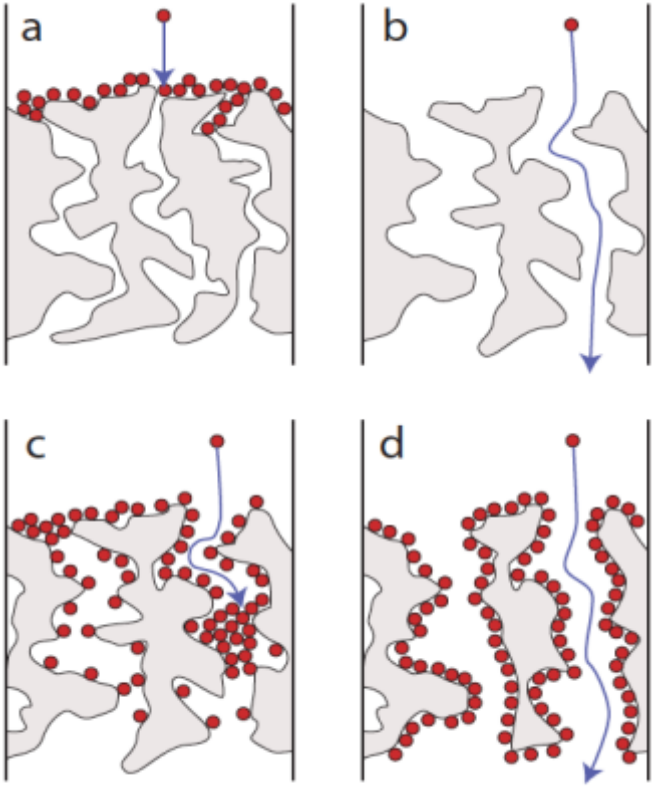
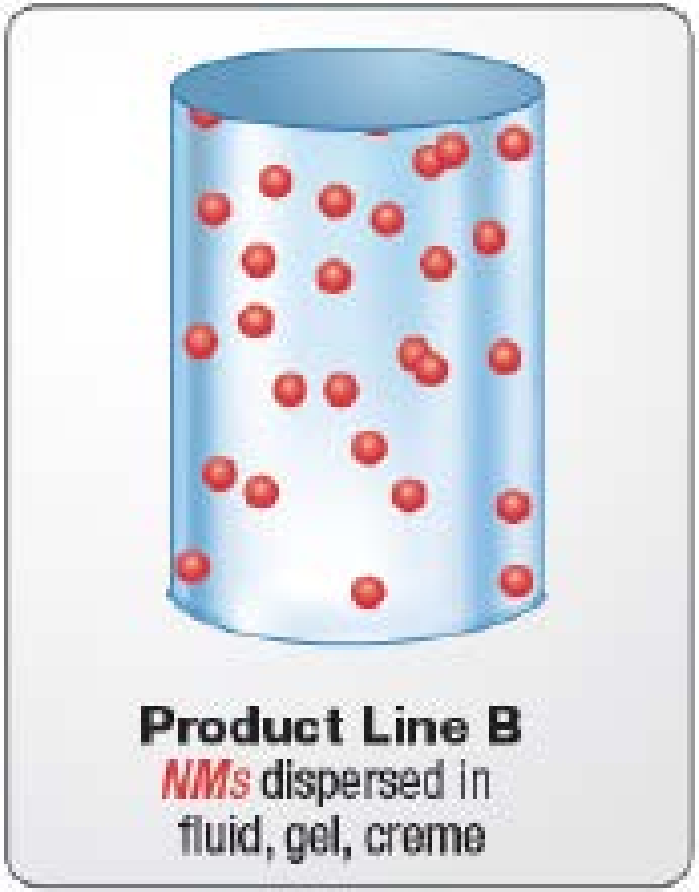


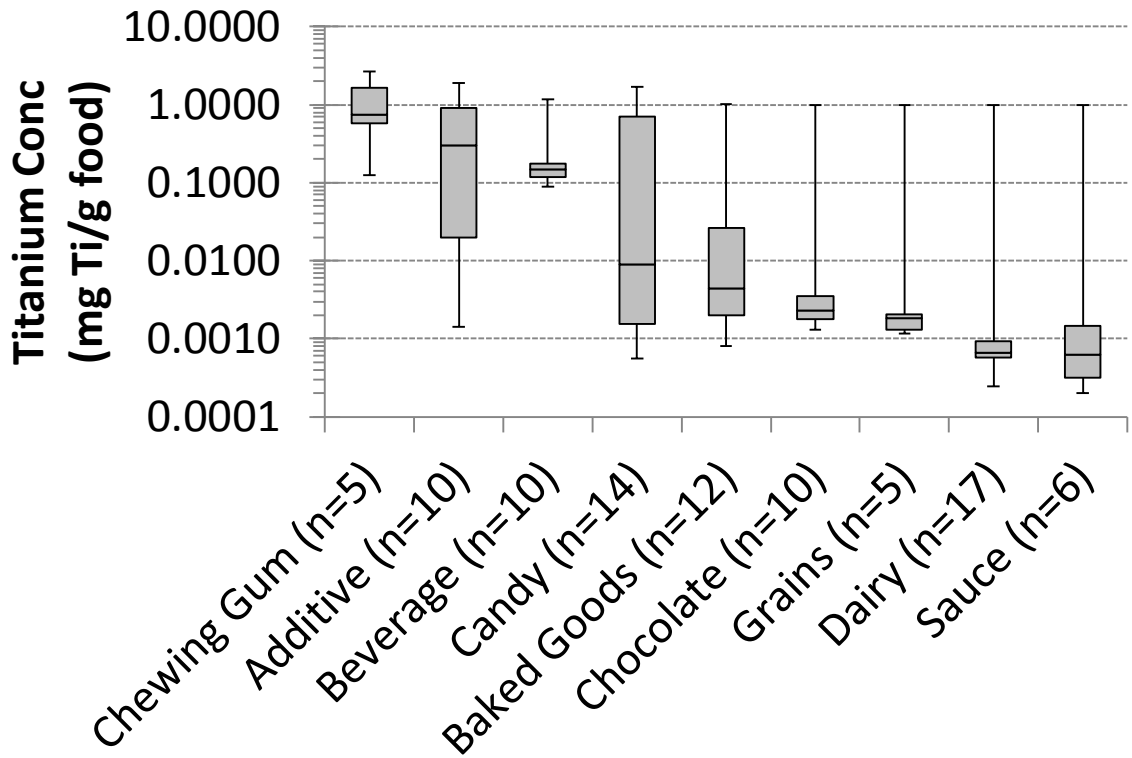
Fig. 3. Normalized permeate concentrations of NPs passed ten syringe filters (0.22-µm pore size) made of five different polymeric trol samples were passed through the filtration device with no men

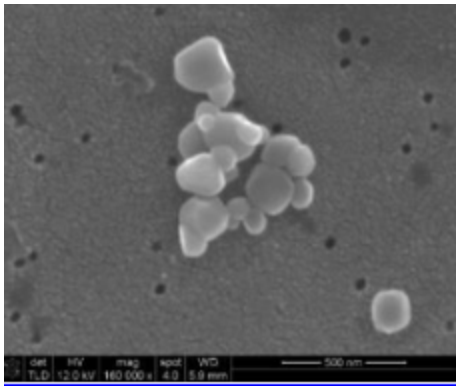
Product Line B
Nanomaterials in foods

- Nanomaterials added to food for a variety of reasons:
  - Texture
  - Anti-caking
  - Color
  - Oxygen barrier
  - Abrasives
  - Antimicrobial
- Little to no regulation exist
- Difficult to monitor



Nanomaterials Dispersed in Products



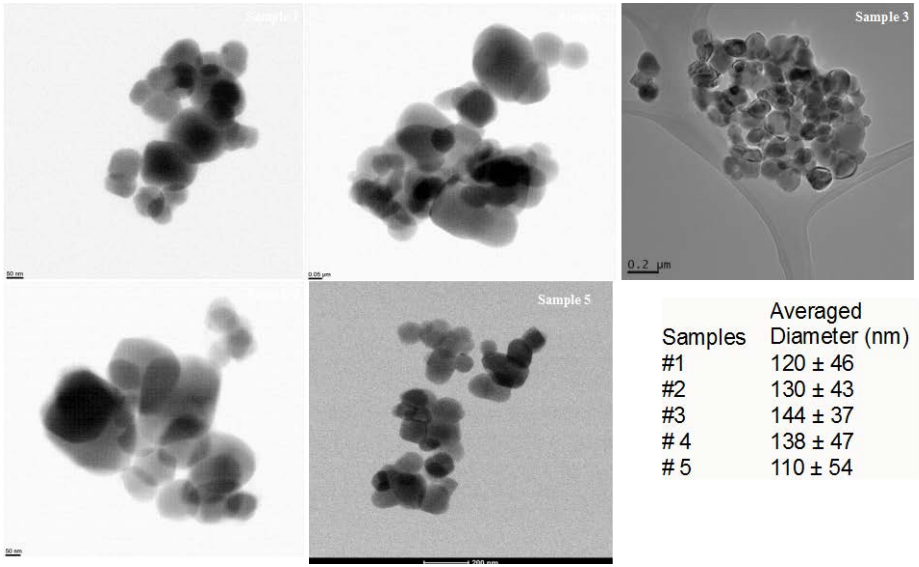


Weir et al., ES&T (2012)

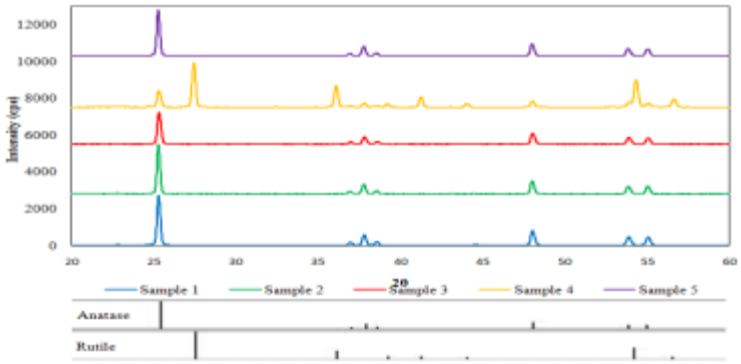
Benn et al., J. Environmental Quality, 39:1-8 (2010)

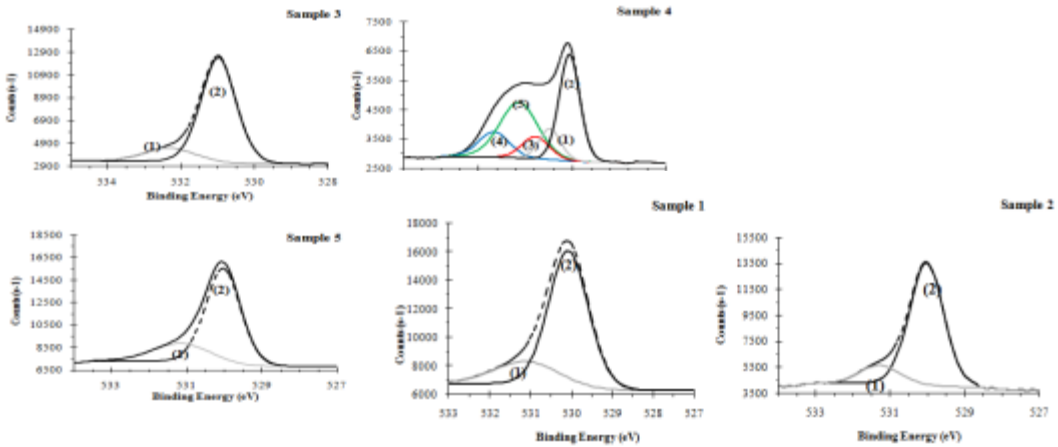
Test thousands of products?

- *Go to suppliers instead of food grade products*
- Can assess fundamental properties of NPs
- Example: food grade TiO_2 contains P-surface groups & is primarily anatase



Samples	Averaged Diameter (nm)
#1	120 ± 46
#2	130 ± 43
#3	144 ± 37
# 4	138 ± 47
# 5	110 ± 54





Yang, et al., ES&T, 48:11:6391-6400 (2014)

Beverages contain all types of nanoparticles

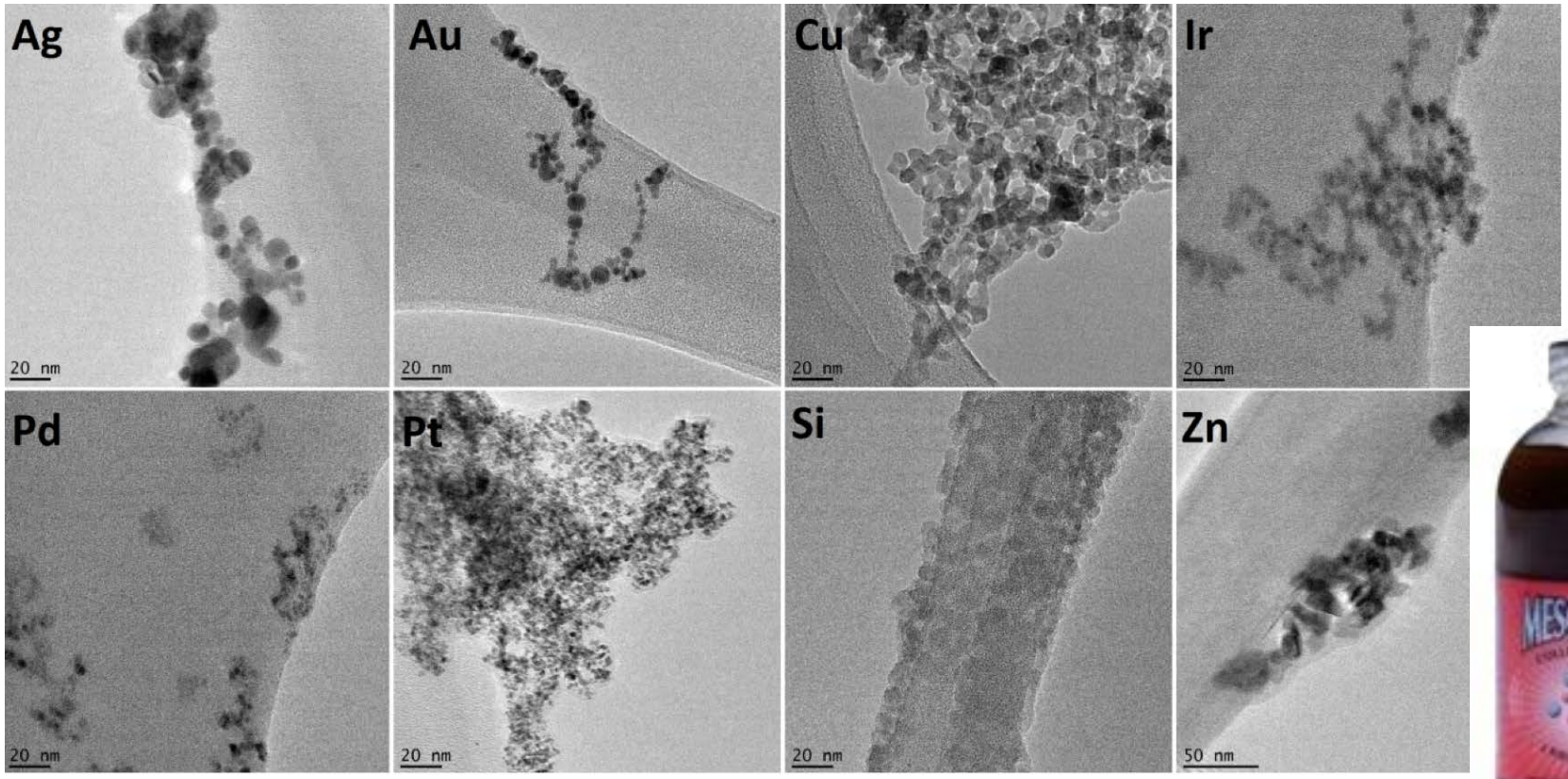


Figure 1. Representative TEM images of NMs found in supplement drinks.

ACS Sustainable Chem. Eng. 2014, 2, 1616−1624

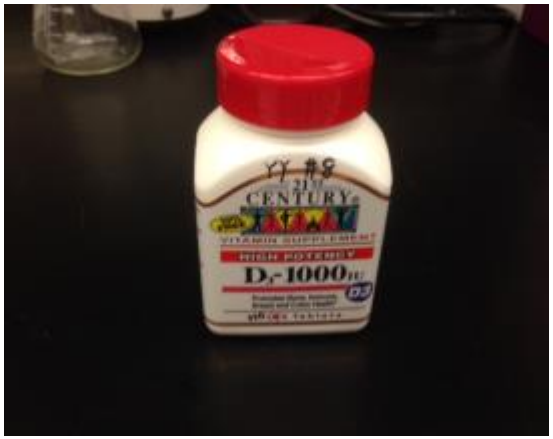
Silica , Anti-caking agent in food

In the United States, the Food and Drug Administration allows up to 2% by weight of silica to foods as an anti-caking agent.

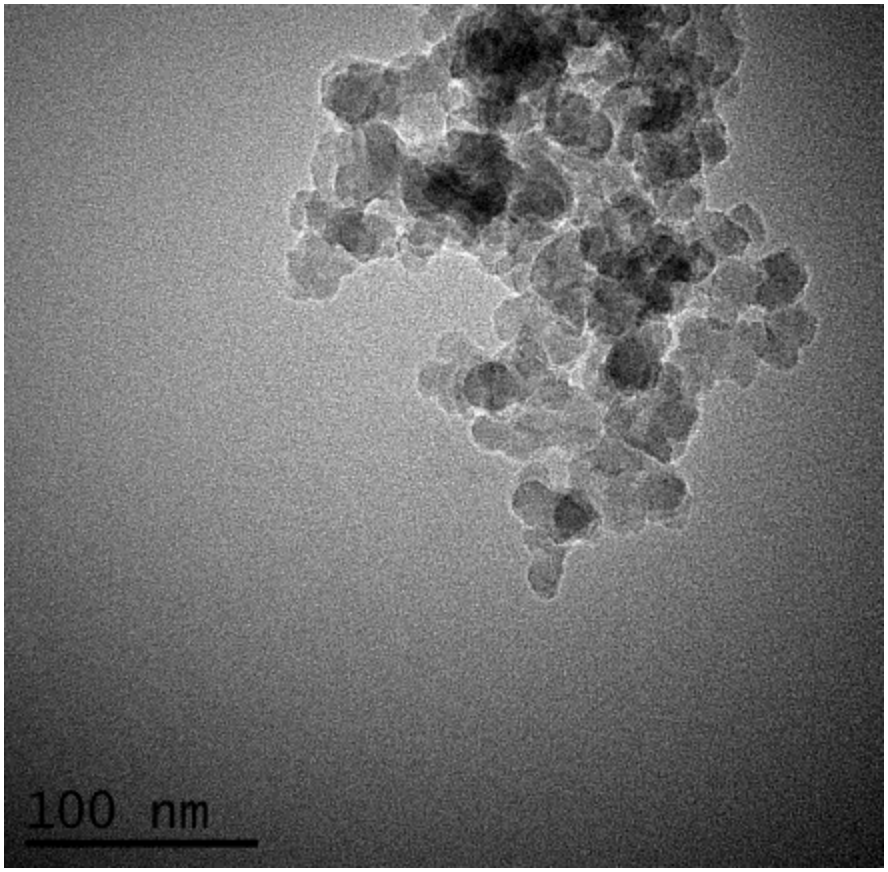
Nature Nanotechnology 9, 658–659 (2014) doi:10.1038/nnano.2014.196

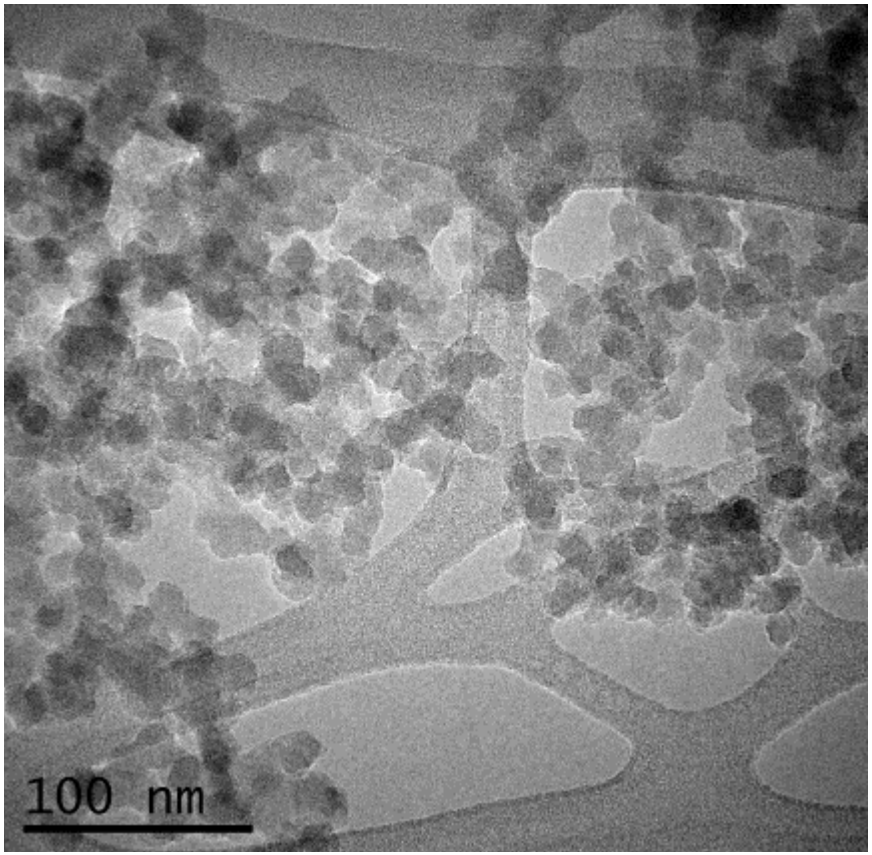
http://www.reddit.com/r/FanTheories/comments/1caz5e/the_cookie_monsters_eating_disorder_and_failed/

Foods Claim Containing Silica

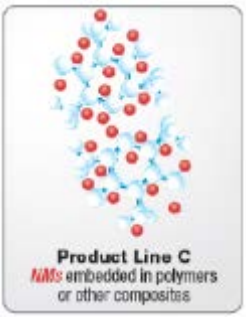


Transmission Electron Microscopy (TEM) on Separated Silica from Foods





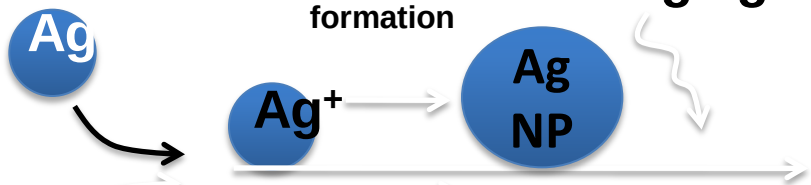
→ **Nano silica present in foods**



Product Line C

Example: nano-Ag in plastics

Ag^+-doped polymers



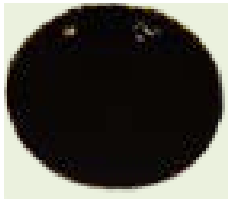
in situ NP formation

curing agents

monomer

compatibilizers/ additives

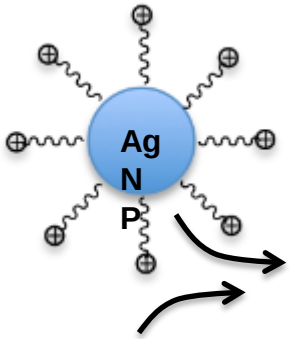
e.g.,



1% MWCNT

5% TiO_2

Ag-NP-doped polymers



curing agents

monomer

compatibilizers/ additives

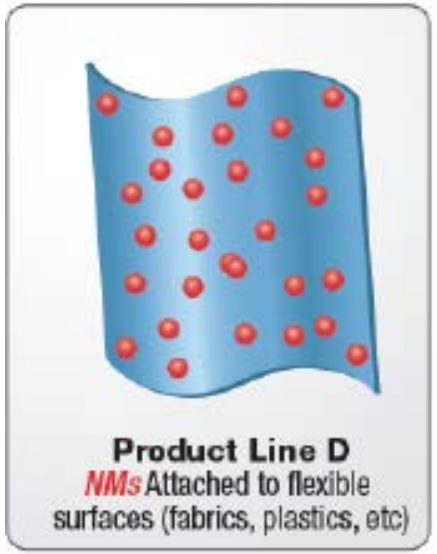
Ag-impregnated Tupperware

amazon.com

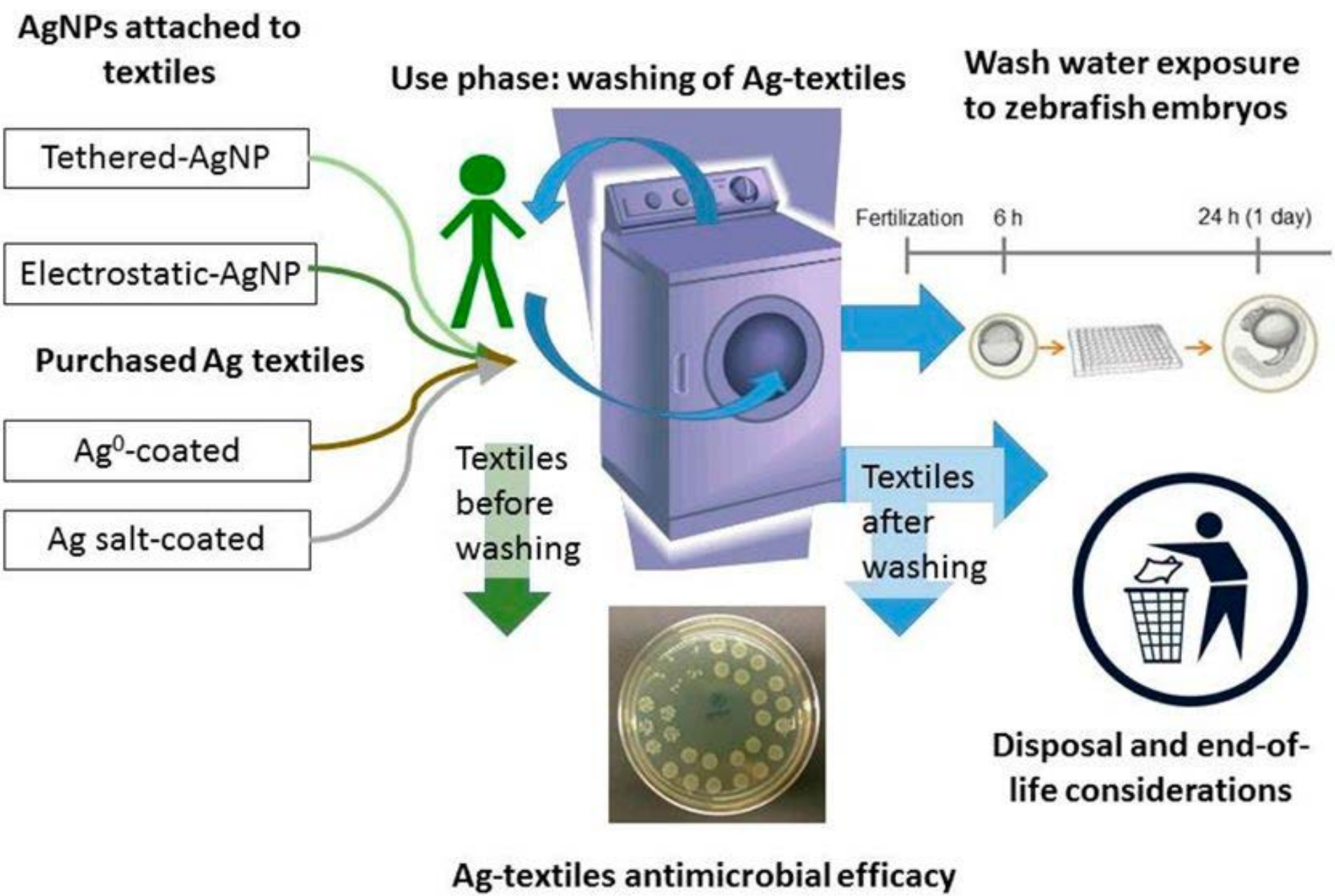
Sharper Image

Product Line D – Nano-enabled fabrics

- Why?
  - Anti-microbial (no stink)
  - Flame Retardant
  - Self cleaning
- Common nanomaterials:
  - Silver
  - Silica
  - CNT
- What happens during use (wearing & washing)?

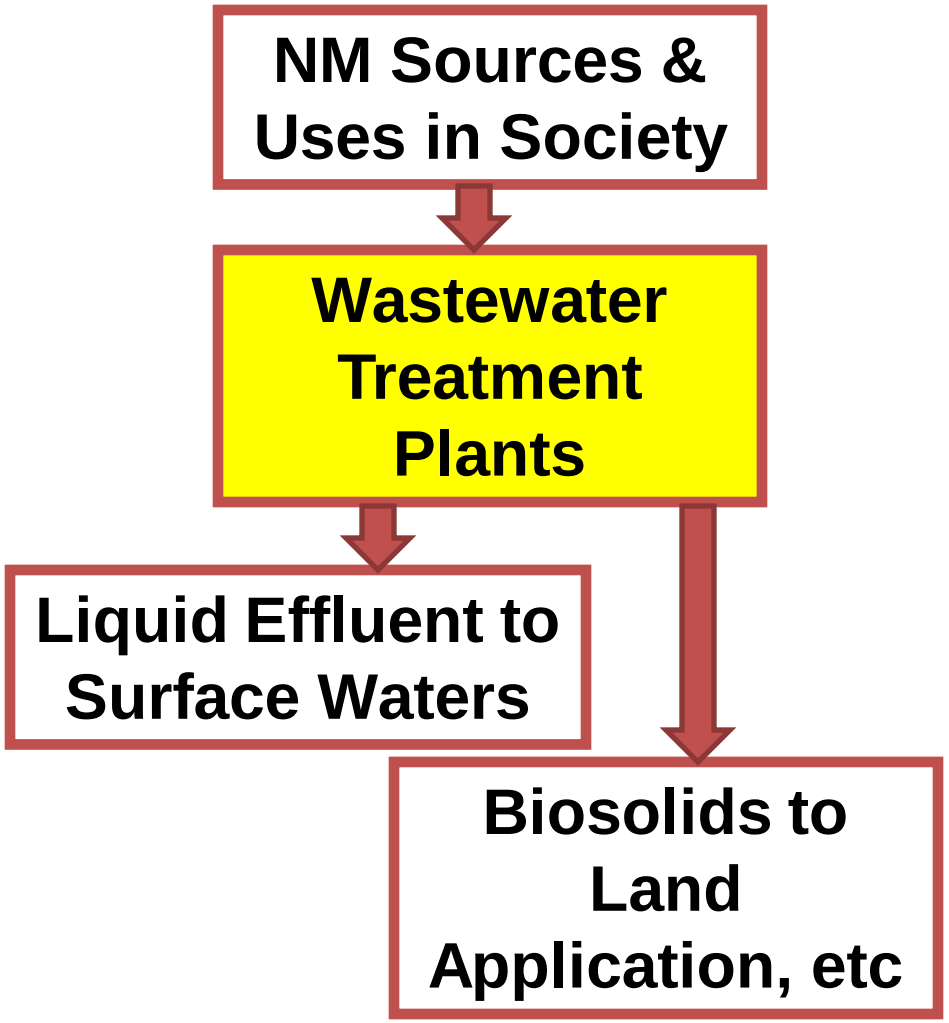


Environ. Sci. Technol. 2016, 50, 4018−4026

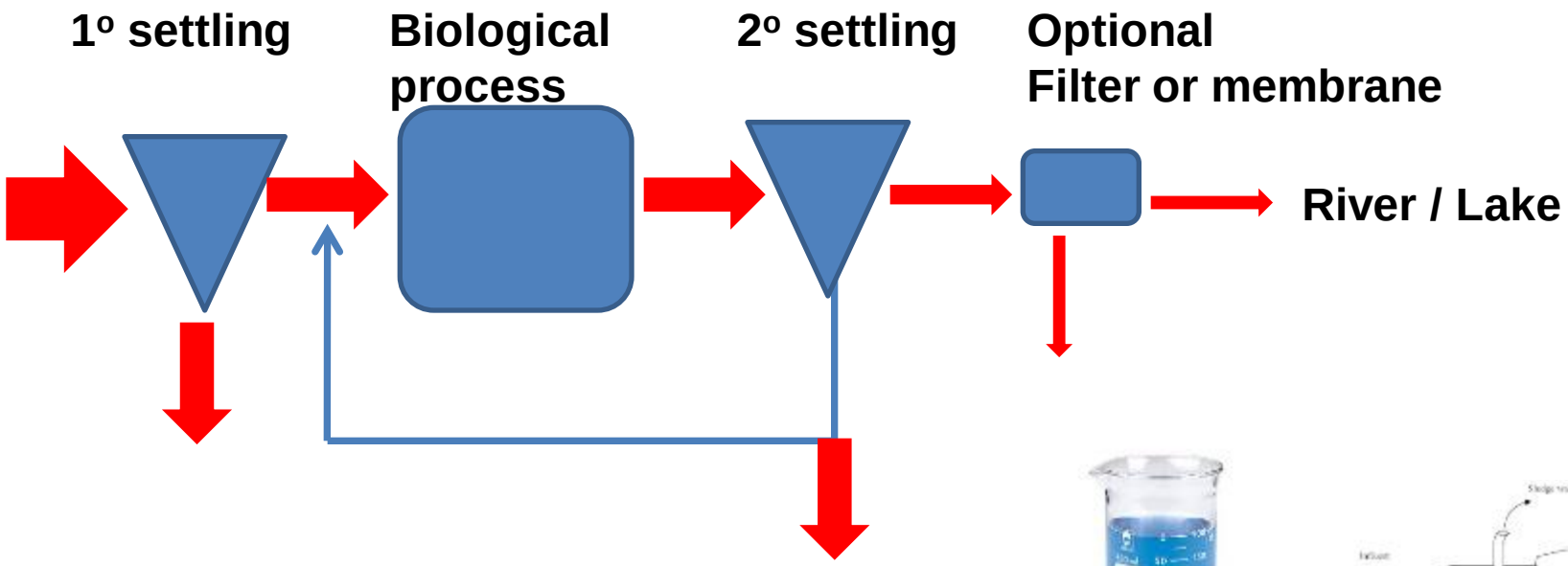


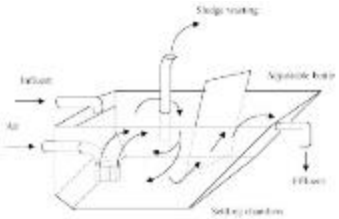
Part I - Summary

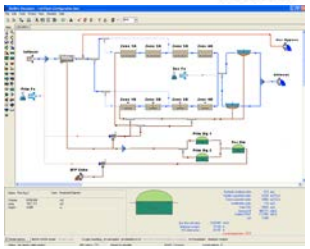
- NMs are released from commercial products into sewage wastewater
- The functionality of the product influences how NMs are used in different product lines



Nanomaterial removal in Wastewater Treatment Processes

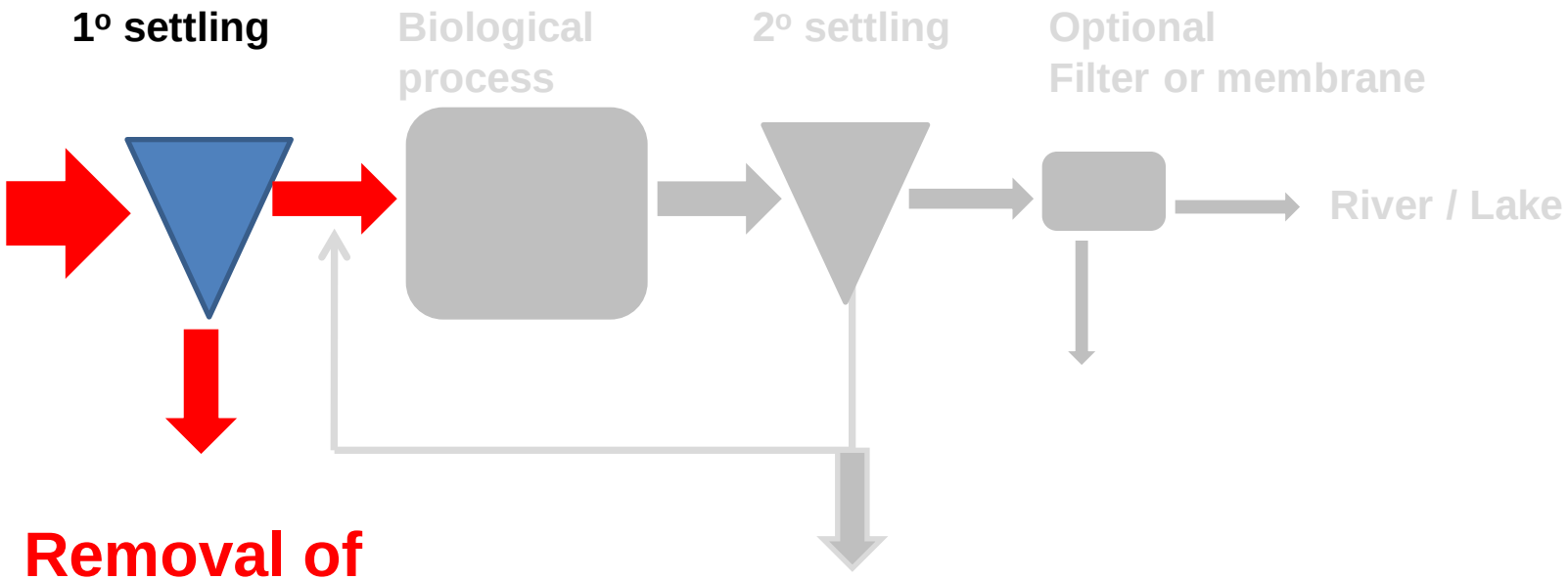






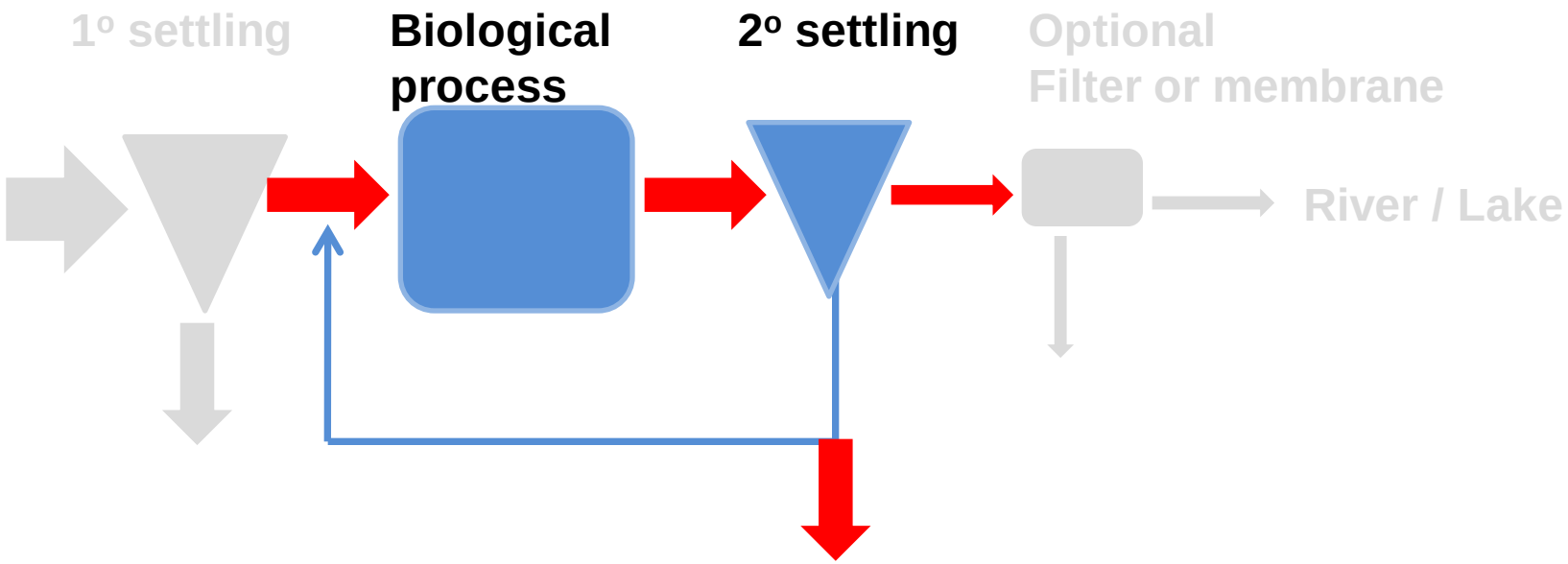
Red Arrows represent flux of nanomaterials

Primary Settling



Removal of nanomaterials that are aggregated to clays, bacteria or other solids > 20 um in size

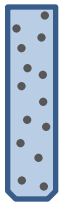
Biological Treatment



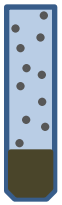
Removal of nanomaterials occurs when they interact with biofilms or biosolids

Batch Sorption Experiments

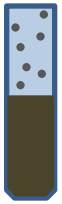
- Fresh wastewater biomass
- Mixing and settling times mimic hydraulic residence times at plant
- Analyze settled supernatant
- Can readily screen many properties
- Quick test
- Standard EPA method exists for organic pollutants using freeze-dried biomass too



Nanoparticle Control (No Biomass Sorbent)



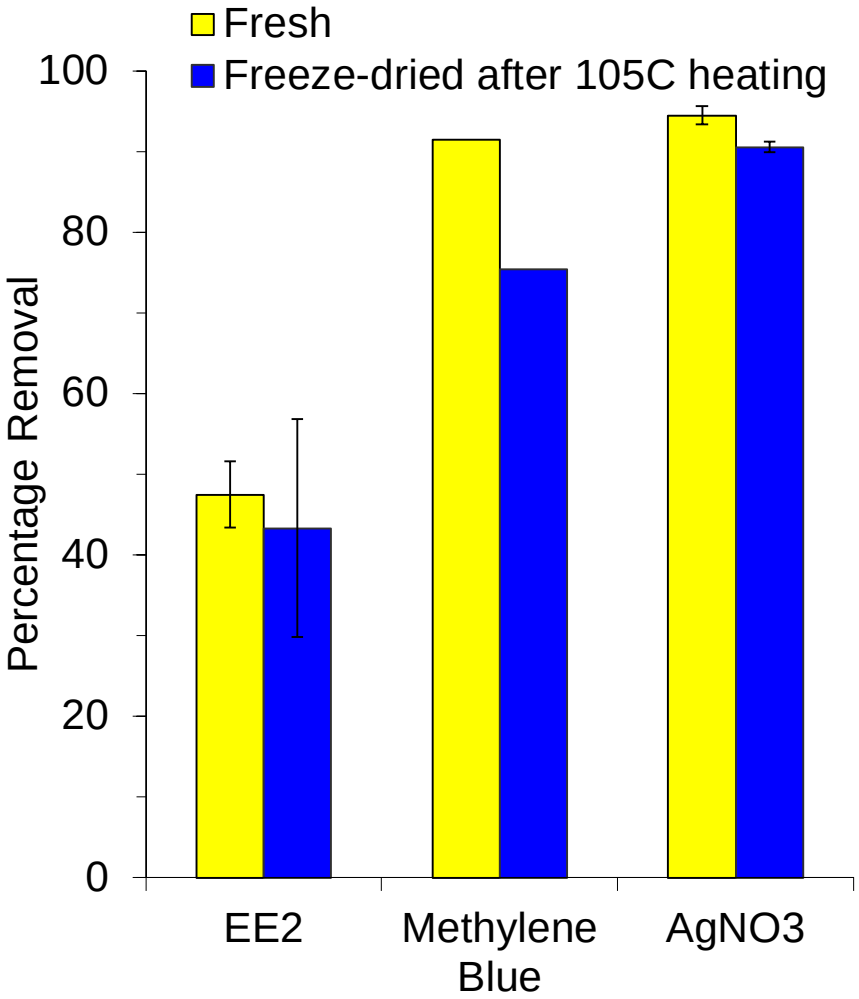
NP + 400 mg TSS/L Biomass Sorbent



NP + 800 mgTSS/L Biomass Sorbent

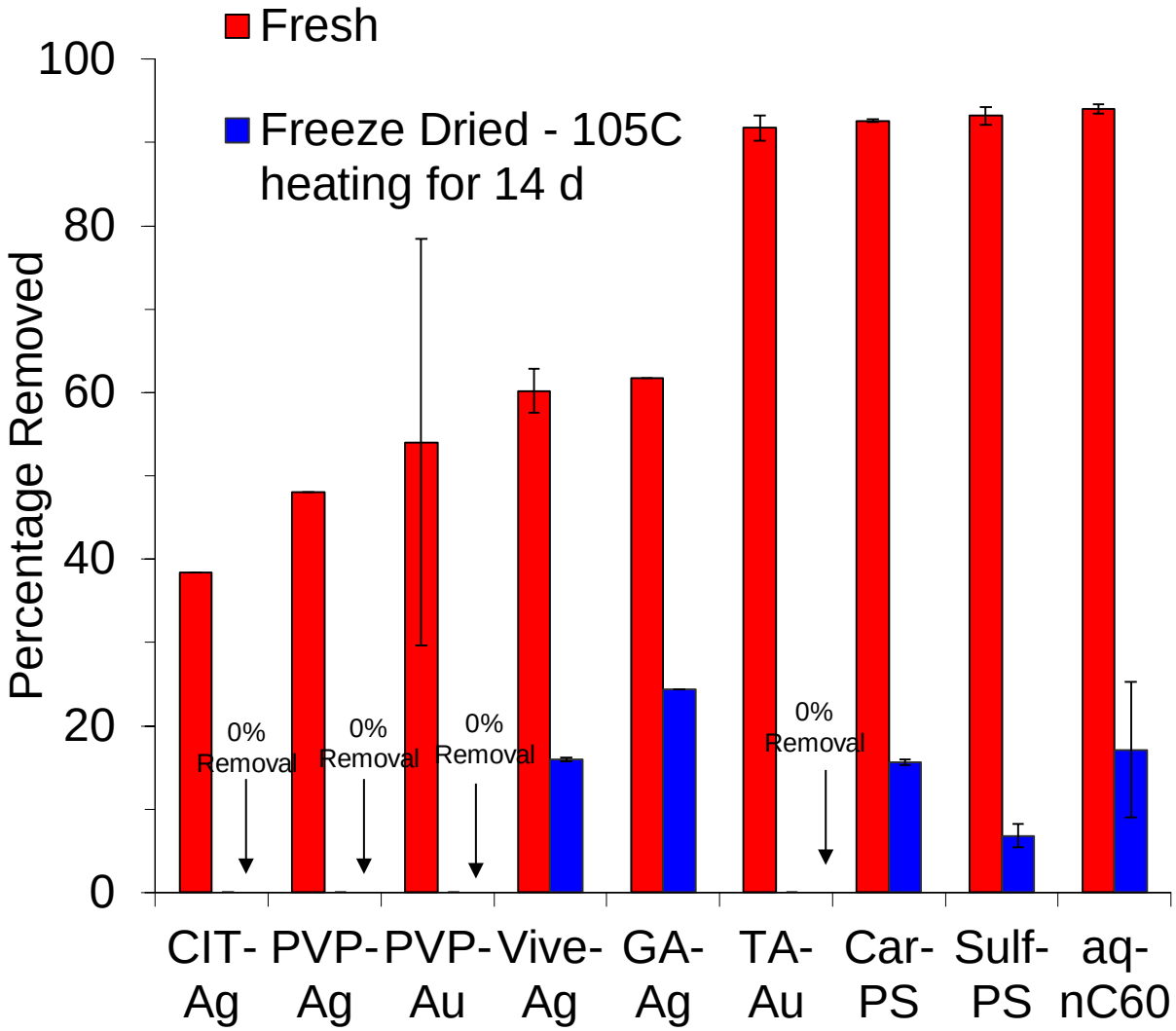
Standard Batch Methods

- OPPTS 835.1110 Activated Sludge Sorption Isotherm
- Uses freeze-dried biomass
- Validated for organics, and has been used for metals
- Data here shows fresh and freeze-dried biomass provide comparable removals when applied at similar mgTSS/L biomass

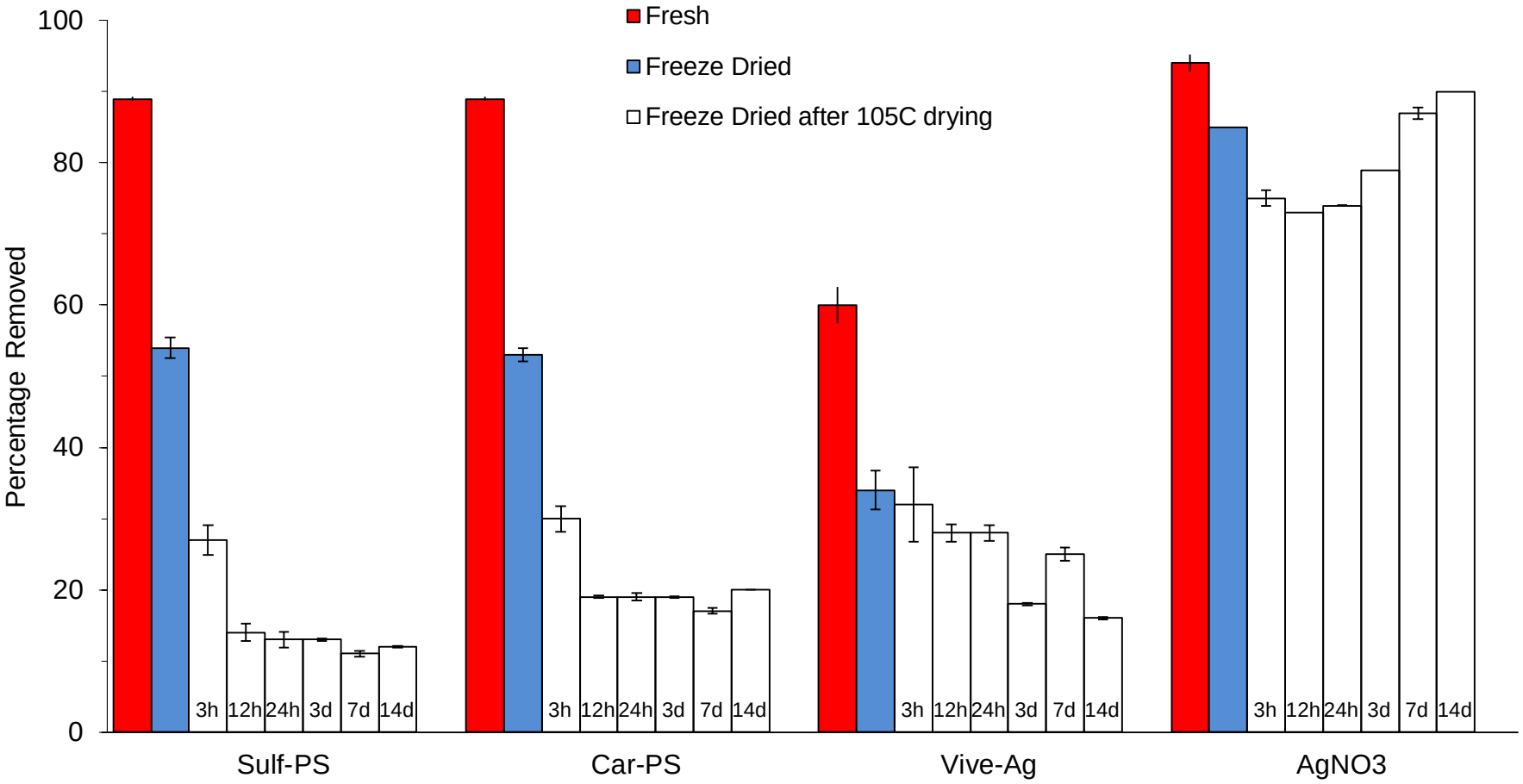


Does OPTT Test work for NPs? NO!

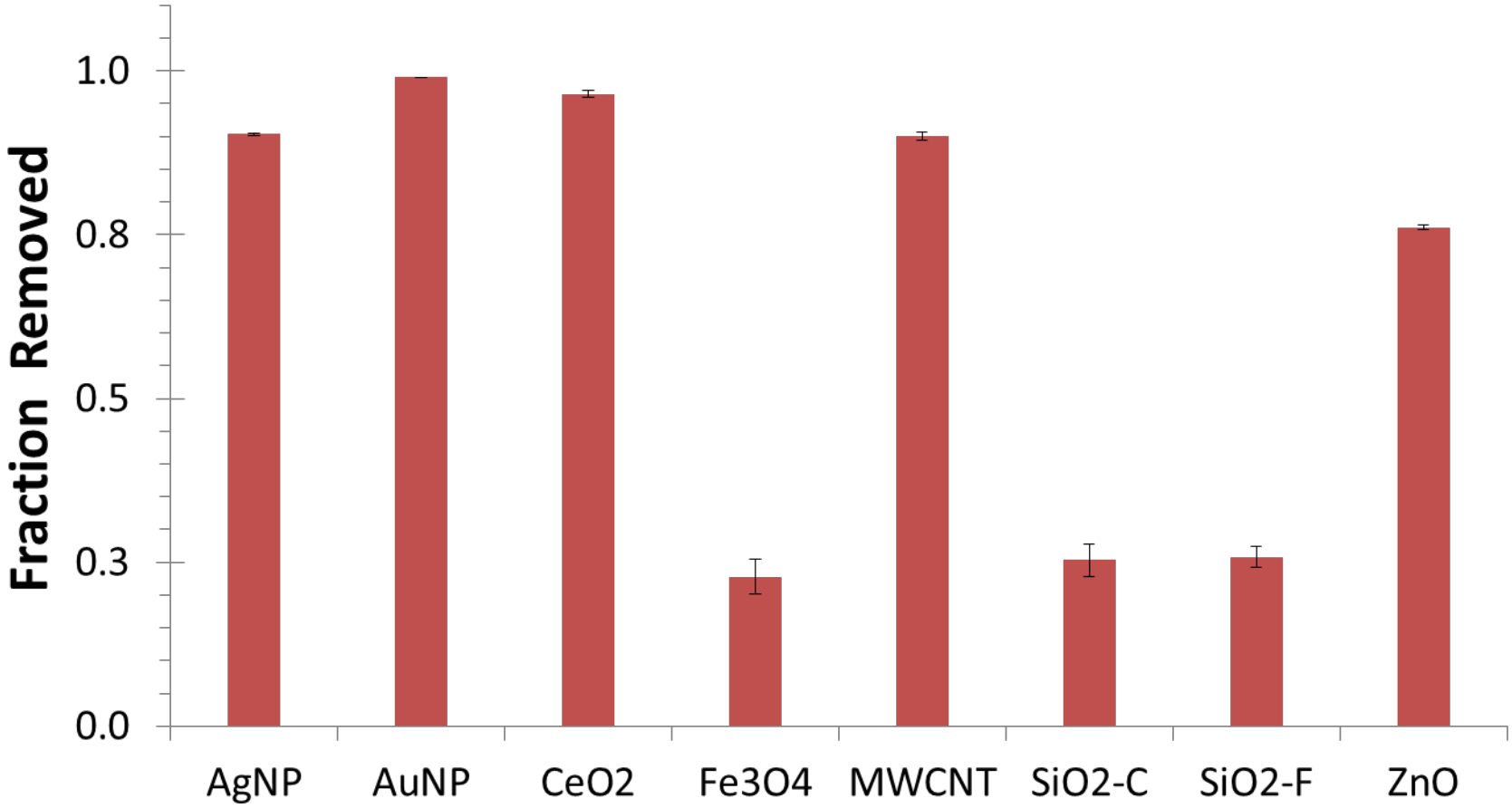
- X-axis is different types of nanoparticles
- Fresh and rinsed biomass shows much more capacity for NMs than freeze-dried biomass



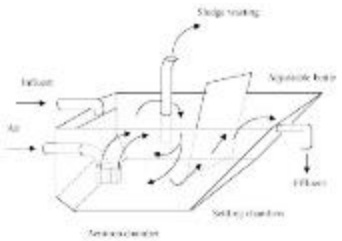
Freeze-drying and heating denatured proteins & released bacterial "surfactants"

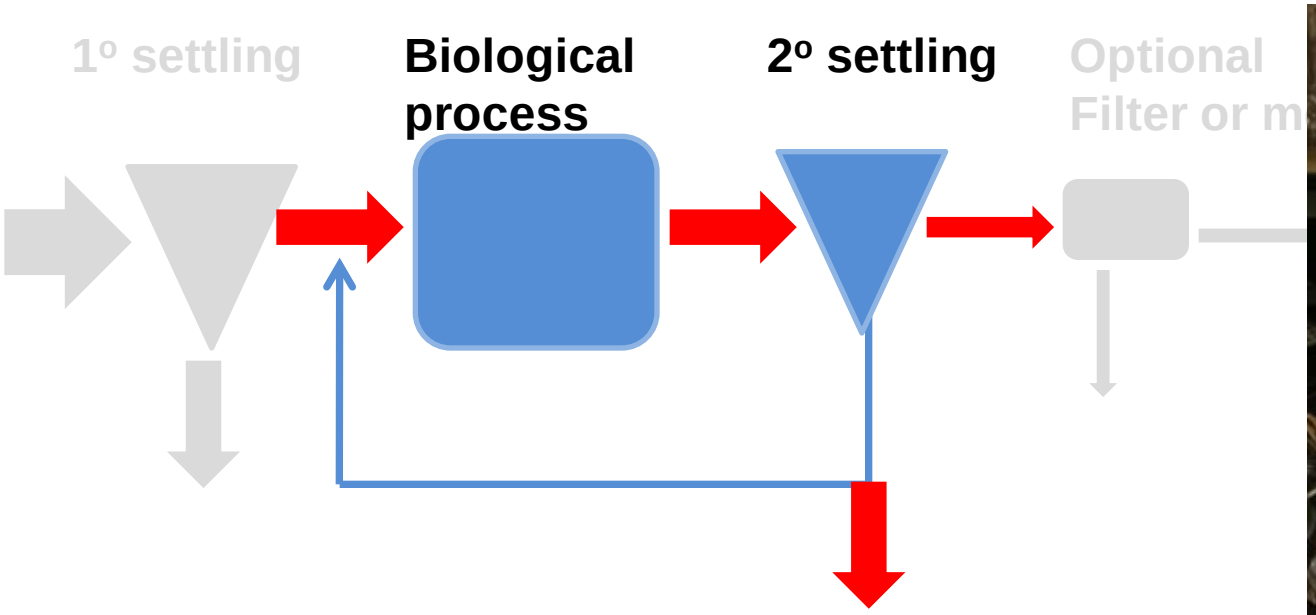


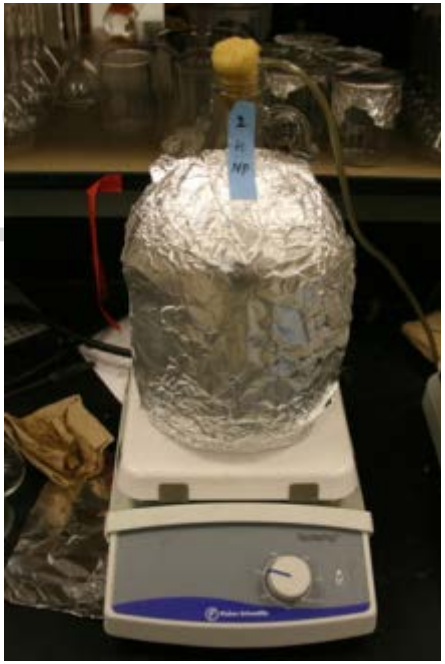
Removal by biomass of different Nanoparticles (1 gTSS/L)



Biological Treatment





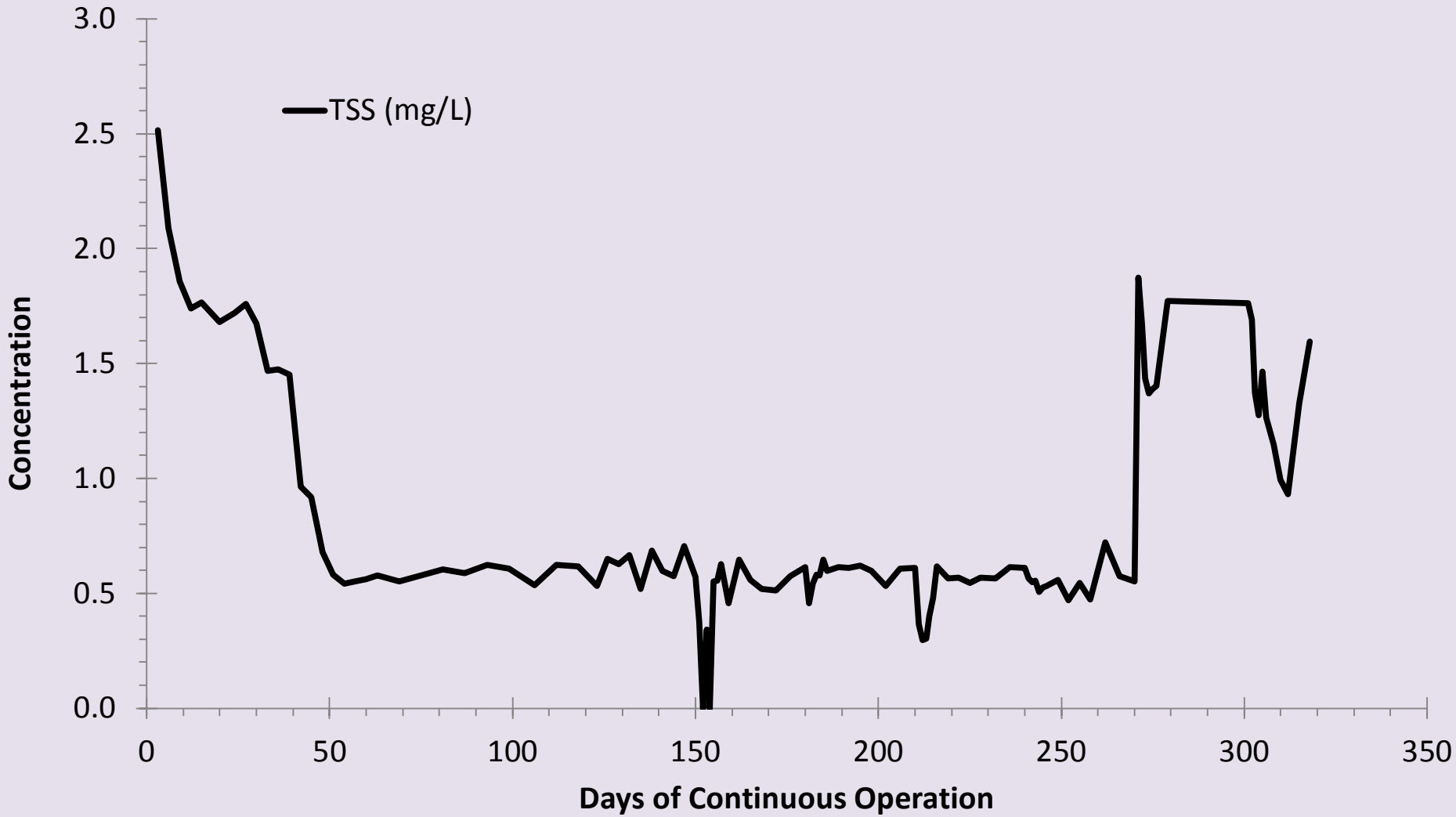


Removal of nanomaterials occurs when they interact with biofilms or biosolids

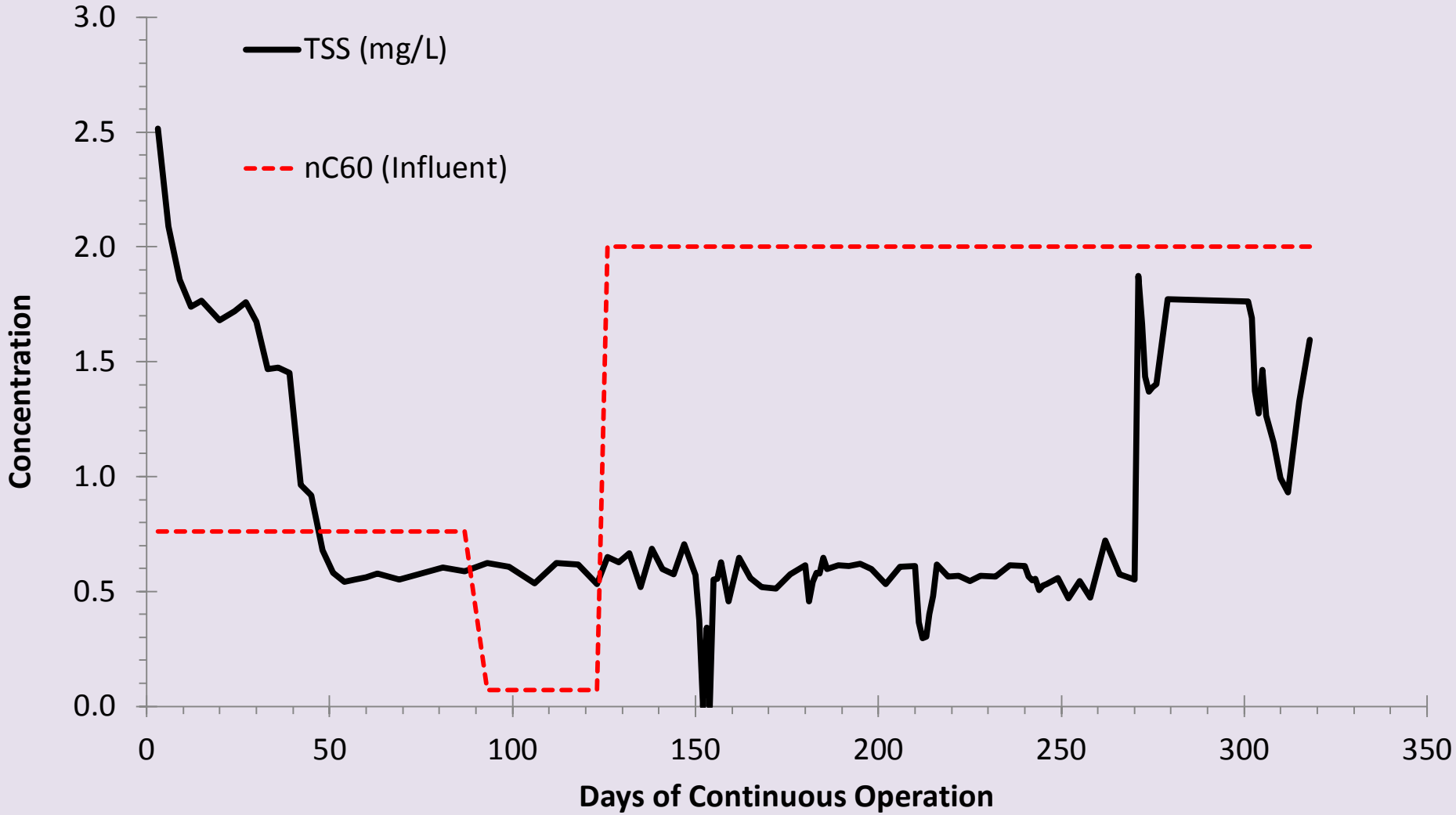
2.5 L
SRT = 6 to 10 days
Influent COD: ~750 mg/L
Influent NP: 0.07 to 2 mg/L

Results of SBR tests with continuous, daily addition of Nanoparticles

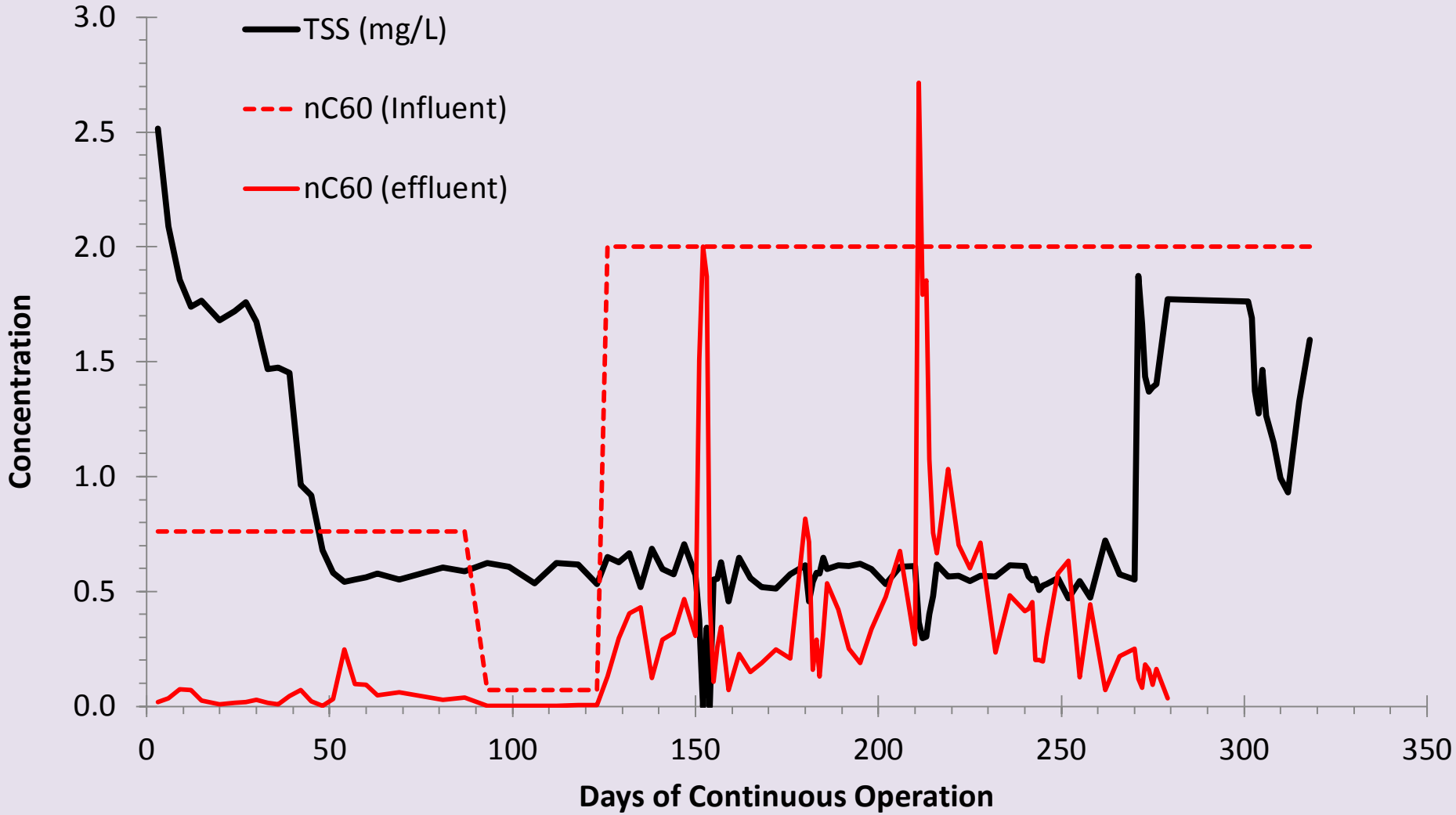
Results of SBR tests with continuous, daily addition of Nanoparticles



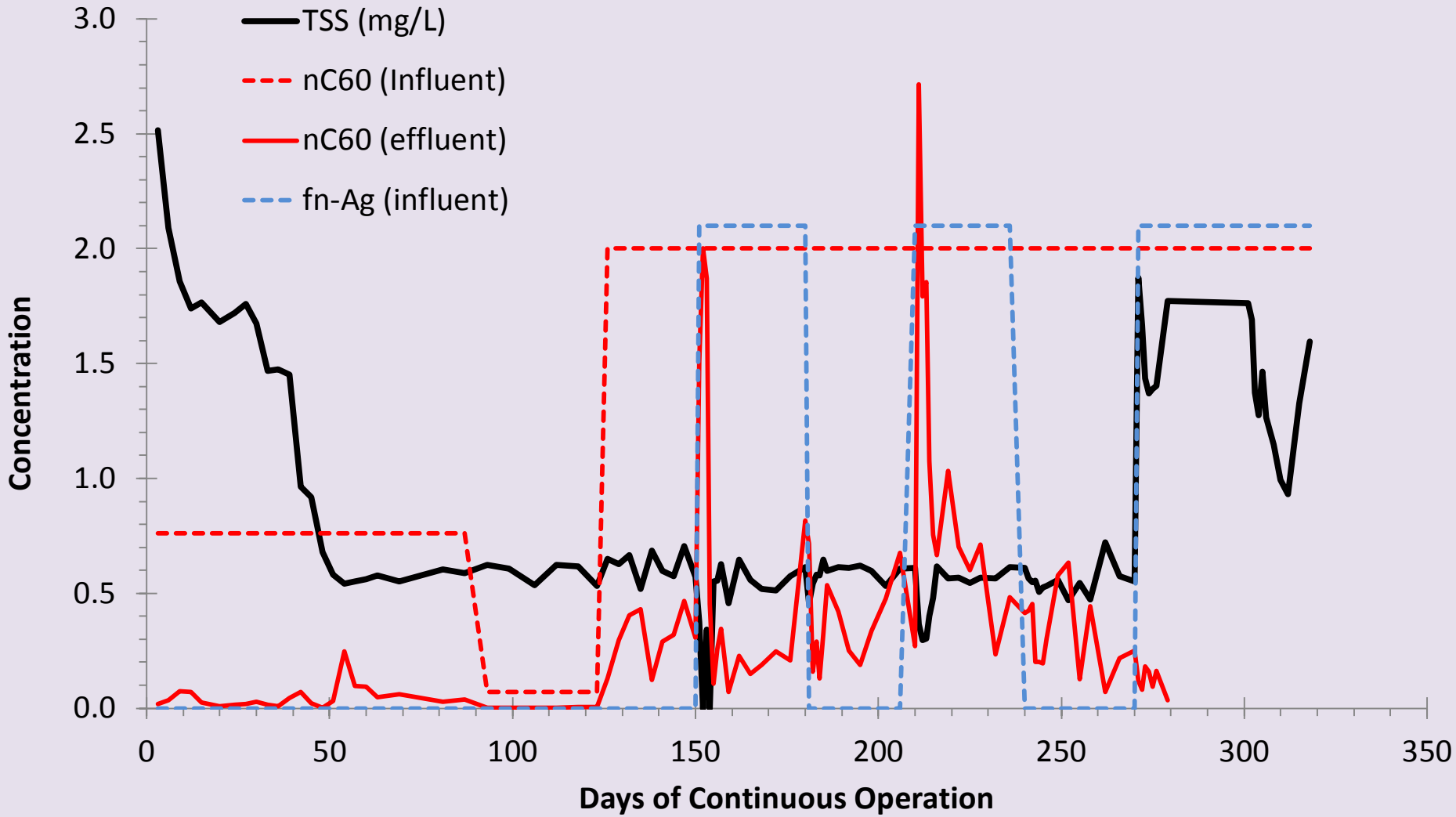
Results of SBR tests with continuous, daily addition of Nanoparticles



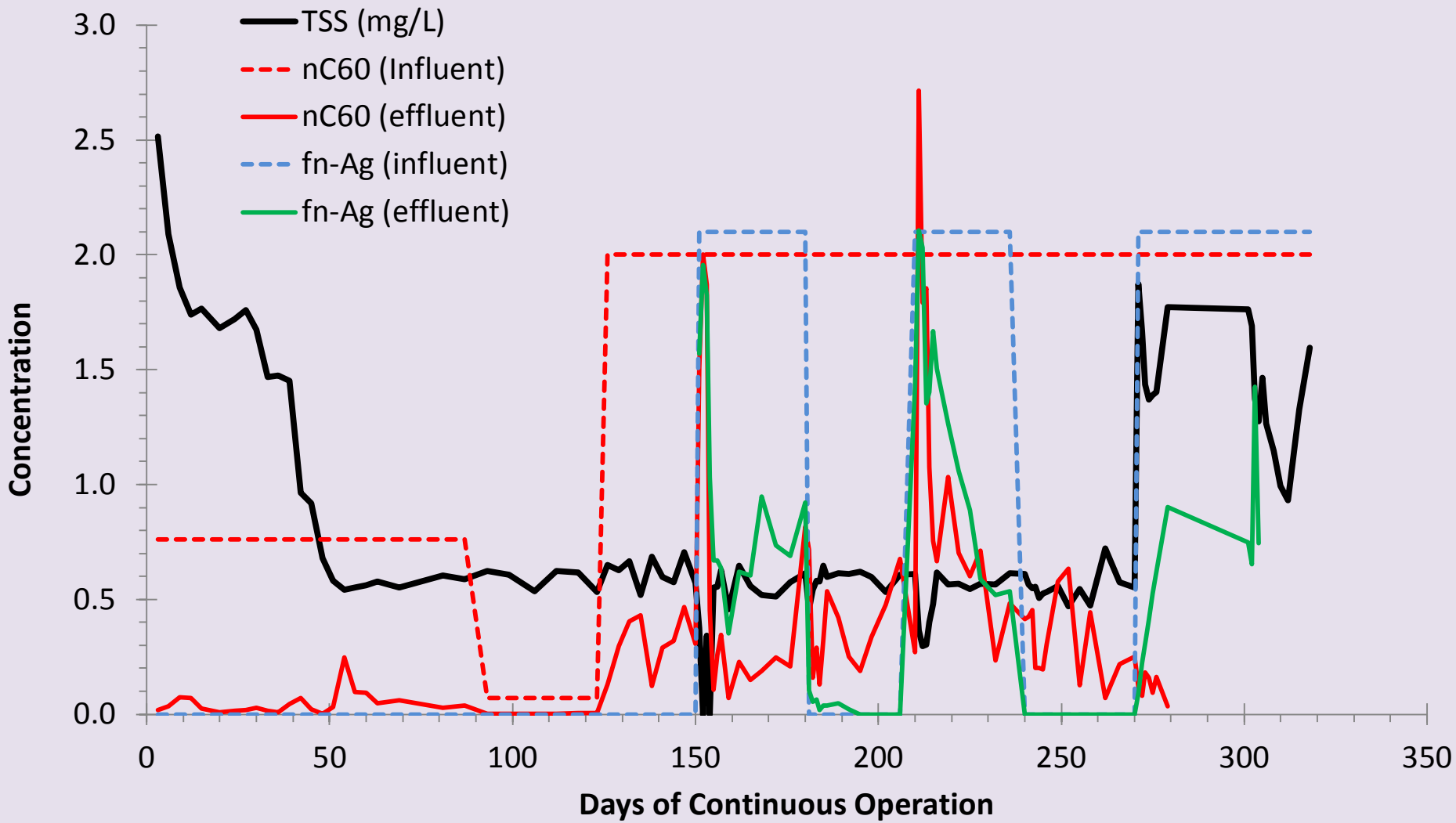
Results of SBR tests with continuous, daily addition of Nanoparticles



Results of SBR tests with continuous, daily addition of Nanoparticles

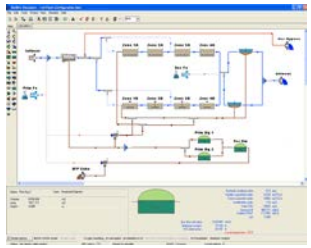


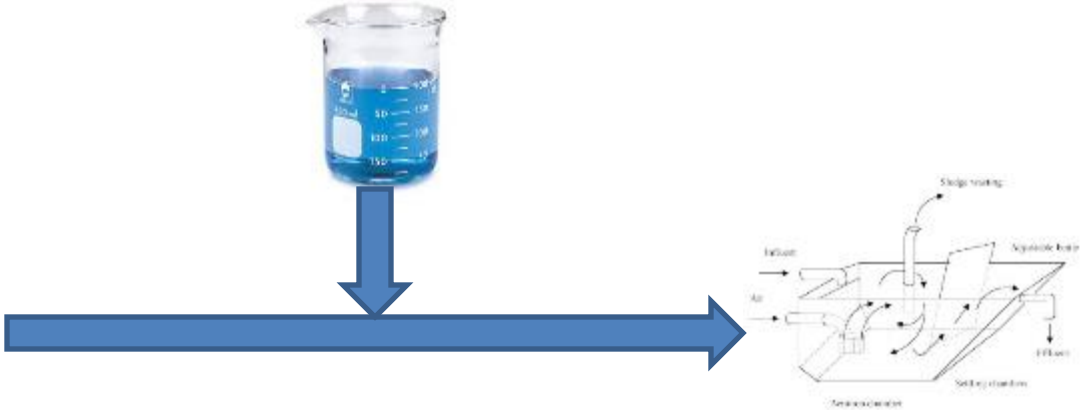
Results of SBR tests with continuous, daily addition of Nanoparticles



Modeling NP Removal

Kiser et al.,
Sep. Sci Tech. 2010



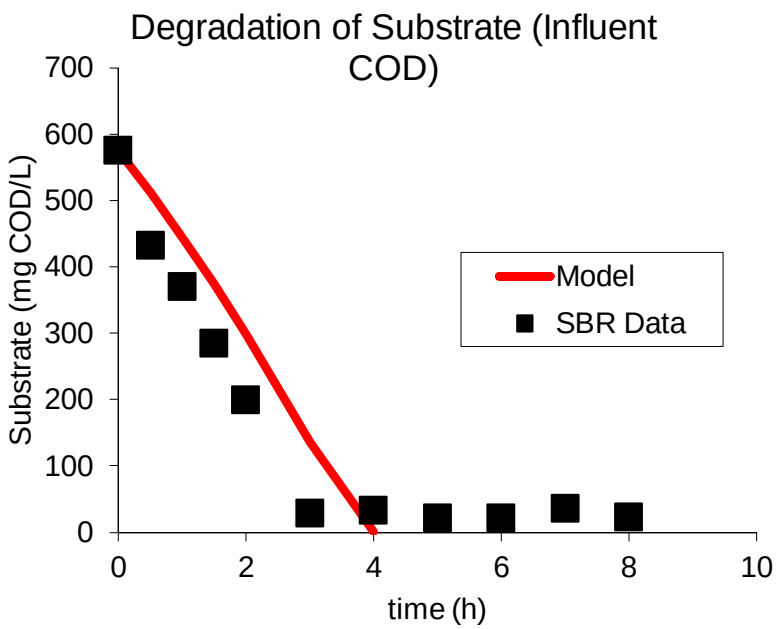


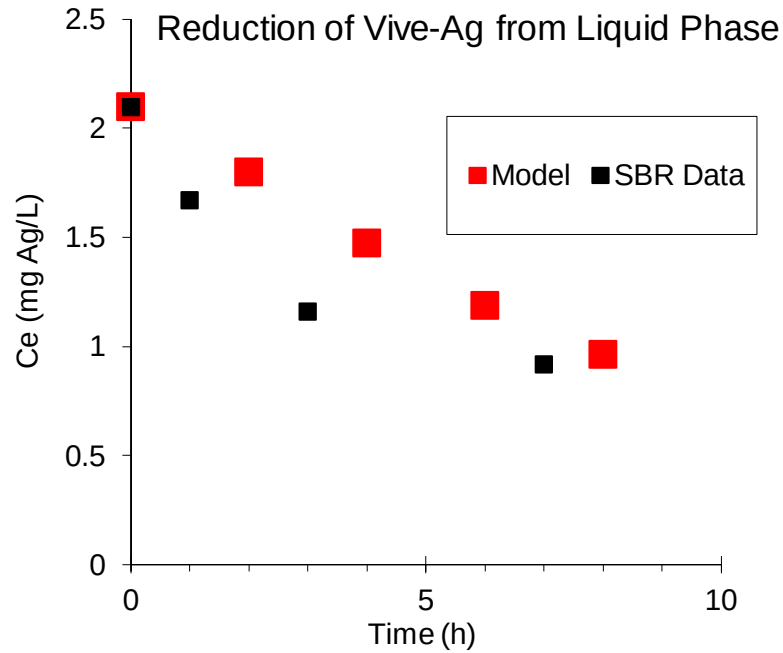
Hypothesis: Batch NP sorption experiments linked with dynamic bacterial growth models and reactor models can predict nanomaterial removal

Example:
Isotherm in batch reactor
Fresh biomass
10 nm diameter citrate functionalized nano Silver
Linear Partition Coefficient for : K = 0.0144 L/g

Model Predictions

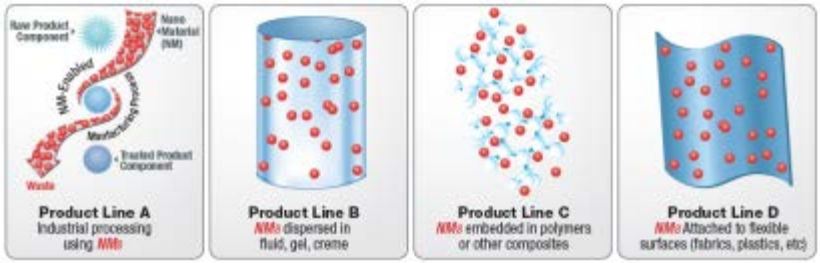
"Isotherms" with NPs predict removal in Sequencing Batch Reactors





Conclusion: Preliminary confirmation exists that we can go from batch experiments to simulations of continuous flow performance. Difference in NP effluent concentration probably related to NP association with non-settlable colloids

Part I - Summary



- Products potential to release NMs into the environment can be grouped into 4 product lines

- NMs are released from commercial products into sewage wastewater

NM Sources & Uses in Society

↓

Wastewater Treatment Plants

↓

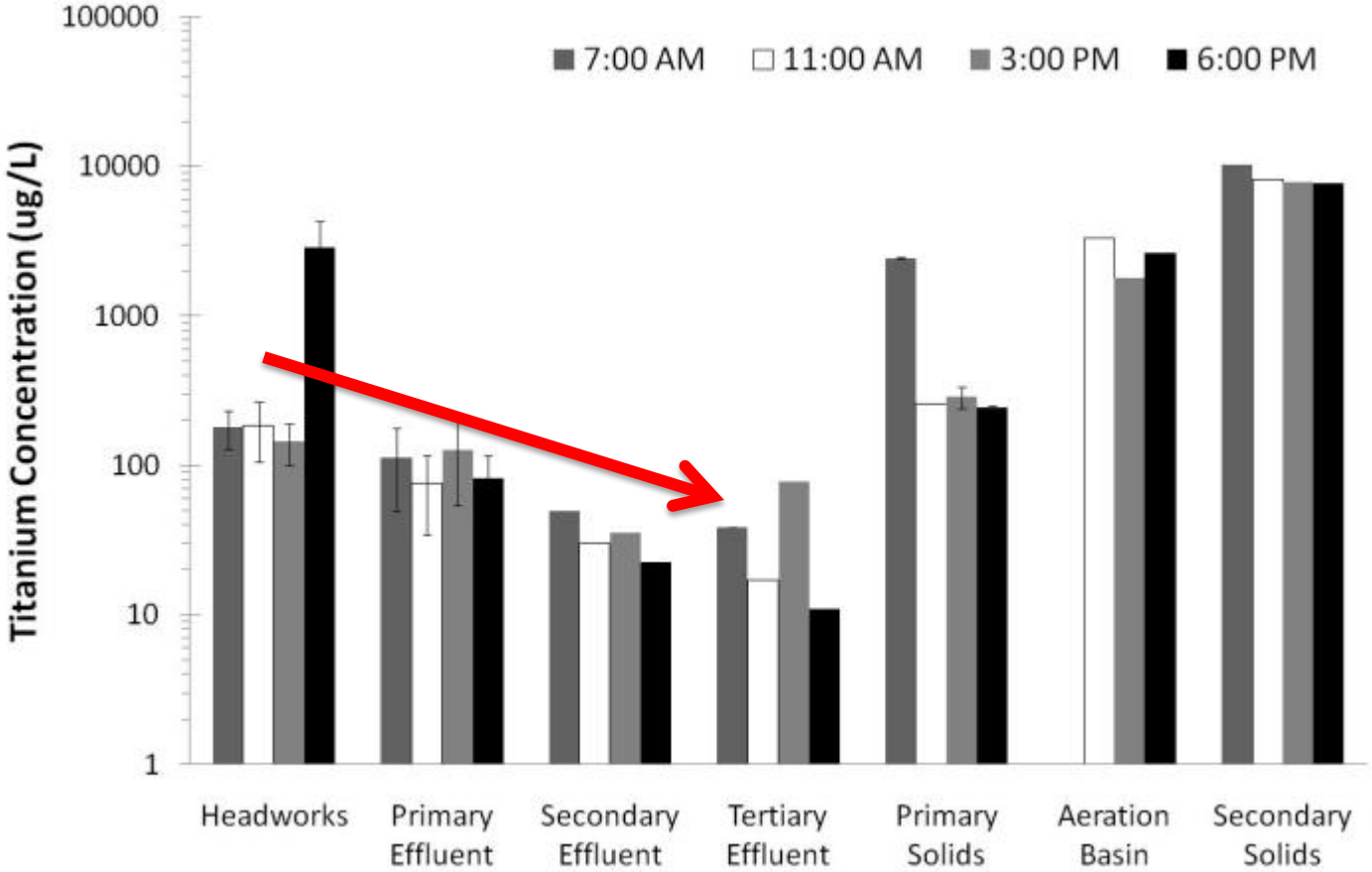
Liquid Effluent to Surface Waters

↓

Biosolids to Land Application, etc

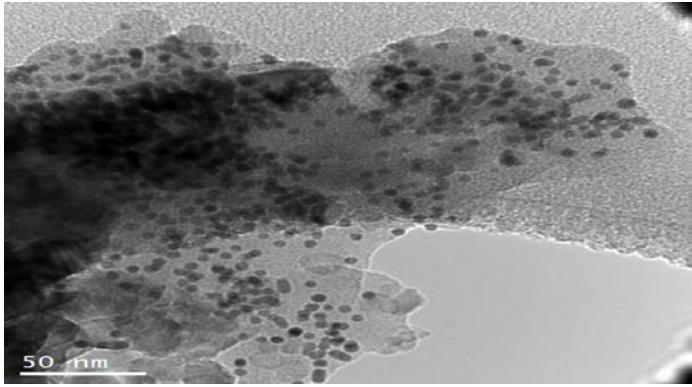
Titanium at Full Scale WWTPs

Titanium is removed from liquid & accumulates in biomass

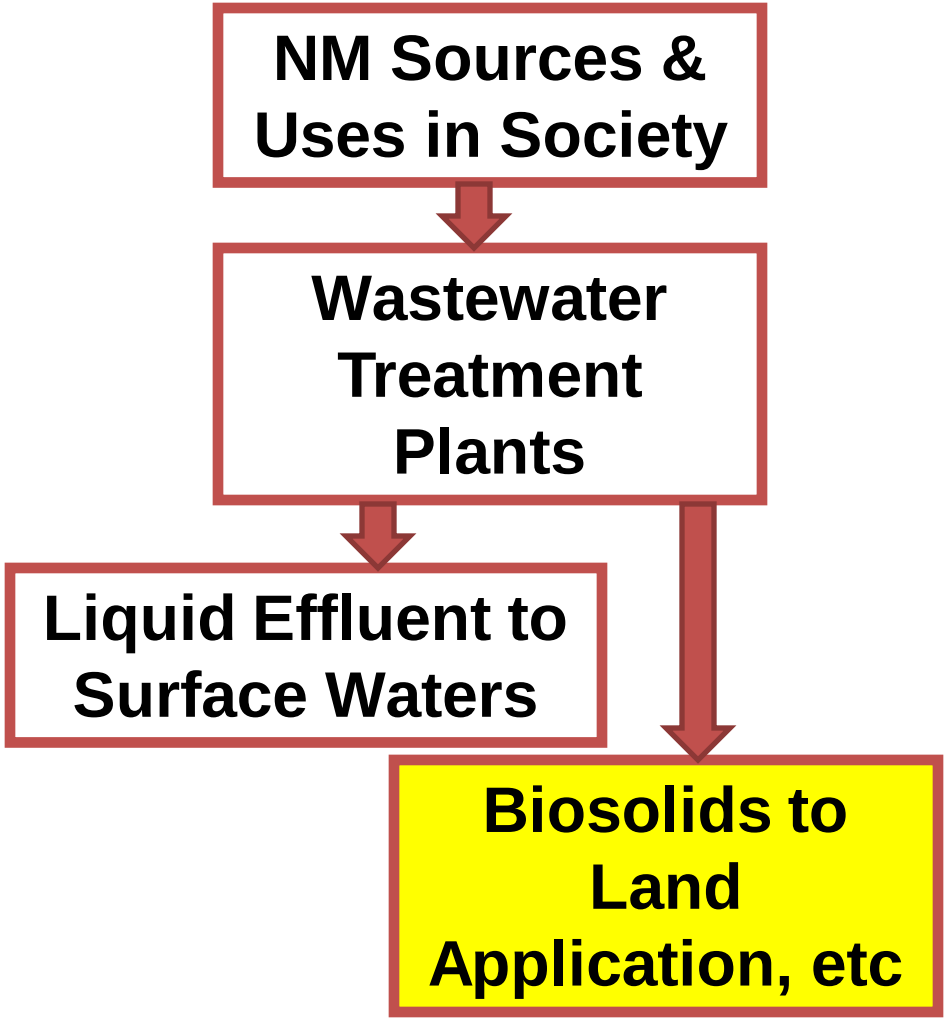


Kiser et al.,EST 2010; Westerhoff et al., JEM 2011

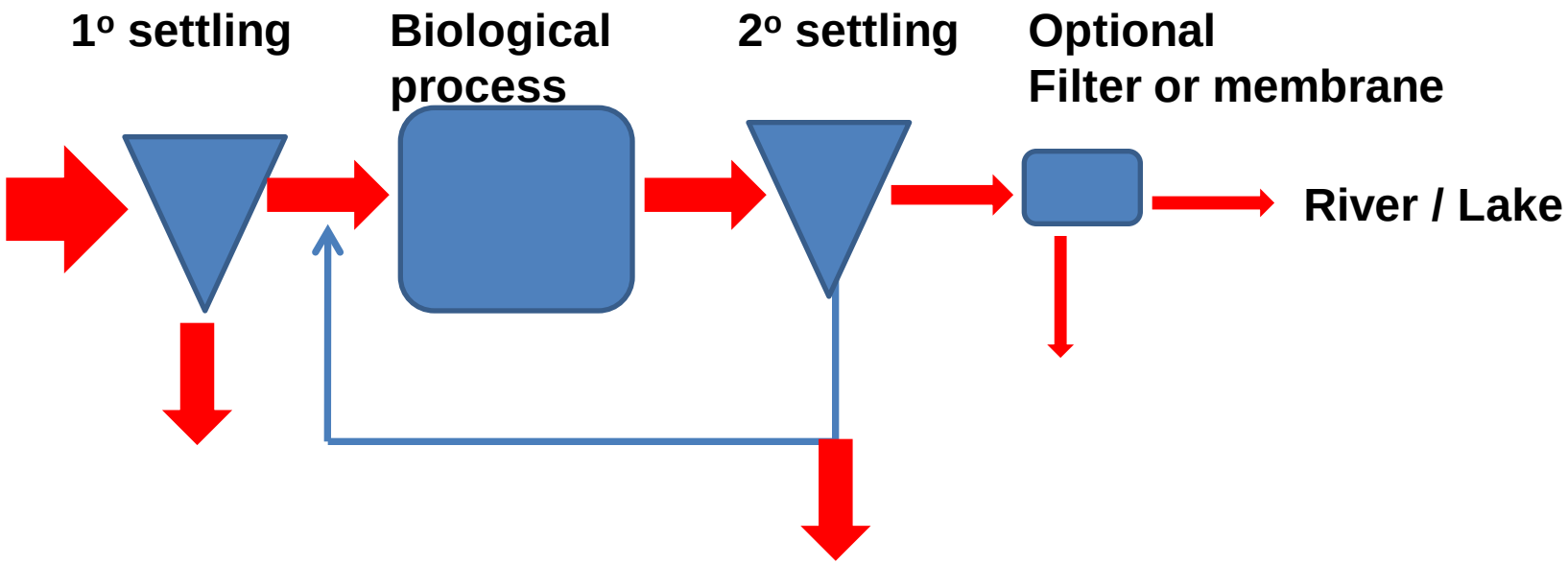
Titanium at Full Scale WWTPs



Different Facilities	Titanium Content of water (ugTi/L)	
	Headworks	Effluent
Activated sludge	615	5
Act. Sludge + filter	180	7
Activated sludge	363	3
Activated sludge	141	2
Activated sludge	581	18
Activated sludge		8
Activated sludge	233	2
Trickling filter	549	13
Membrane bioreactor (MBR)	310	1
MBR	422	4
Average	377	6


NM Sources & Uses in Society
Wastewater Treatment Plants
Liquid Effluent to Surface Waters
Biosolids to Land Application, etc

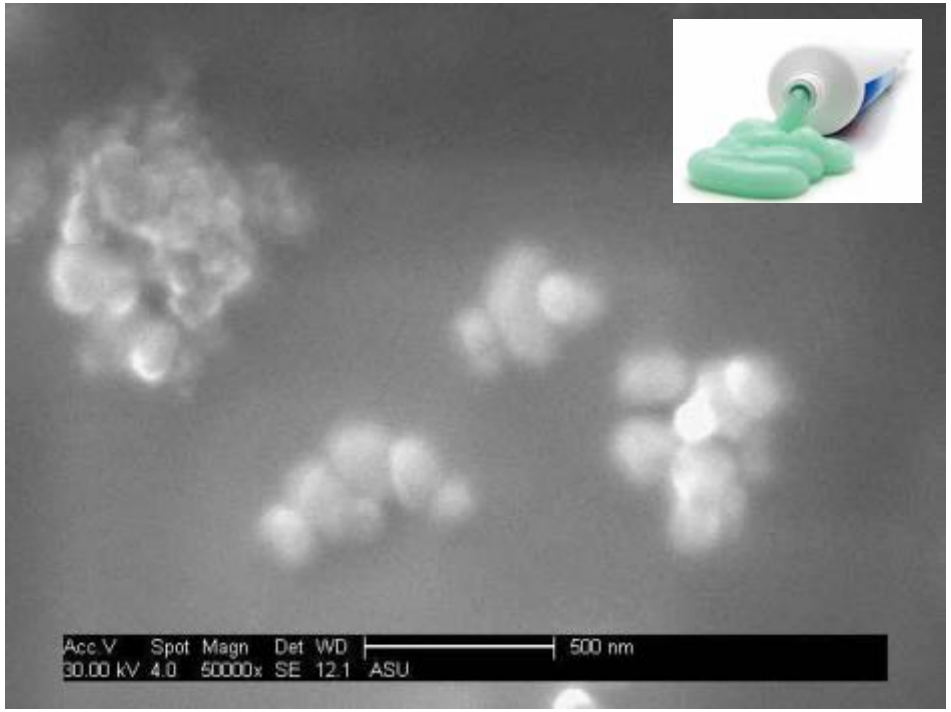
Under typical TSS levels (1500-3000 mg/L) greater than 90% of even highly negatively charged NMs will *distribute* into biomass

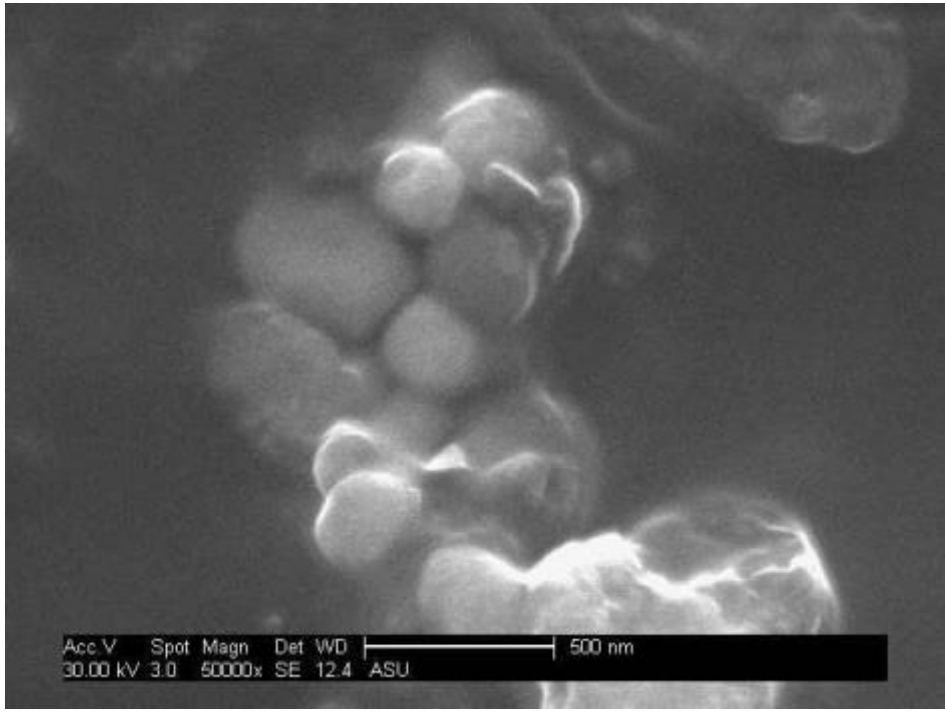


Let's go Nanoprospecting

What type of NMs do we find in real biosolids?

TiO_2 in commercial products are similar to TiO_2 extracted from biosolids

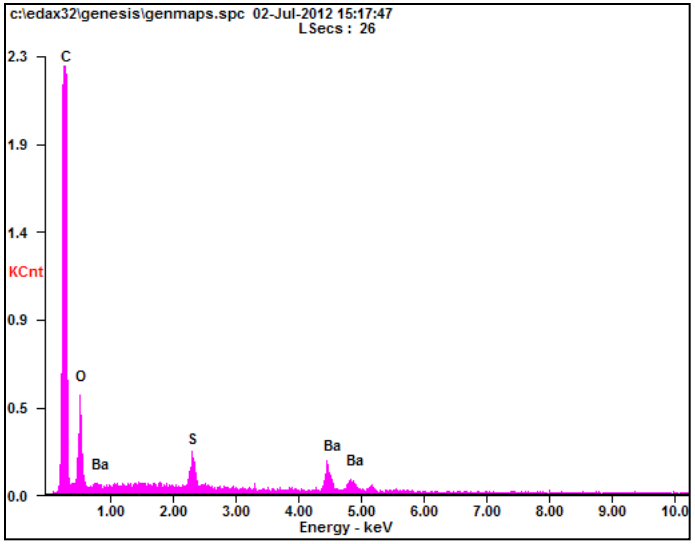


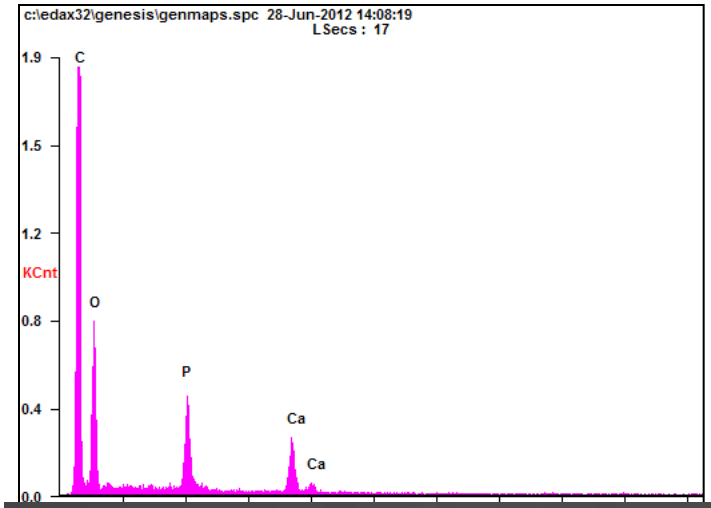


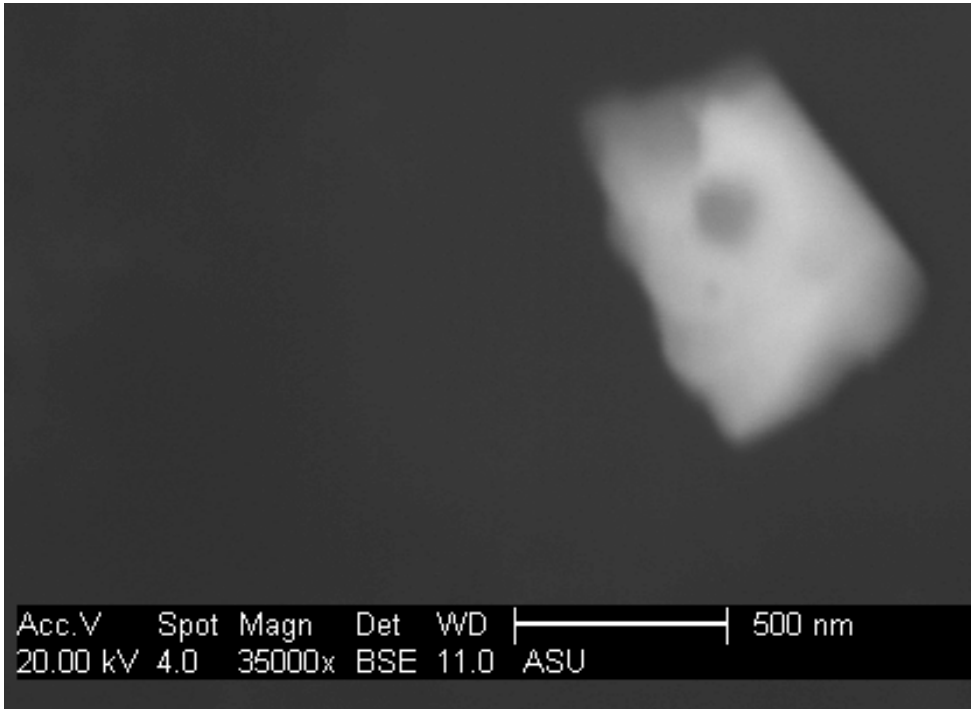
TiO_2 in Toothpaste

TiO_2 in Biosolids

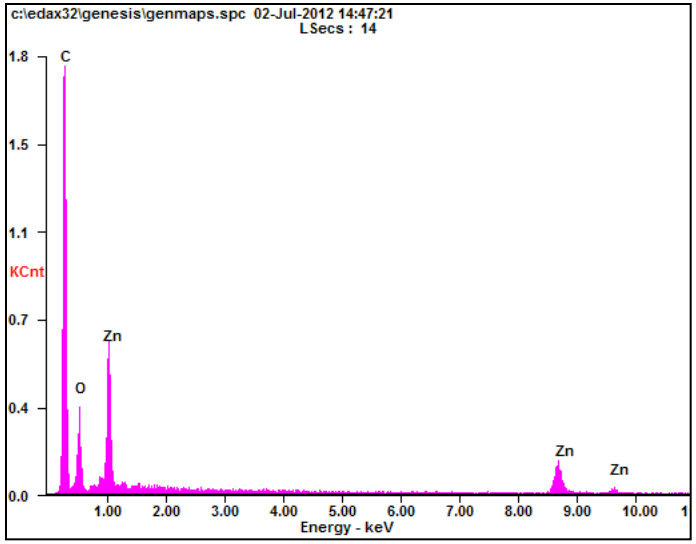
Barium Sulfate & Calcium Phosphates

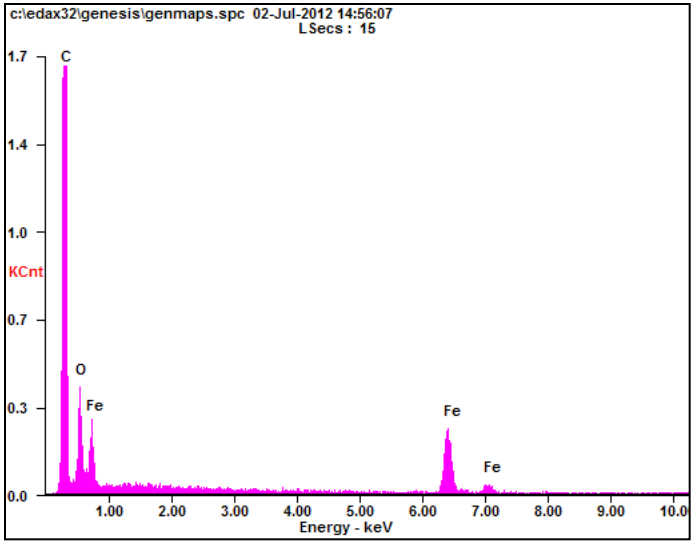


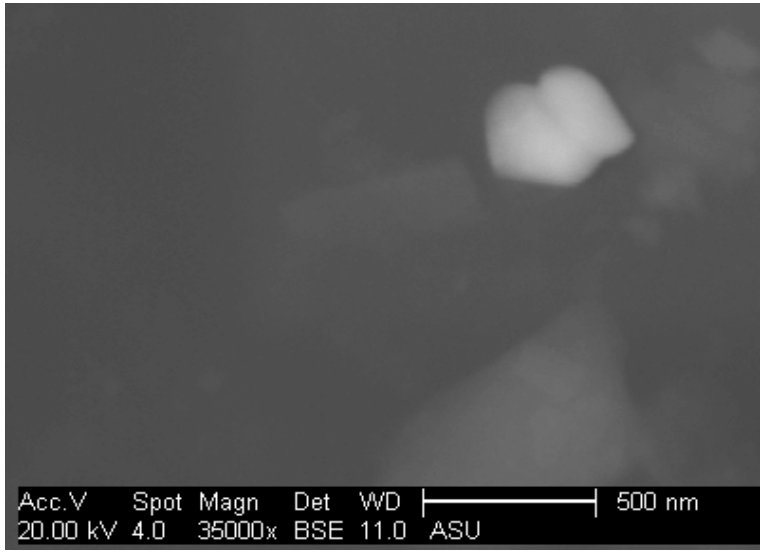




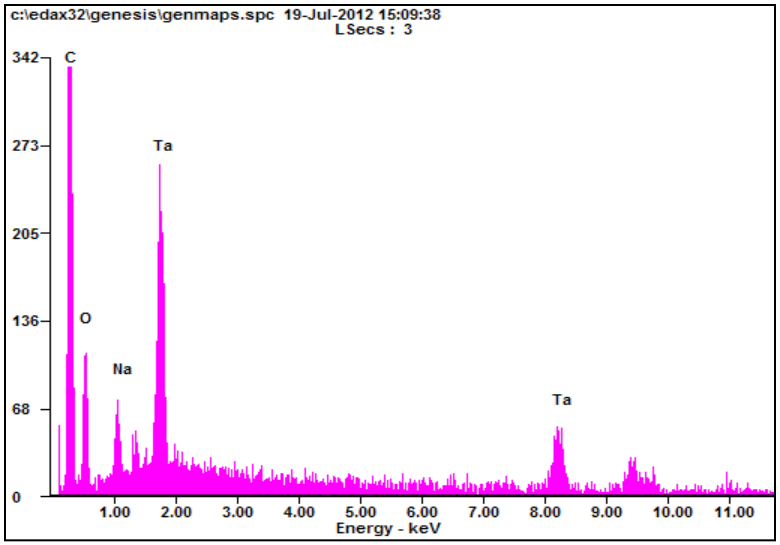
Zinc & Iron Oxides

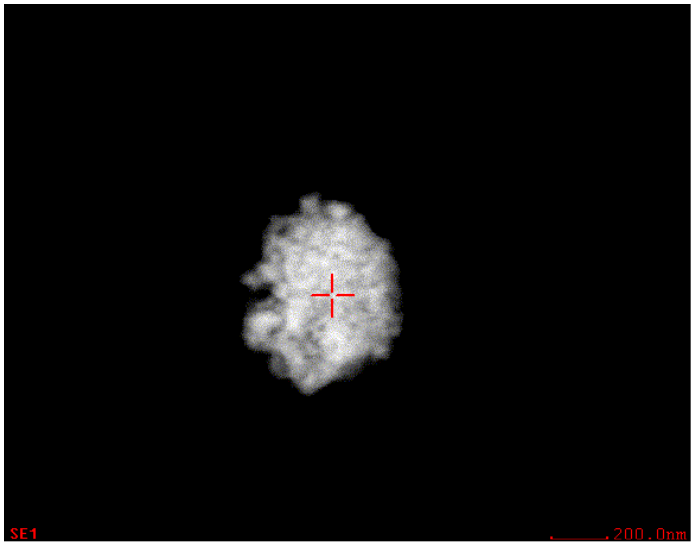


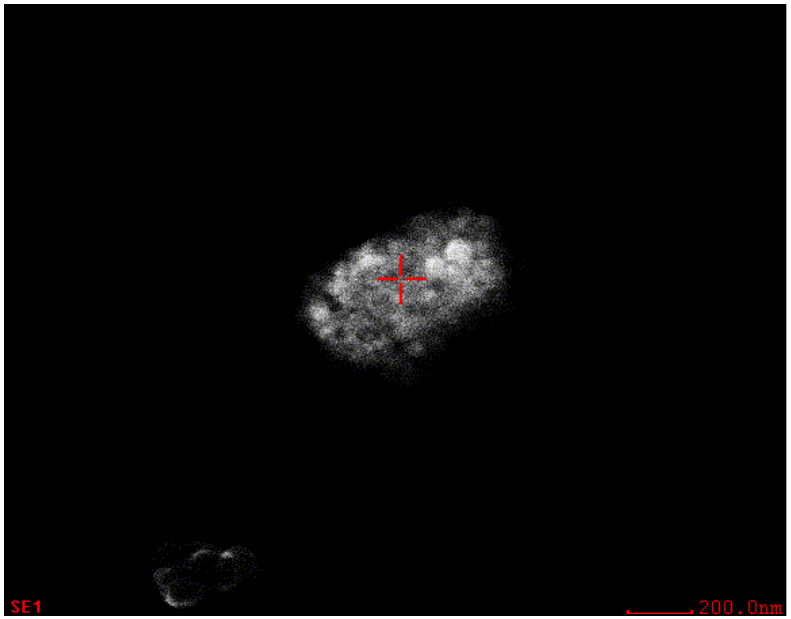




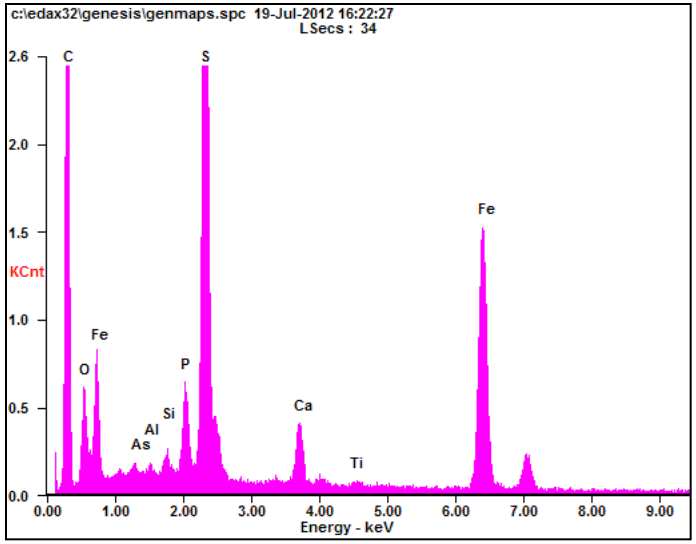
Sodium Tantalate Catalysts

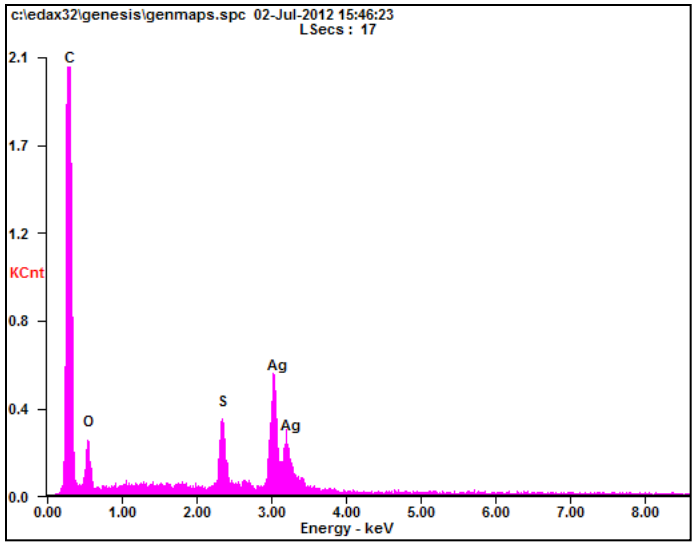


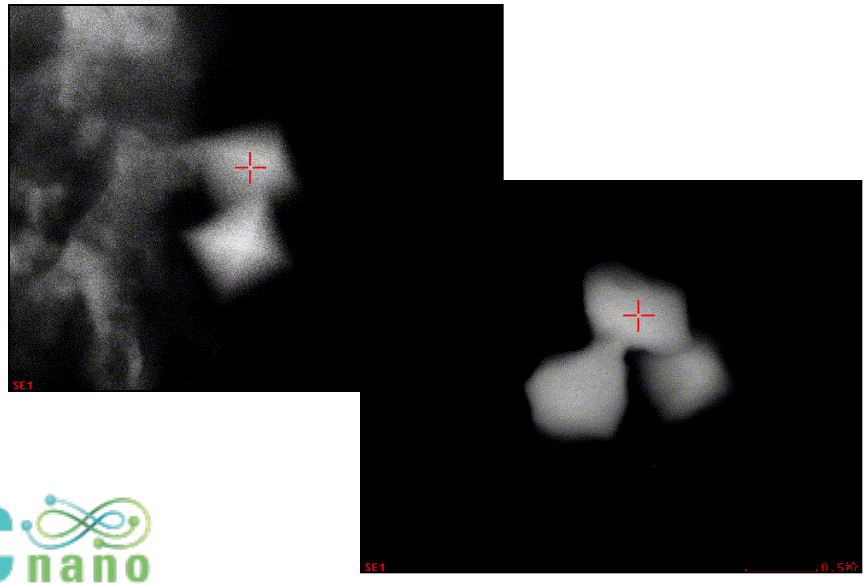


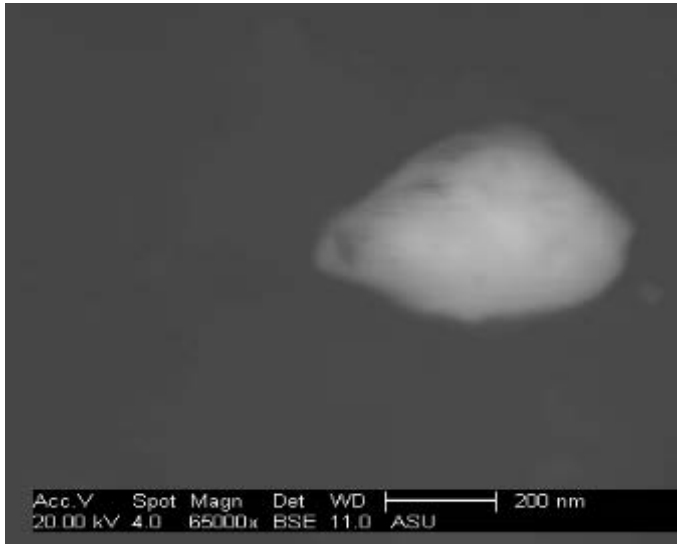


Iron & Silver Sulfides

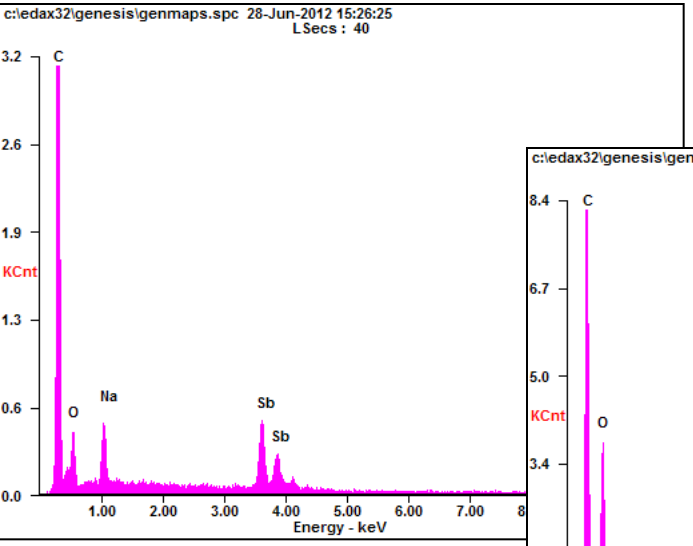


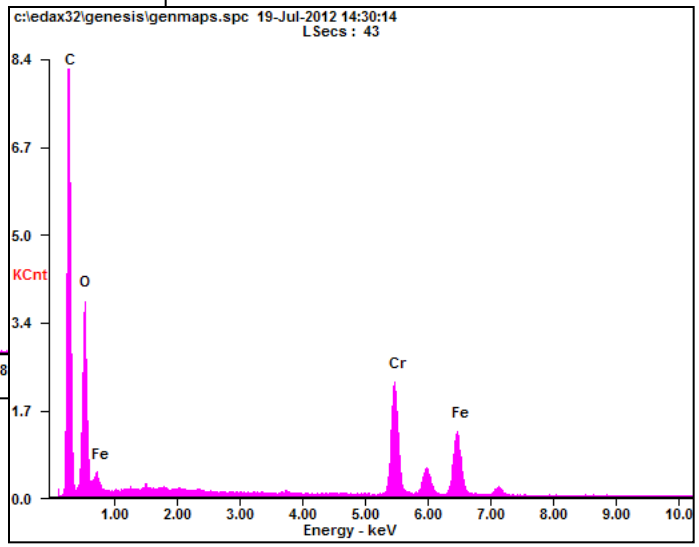


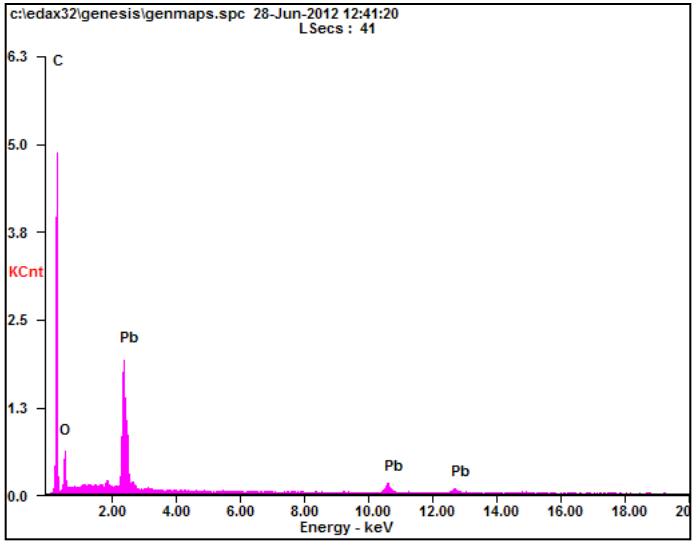


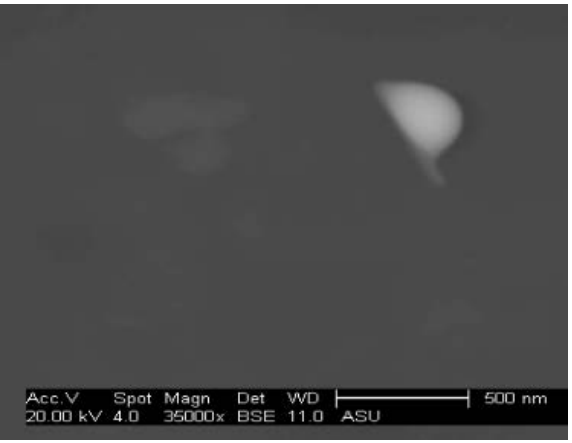


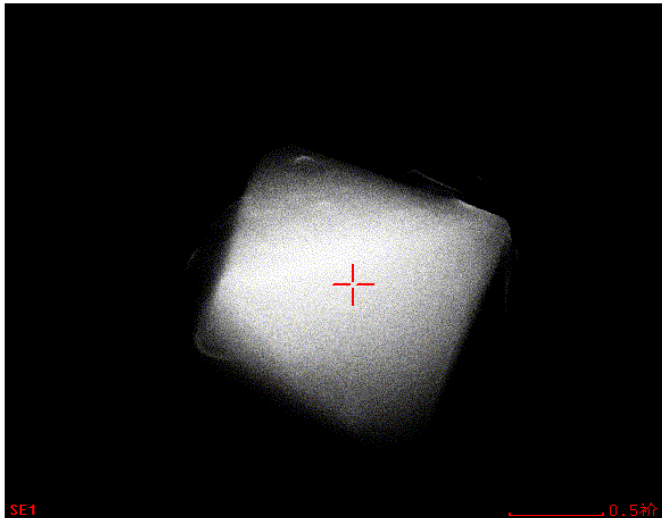
Solder & Facet “released” material

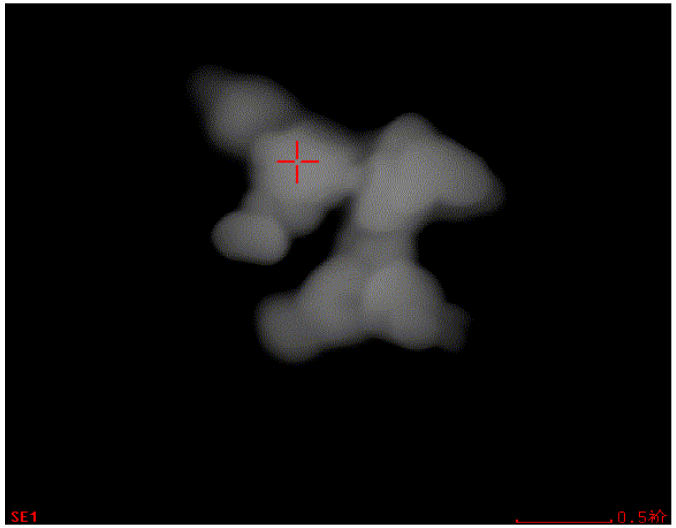




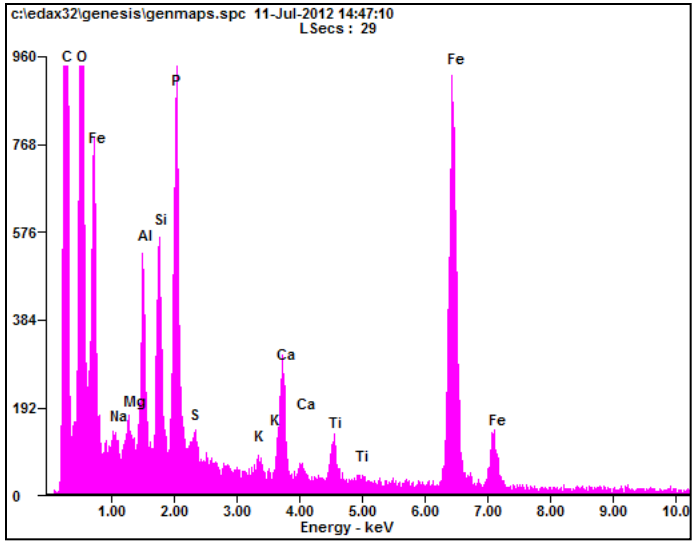


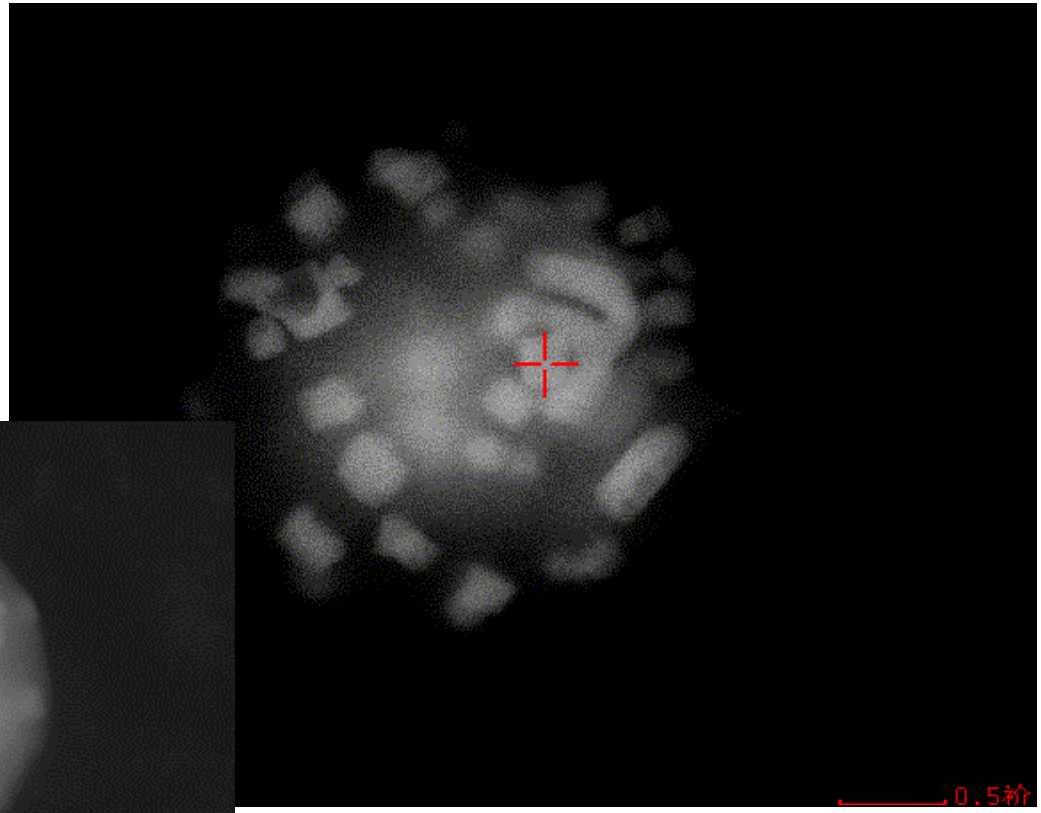


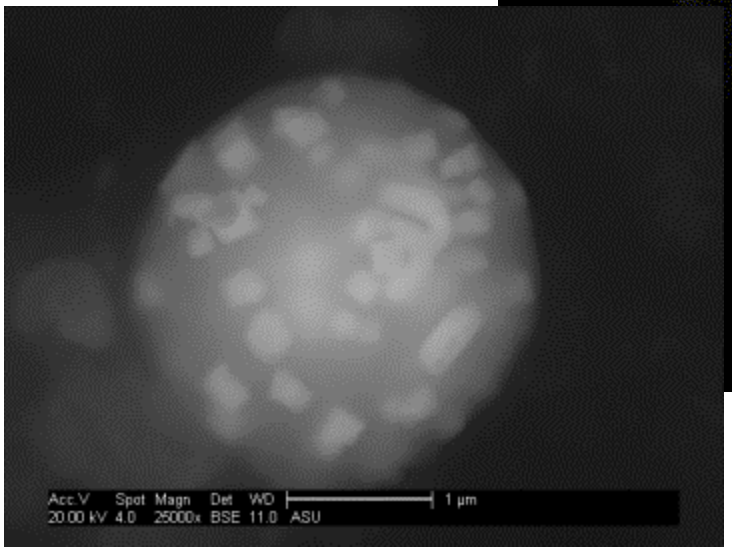




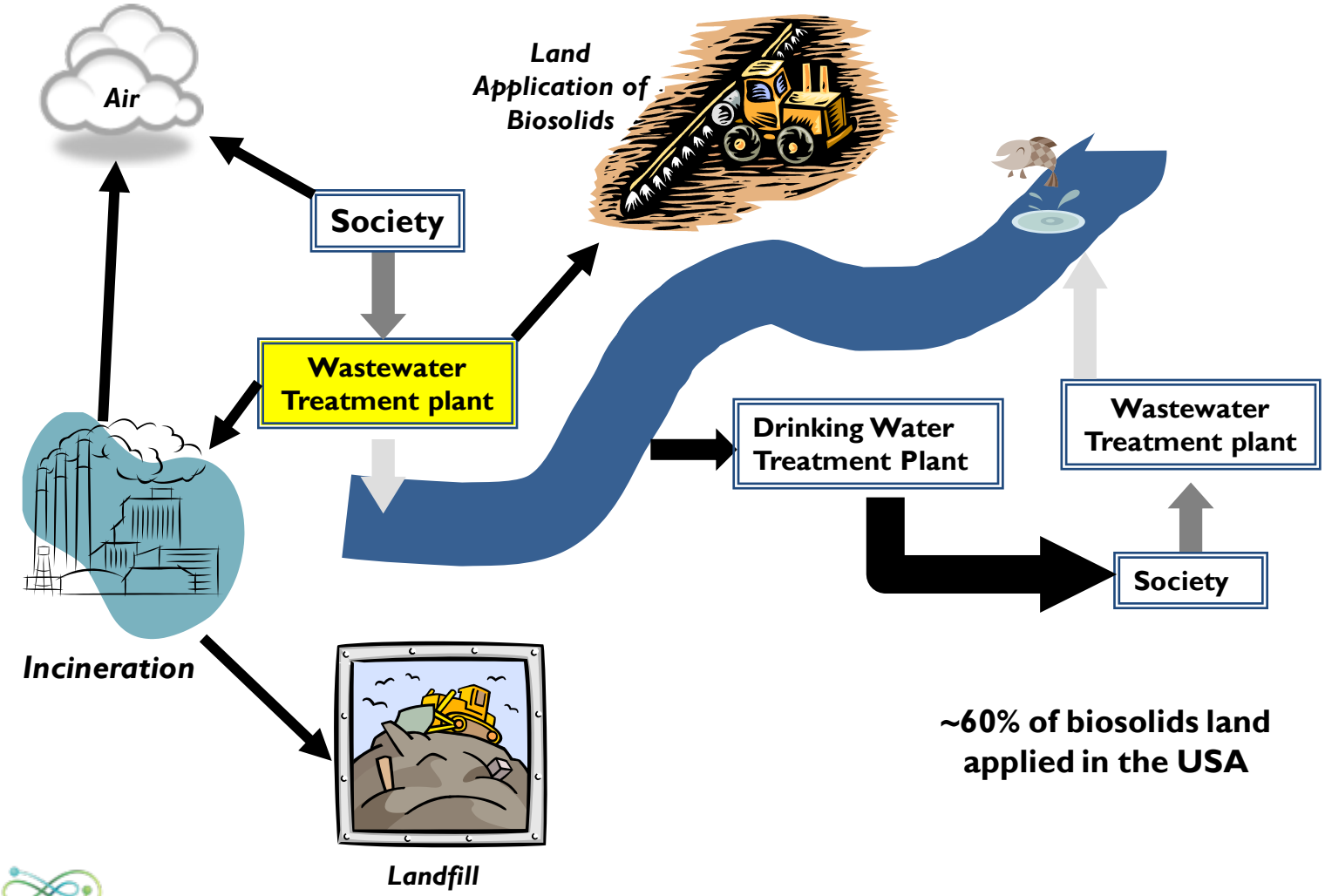
Fun – Complex Stuff





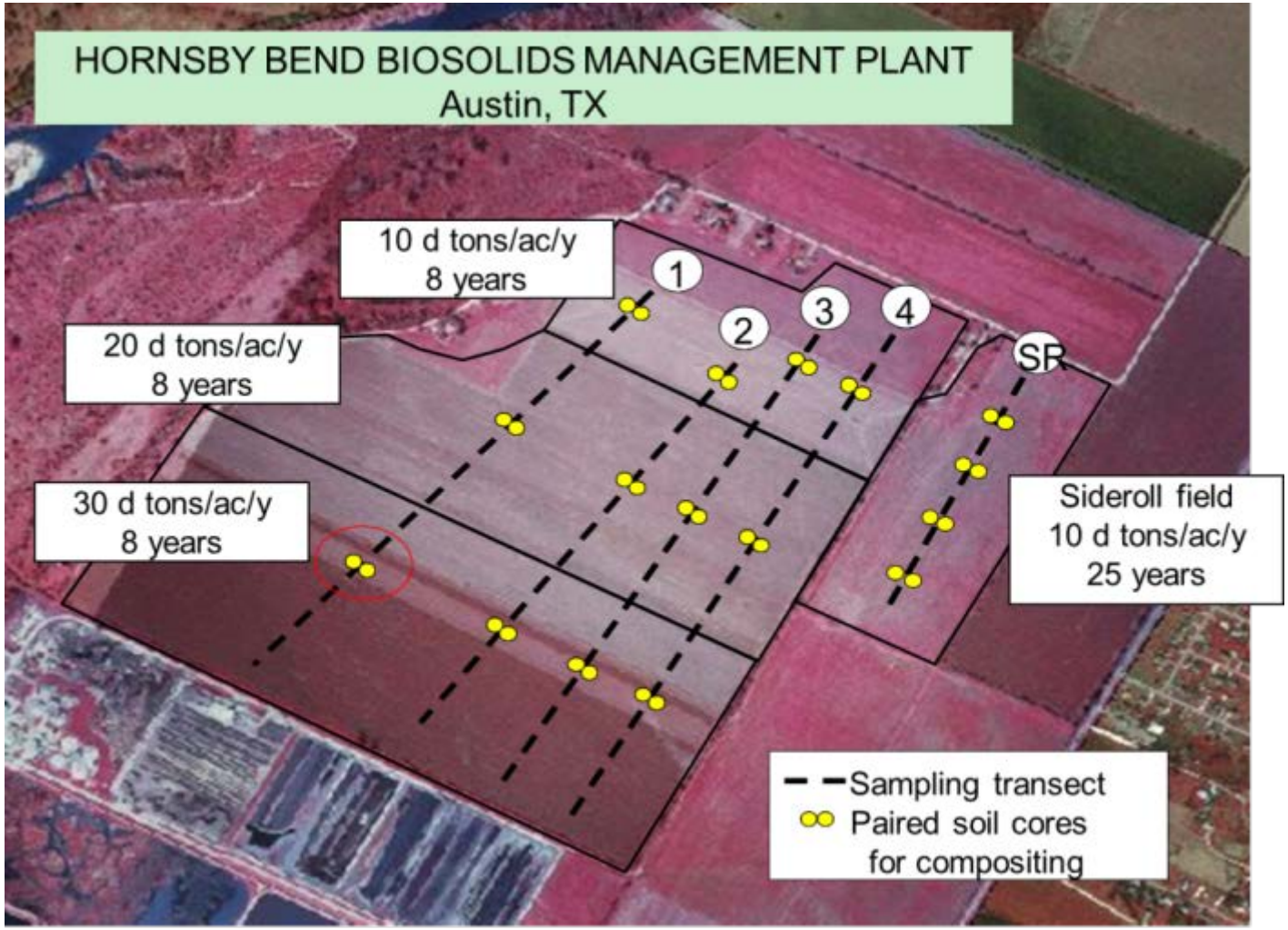


Where do Biosolids Go?

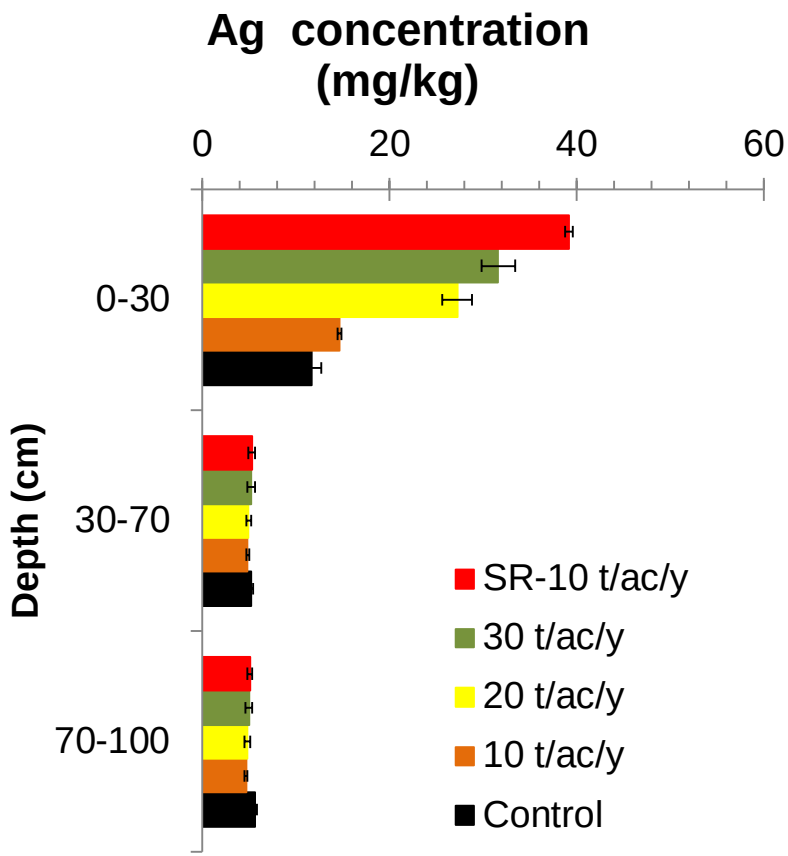


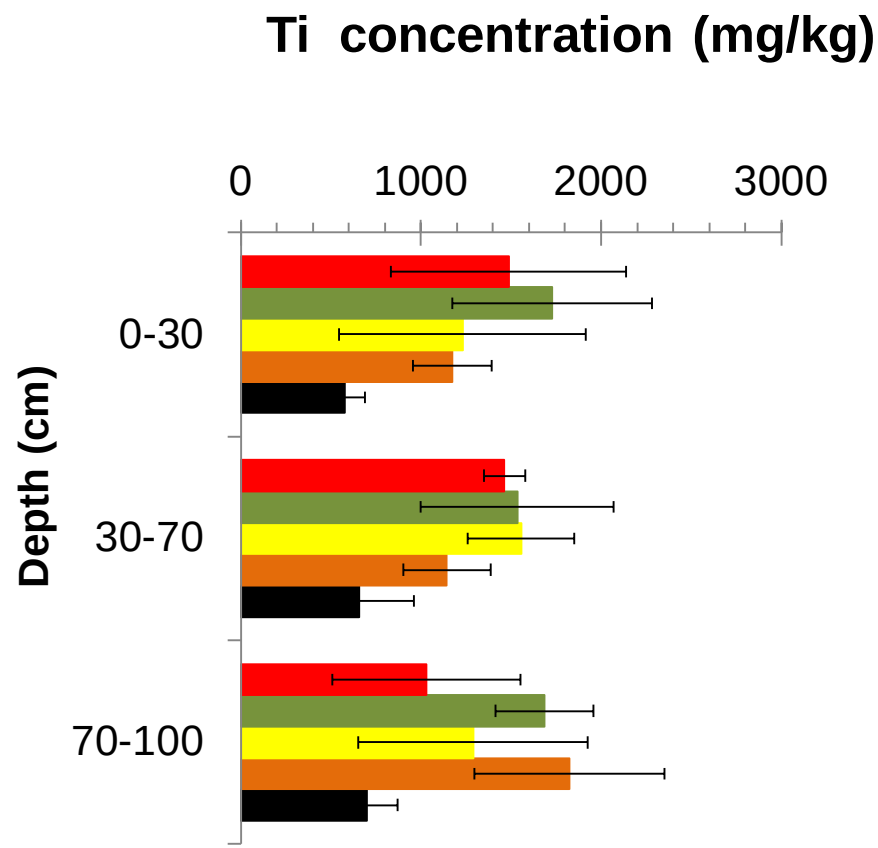
~60% of biosolids land applied in the USA

USDA Field Site Near Austin, TX
Long-term Biosolid Applications

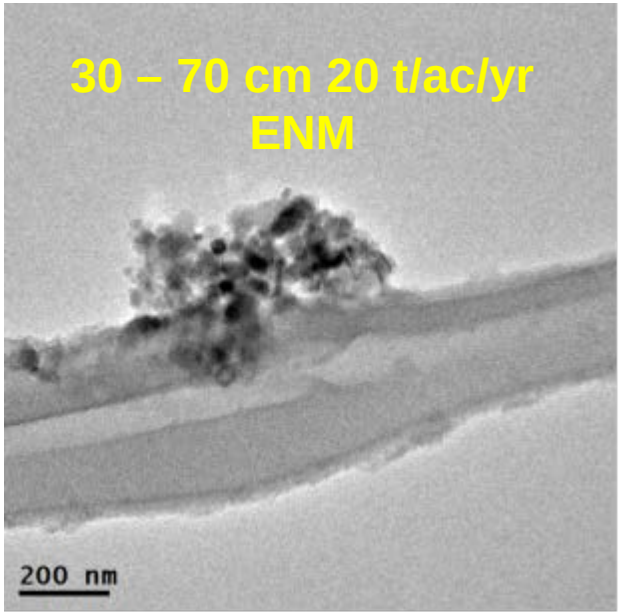


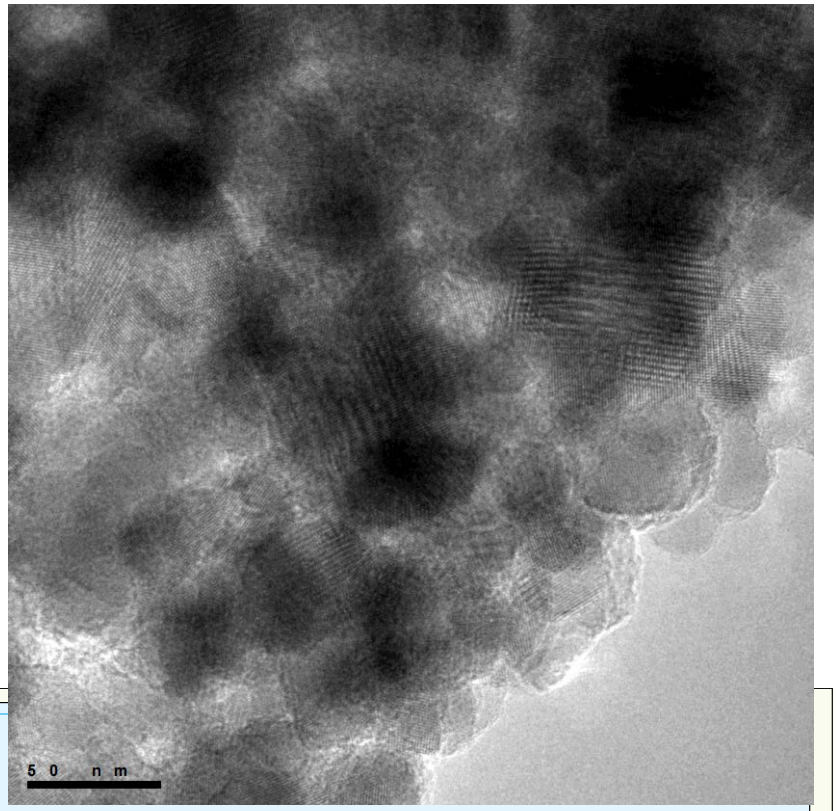
Each element has different soil profile after applying biosolids

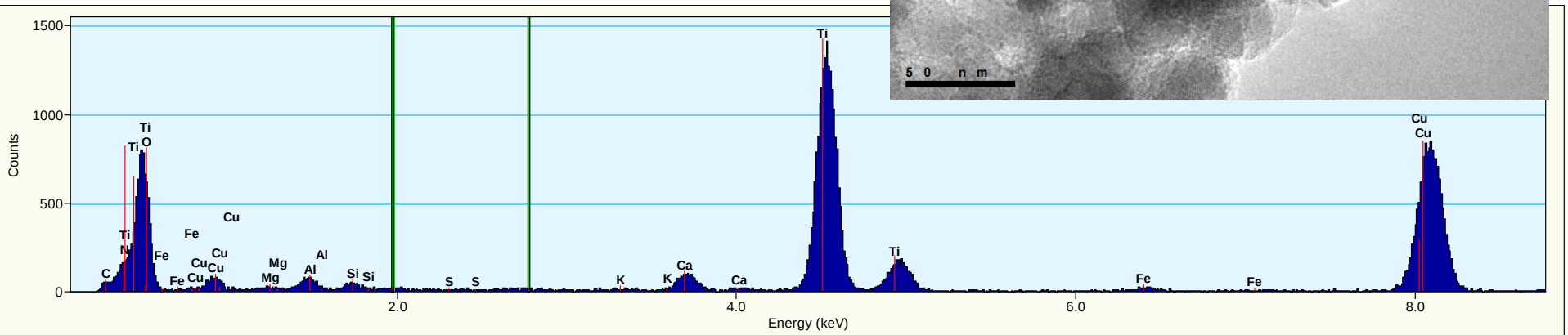




TiO_2 Nanomaterials are present in Biosolid Ammended Fields

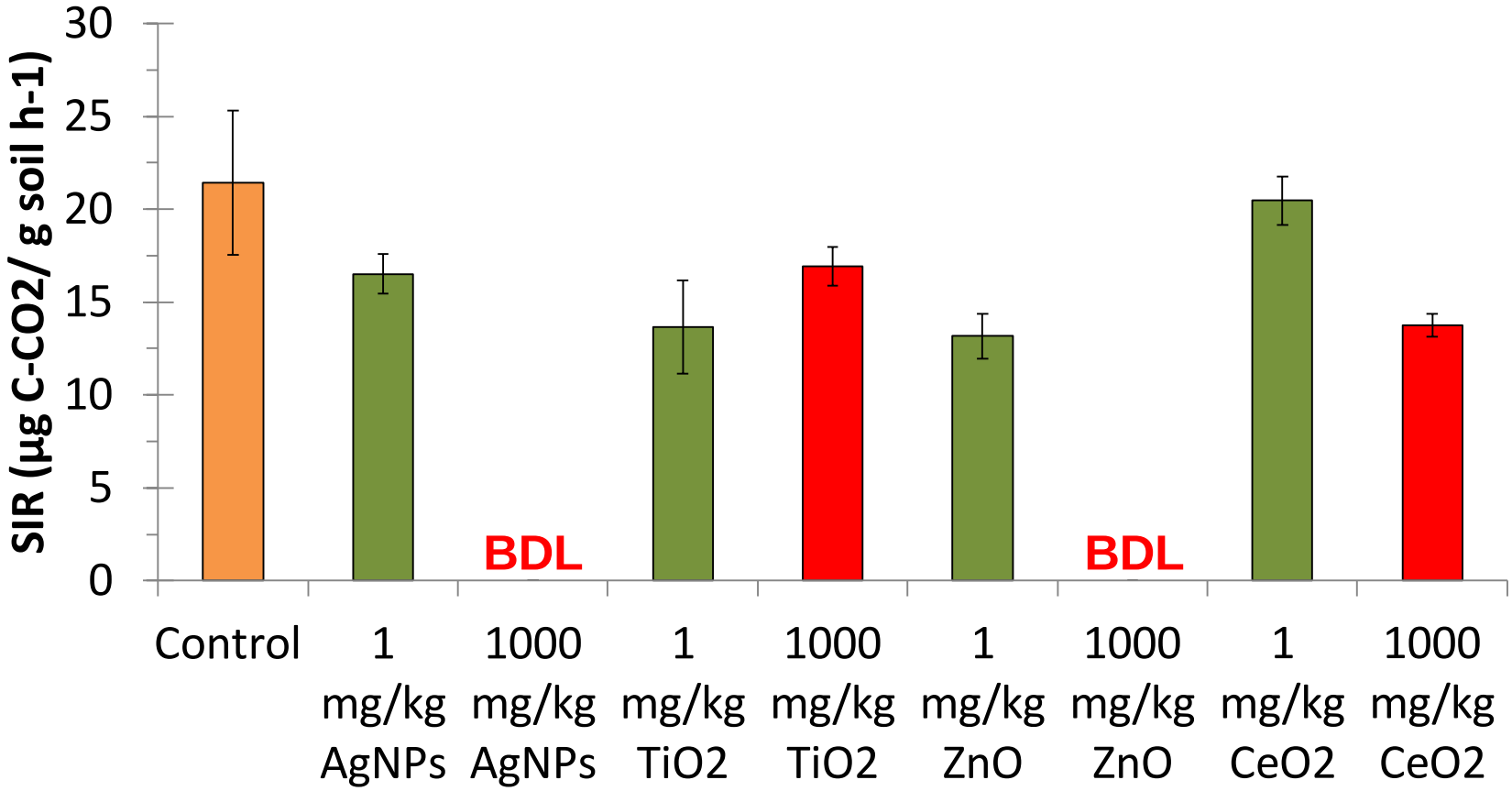






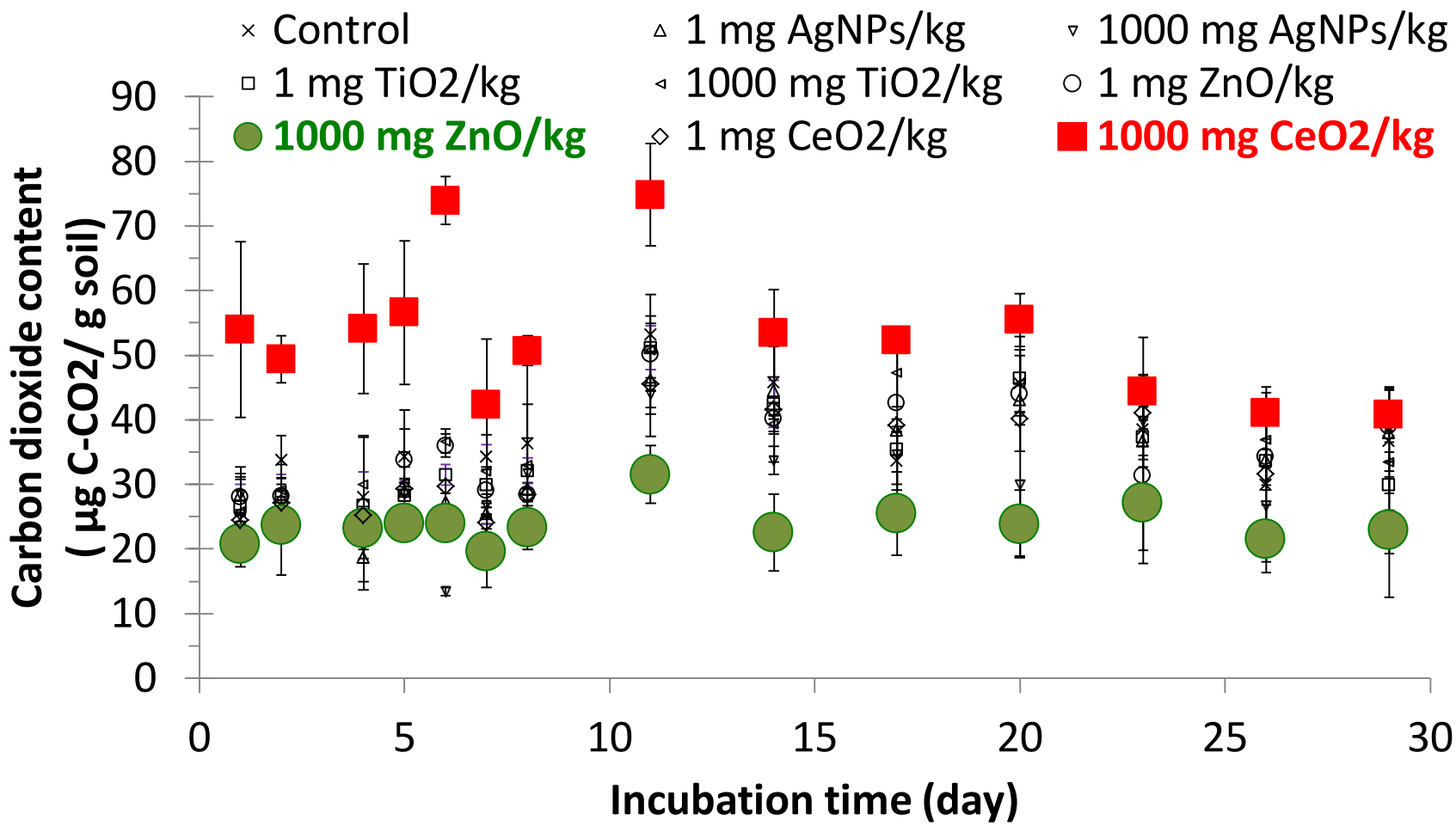
Do NMs in Biosolids Amended Soils Impact Biological Activity ?

Substrate Induced Respiration (28 day)



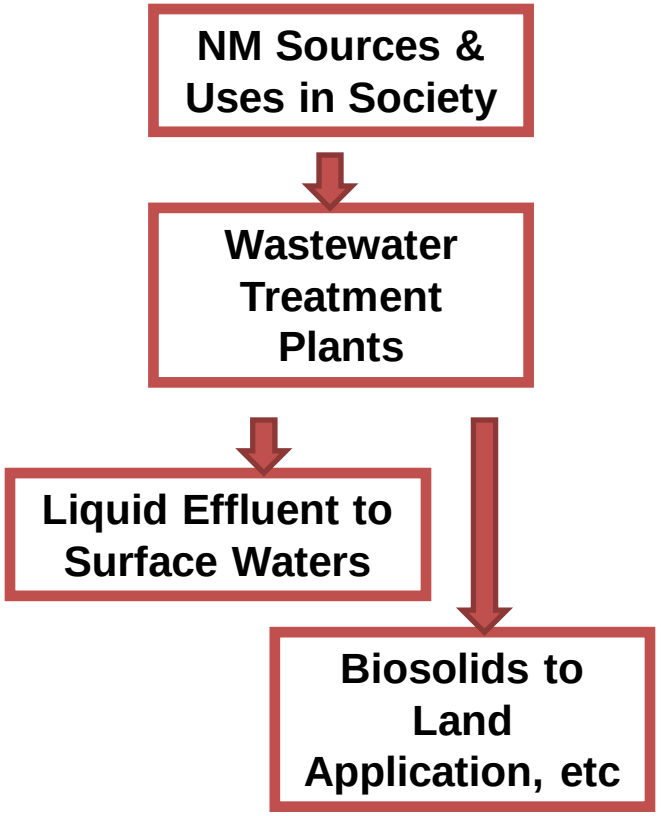
Basal Respiration Tests

CeO_2 increases CO_2 production



Summary

- Nanomaterials will be emitted from various industrial, commercial and residential products into sewers
- On-site treatment systems (lime, membranes) can be effective
- Uniqueness of Nanomaterials: They "accumulate" at interfaces
- At current levels, engineered NMs are UNLIKELY to impact WWTP operations



Acknowledgements

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  - Paul L. Busch Award 2006
  - Project U1R10
- NIH/NIEHS - NIH/NIEHS Nano-Go Funding: RES018801Z
- NSF *(CBET 1336542)*
- EPA (RD83322 & RD835580)
- SRC 425.040 & 425.052

- Contact: p.westerhoff@asu.edu

Semiconductor Research Corporation

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DOE BER
Grant number: DE-FG02-08ER64613

Upcoming Webinars

Monday, June 13, 2016 - 1pm Eastern Time

Self-Powered Wearable Devices for Monitoring Personal Health

Presenter: Veena Misra, Ph.D.

Director, NSF ASSIST Nanosystems Center

Professor, Department of Electrical Engineering

The effects of slurries on the proliferation, viability, or membrane integrity of model organisms.

Table 4 The effects of slurries on the proliferation, viability, or membrane integrity of model organisms. IC-50 levels were not determined (ND) under several conditions as noted

	IC-50 (mg mL^{-1})			
Assay	c-SiO_2	f-SiO_2	CeO_2	Al_2O_3
Bioluminescence of *A. fischeri*	ND[a]	ND[b]	ND[c]	ND[d]
Proliferation of A549 cells	3.8 ± 1.3	3.6 ± 0.2	ND[e]	ND[f]
Viability of A549 cells	1.2 ± 0.2	1.5 ± 0.2	ND[g]	ND[h]
Integrity of A549 cells	4.6 ± 0.2	3.1 ± 0.2	ND[g]	ND[h]

Fig. 11 Ecotoxicity findings determined in bioassays with freshwater crustaceans (*Cladocera*) (A) and algae (B) for three major classes of metal-based nanoparticles used in CMP slurries. Note: *D. similis* = *Daphnia similis*; *D. magna* = *Daphnia magna*; *D. pulex* = *Daphnia pulex*; *C. dubia* = *Cerodaphnia dubia*; *P. subcapitata* = *Pseudokirchneriella subcapitata*. Legends: Data for CeO_2 (■), Al_2O_3 (□), and SiO_2 (▨).

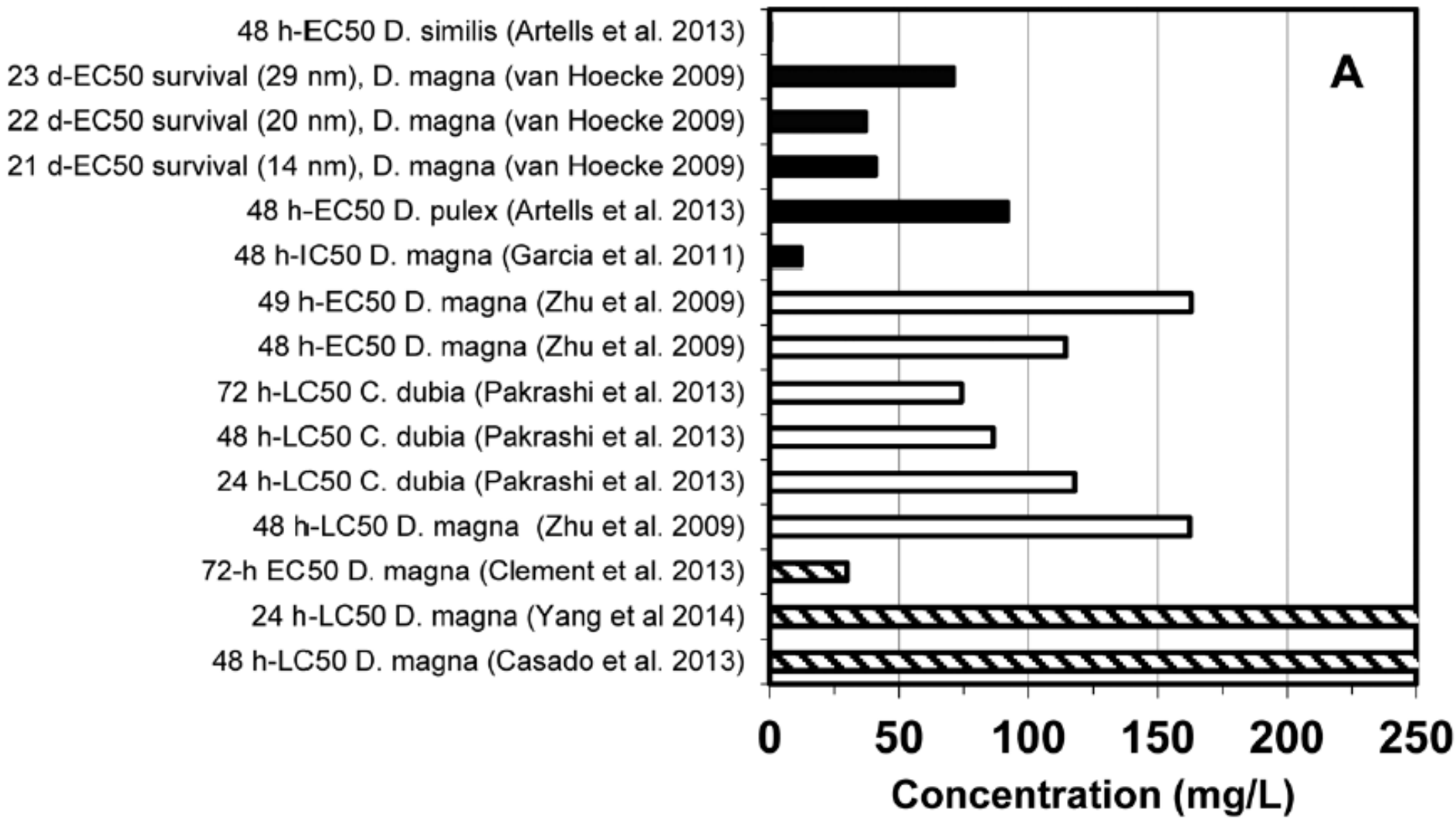
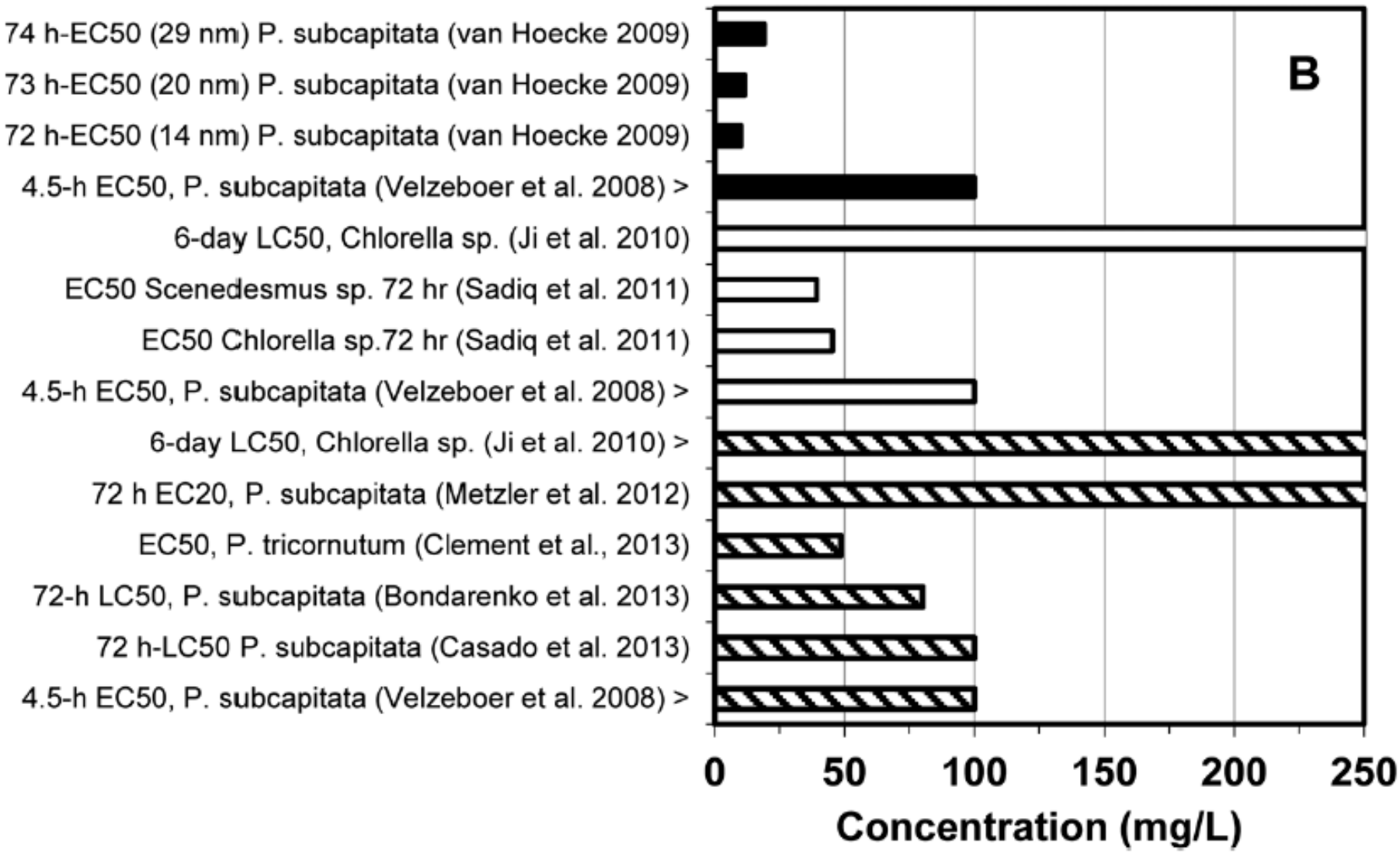


Fig. 11 Ecotoxicity findings determined in bioassays with freshwater crustaceans (*Cladocera*) (A) and algae (B) for three major classes of metal-based nanoparticles used in CMP slurries. Note: *D. similis* = *Daphnia similis*; *D. magna* = *Daphnia magna*; *D. pulex* = *Daphnia pulex*; *C. dubia* = *Cerodaphnia dubia*; *P. subcapitata* = *Pseudokirchneriella subcapitata*. Legends: Data for CeO_2 (■), Al_2O_3 (□), and SiO_2 (▨).



Lifecycle Perspective of NMs

Societal Use of Products

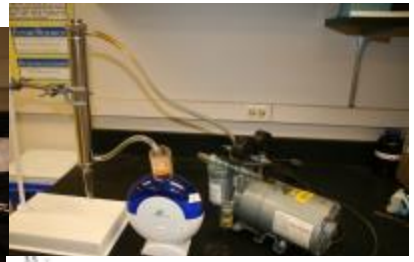
Measuring Releases of NPs in various media

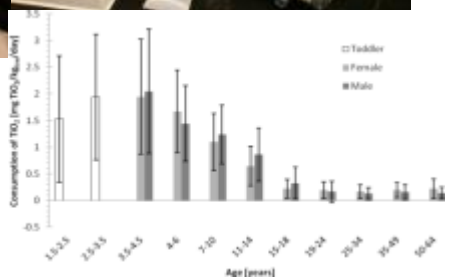
Removal of NPs at WWTPs

NPs in biosolids that are land applied

Lifecycle Perspective of NMs

Societal Use of Products





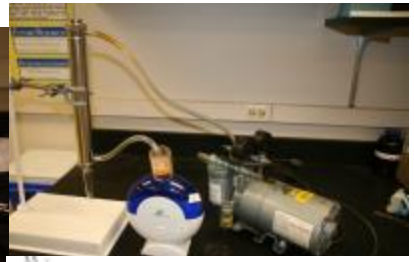
Measuring Releases of NPs in various media

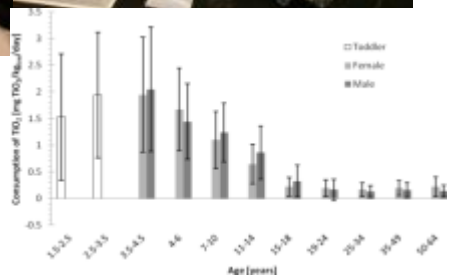
Removal of NPs at WWTPs

NPs in biosolids that are land applied

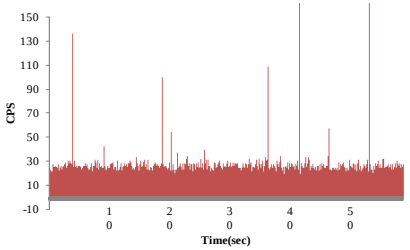
Lifecycle Perspective of NMs

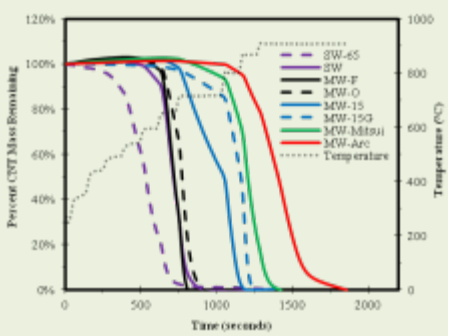
Societal Use of Products





Measuring Releases of NPs in various media



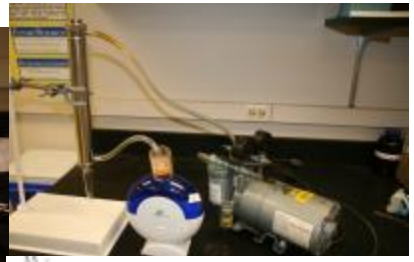


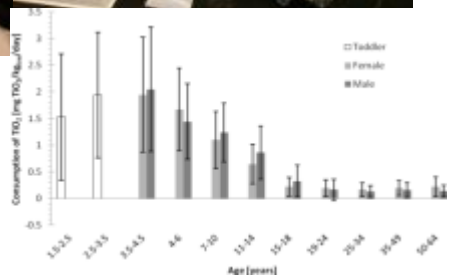
Removal of NPs at WWTPs

NPs in biosolids that are land applied

Lifecycle Perspective of NMs

Societal Use of Products





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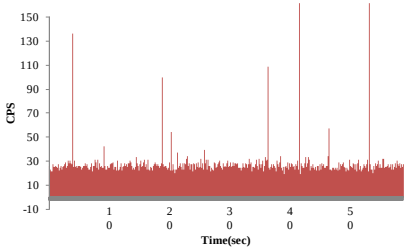
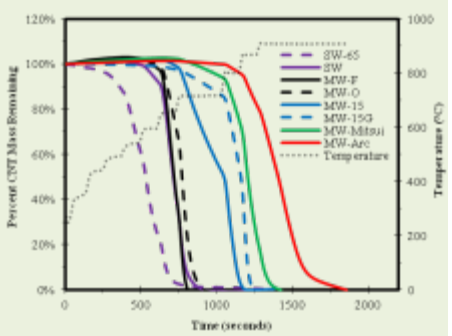
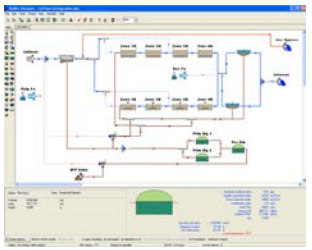
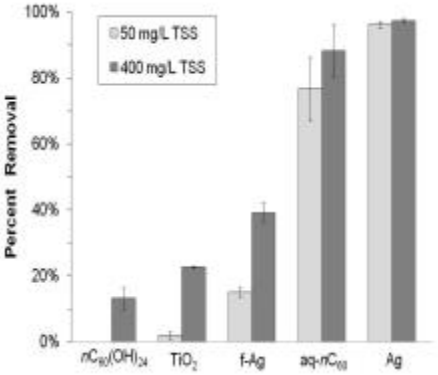




Removal of NPs at WWTPs

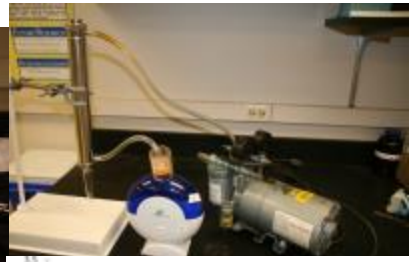


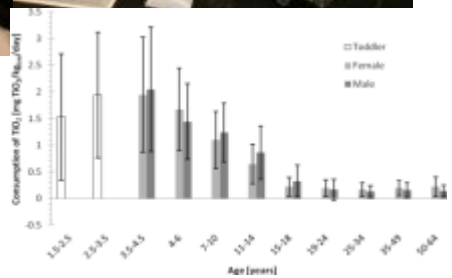


NPs in biosolids that are land applied

Lifecycle Perspective of NMs

Societal Use of Products





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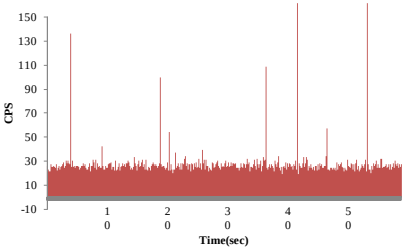

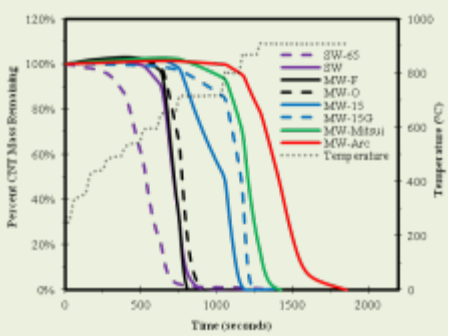

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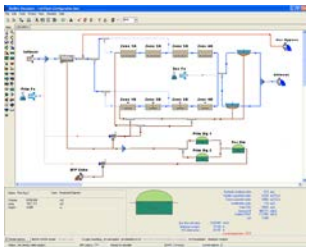
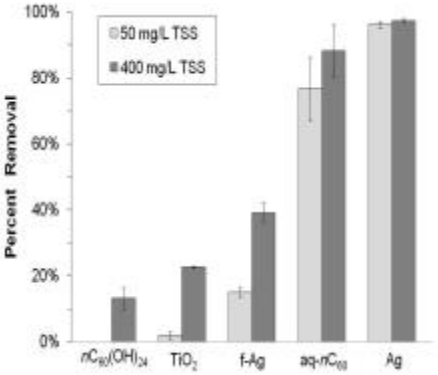
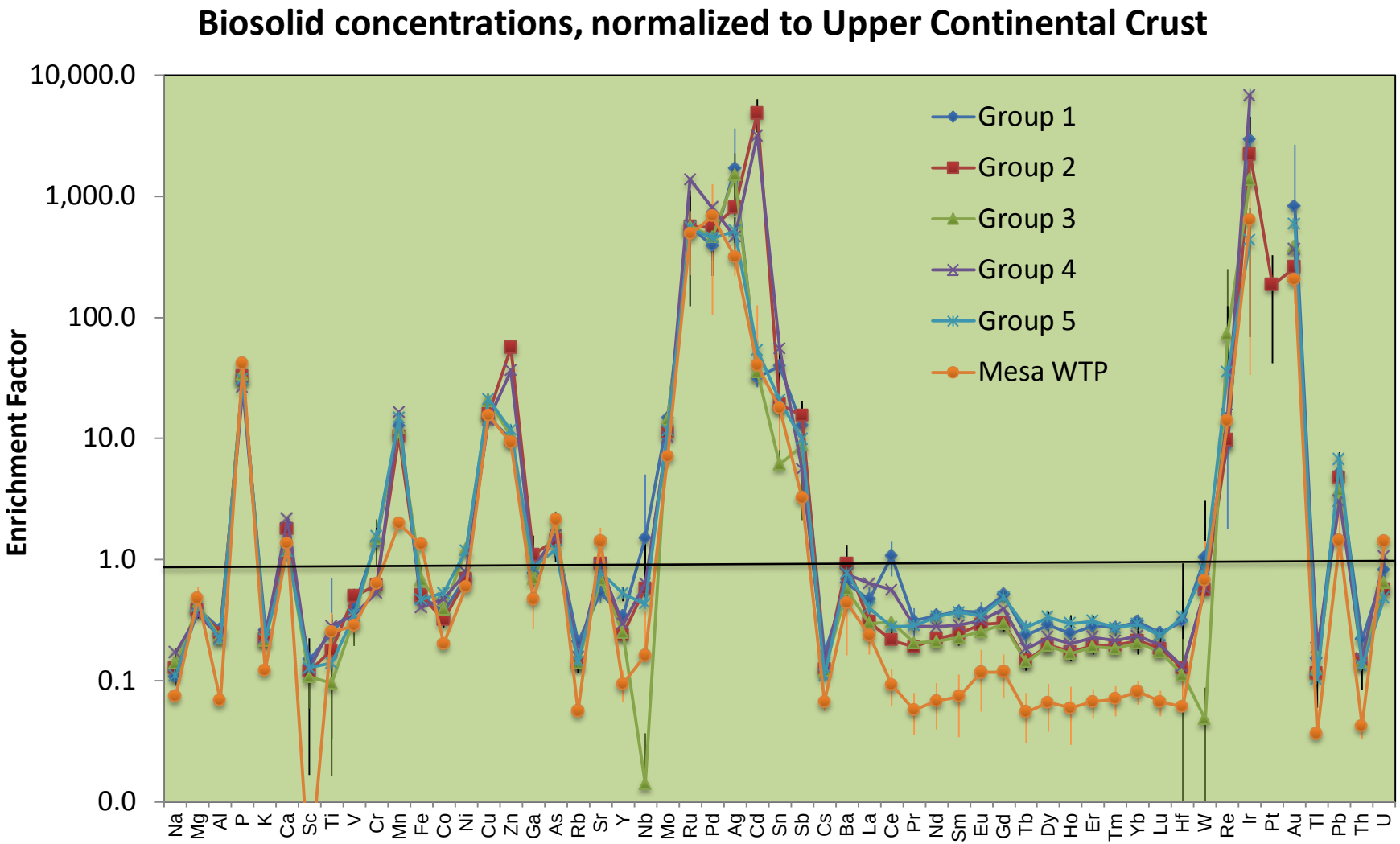




NPs in biosolids that are land applied

Big Picture – EPA Composite Biosolids



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