Gordon Research Conference
Environmental Nanotechnology

http://www.grc.org/programs.aspx?id=14914

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West Dover, VT

Fate of Engineered Nanomaterials in Wastewater Biosolids, Land Application and Incineration (*WERF #U1R10*)

Paul Westerhoff, Ph.D., PE

Professor of Environmental Engineering & Associate Dean For Research

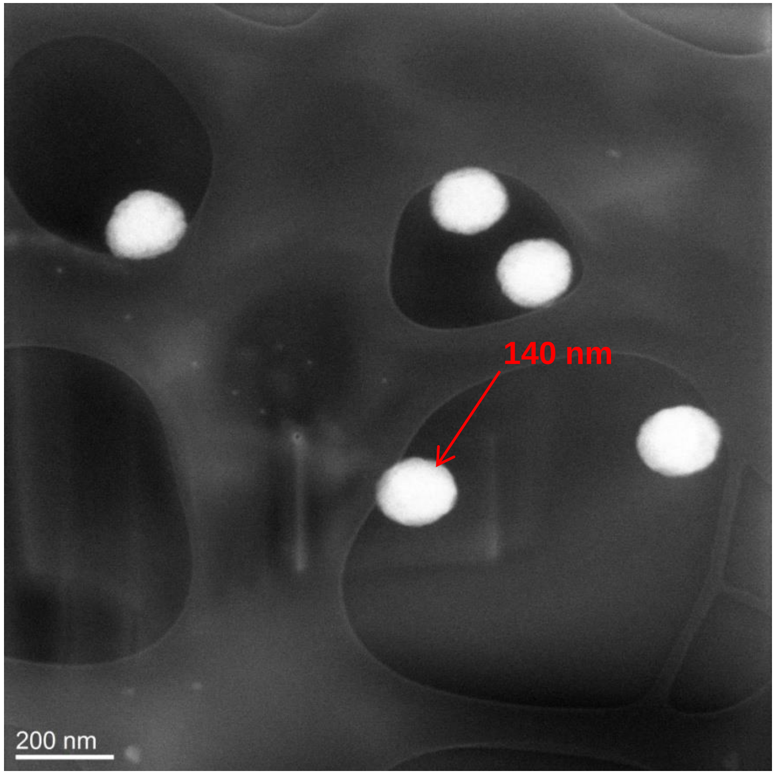
Arizona State University (Tempe, AZ)

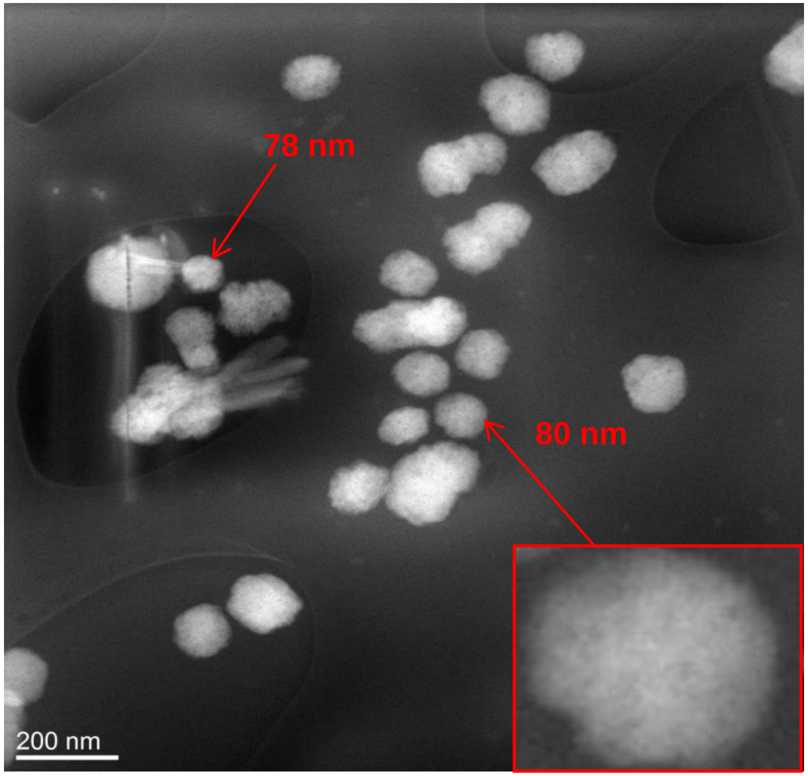
Contributors:

K. Hristovski, Yu Yang, P. Herckes

Nanoparticles in effluent from Arizona Wastewater Treatment Plants

Should we be concerned?





Should the public be concerned?
History of Emerging Pollutants in Water

Emerging Pollutants Are <u>things</u> in our water we know little about but <u>scare</u> us

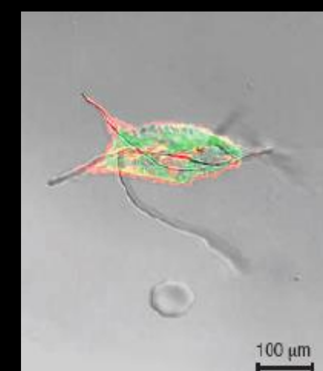
All nano is

US Invests ~ $1.5B/year in Nano R&D

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

Where is Nano being Used in Society?

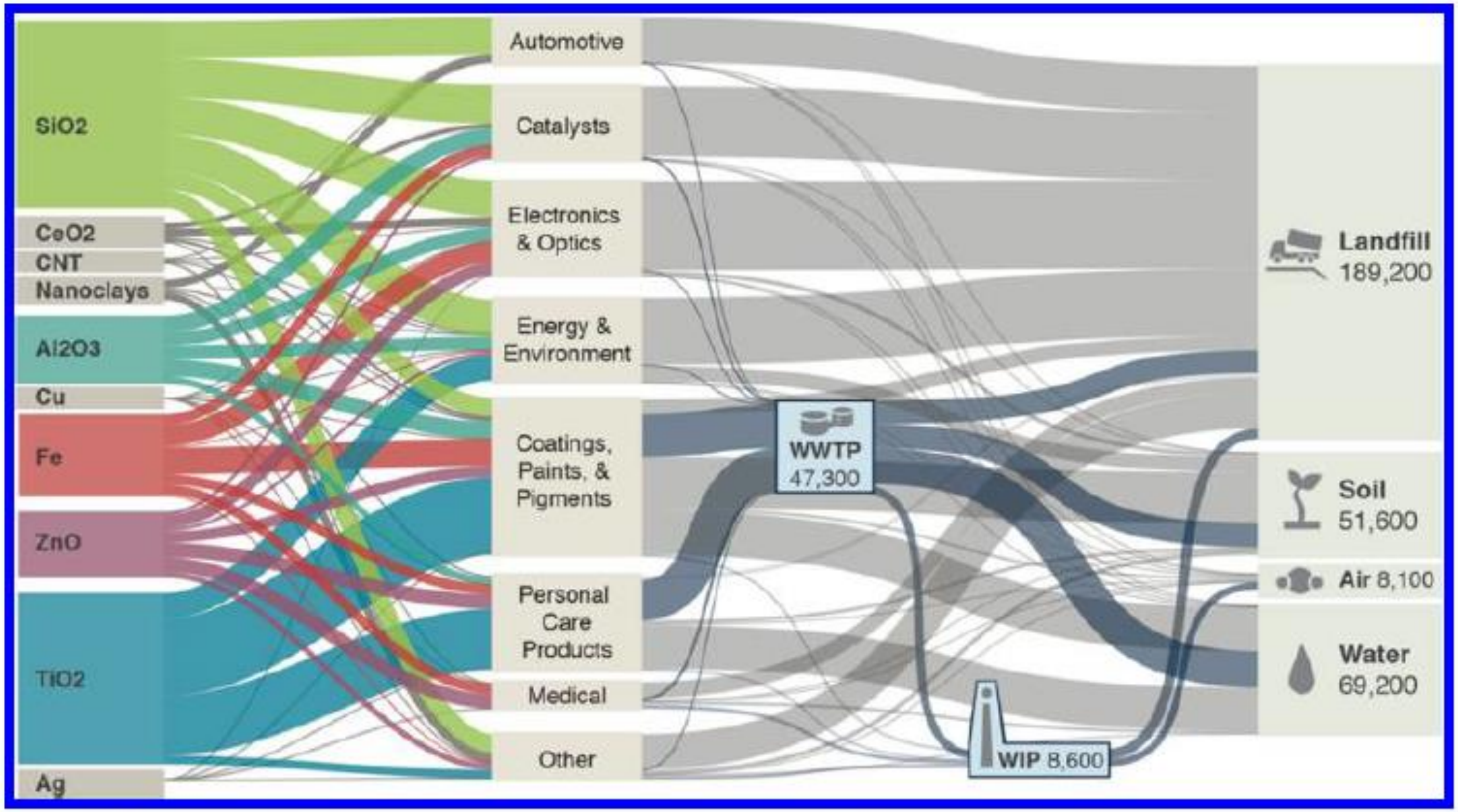
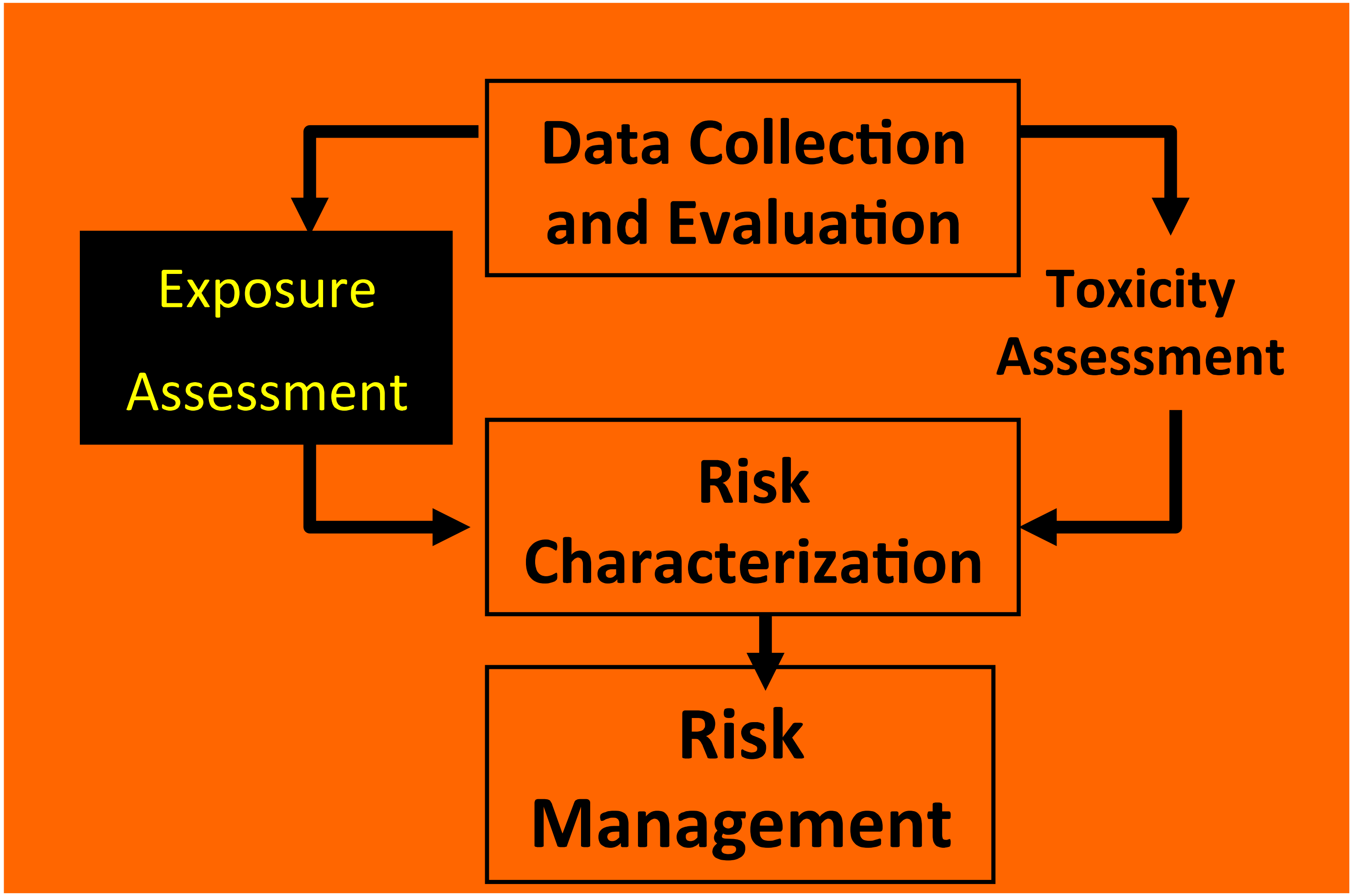


Figure 1. Estimated global mass flow of ENMs (in metric tons per year) from production to disposal or release, considering high production and release estimates as of 2010. Production data are from ref 14, without modification.

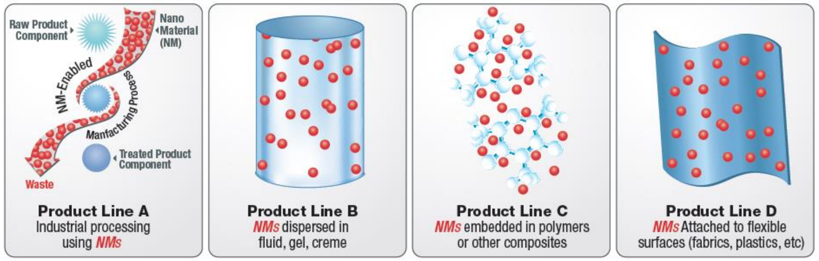
Predicted Releases of Engineered Nanomaterials: From Global to Regional to Local

Arturo A. Keller* and Anastasiya Lazareva

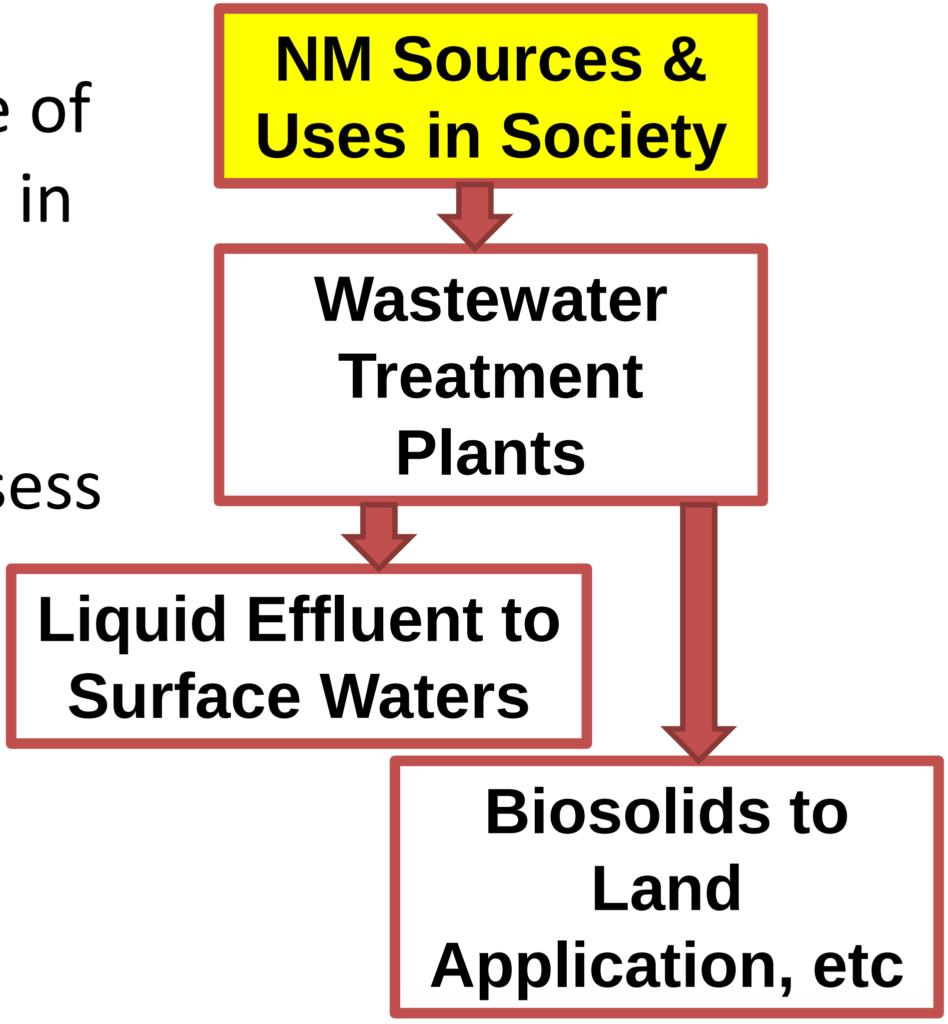
Westerhoff Lab Focus



Presentation Outline & Goals

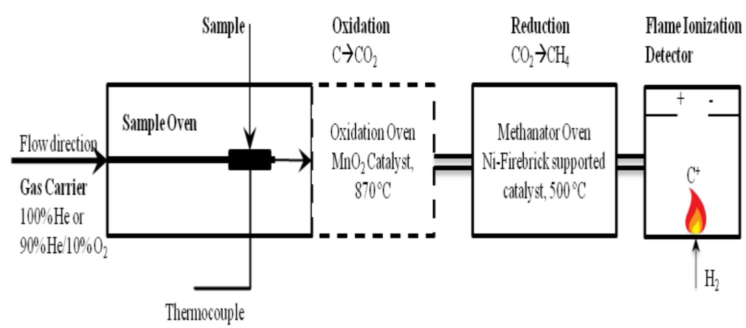


- Understand sources & fate of engineered nanomaterials in sewage systems
- Demonstrate analytical techniques required to assess nanomaterial exposures
- Begin dialog on a national nanomaterial monitoring program



Exposure Assessments for Nanomaterials Requires Rethinking **Analytical Methods**

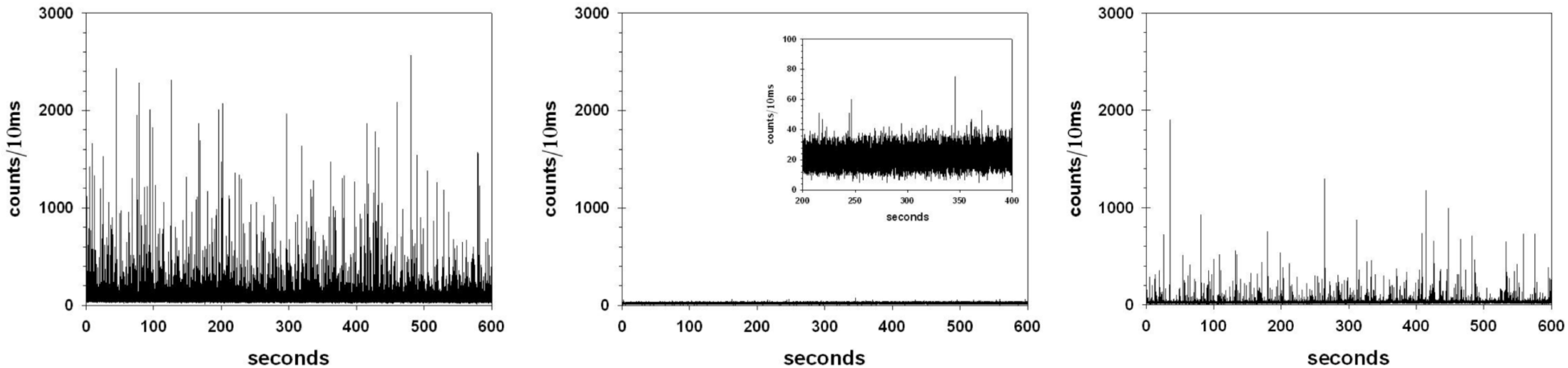
- Metalic NPs: TiO_2, Ag, SiO_2, CeO, Au
  - Single-Particle ICP-MS
  - FFF/SEC-ICP-MS
  - TEM / SEM
- Carbonaceous: fullerenes (C_{60}) & nanotubes & graphene
  - LC/MS
  - HPLC
  - Thermal combustion
  - Raman



Nanoprospecting across urban water gradient

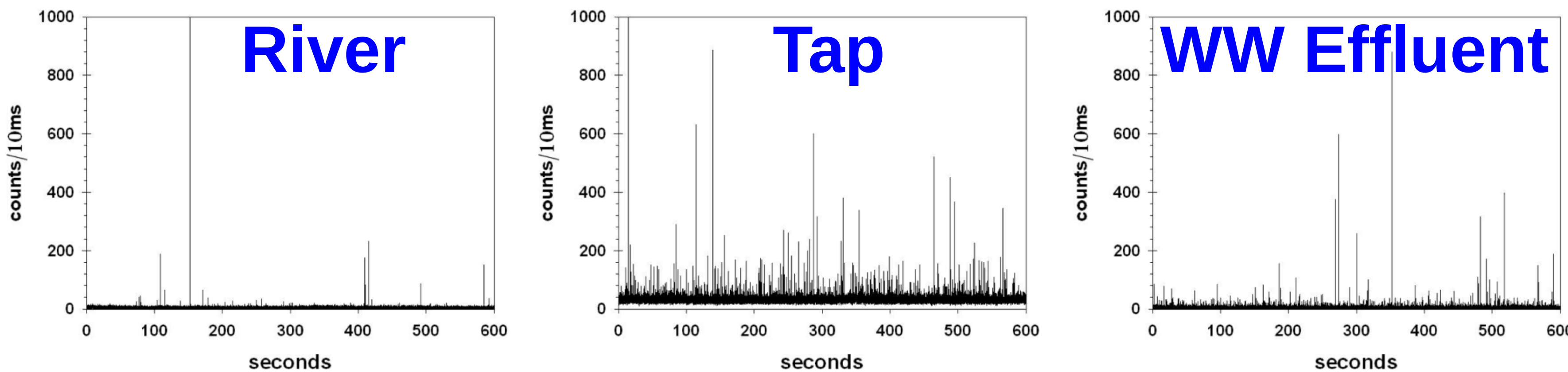
using Single Particle-ICP-MS

River **Tap** **WW Effluent**



(a) (b) (c)

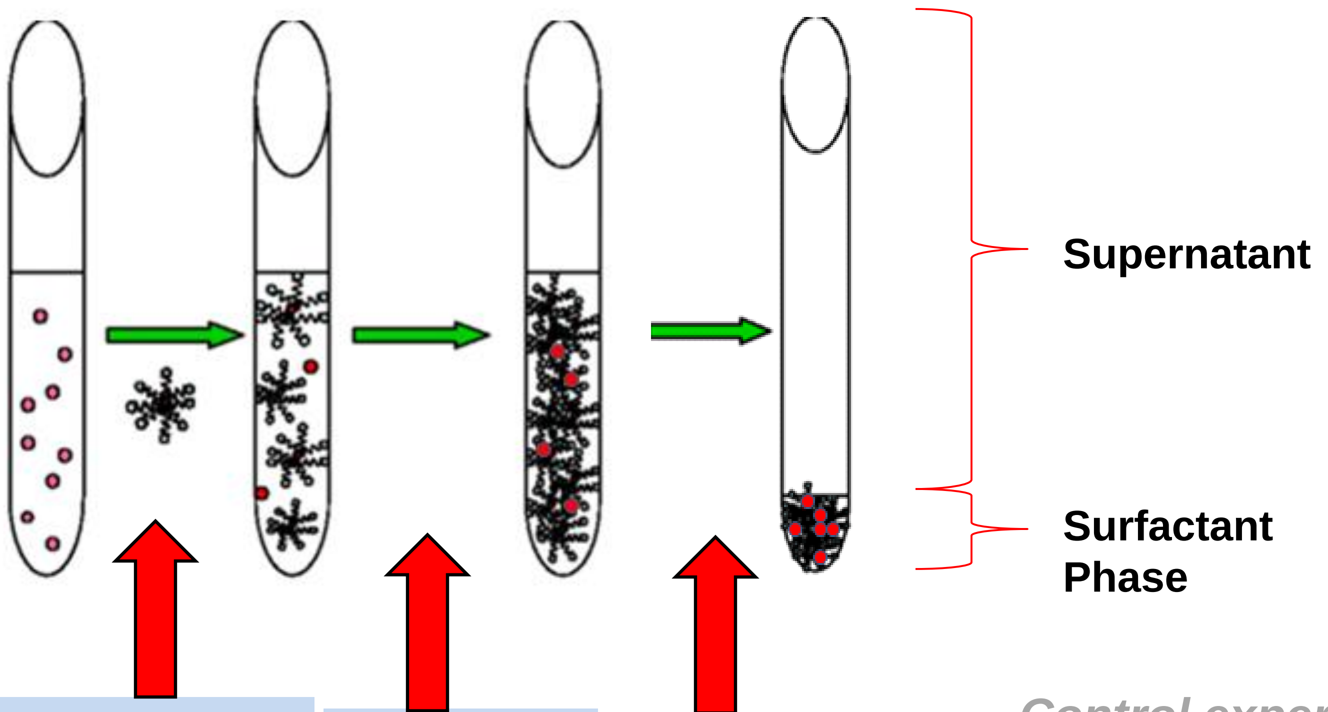
Titanium (↑) **Silver (↓)**



(g) (h) (i)

Lee et al. (in-prep)

Cloud-point Extraction of Waters



Step 1.
Adding surfactant (Triton 114) to get a final concentration of 5% (W/V)

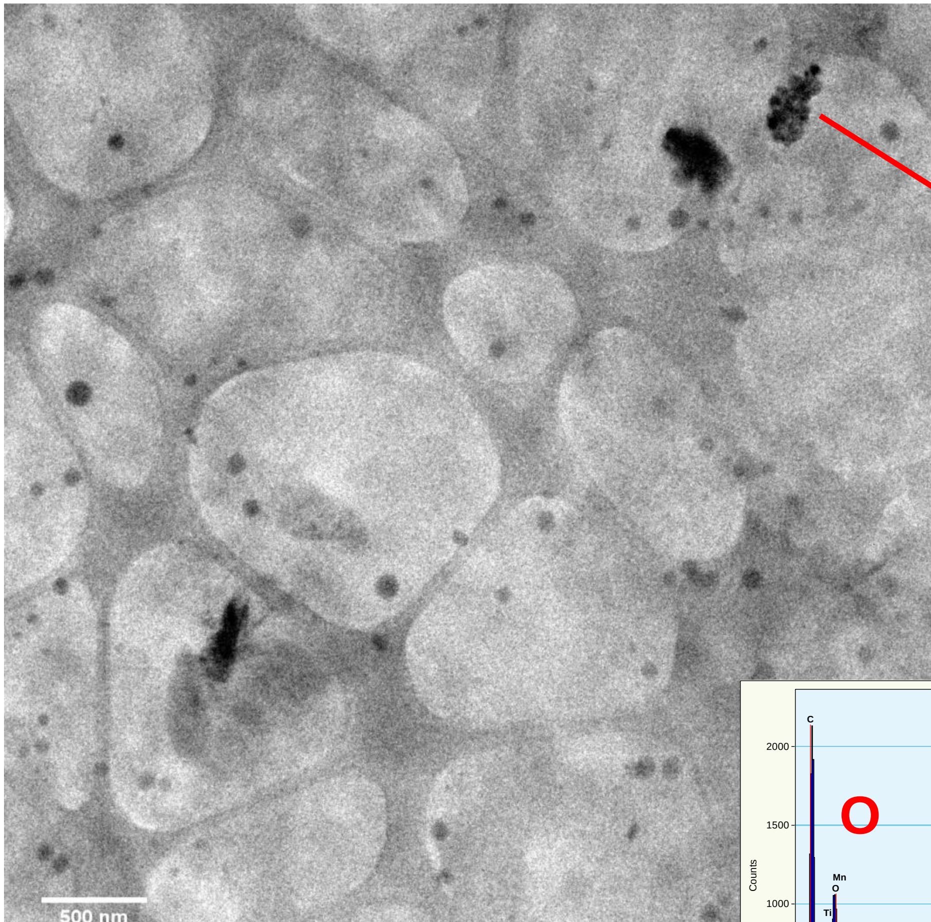
Step2.
Water bath at 40 °C for 30 minutes

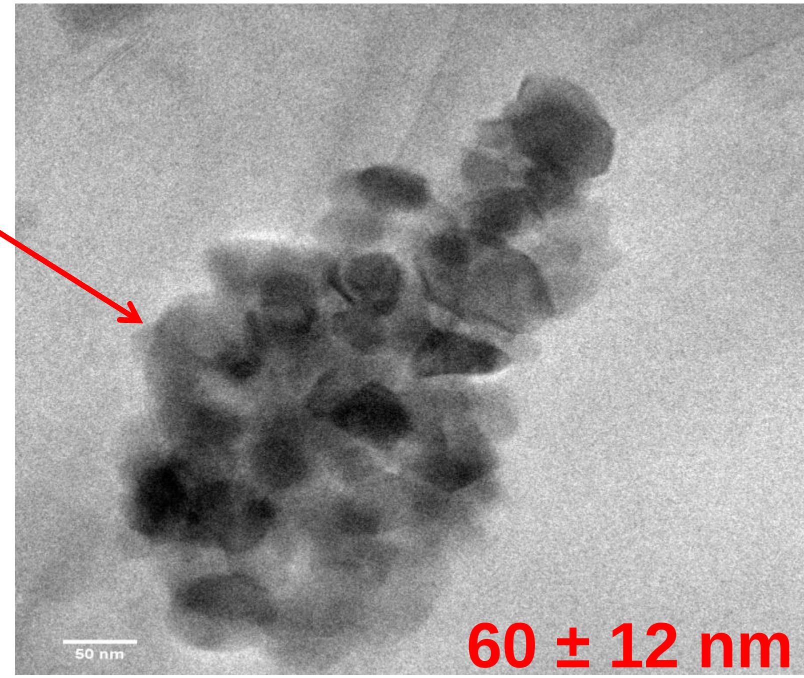
Step 3.
Cooling down, and centrifuge

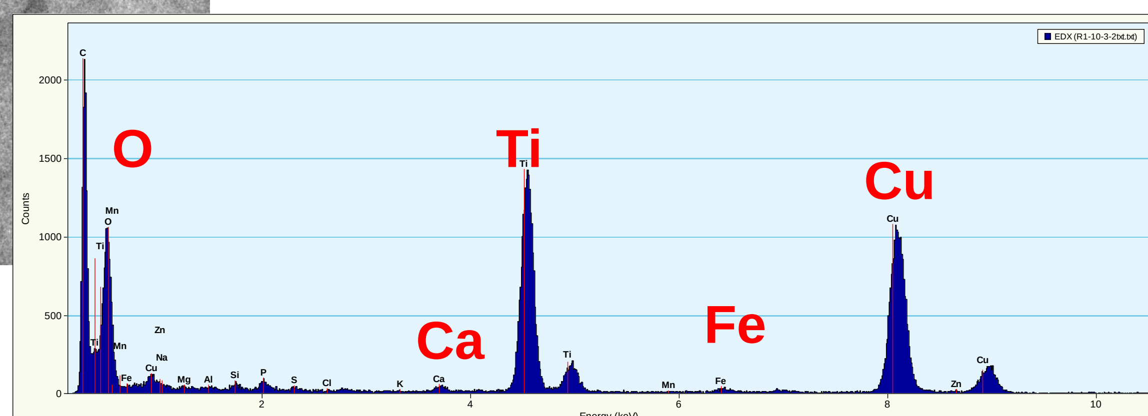
Control experiments with several NMs showed >85% recoveries at ~0 °C

Ojeda.,et.al., Microchimica Acta, 2012
Hartmann et al., Anal. Chem, 2014

TEM on Cloud-Point Extracted water sample from Salt River, AZ

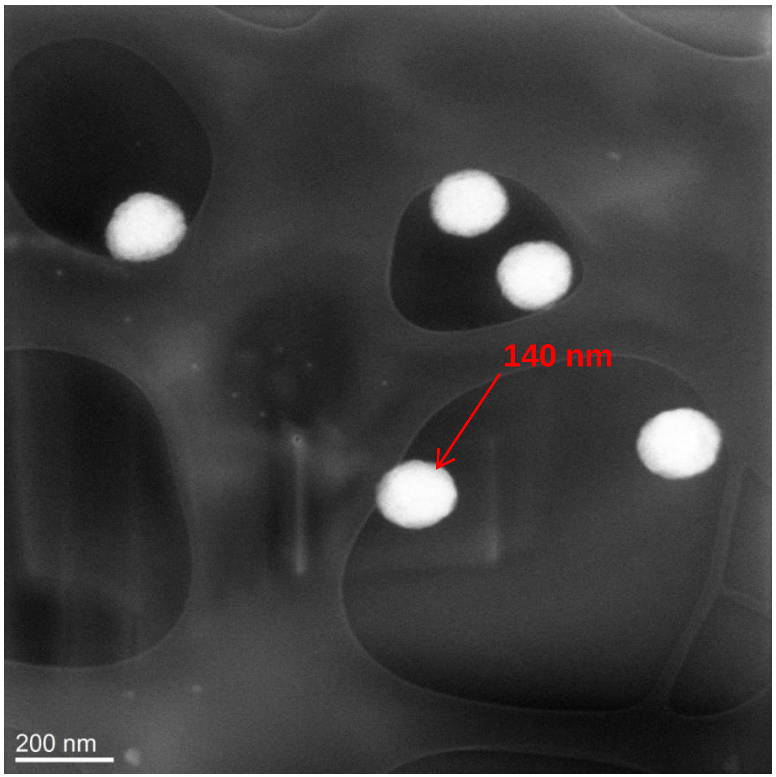


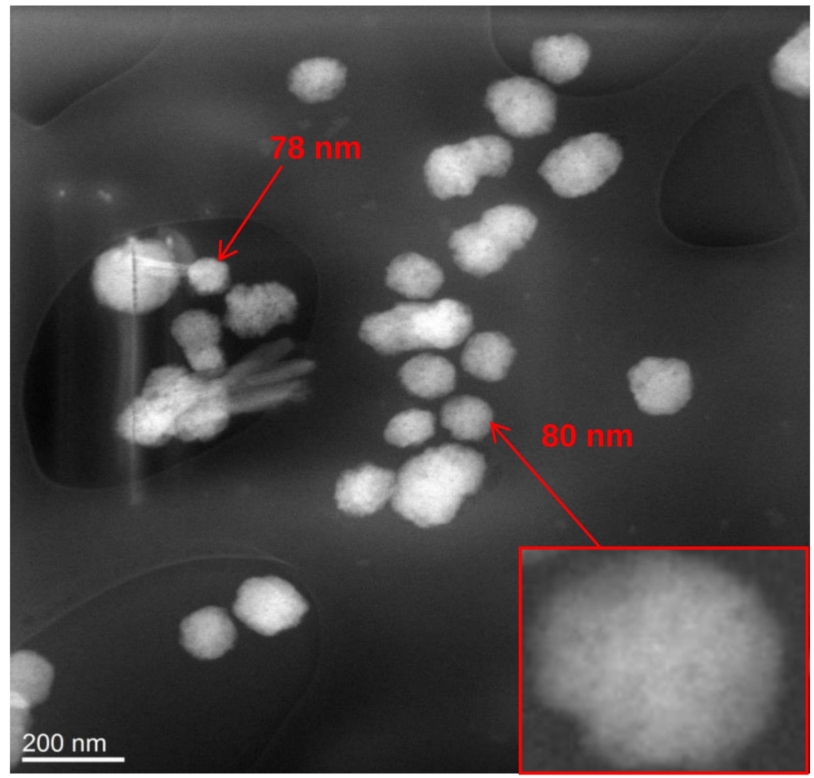




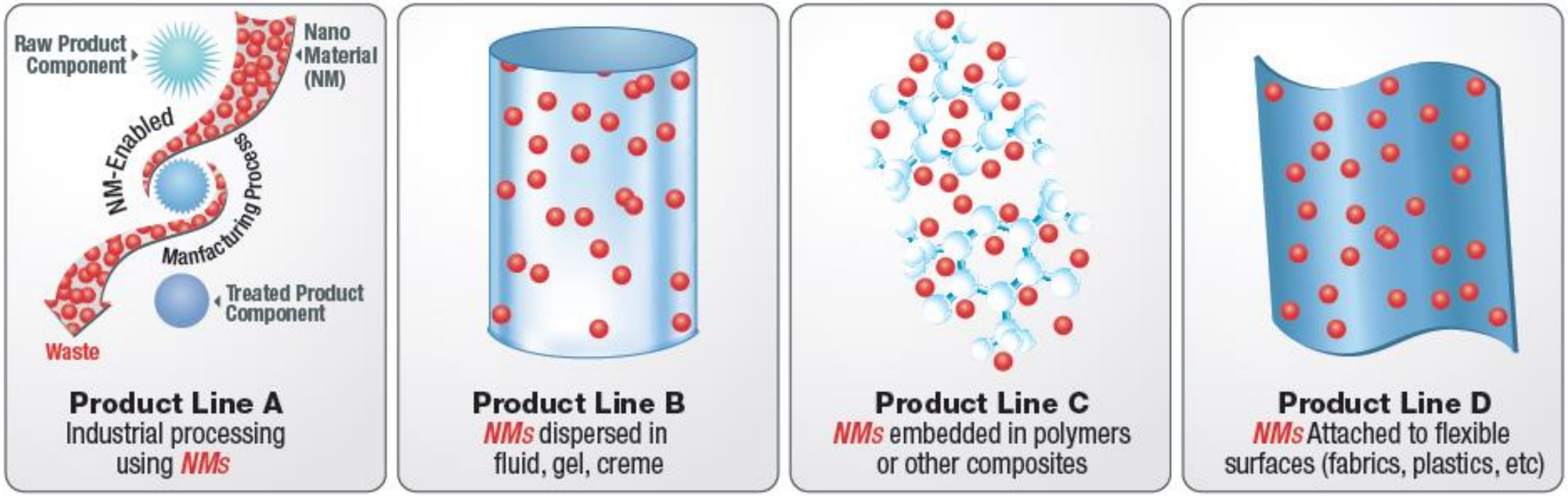
Nanoparticles in effluent from Arizona Wastewater Treatment Plants

Where did they come from?



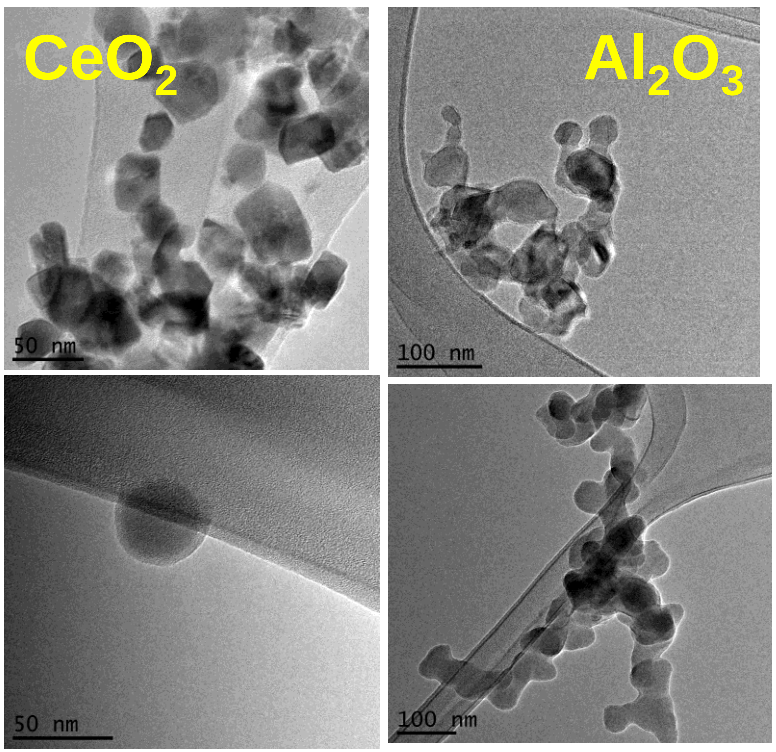


Sources of Nano Into Sewers



Product Line A – Polishing Agents

Chemical-Mechanical Polishing (CMP) fluids



Colloidal Silica **Fumed Silica**

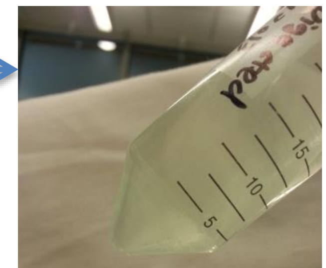
- CMP Use is ~100 mL / wafer: **0.2 mg/L in sewage** (5%NP @ 100 galCMP/d into 25 MGD)
- On-site industrial treatment designed to remove Cu, As, F, etc in wastestreams & NOT CMP nanoparticles
- Release Potential: One full-scale system removed >98% of Al and Ce, but only 50% of Si
- NPs accumulate in settled solids which are landfilled
- NPs in treated effluent enter municipal sewer system

Product Line C

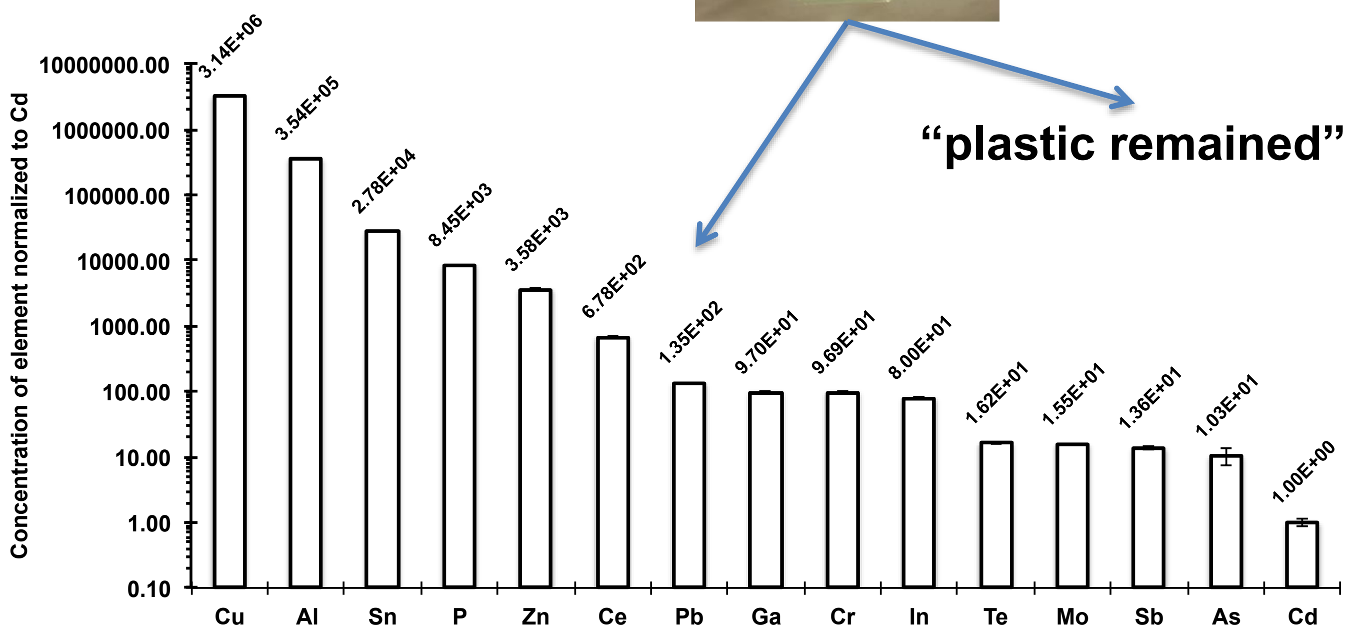
Example: LED lighting

LED light strip from Home Depot

Multiple types of acid digestion (hot plate / microwave)



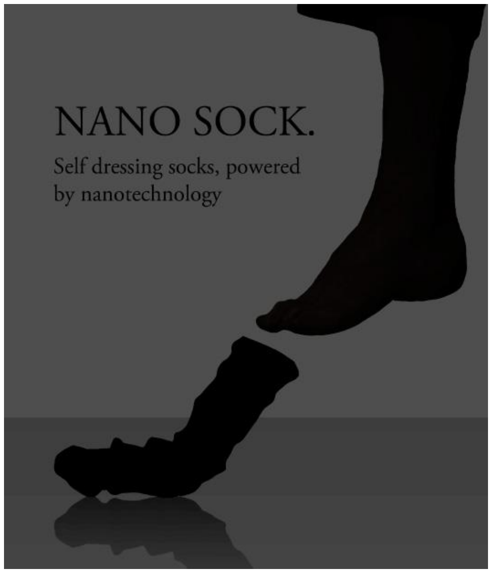
"plastic remained"



HF and HNO3(1:4 v/v). 0.041g substrate was used, the sample was diluted into 25.25mL.

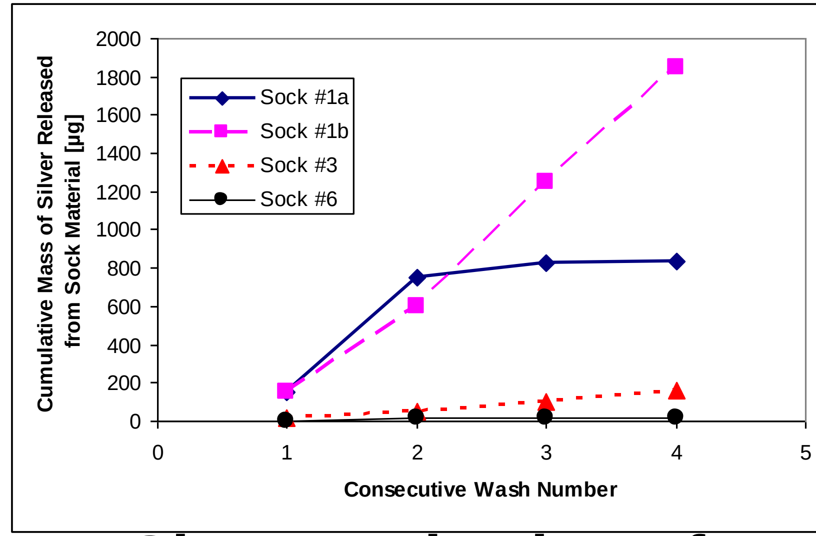
Product Line D

Example: Silver from fabrics



Water

Quantity Leached



Characterization of Leached Material

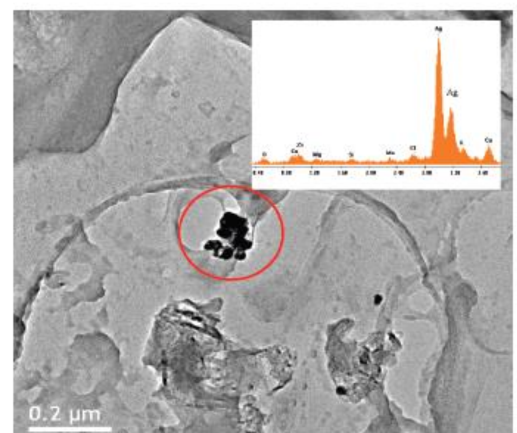


FIGURE 4. TEM image of colloidal material from sock 1a washwater. Inset: EDX confirmation that the dark particles within the circle are predominantly silver.

- Tremendous press
- Assessed removal by activated sludge at wastewater facility
- Others developed standardized approaches using soap, heat, mixing
- Others have looked at LCA views
- Data used to estimate potential exposure levels and loading

Benn & Westerhoff, ES&T 42:11:4133-4139 (2008)

Silver from other fabrics

Product	Silver content (ug Ag per gram product)	Size Fraction of Silver released into 500 mL tap water [µg]			
		Total	< 100 nm	< 20 nm	Total silver released per product mass [µg-Ag/g-product]
Athletic Shirt	30	27 ± 1.4	20 ± 0.5	11 ± 1.2	0.56 ± 0.01
Unfinished Cloth Fabric	44	22 and 47	12 and 16	12 and 13	0.5 and 1.1
Medical Mask	270,000	15.8	14.8	14.8	11
Medical Cloth	230,000	13.8	13.3	13.3	46
Yellow Cloth (towel)	270	< 5	< 5	< 5	< 1.0
Teddy Bear	70 (foam)	< 5	< 5	< 5	< 0.2

Only some fabrics leached nano-sized silver

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

Product Line B – Dispersed in Products

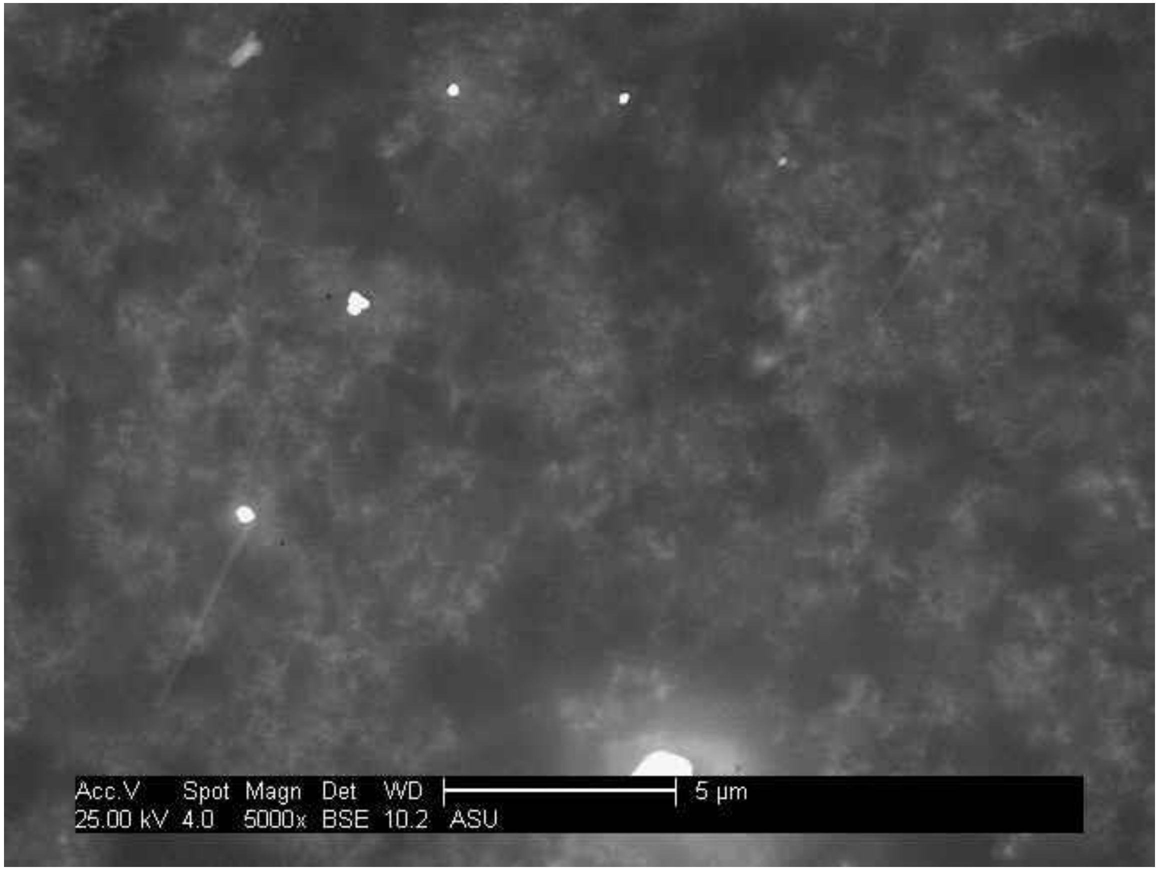
Water

Product	Size Fraction of Silver released (%)		
	< 100 nm	< 20 nm	Total silver released per product mass [µg-Ag/g-product]
Toothpaste	40%	12%	18
Shampoo	41%	32%	0.9
Detergent	16%	4%	1.8

Highly variable silver content observed because unequal distribution in products

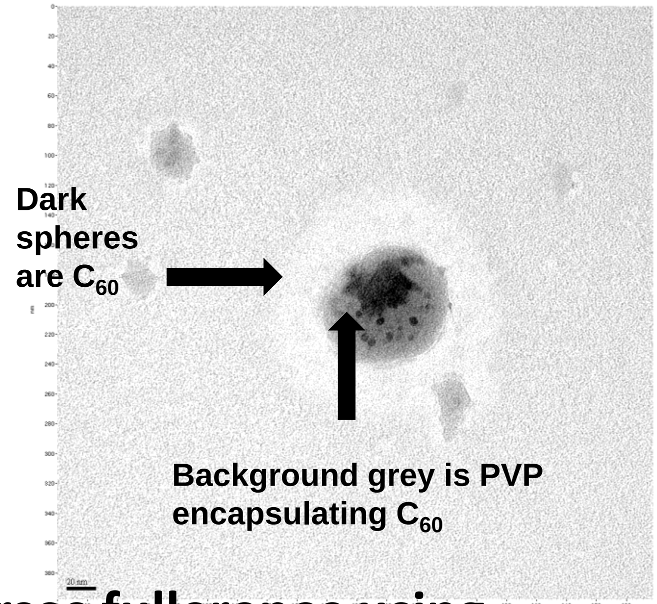
Benn et al., J. Environmental Quality, 39:1-8 (2010)

Silver Nanoparticles in washwater from toothpaste (advertized to contain 100 pm Ag)



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

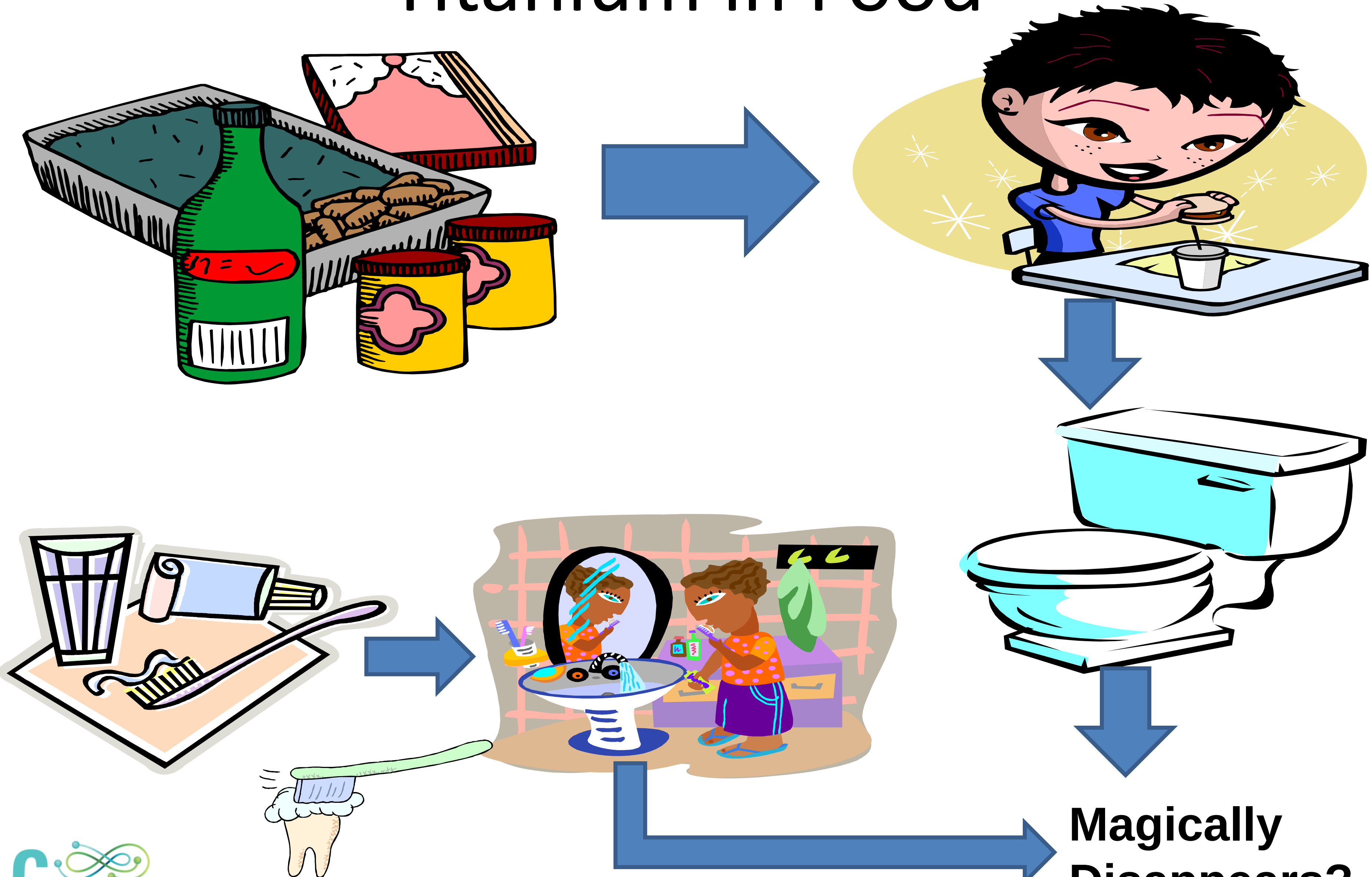
Fullerenes From Cosmetics



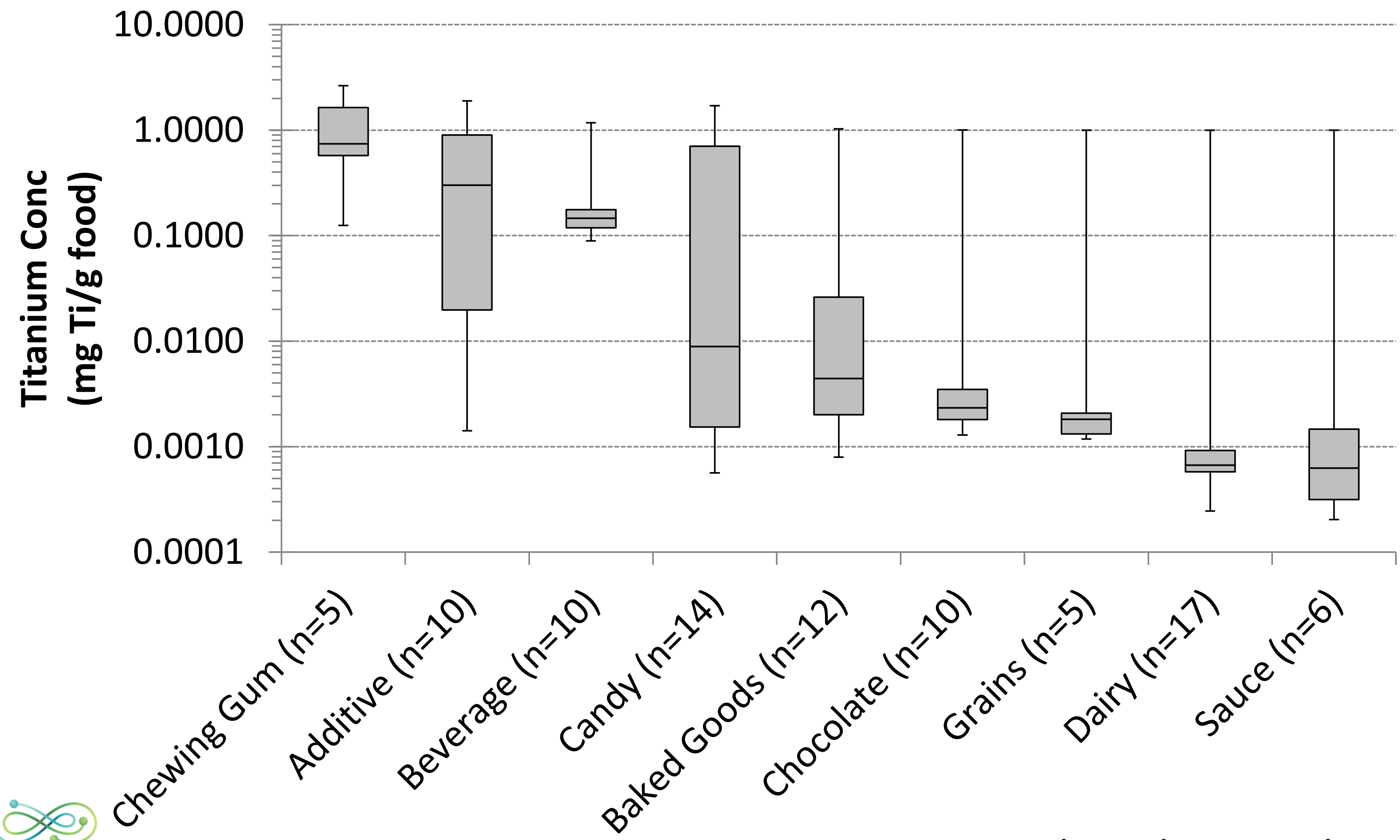
- Five cosmetic products evaluated
- **Common cosmetic formulation disperses fullerenes using polyvinylpyrrolidone (C_{60}-PVP)**
- LC/SMused to detect fullerenes (C_{60} and C_{70}).
- **C_{60} was detected in four commercial cosmetics ranging from 0.04 to 1.1 µg/g, and C_{70} was qualitatively detected in two samples**.
- A single-use quantity of cosmetic (0.5 g) may contain up to 0.6 µg of C_{60} and demonstrates a pathway for human exposure to engineered fullerenes.

Benn et al., Environ. Poll. (2011)

Titanium in Food

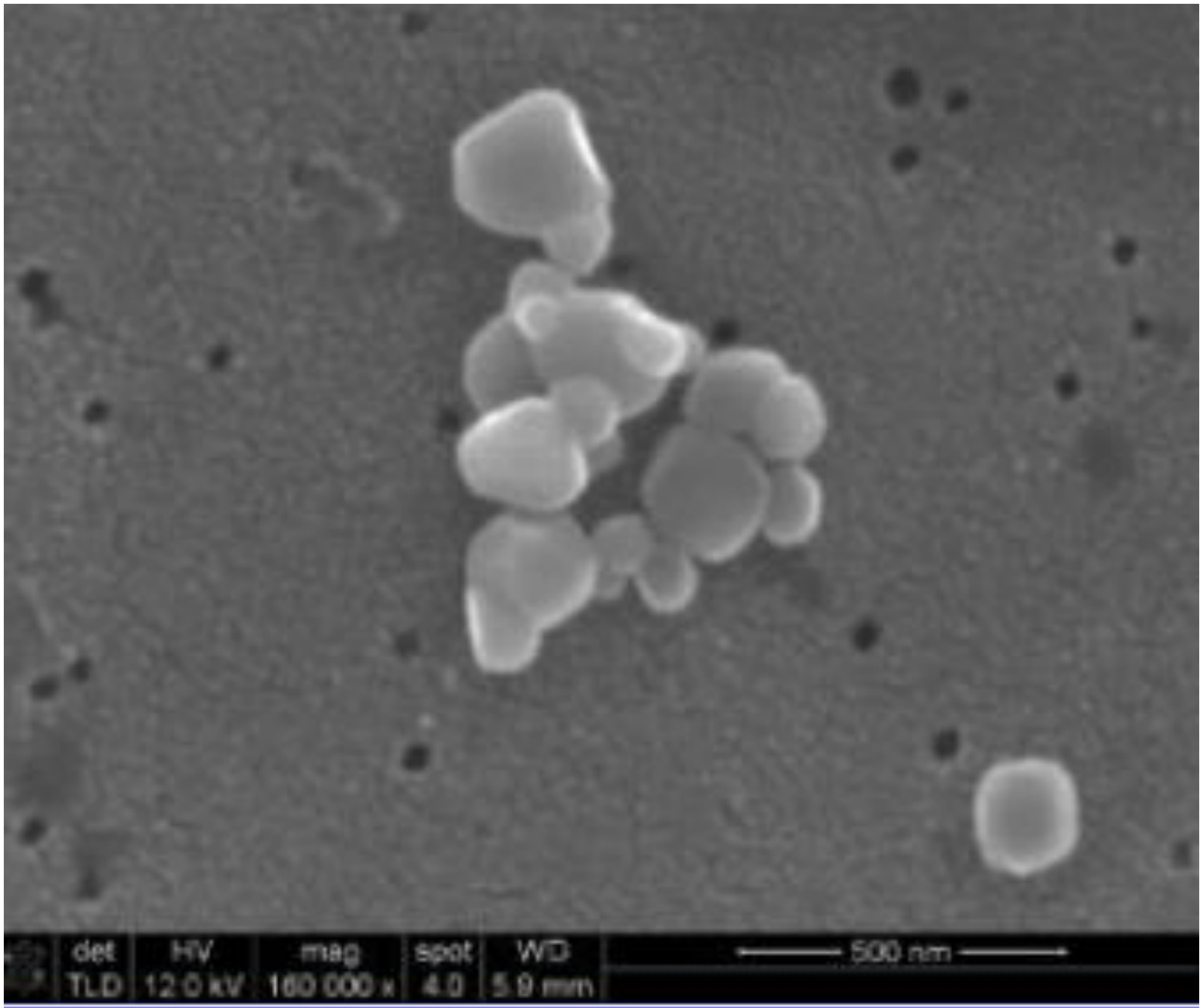


Titanium content of foods



Weir et al., ES&T (2012)

TiO_2 from Candy Coating on Chewing Gum



Multi-phase products have un-even TiO_2 distribution

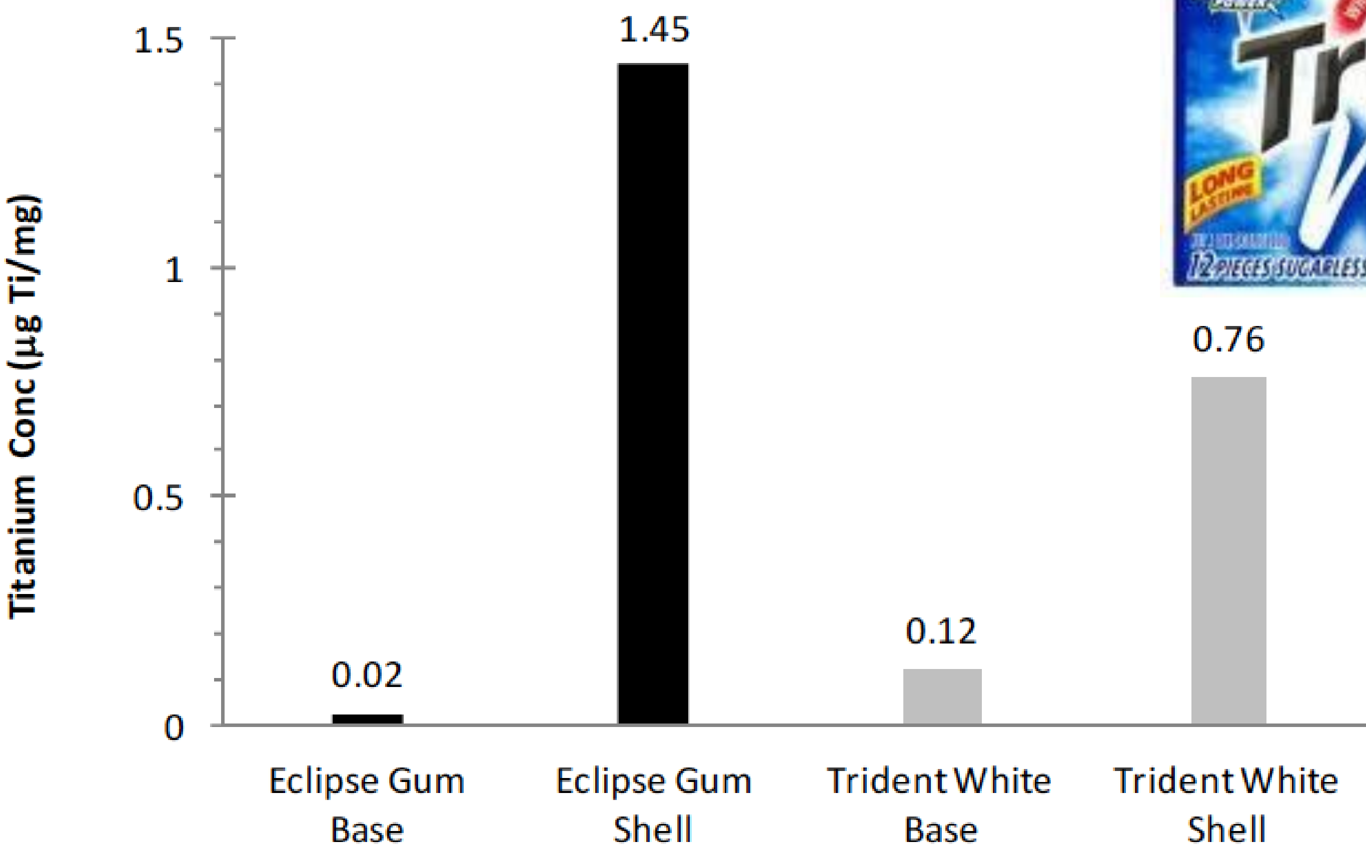
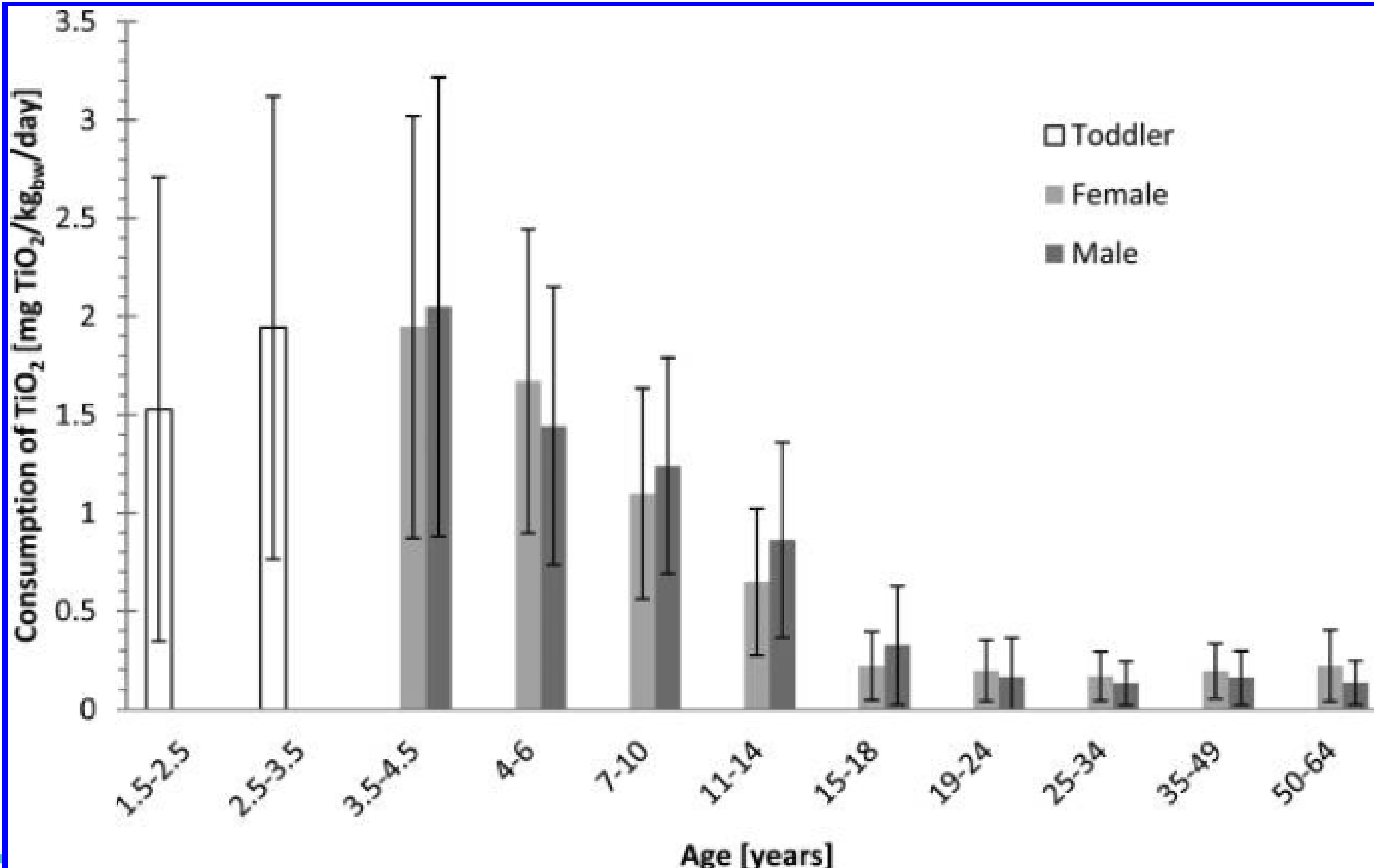
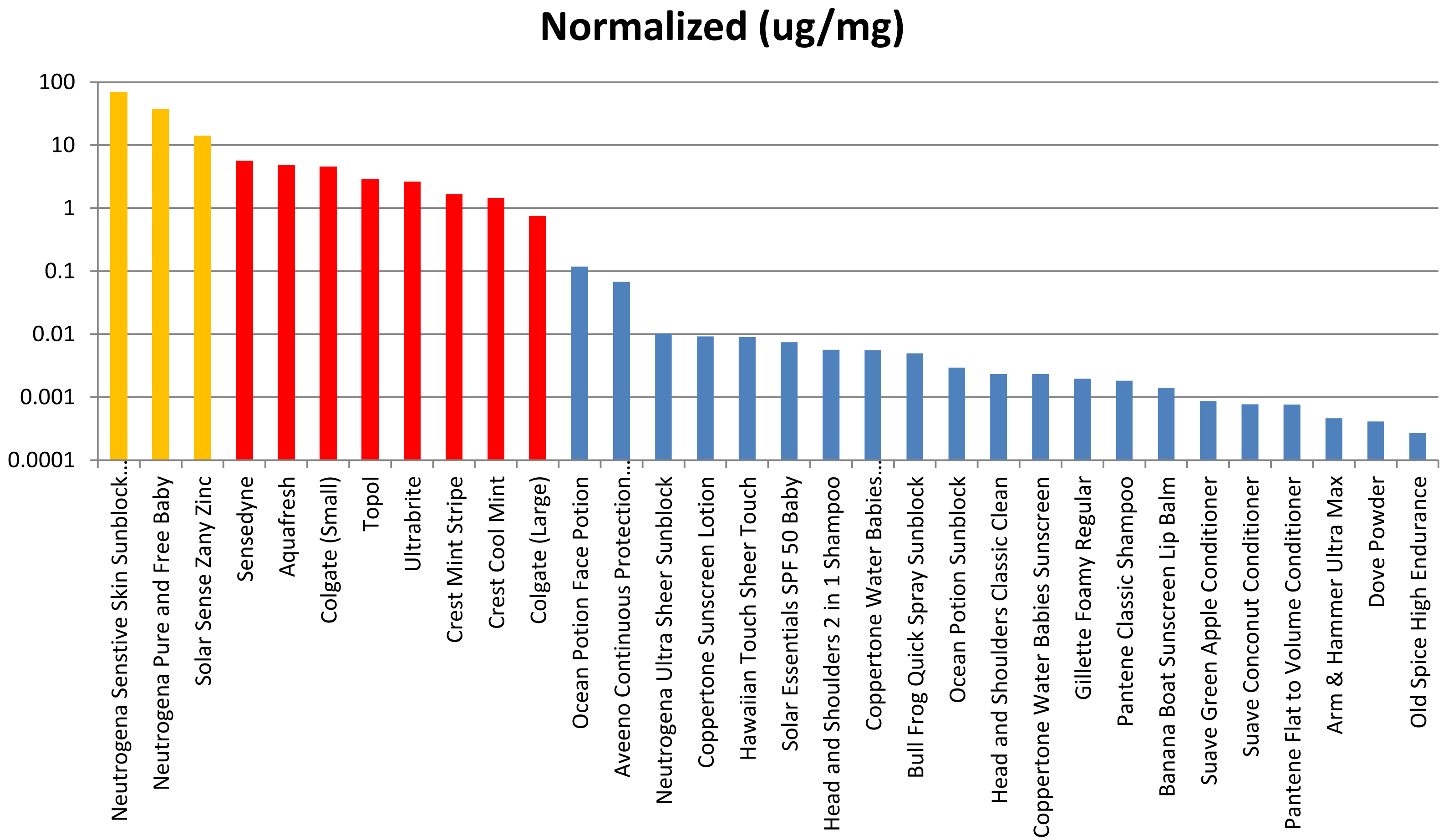


Figure SI.3 Comparison of titanium content in outer chewing gum shell versus inner gum base for two types of chewing gums

Human exposures to Nano is real



Sunscreens, Toothpaste, and Personal Care Products (titanium)



Orange: Sunscreen with Ti listed on label

Red: Toothpaste with Ti listed on label

Weir et al., ES&T (2012)

But is there hazard?

Characterization of nanomaterials in metal colloid - containing dietary supplement drinks and assessment of their potential interactions after ingestion

Robert B. Reed[1*], James J. Faust[2], Yu Yang[1], Kyle Doudrick[1], David G. Capco[2], Kiril Hristovski[3], and Paul Westerhoff[1]

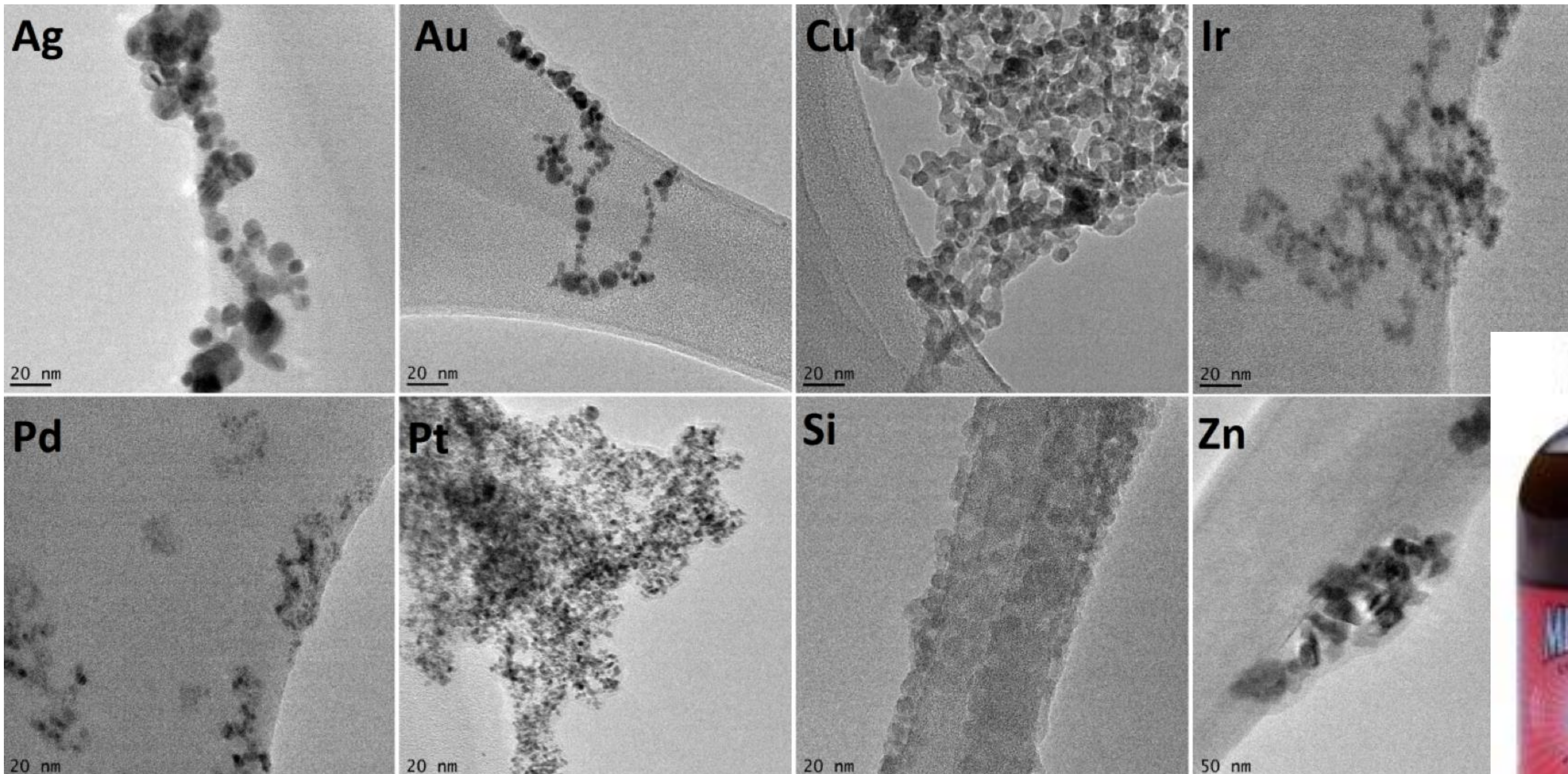


Figure 1. Representative TEM images of NMs found in supplement drinks.

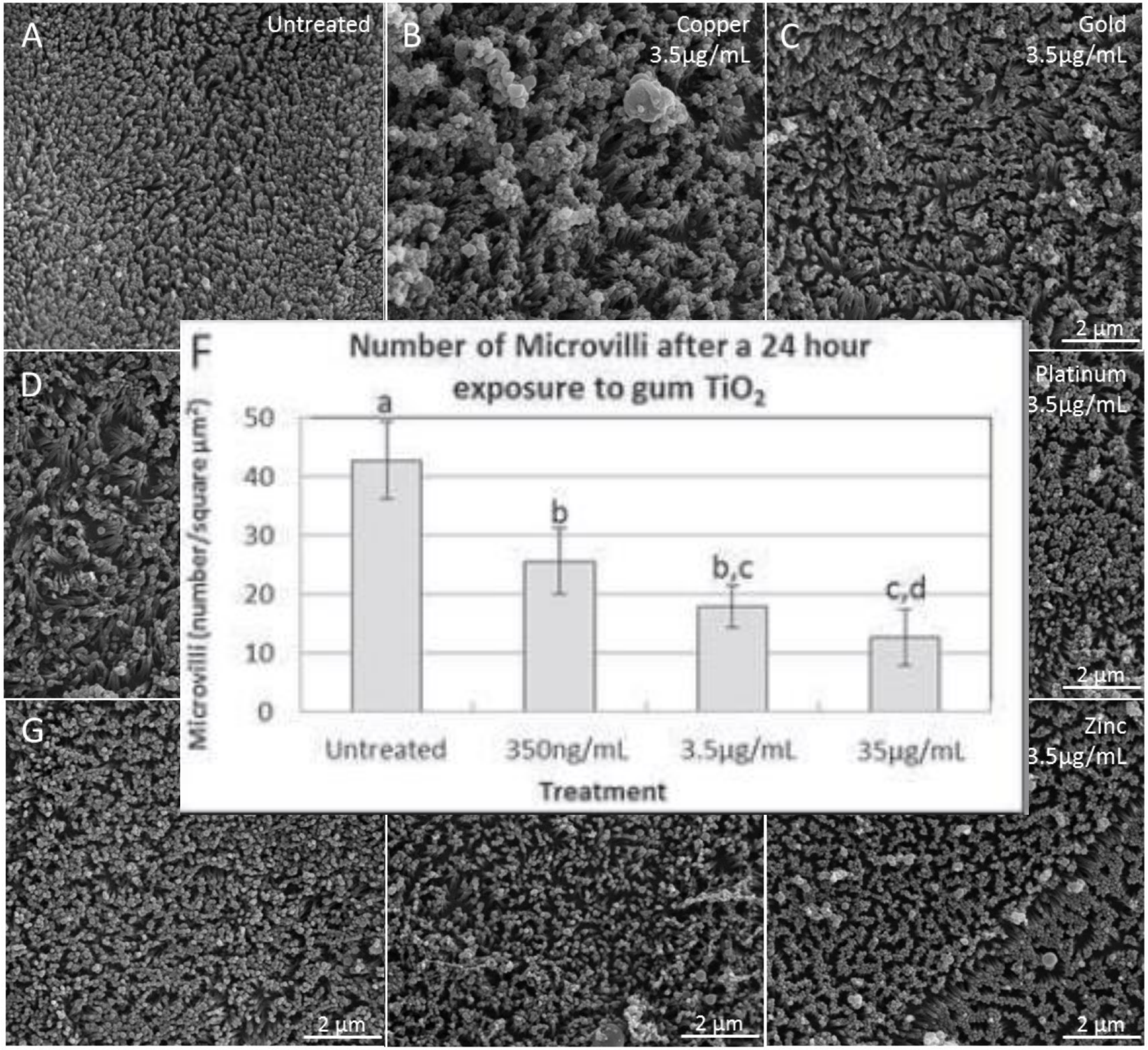
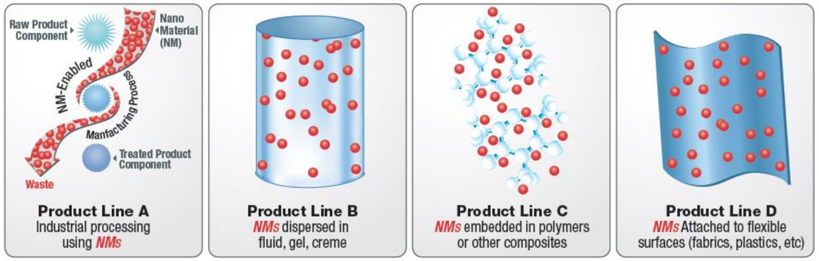


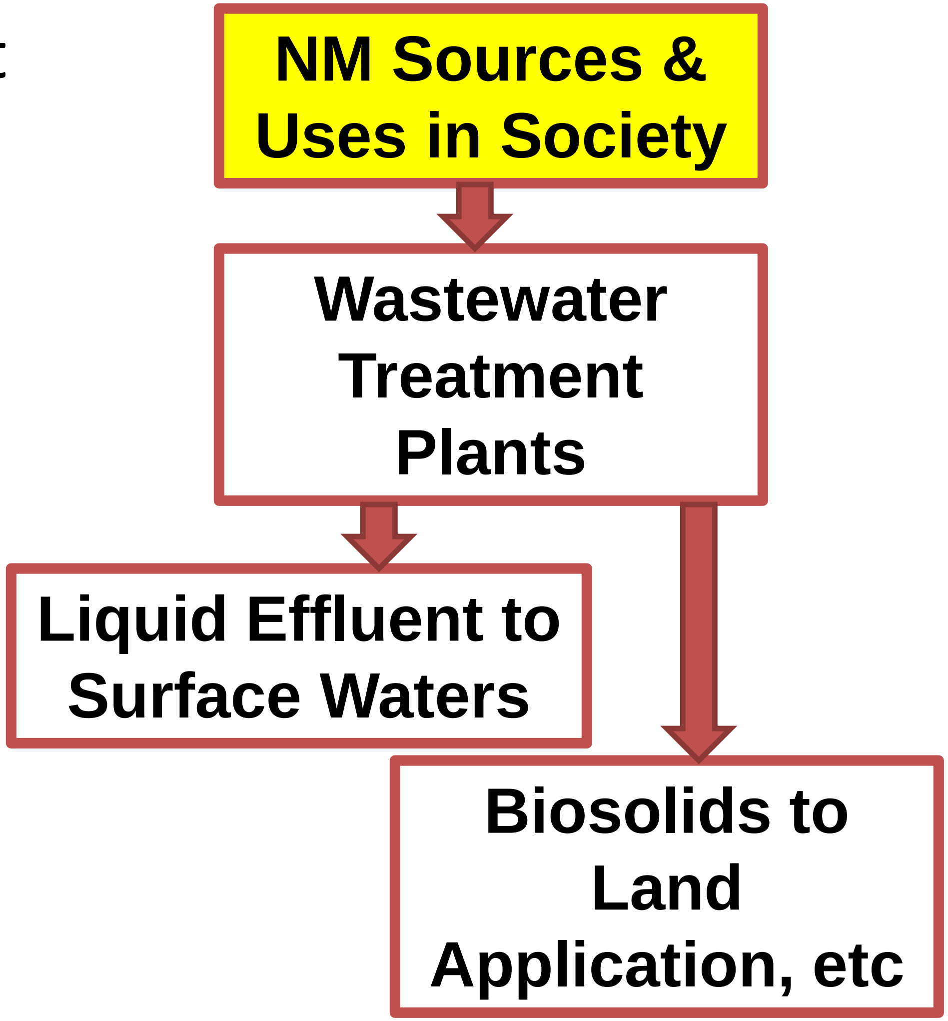
Figure 4. SEM images of microvilli exposed to 1 µg/cm^2 NMs (3.5 µg/mL), except "A", which is an untreated control. After exposure to NMs from supplement drinks, both the normal organization and the number of microvilli changed compared to untreated controls. Large spherical particles (>250 nm) are membrane blebs.

Part I - Summary

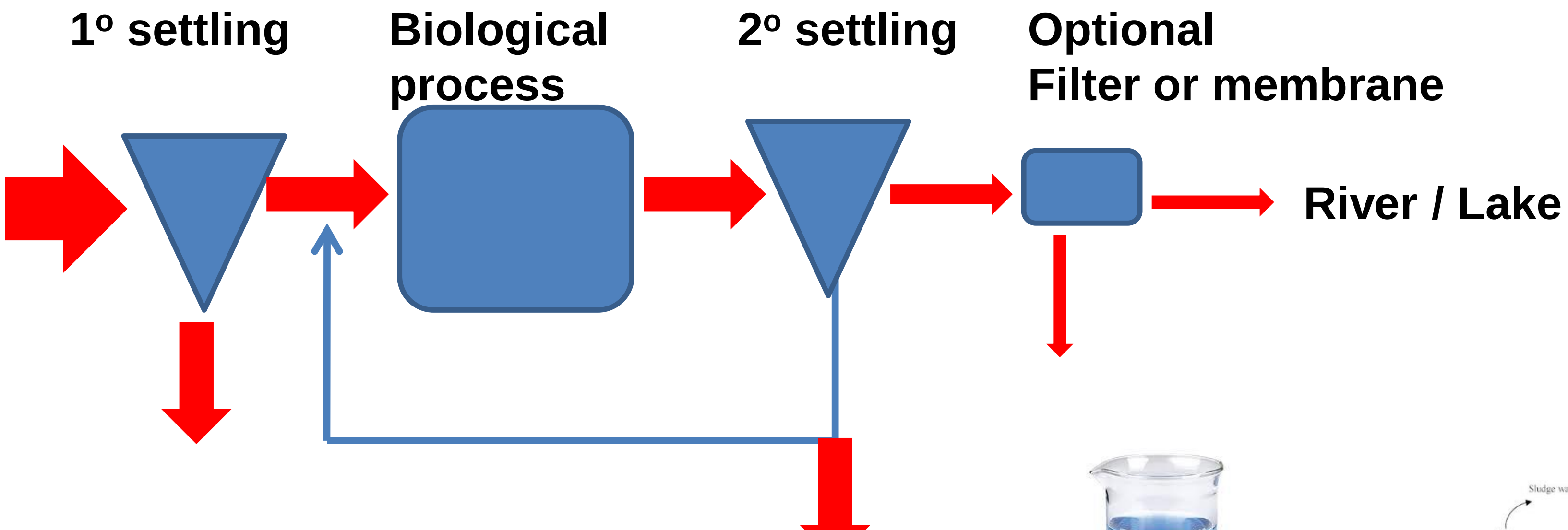


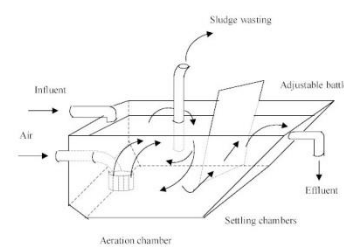
- Products potential to release NMs into the environment can be grouped into 4 product lines

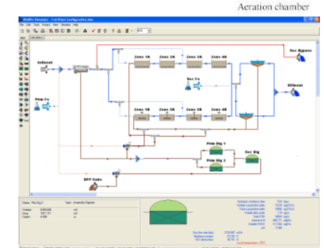
- NMs are released from commercial products into sewage wastewater



Part 2 – NM removal in Wastewater Treatment Processes

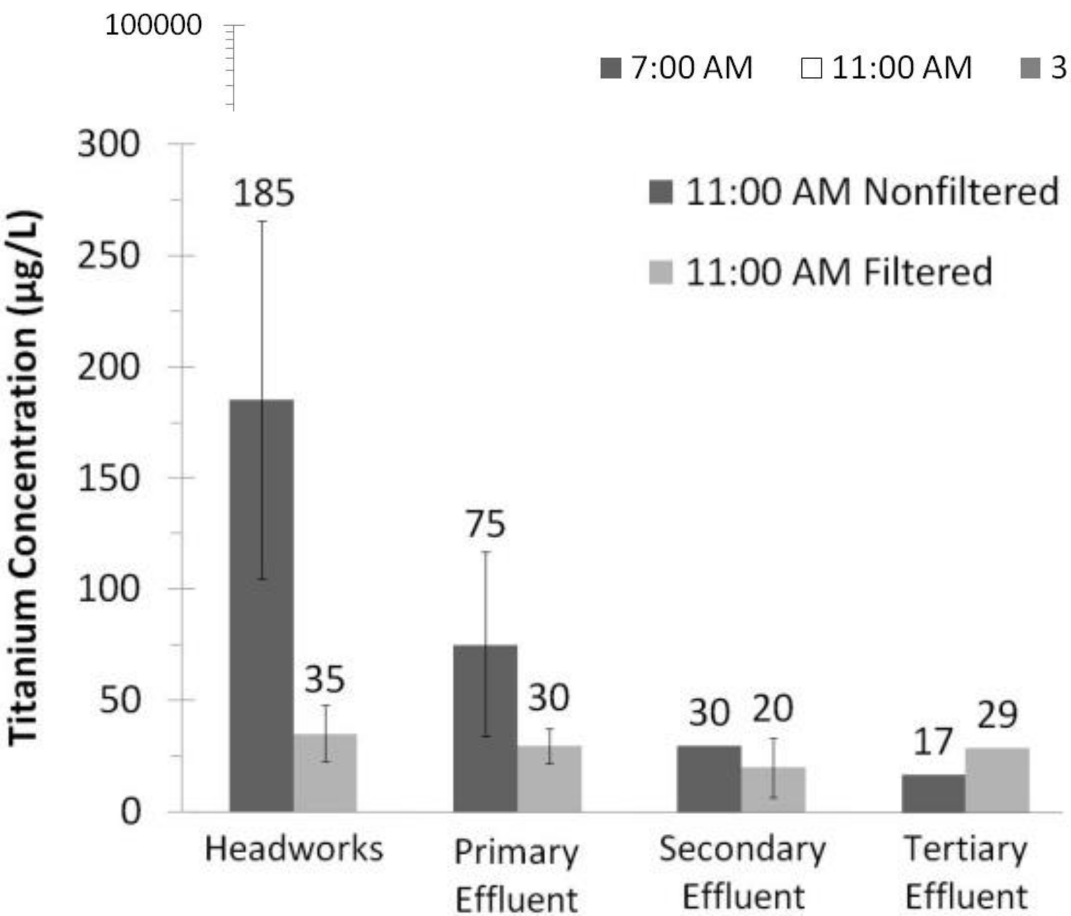


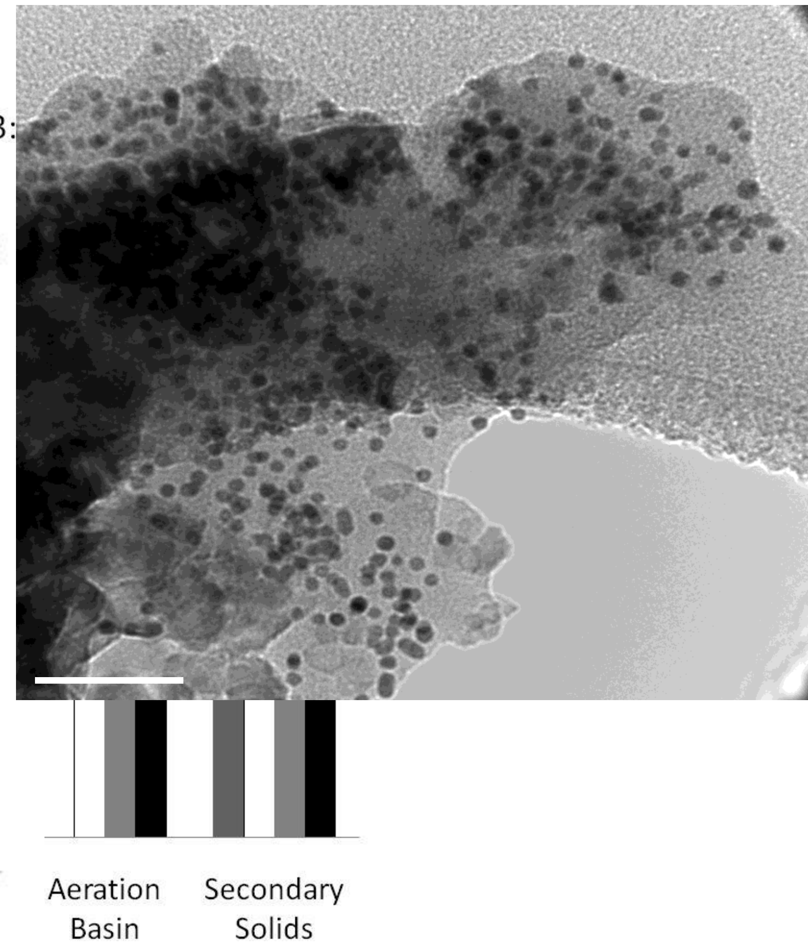




Red Arrows represent flux of nanomaterials

Titanium at Full Scale WWTPs



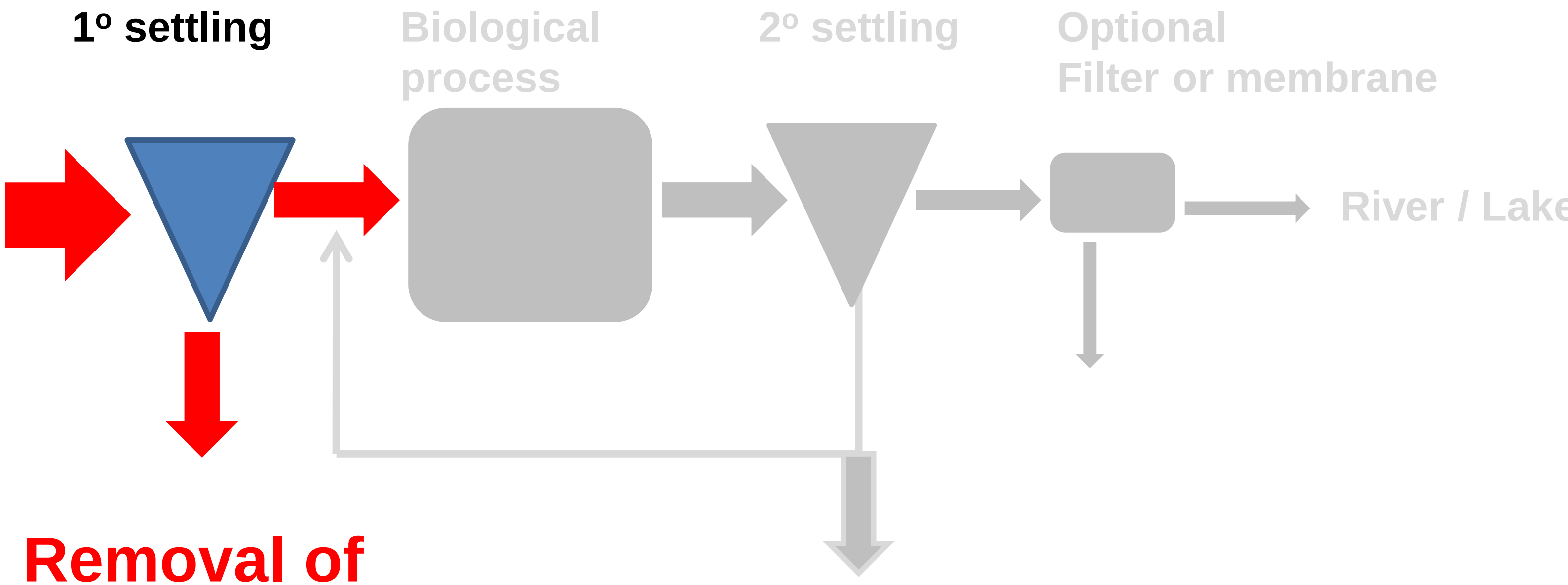


Kiser et al.,EST 2010; Westerhoff et al., JEM 2011

Titanium at Full Scale WWTPs

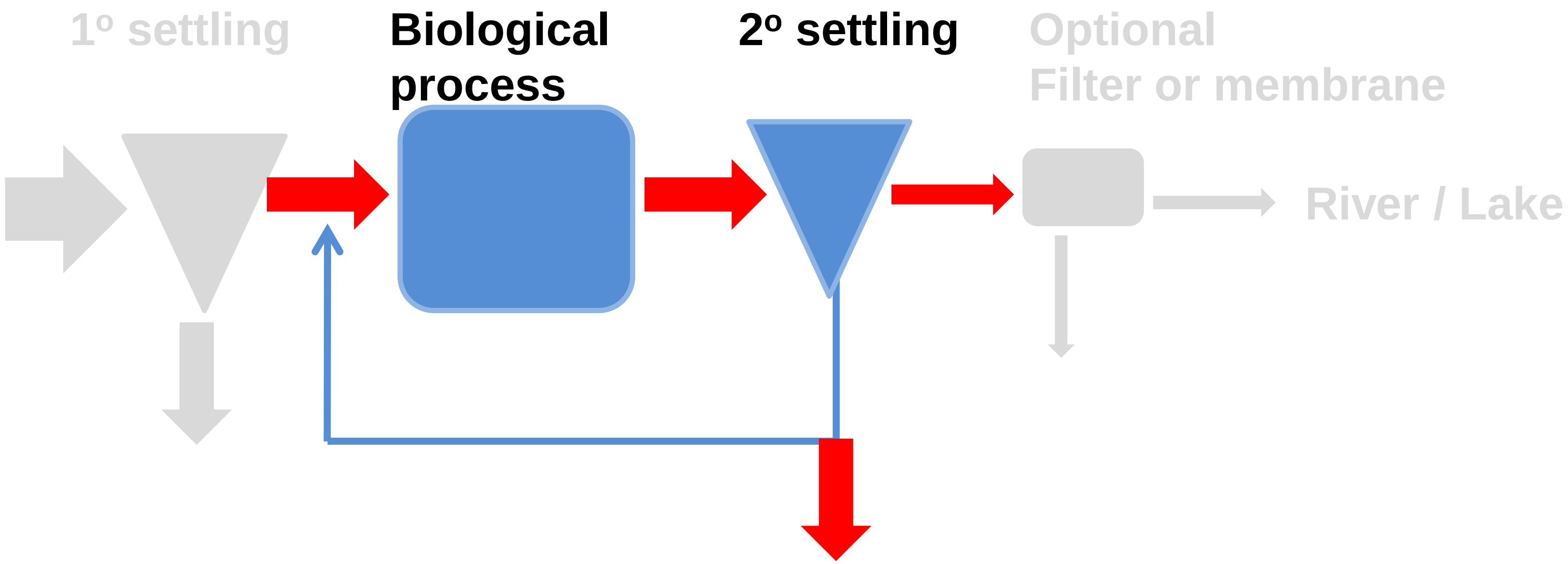
Different Facilities	Titanium Content of water (ugTi/L)	
	Headworks	Effluent
Activated sludge	615	5
Act. Sludge + filter	180	7
Activated sludge	363	3
Activated sludge	141	2
Activated sludge	581	18
Activated sludge		8
Activated sludge	233	2
Trickling filter	549	13
Membrane bioreactor (MBR)	310	1
MBR	422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

Primary Settling



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

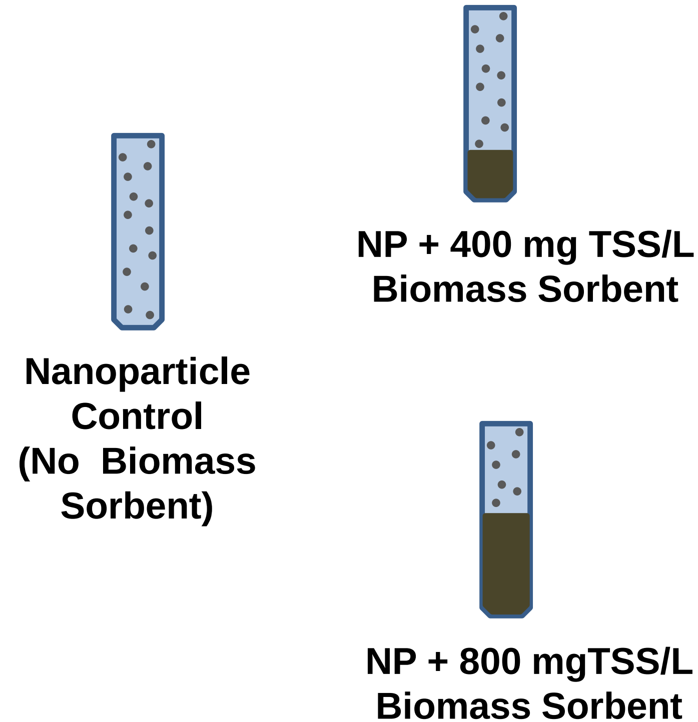
Biological Treatment



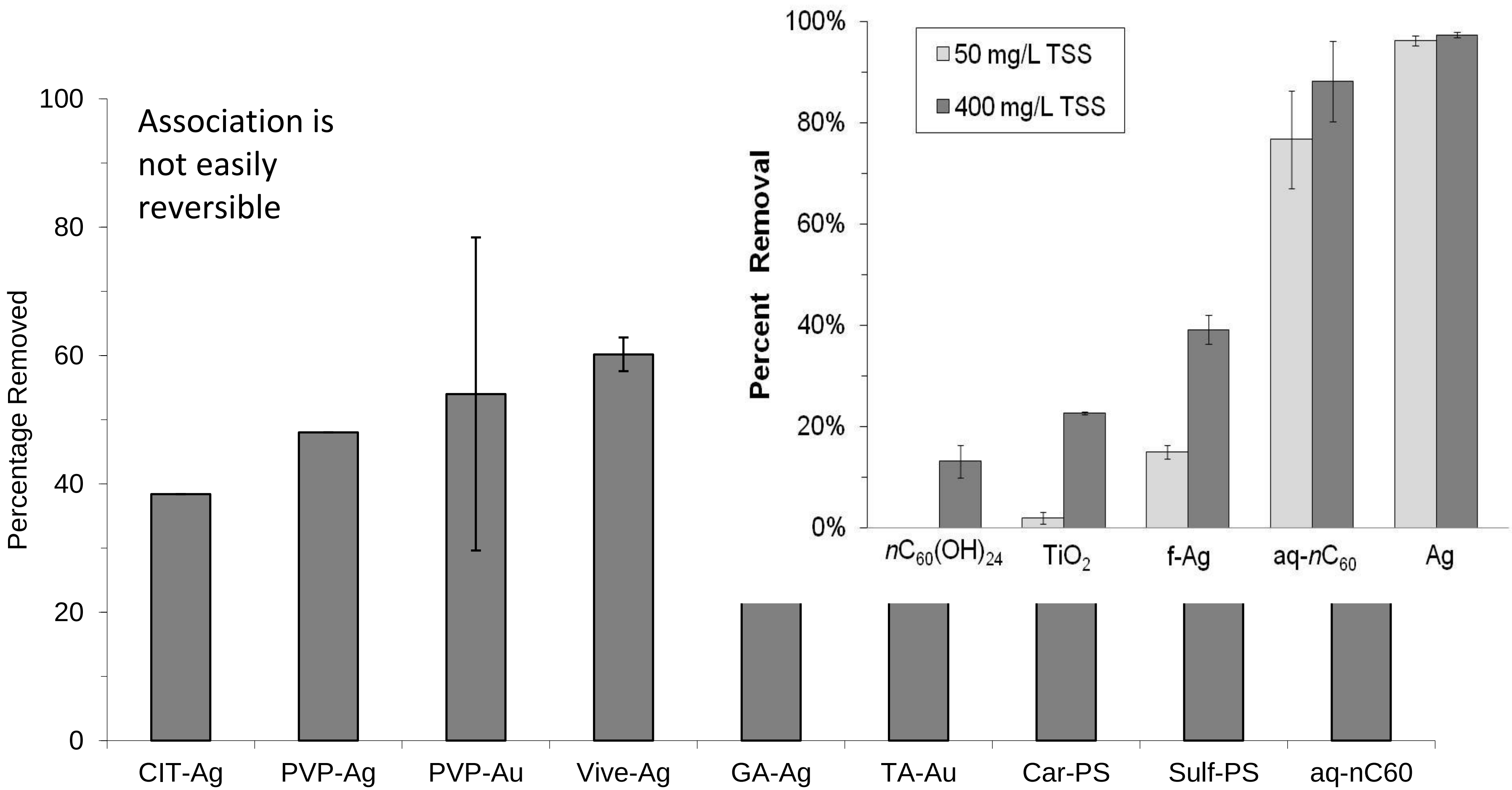
Removal of nanomaterials occurs when they interact with biofilms or biosolids

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



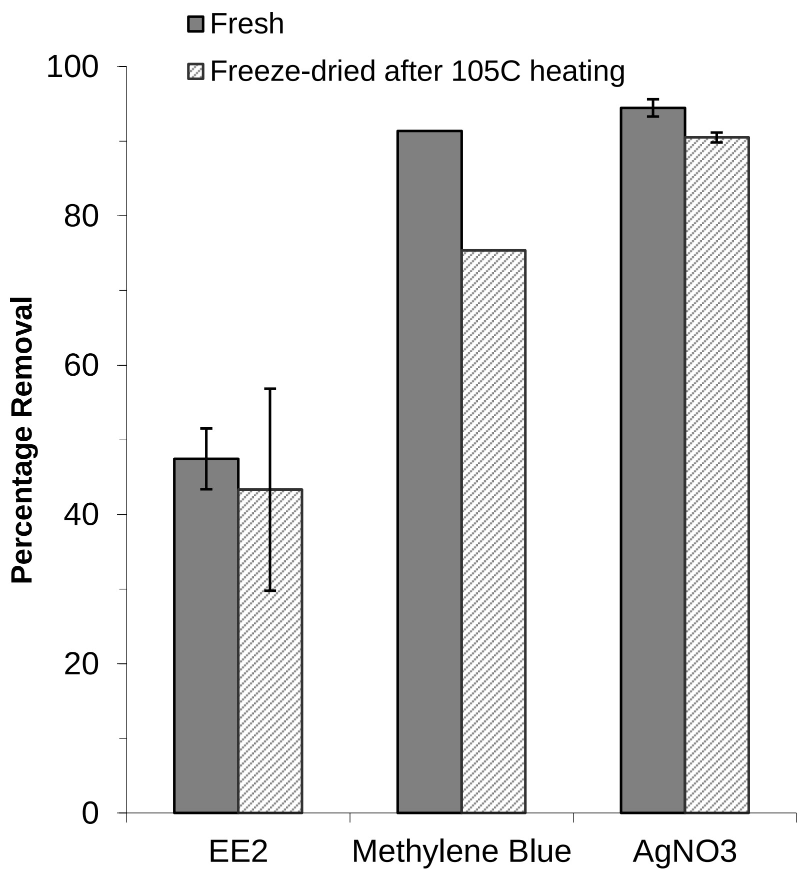
Nanomaterial Interaction with Wastewater biosolids



Kiser et al (in prep); Kiser et al., WR, 2010

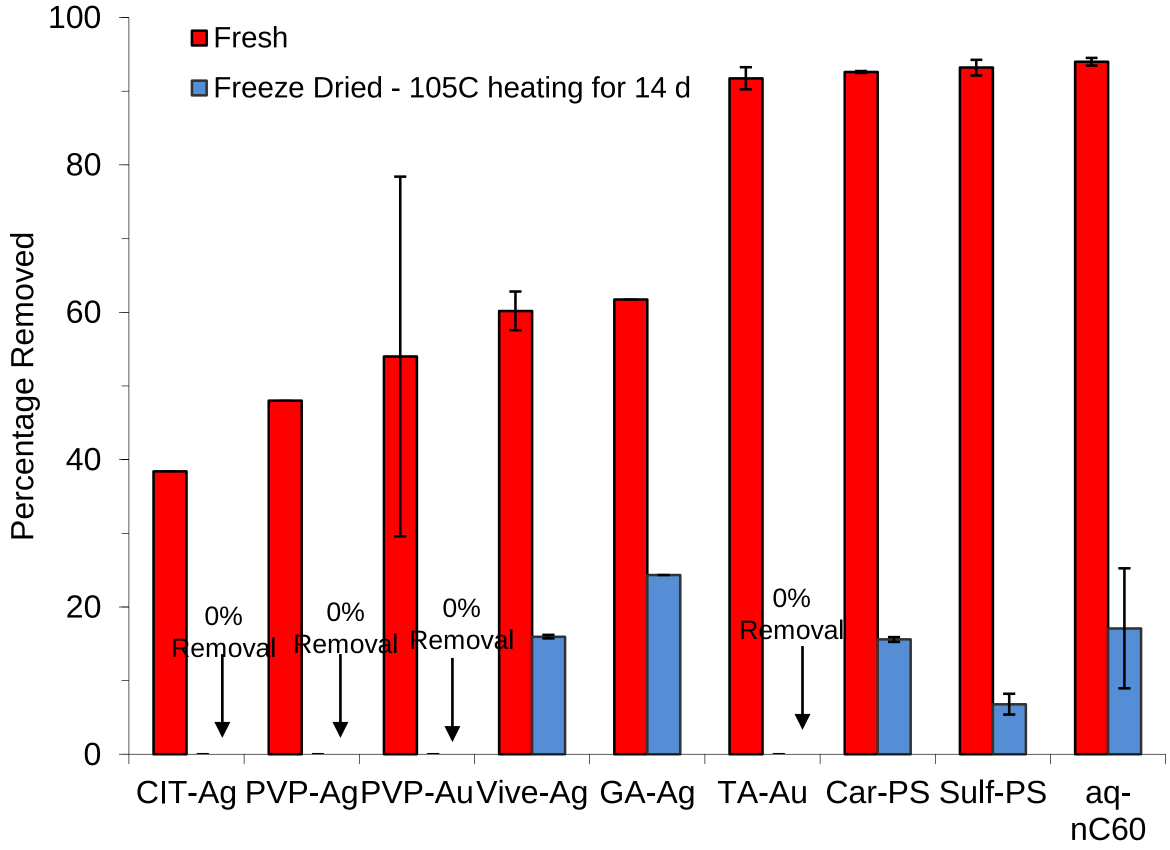
Standard Batch Methods

- 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

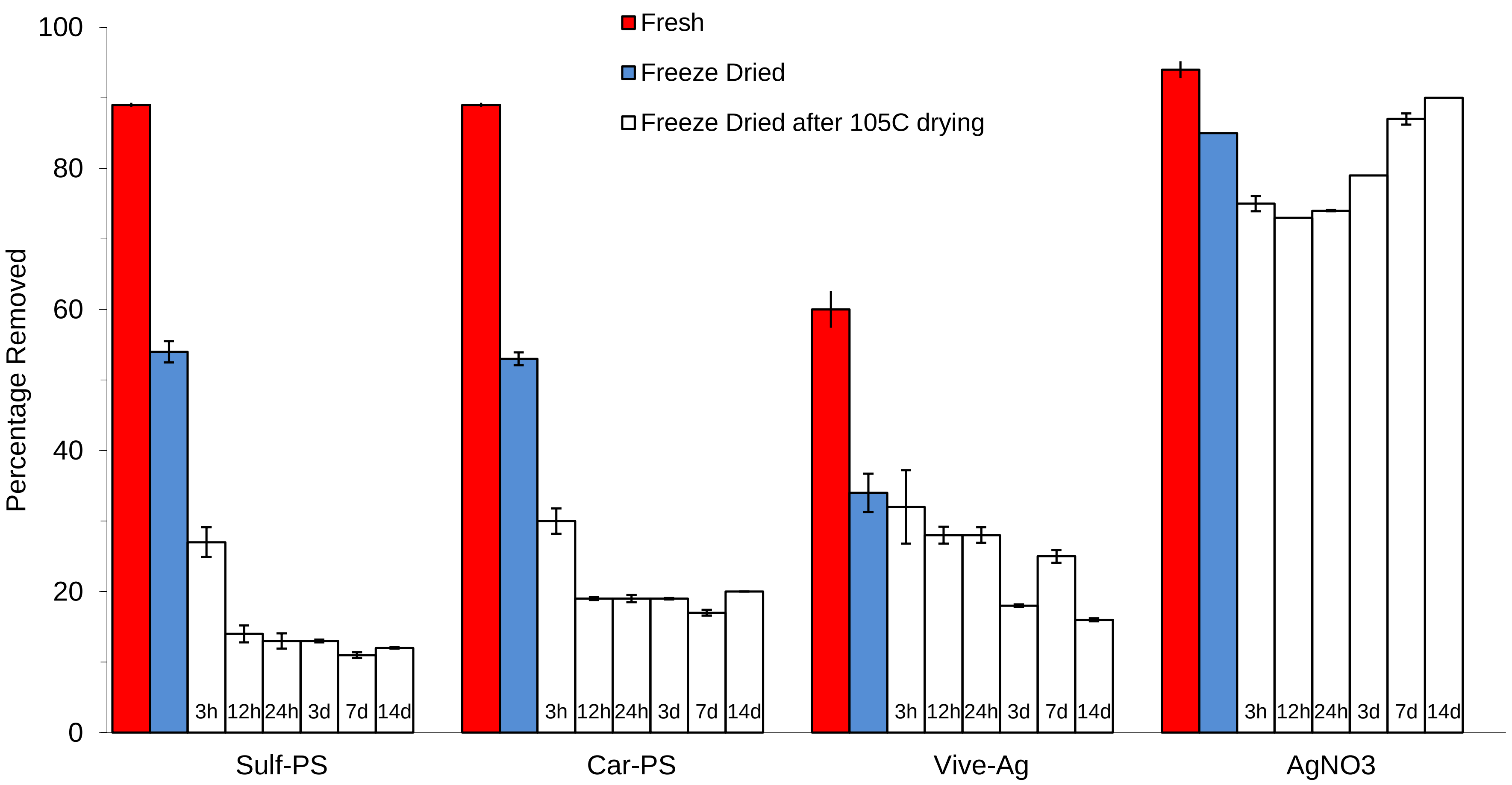


Does OPTT Test work for NPs?

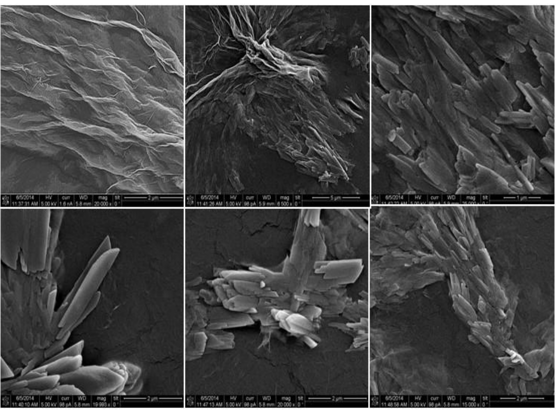
- Fresh and rinsed biomass shows much more capacity for NMs than freeze-dried biomass



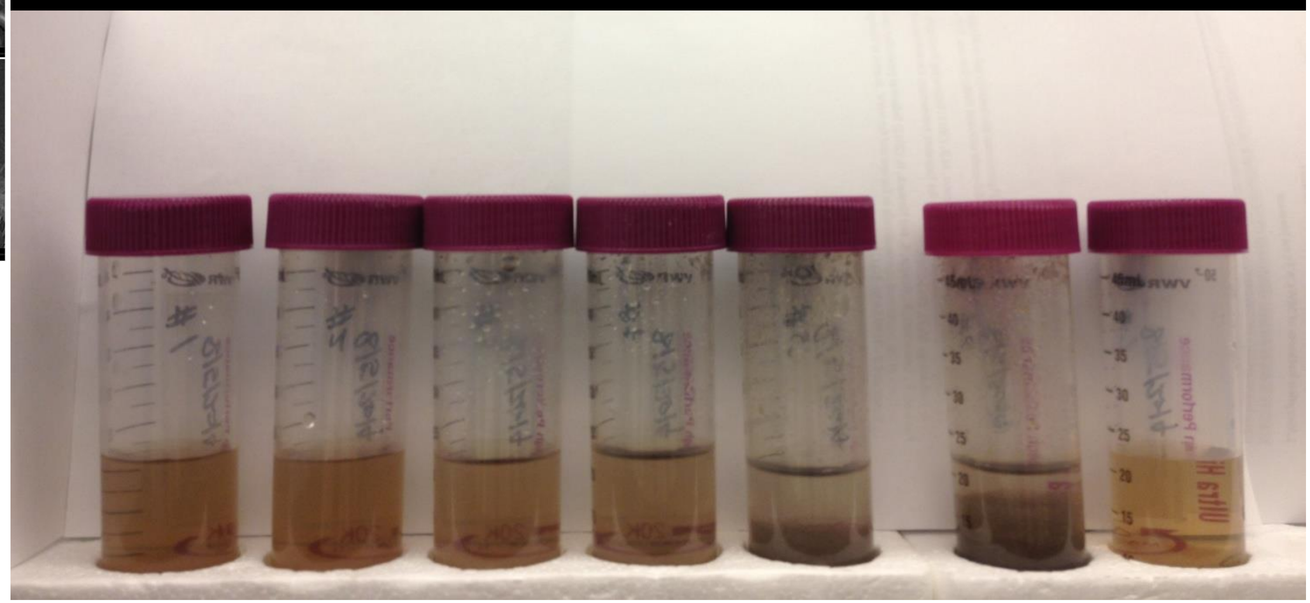
Effect of heating may inform important sorption mechanism



Graphene Oxide
Initial Concentration = 25 mg/L

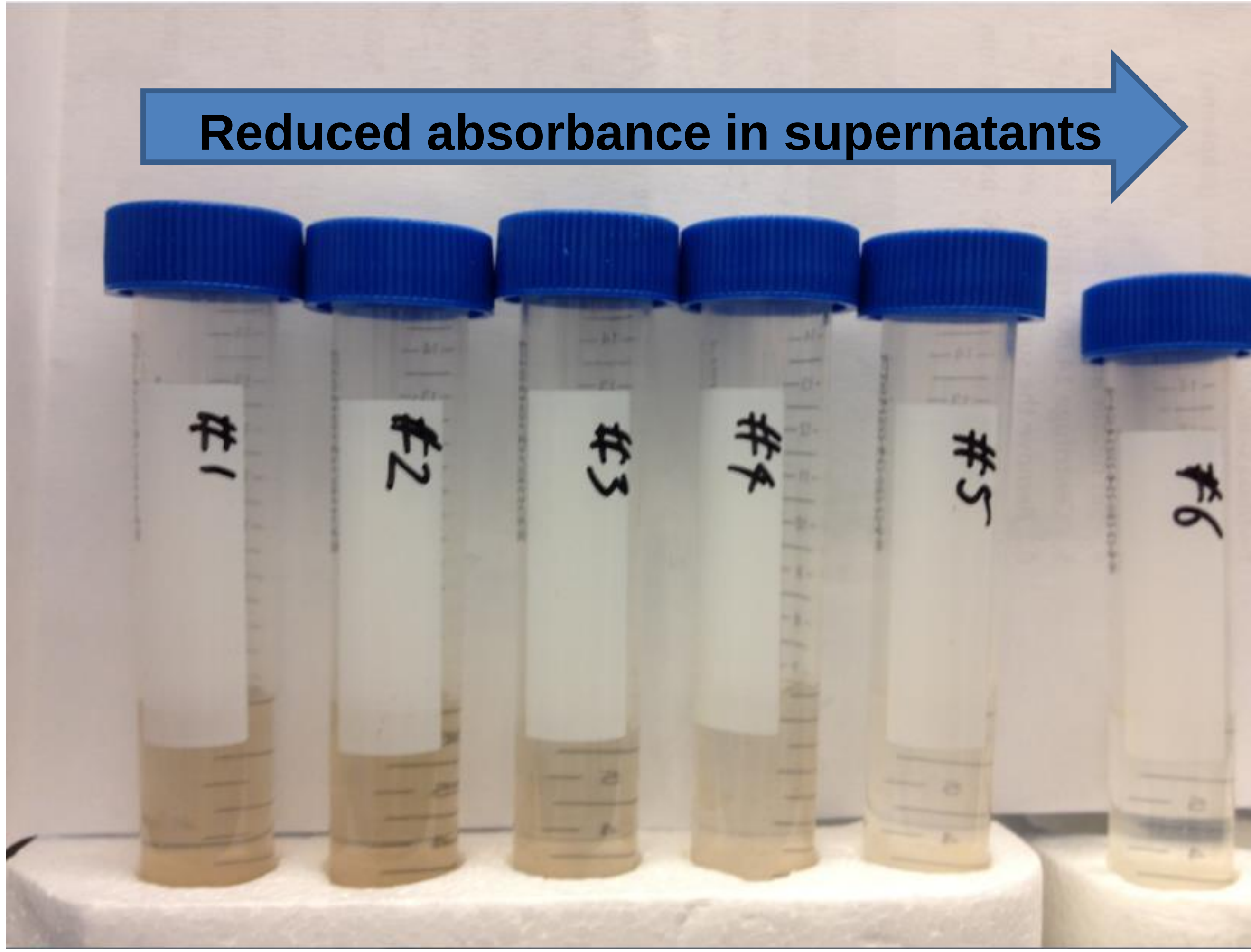


After mixing for
3 hrs and settled for 30 min



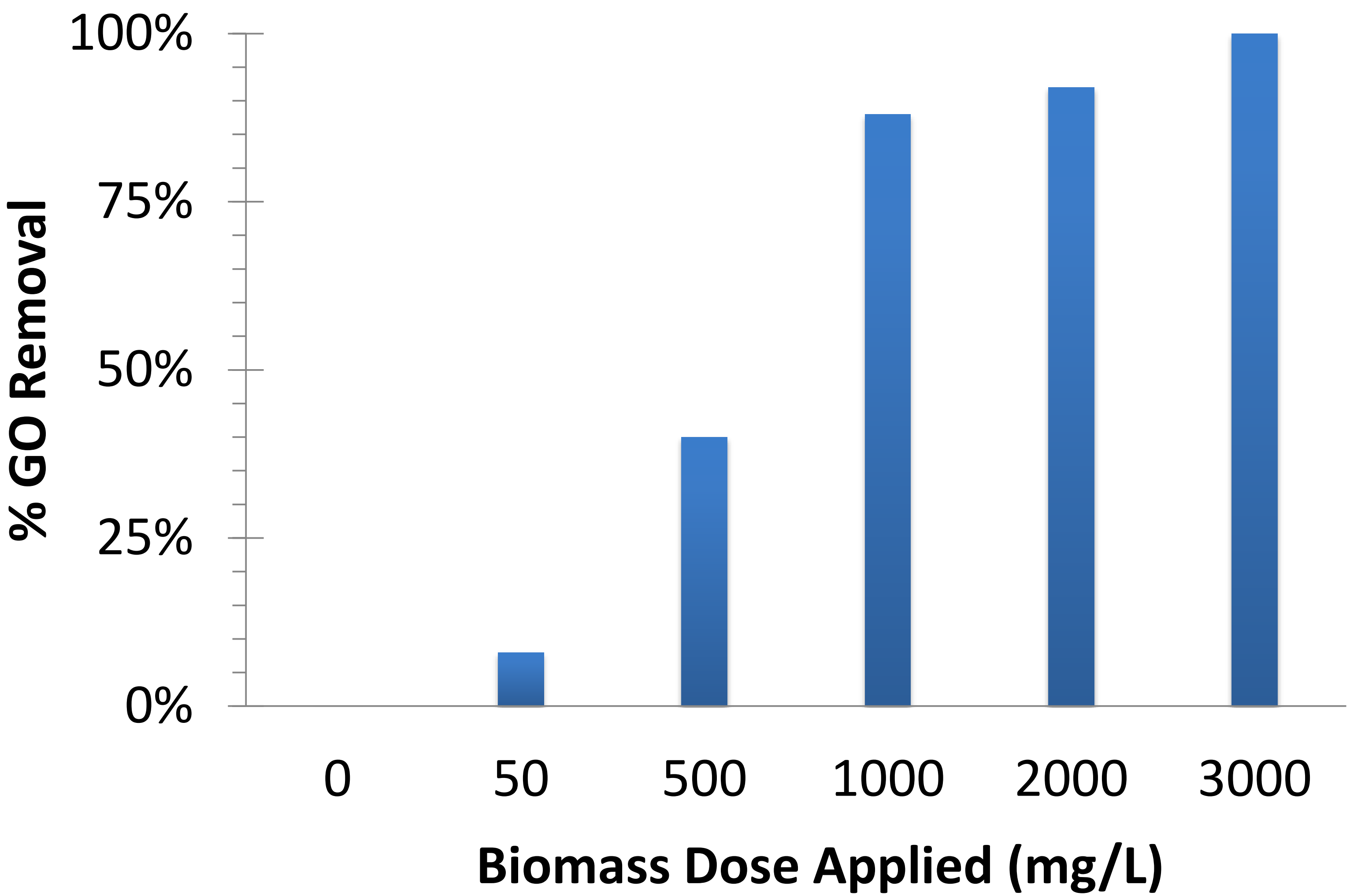
Biomass: 50 mg/L 100 mg/L 500 mg/L 1000 mg/L 2000 mg/L 3000 mg/L GO control

Supernatant after centrifuged at 1000 G for 5 min



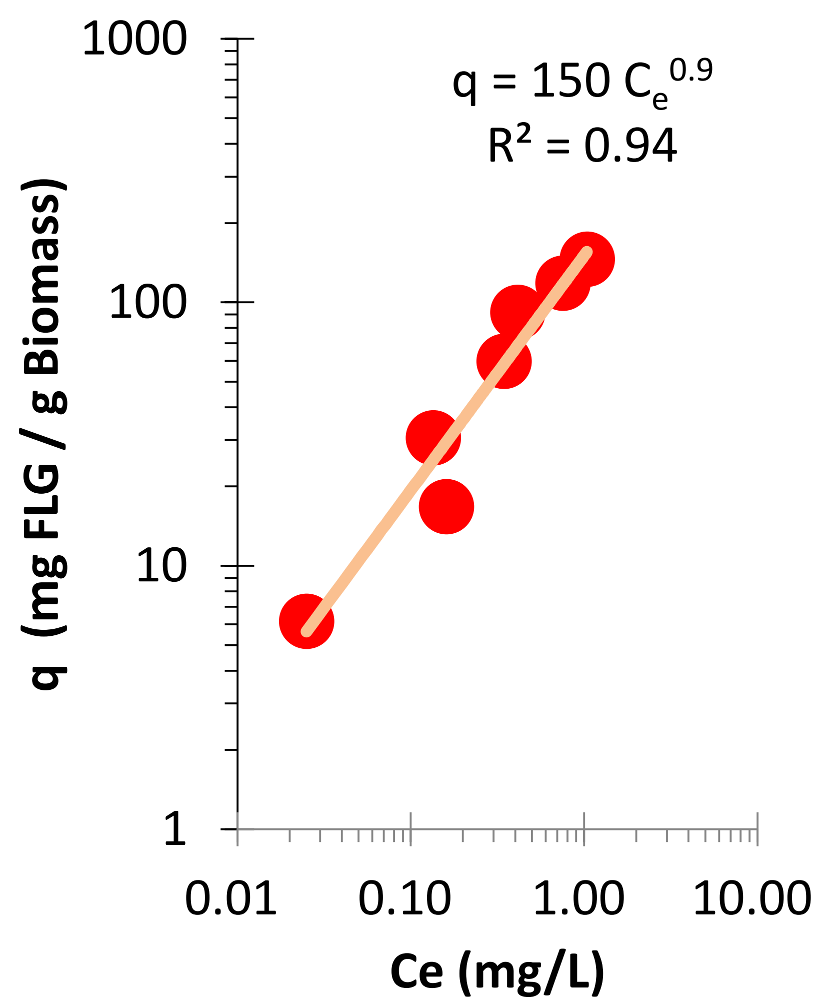
Biomass: 50 mg/L 100 mg/L 500 mg/L 1000 mg/L 2000 mg/L 3000 m

GO Association with Biomass

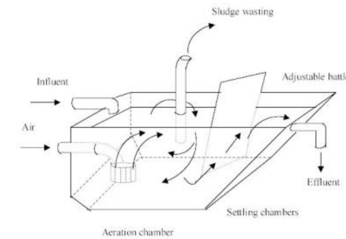


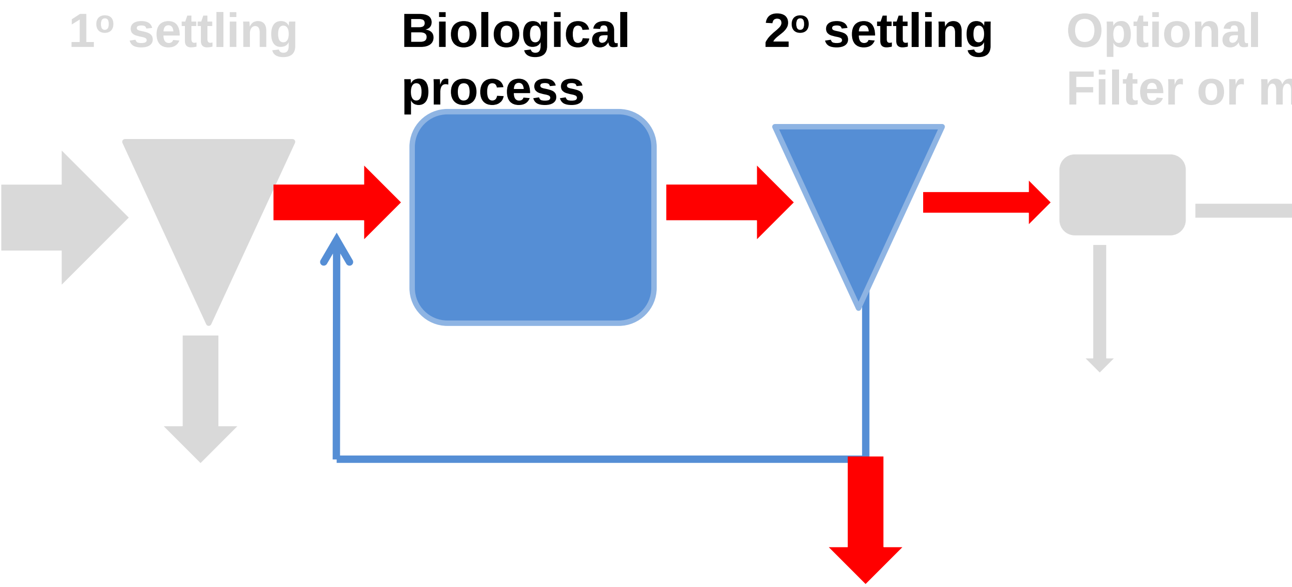
Application to FLG sorption to Biomass

- Fixed biomass concentration
  - 50 mg/L
  - Higher biomass concentrations are now capable with optimized digestion method
- Variable initial graphene concentration
  - 0.3 to 8.3 mg/L
  - Lower than with UV/VIS
  - Very small background PTA signal from 50 mg/L biomass
- Consistent removal (10±3%) of graphene by 50 mg/L biomass



Biological Treatment

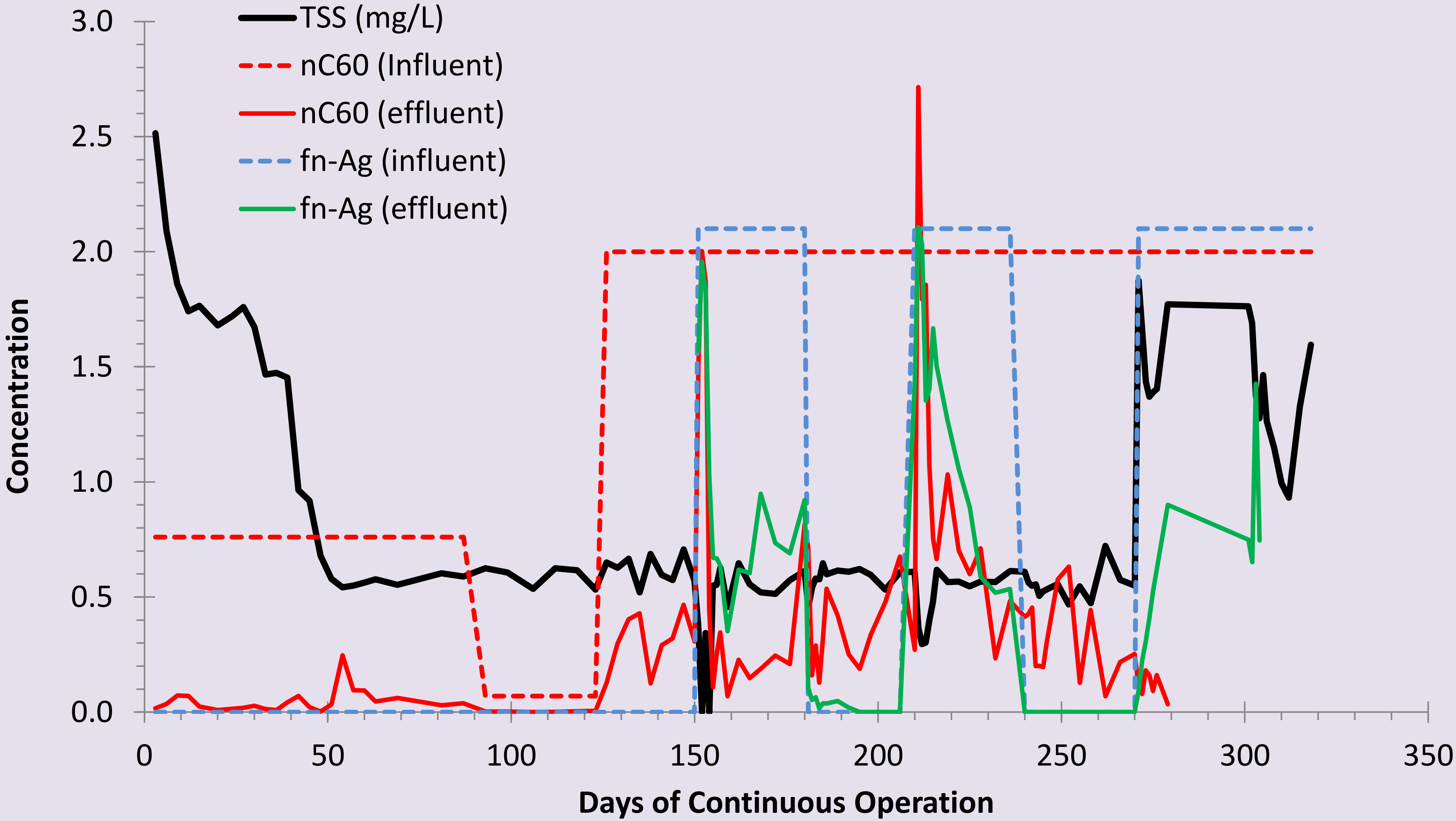




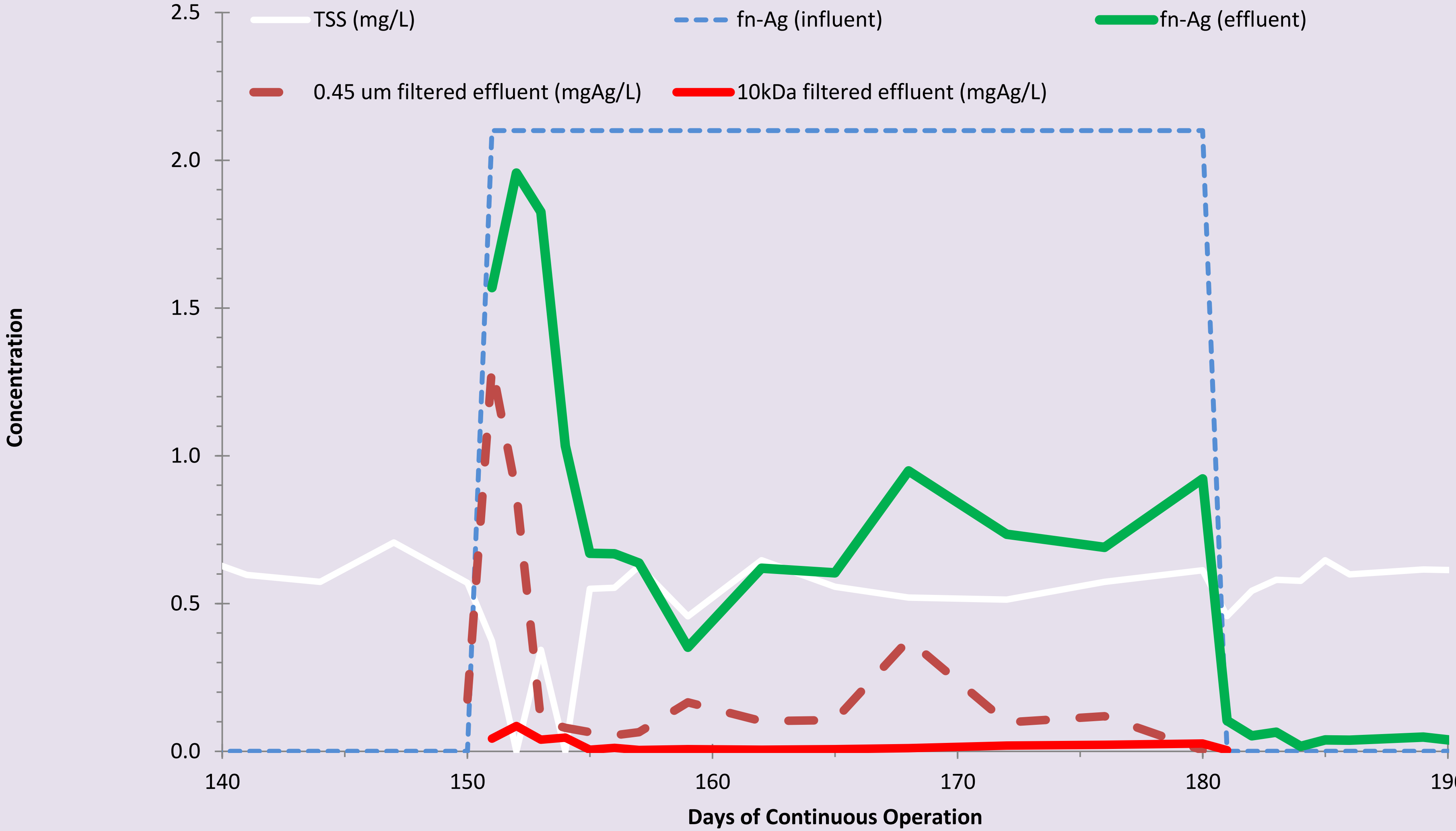
Removal of nanomaterials occurs when they interact with biofilms or biosolids

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

Biological Treatment

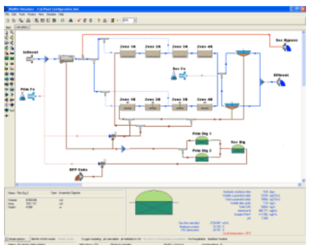


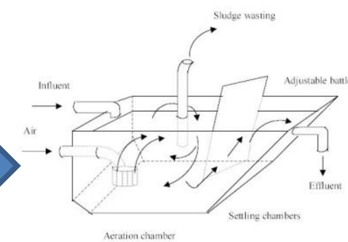
Biological Treatment



Modeling NP Removal

Kiser et al.,
Sep. Sci Tech. 2010

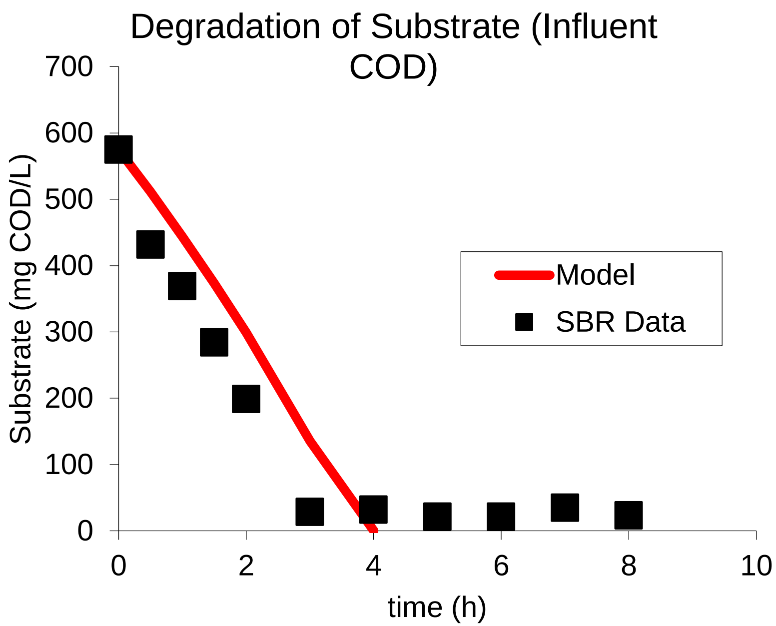


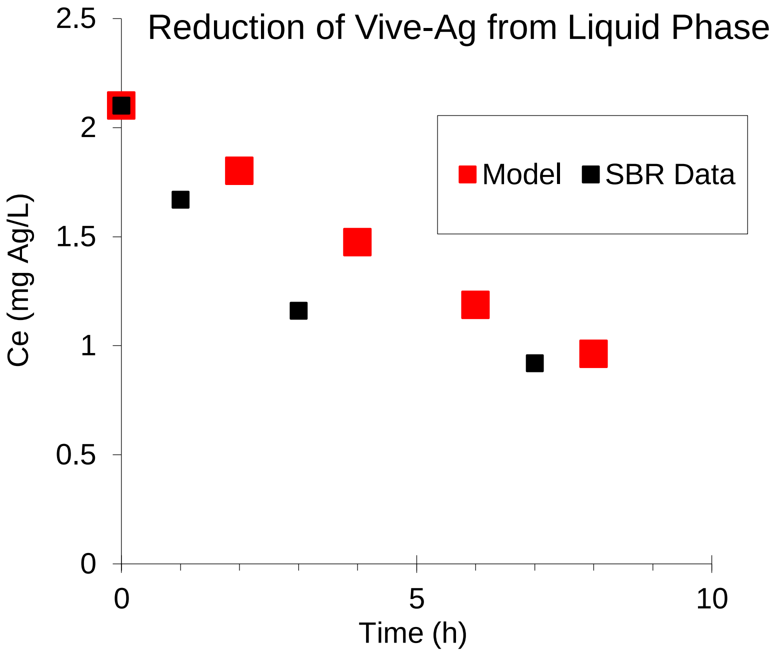


Hypothesis: Batch NP sorption experiments linked with dynamic bacterial growth models and reactor models can predict nanomaterial removal

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

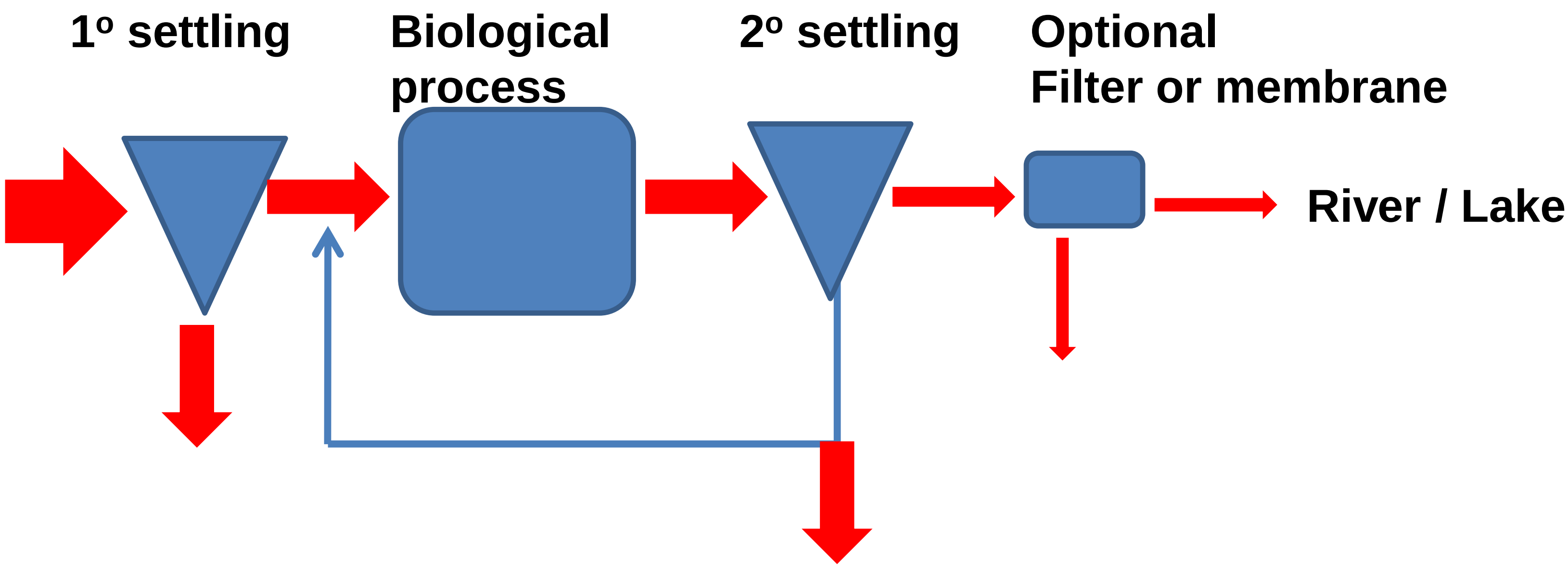
Model Predictions





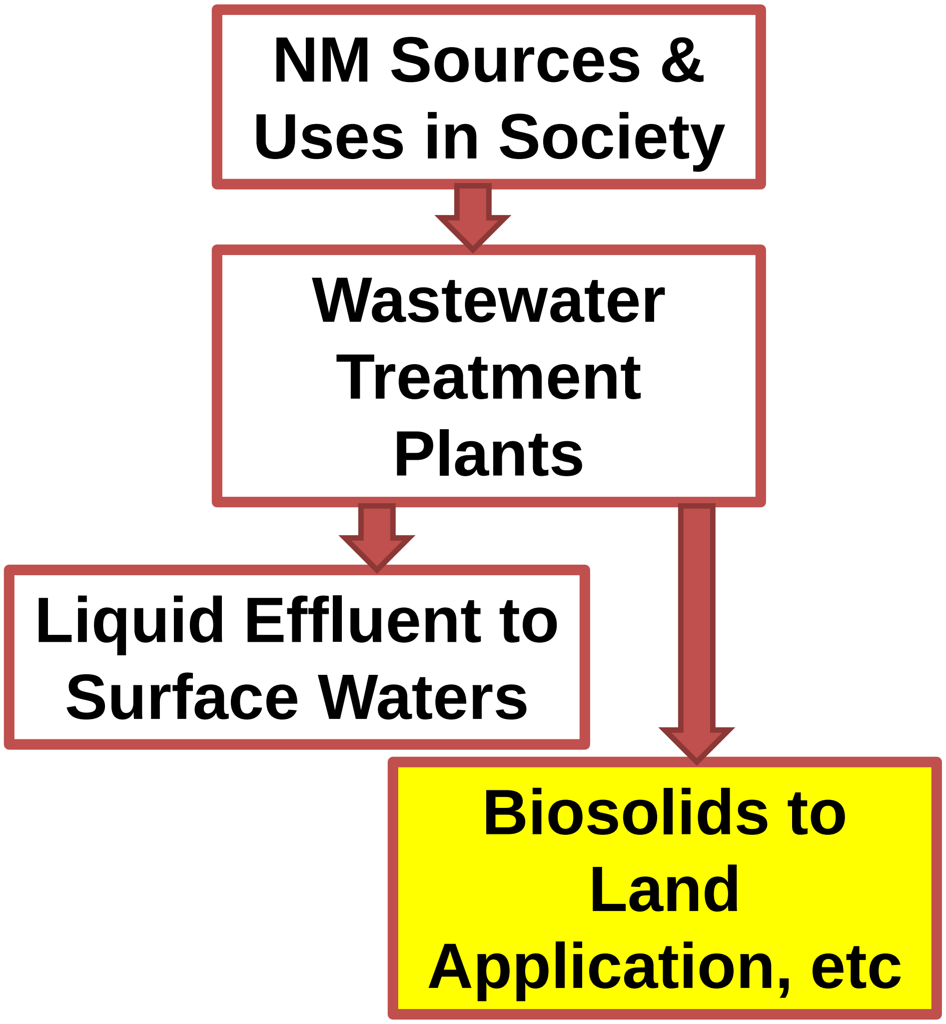
Conclusion: Preliminary confirmation exists that we can go from batch experiments to simulations of continuous flow performance. Difference in NP effluent concentration probably related to NP association with non-settlable colloids

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

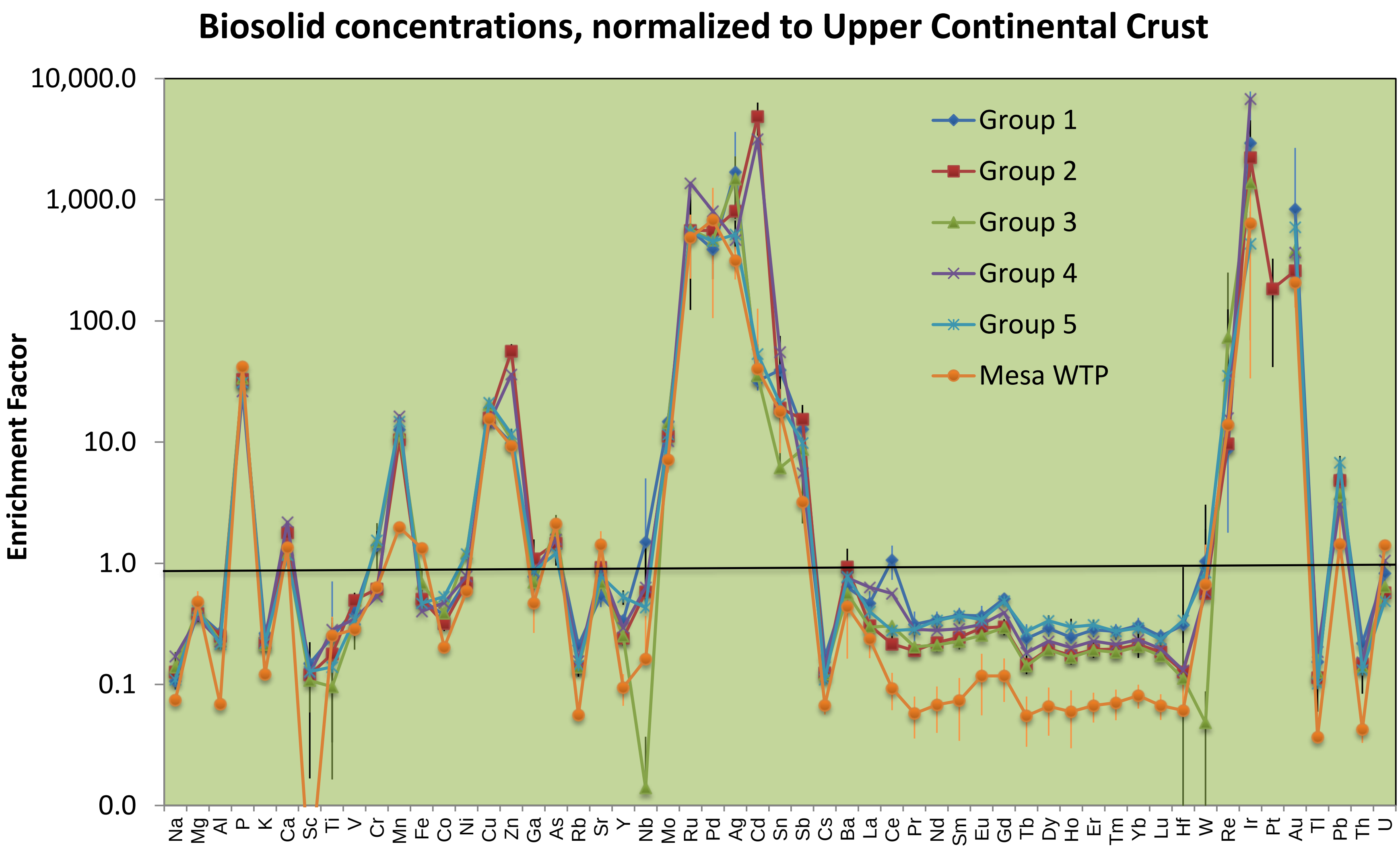


Let's go Nanoprospecting

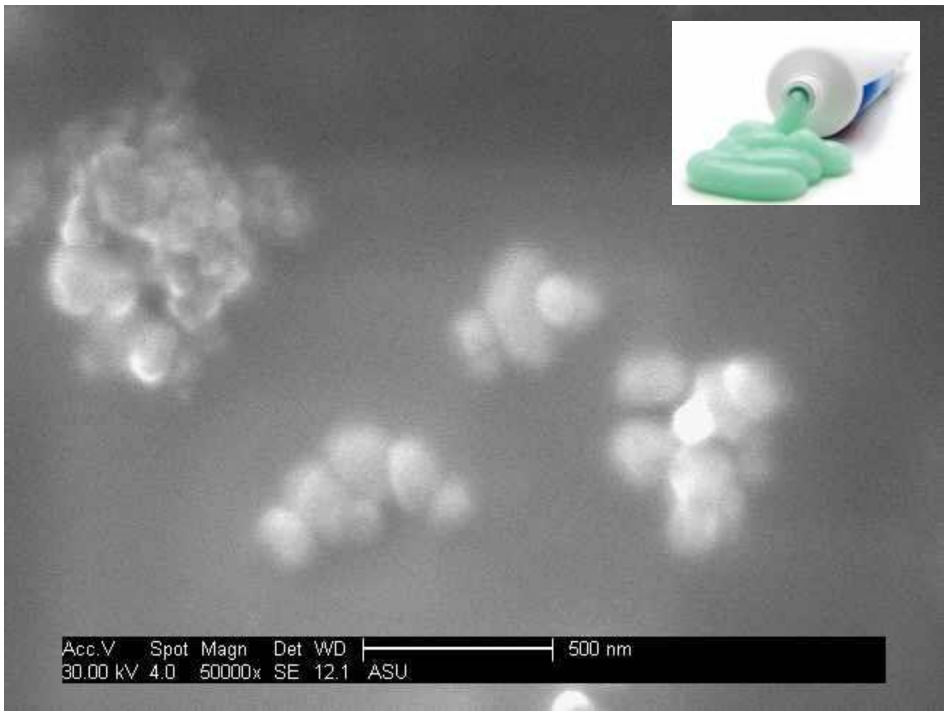
What type of NMs do we find in real biosolids?


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

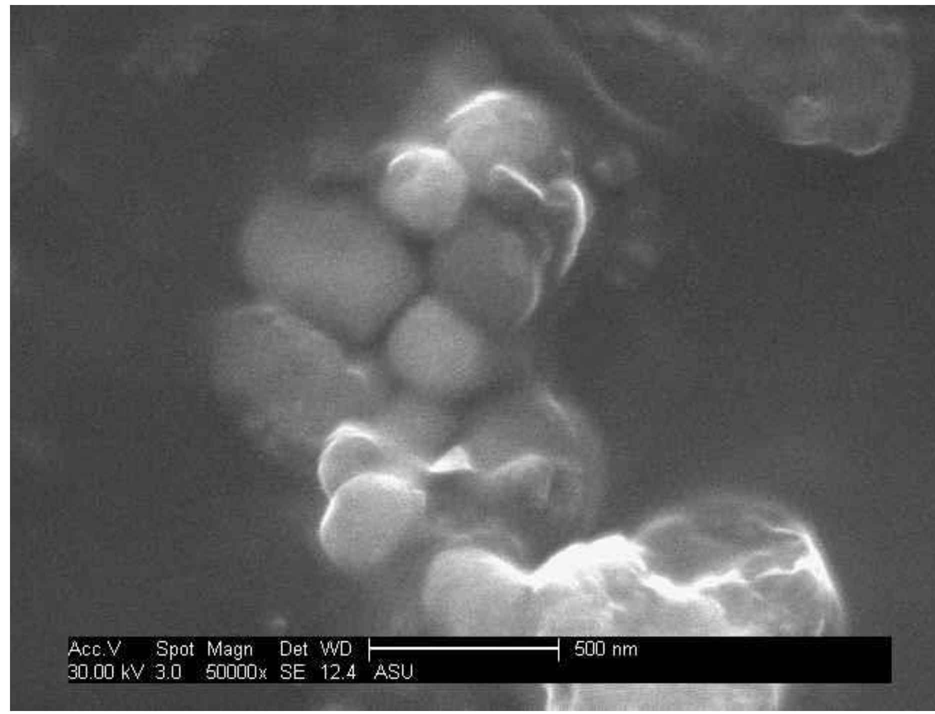
Big Picture – EPA Composite Biosolids



TiO_2 in commercial products are similar to TiO_2 extracted from biosolids

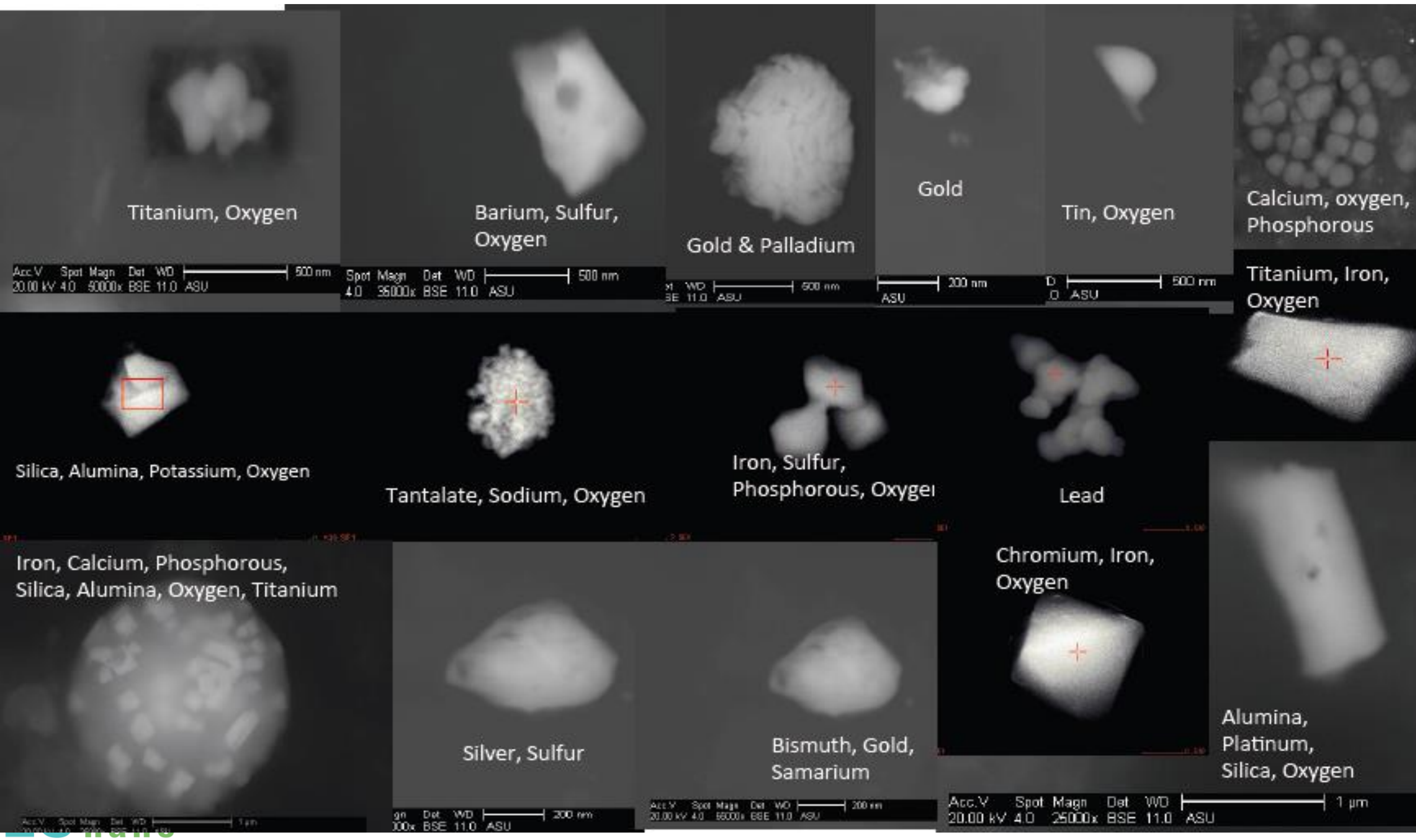


TiO_2 in Toothpaste



TiO_2 in Biosolids

Nano-scale objects found in Biosolids

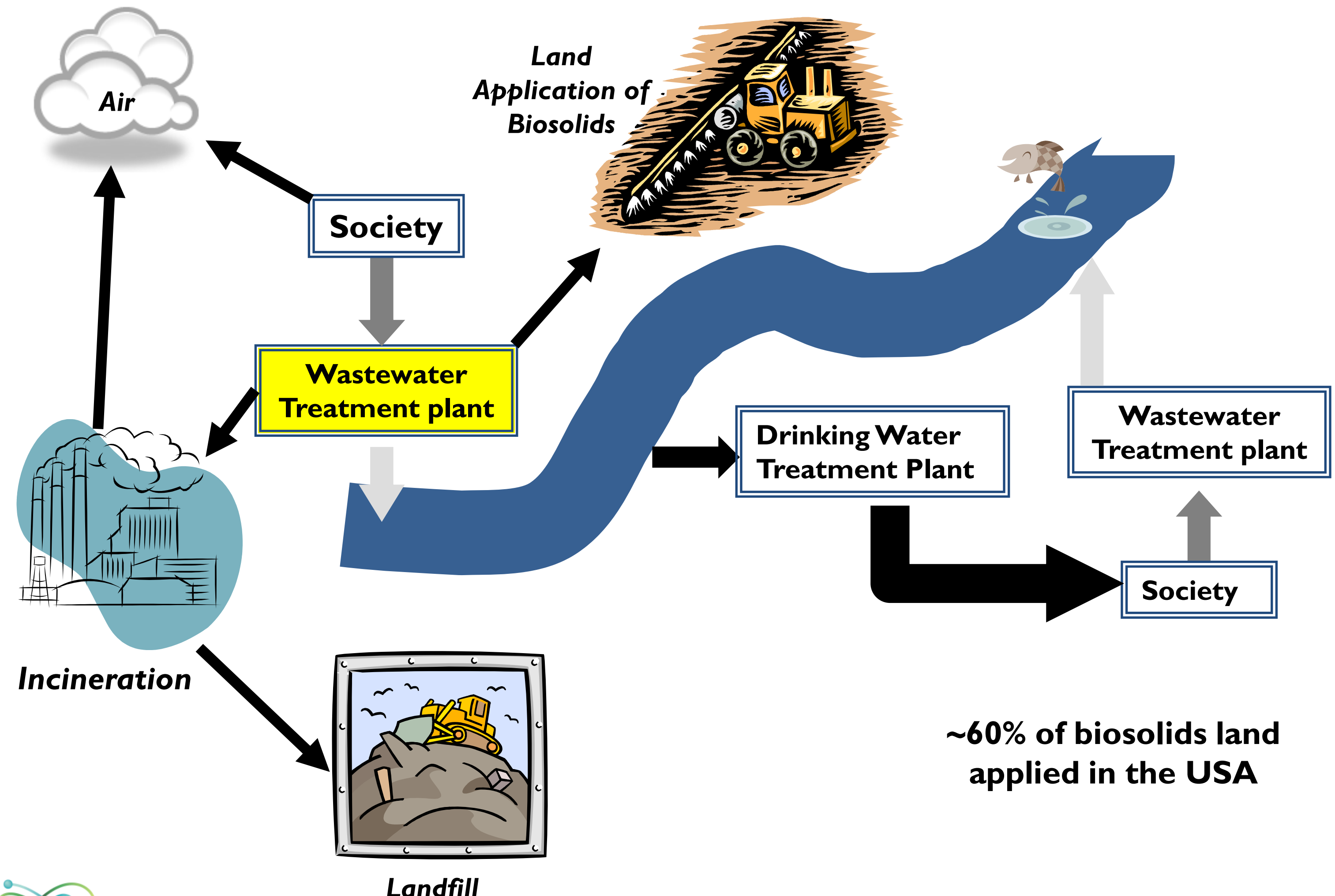


Frequent Nano-structures

Nanomaterial Composition (likely material)	**Approximate size**
Au+ Pd (catalyst)	200 to 500 nm
Au	200 nm
Al+Pt (catalyst)	1000 nm
Ag+S (silver sulfide)	200 nm
Fe+Ti+Si+O (clay)	500 nm
Bi	400-500 nm
Ba+S+O (barium sulfate)	500 nm
Fe + O (iron (hydr)oxide)	400 nm
Zn+O (zinc oxide)	250-400 nm
Ca+O (calcium carbonate)	300-600 nm
Ca+P+O (calcium phosphate)	600 nm
Sb+O+Na	250 nm
Ti+O (titanium dioxide)	100-300 nm
Ti+O+P (phosphate covered TiO2)	300 nm
Pb + O (lead oxide)	100-300 nm
Ta+Na+O (sodium tantalate – catalyst)	<100 nm to 300 nm

LC

Where do Biosolids Go?

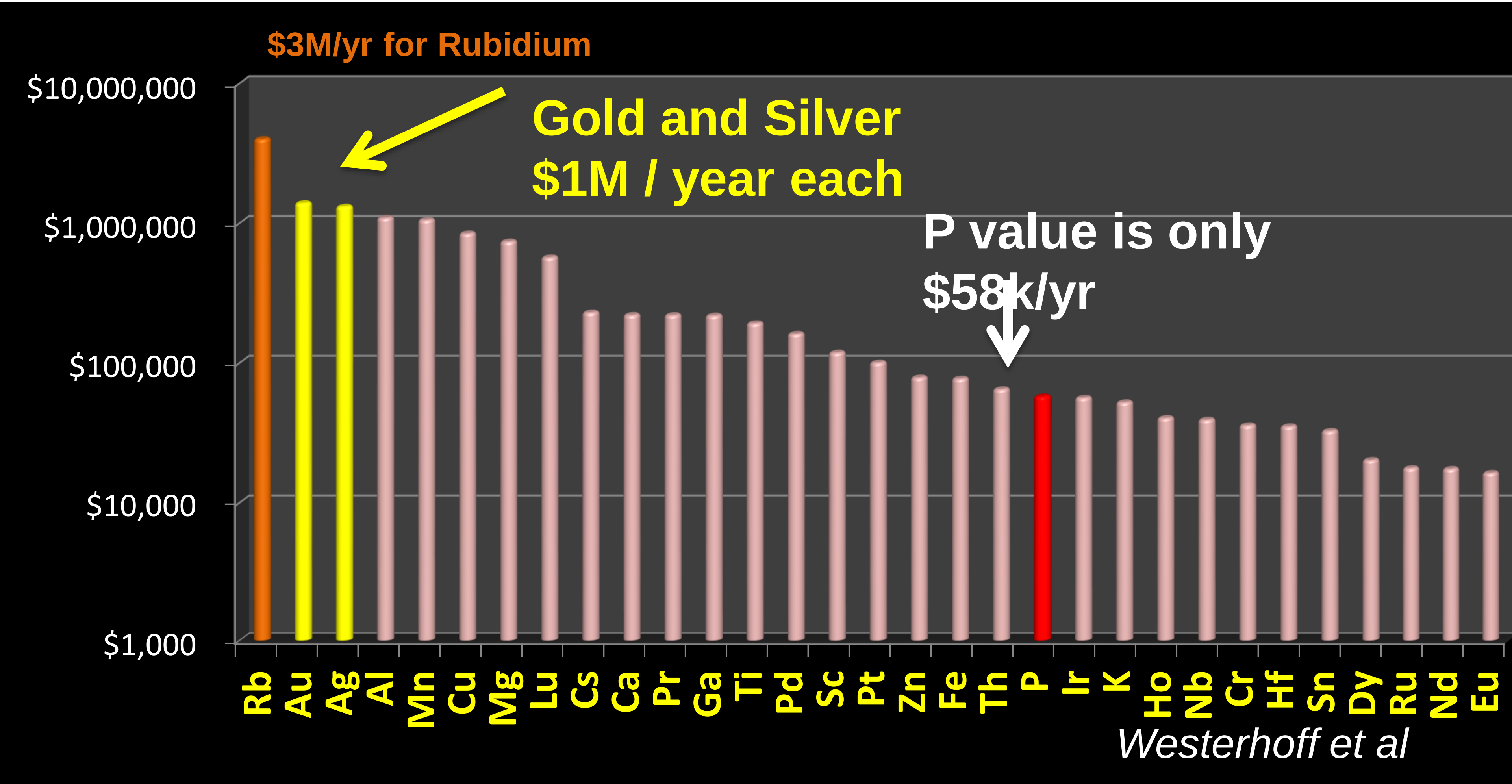


~60% of biosolids land applied in the USA

Value of metals in Biosolids

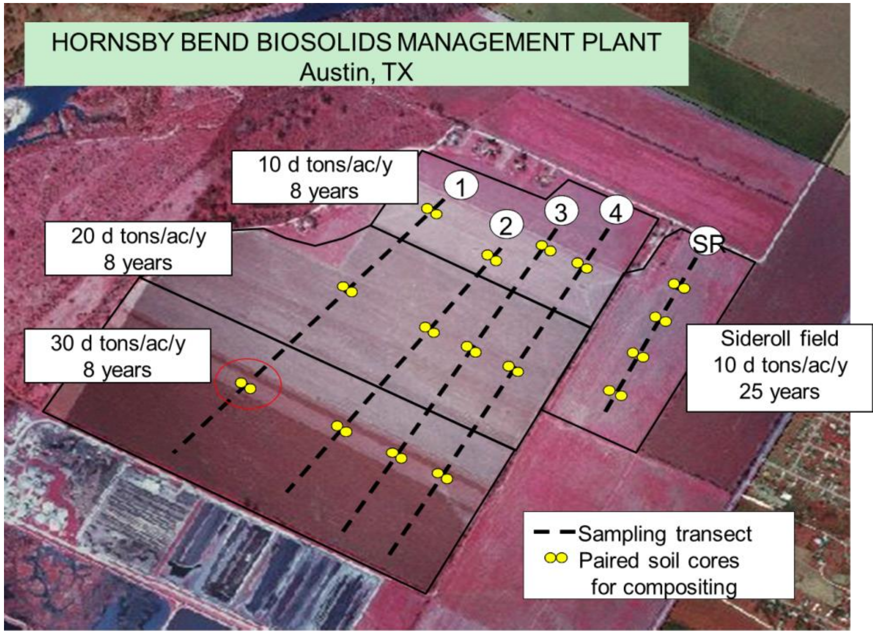
26 kg/year-capita & 1,000,000 people
(2863 tons dry biosolid per year)

Total Value = $12Million / year

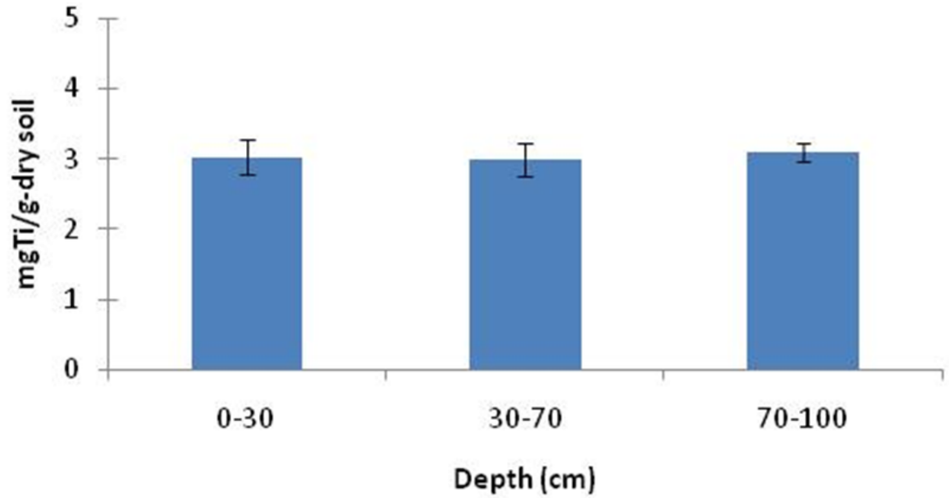


USDA Field Site Near Austin, TX Long-term Biosolid Applications

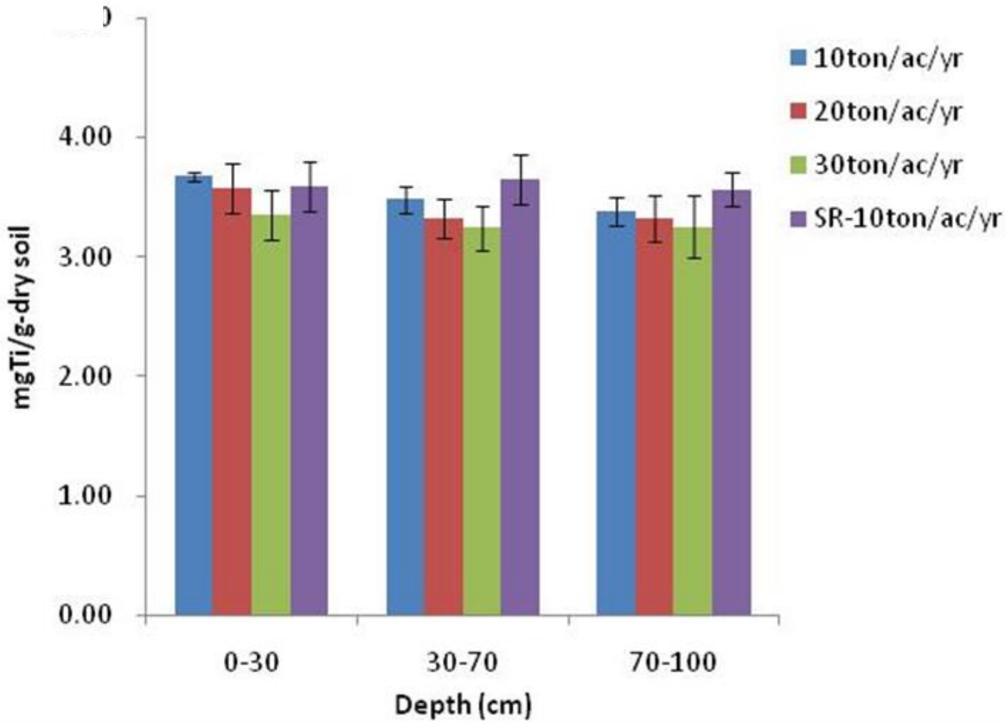
- Composite depth profile samples
  - 0 – 30 cm
  - 30 – 70 cm
  - 70 – 100 cm
- HNO_3/HF digestion
- ICP-OES for Ti, Ce, and Ag
- HR-TEM and EDS analysis



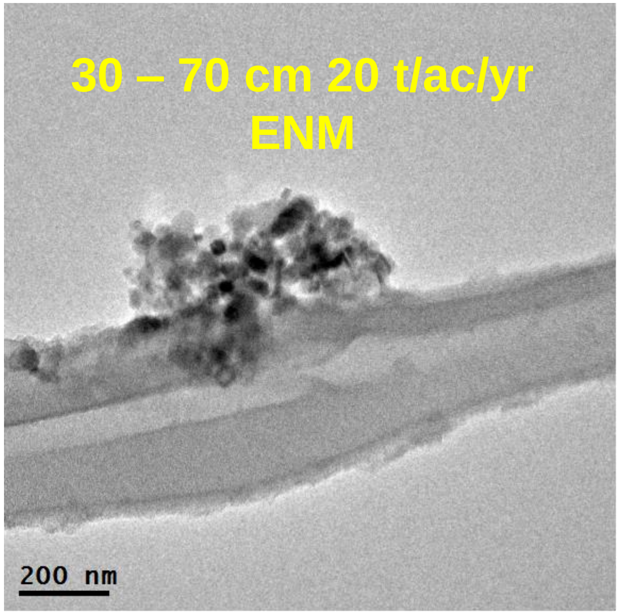
Titanium in Land Applied Fields

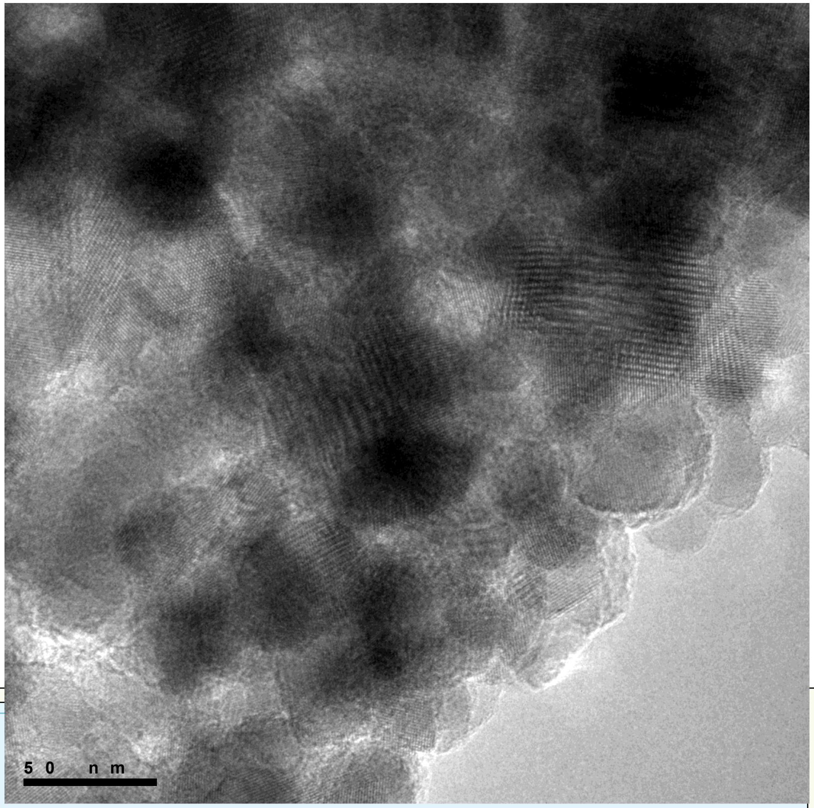


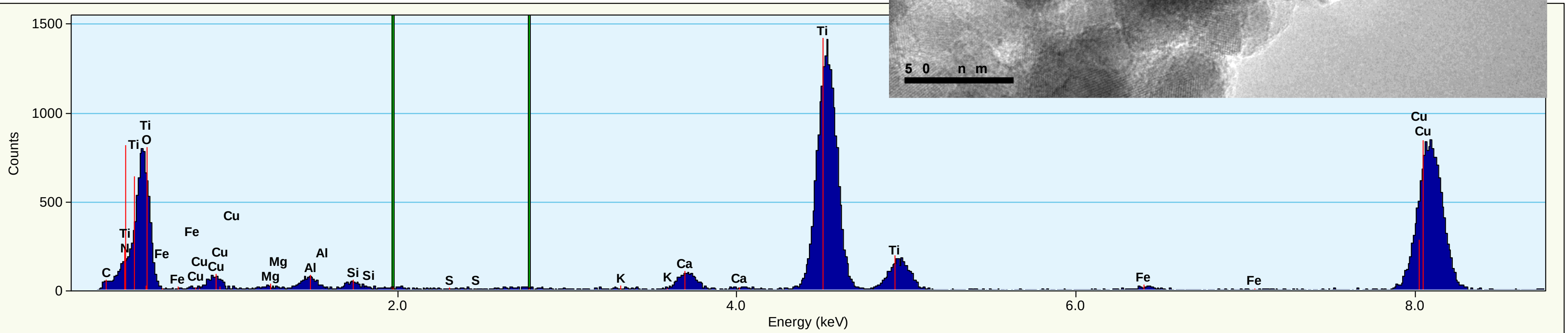
Titanium levels in biosolid amended soils are statistically higher than nearby “control” site



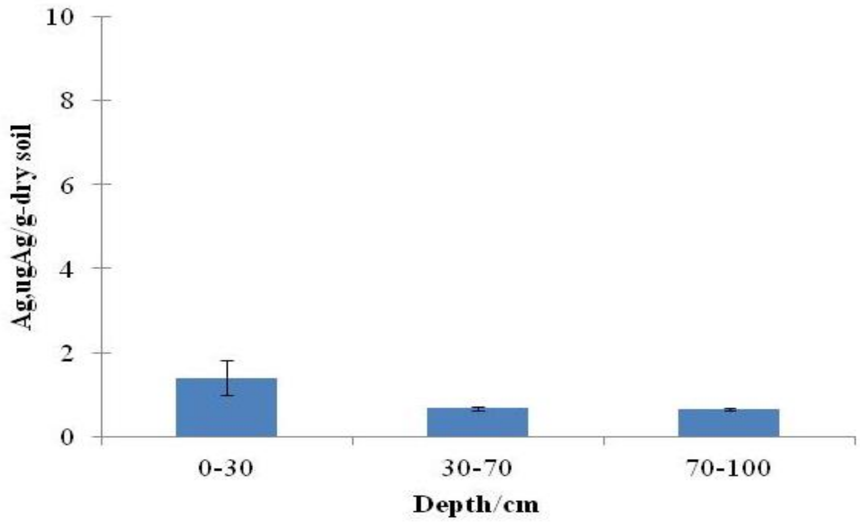
TiO_2 Nanomaterials are present in Biosolid Ammended Fields

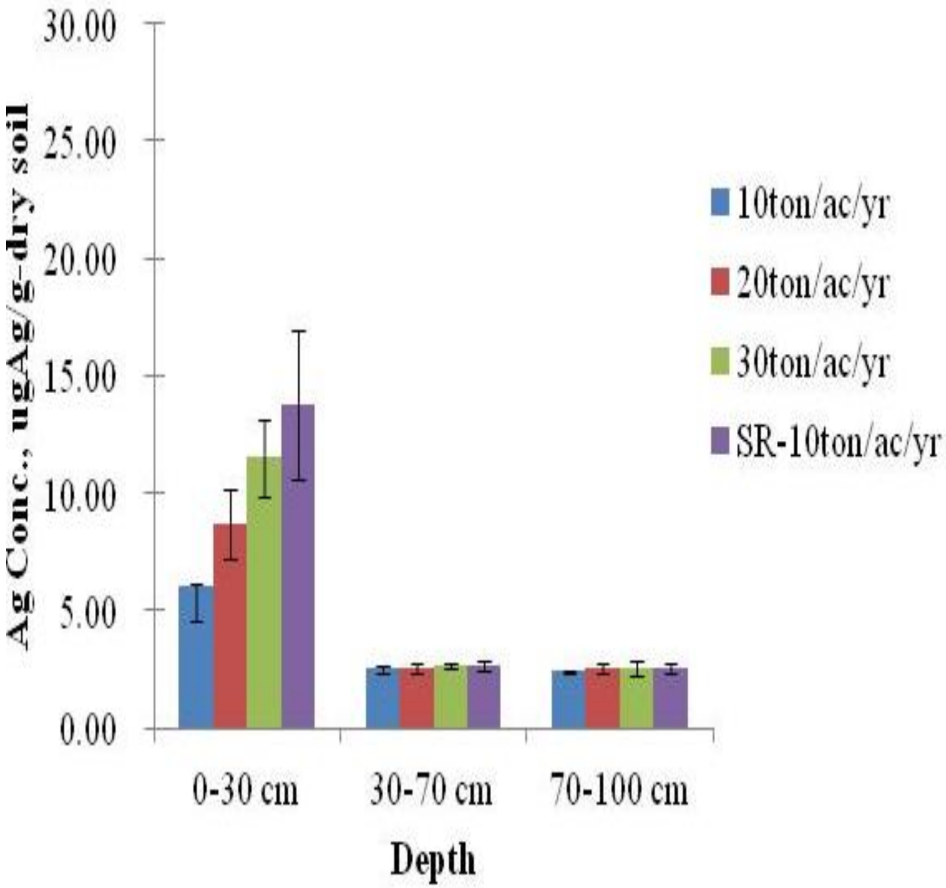






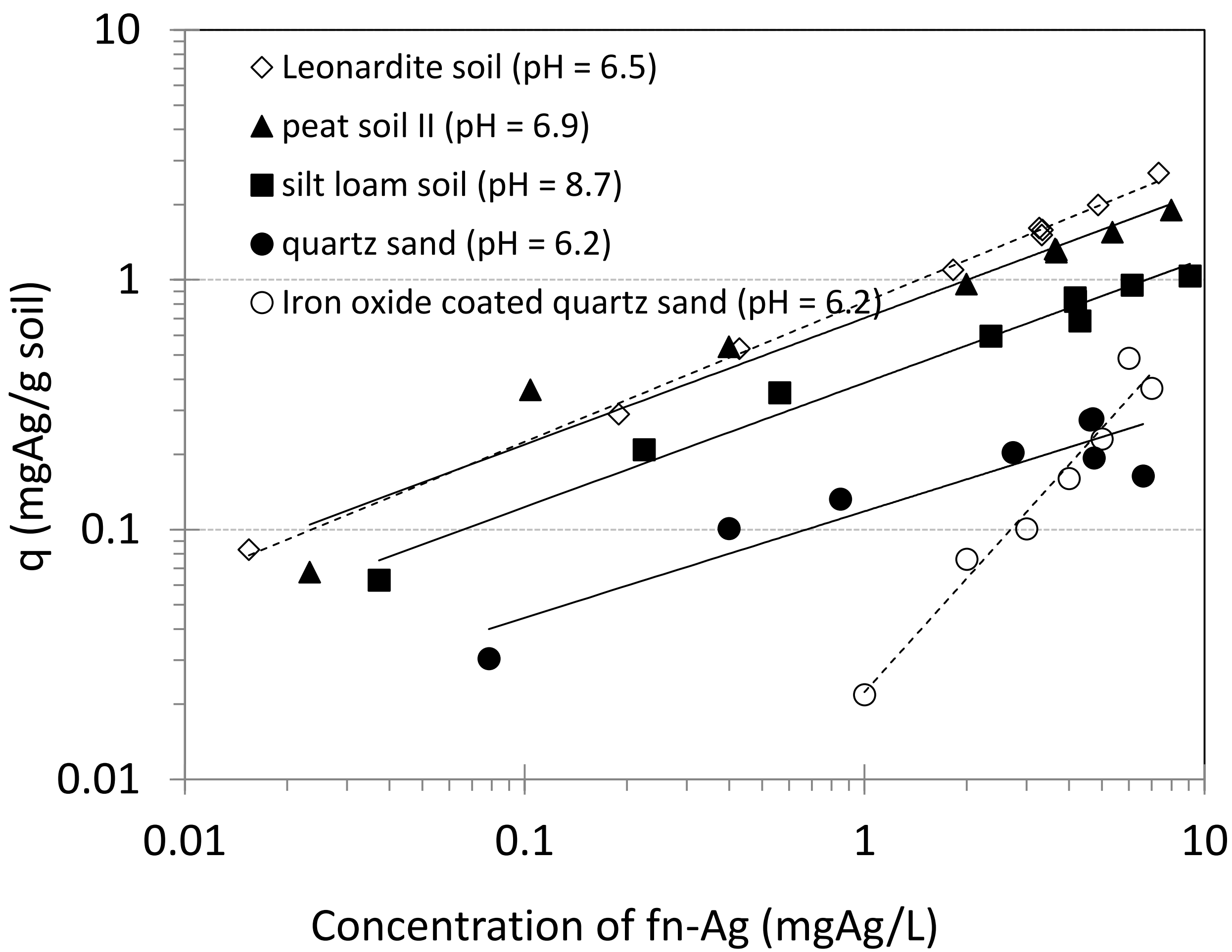
Silver Results





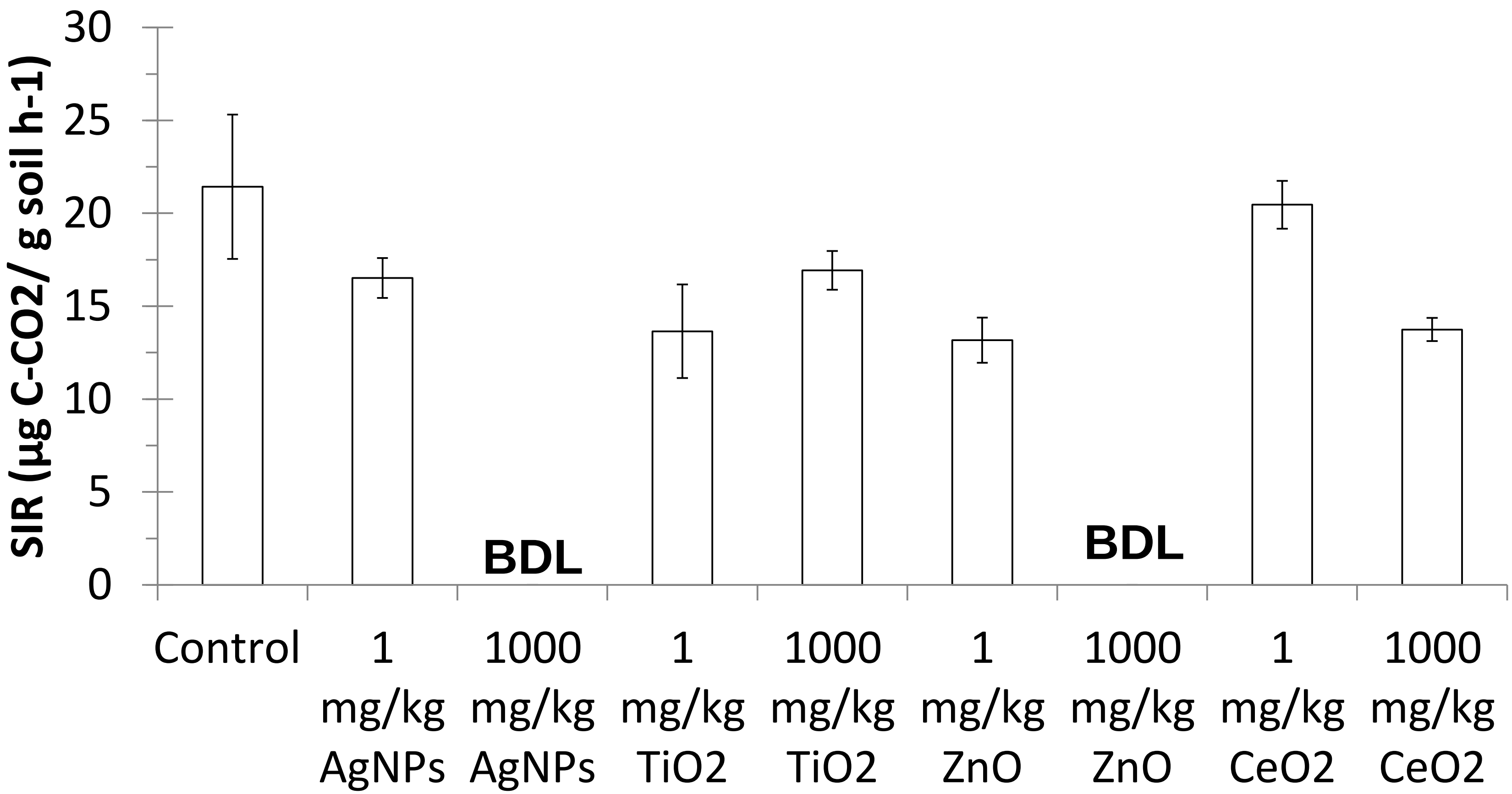
- Background concentration
  - 0.6 – 1.4 μgAg/g dry soil
  - Surface content higher
- Biosolids Field
  - Accumulation in surface soil
  - Accumulation increases with application rates
  - Avg: 6 – 14 μgAg/g dry soil

Soil-Sand Partitioning of NMs

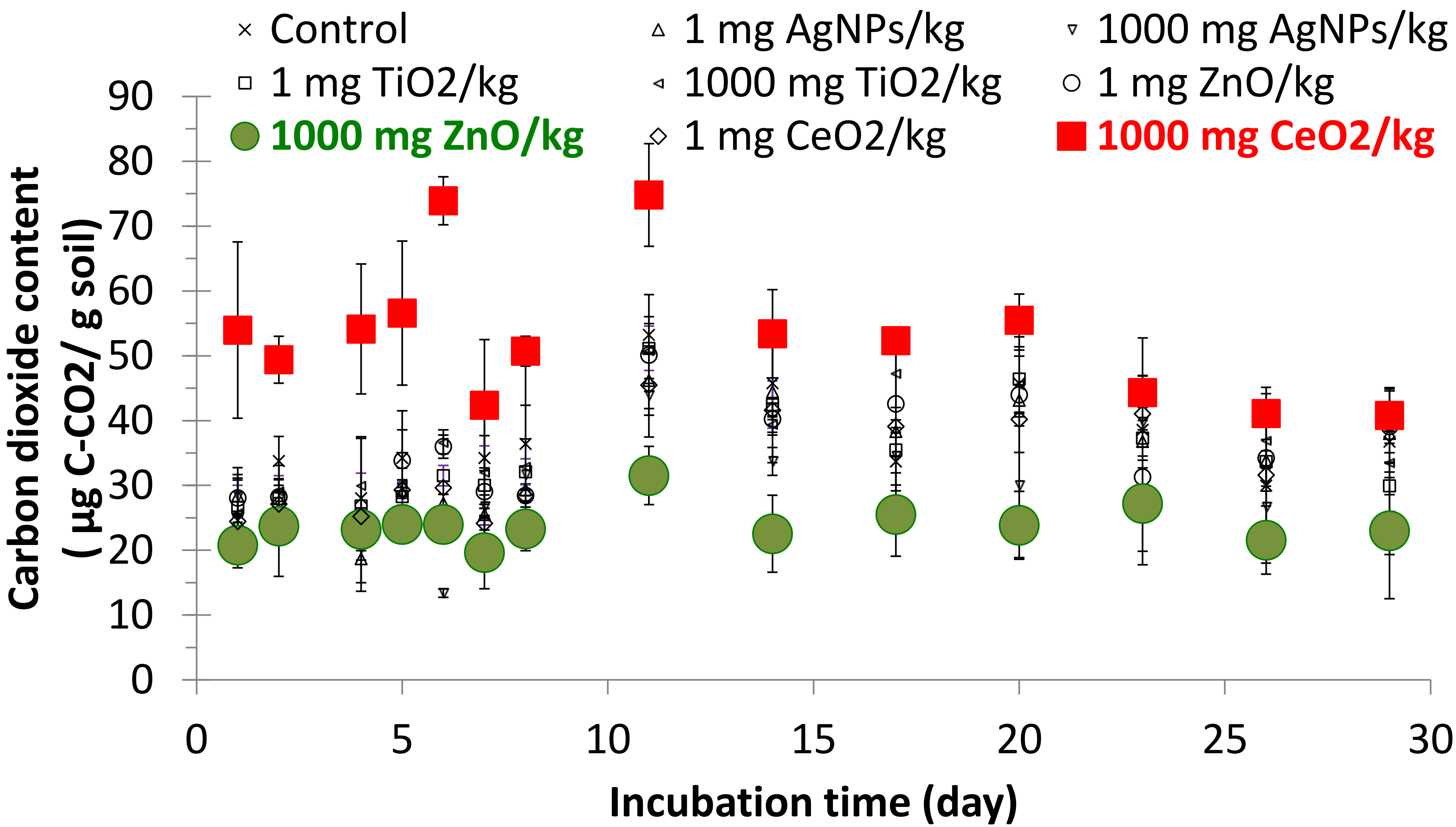


Unpublished work by ASU
Cornelis et al., Solubility and Batch Retention of CeO2 Nanoparticles in Soils, EST, 2011

Substrate Induced Respiration (28 day)



Basal Respiration Tests
CeO_2 increases CO_2 production

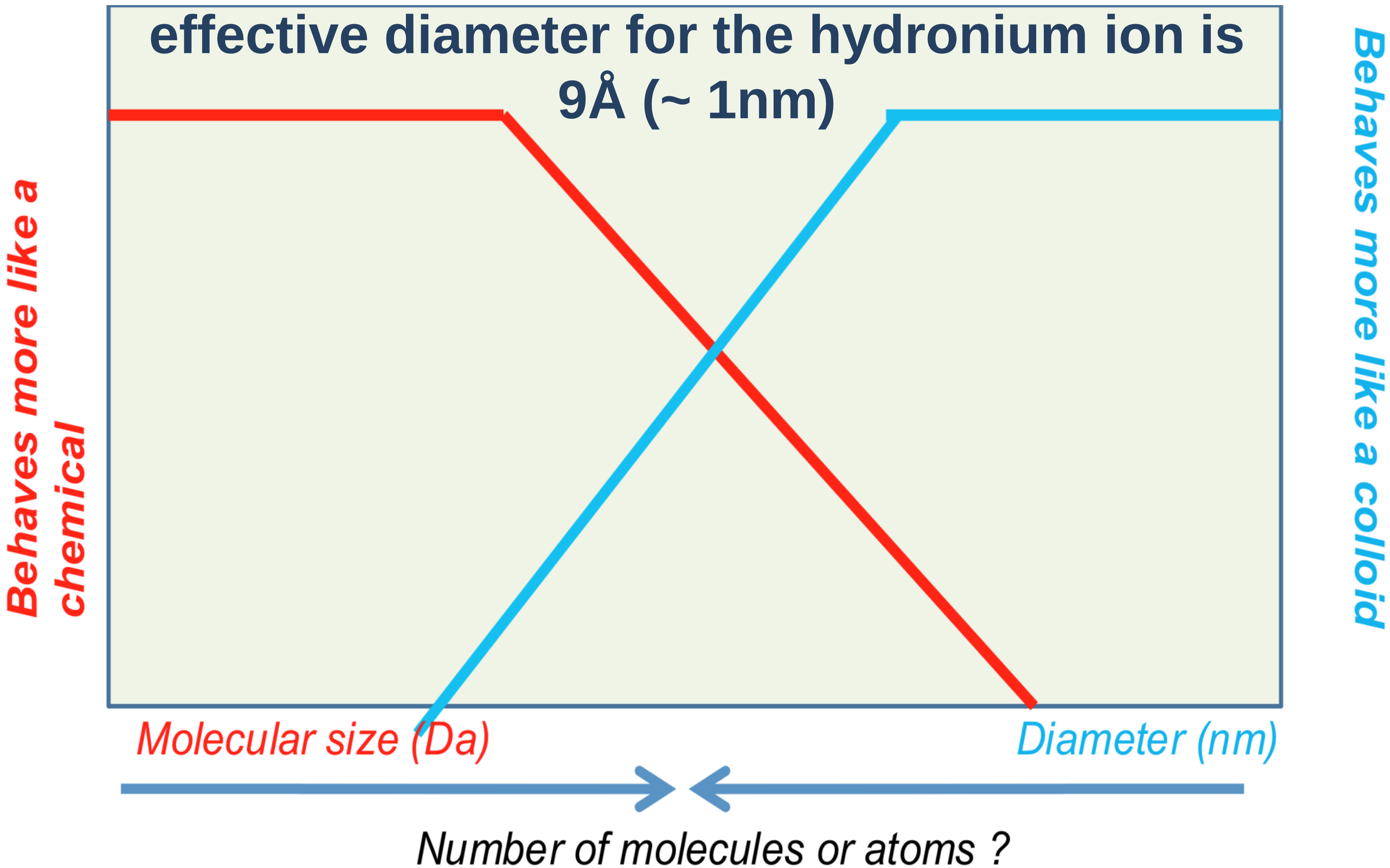


Key Points

- Nano can be "good" or "Bad" & are emerging contaminants
- Nanomaterials are already in use & entering sewage systems
- Nanomaterials generally accumulate in biosolids, but some can be detected in effluents
- New analytical techniques are being applied and needed to track nanomaterials
- Nanomaterials accumulate at interfaces
- Nanomaterials have unique properties that require new fate & transport paradigms

A Matter of Perceptive

when do ENMs behave more like classical colloids rather than dissolved macromolecules?



Westerhoff & Nowack, ACR (2013)

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- NSF *(CBET 1336542)*
- Contact: p.westerhoff@asu.edu

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