Interaction of Nanomaterials with Wastewater Biomass and Their Detection in Water

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Outline

- Life cycle view of nanomaterials and significance of sewer systems
- Fate of nanomaterials during wastewater treatment
- Emerging technologies to monitor nanomaterials in water
- Acknowledgements

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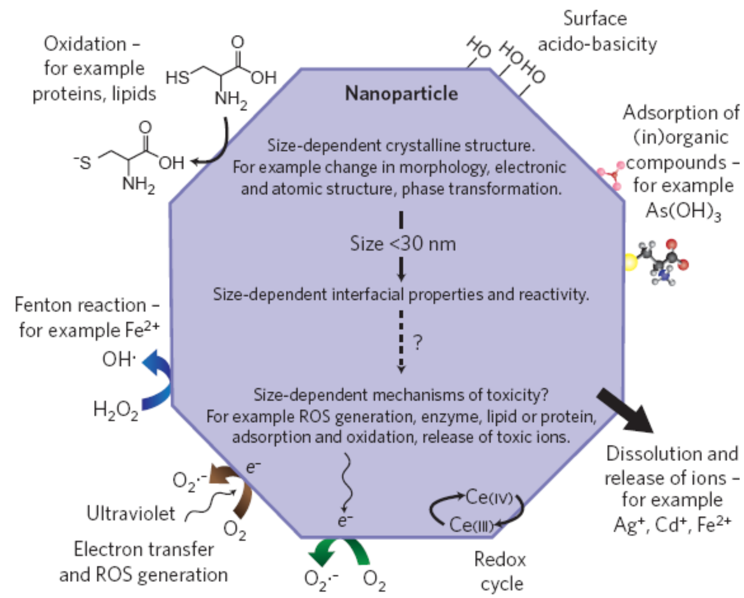
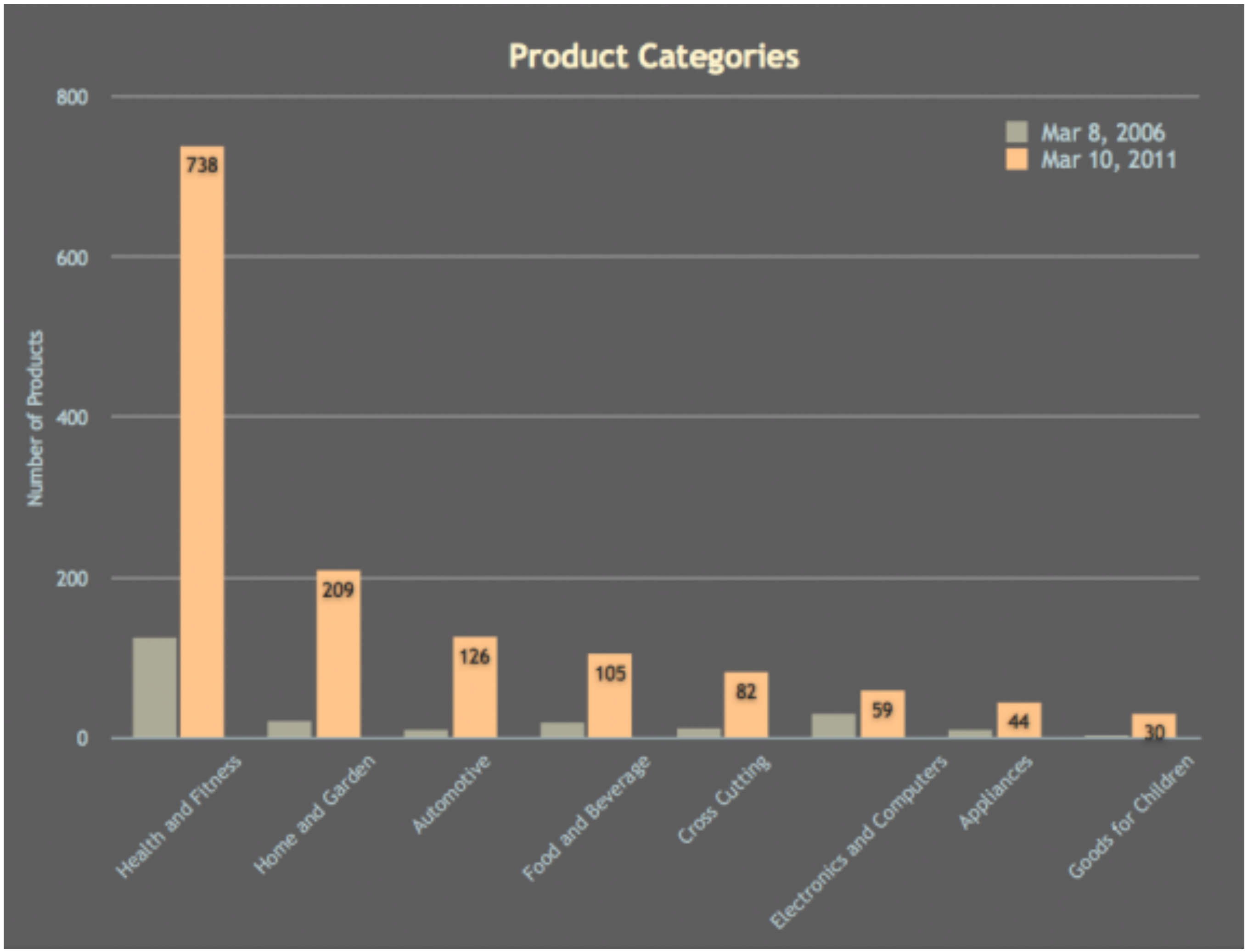
Working Definition of “nano”

- What is “nano”
  - Nanoscale: < 100 nm in one dimension
  - Nanomaterial: has a unique property because of its smallness
- Types:
  - Metalics: TiO_2, Ag, SiO_2, CeO, Au
  - Carbonaceous: fullerenes (C_{60}) & nanotubes



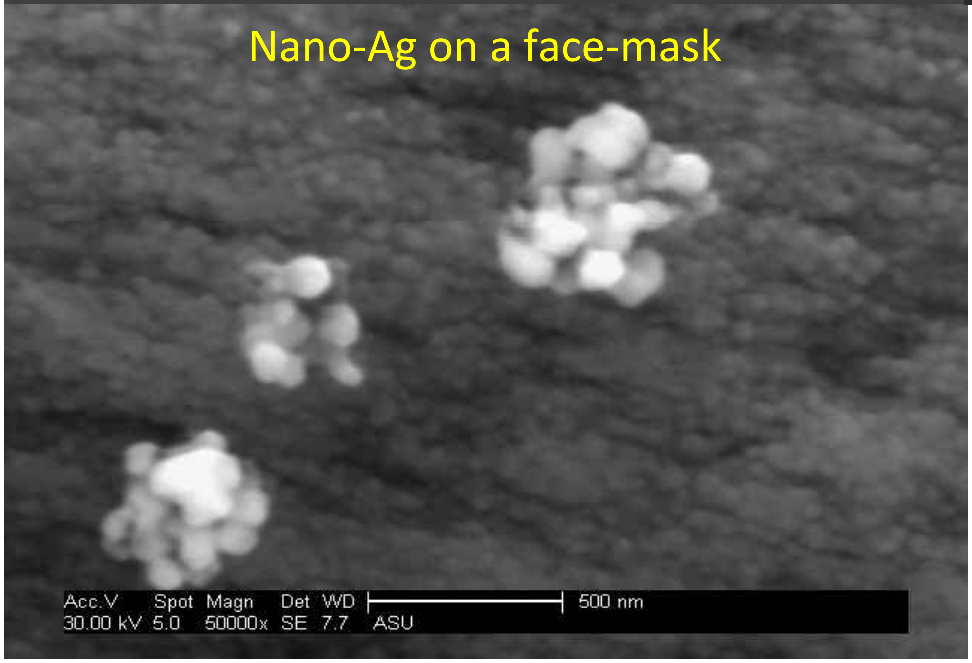
Physicochemical mechanisms for processes that occur on NM surfaces, and can lead to ecotoxicity issues (Auffan et al., 2009)

Many commercial products contain nanomaterials

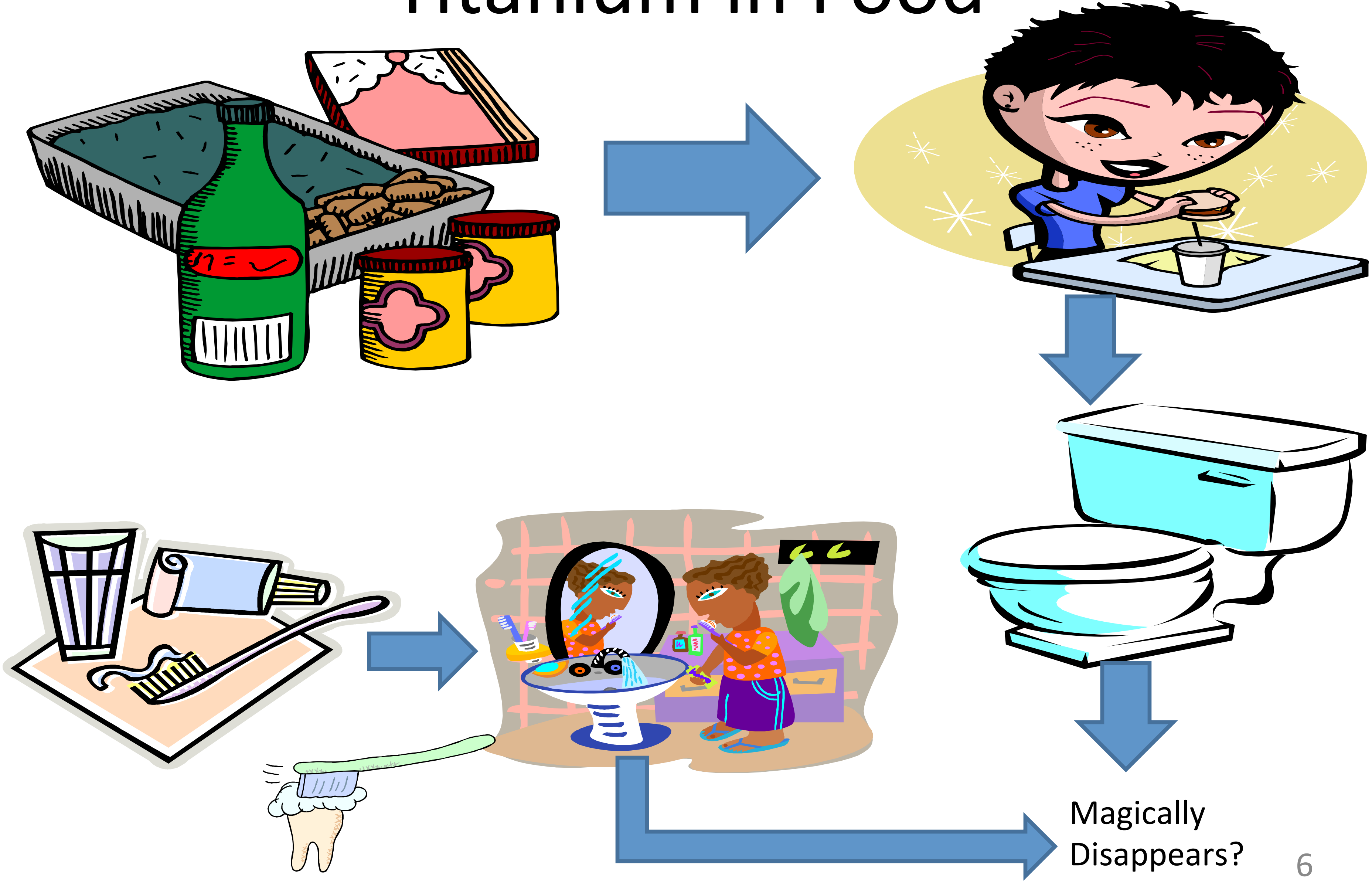


http://www.nanotechproject.org/inventories/consumer/analysis_draft/

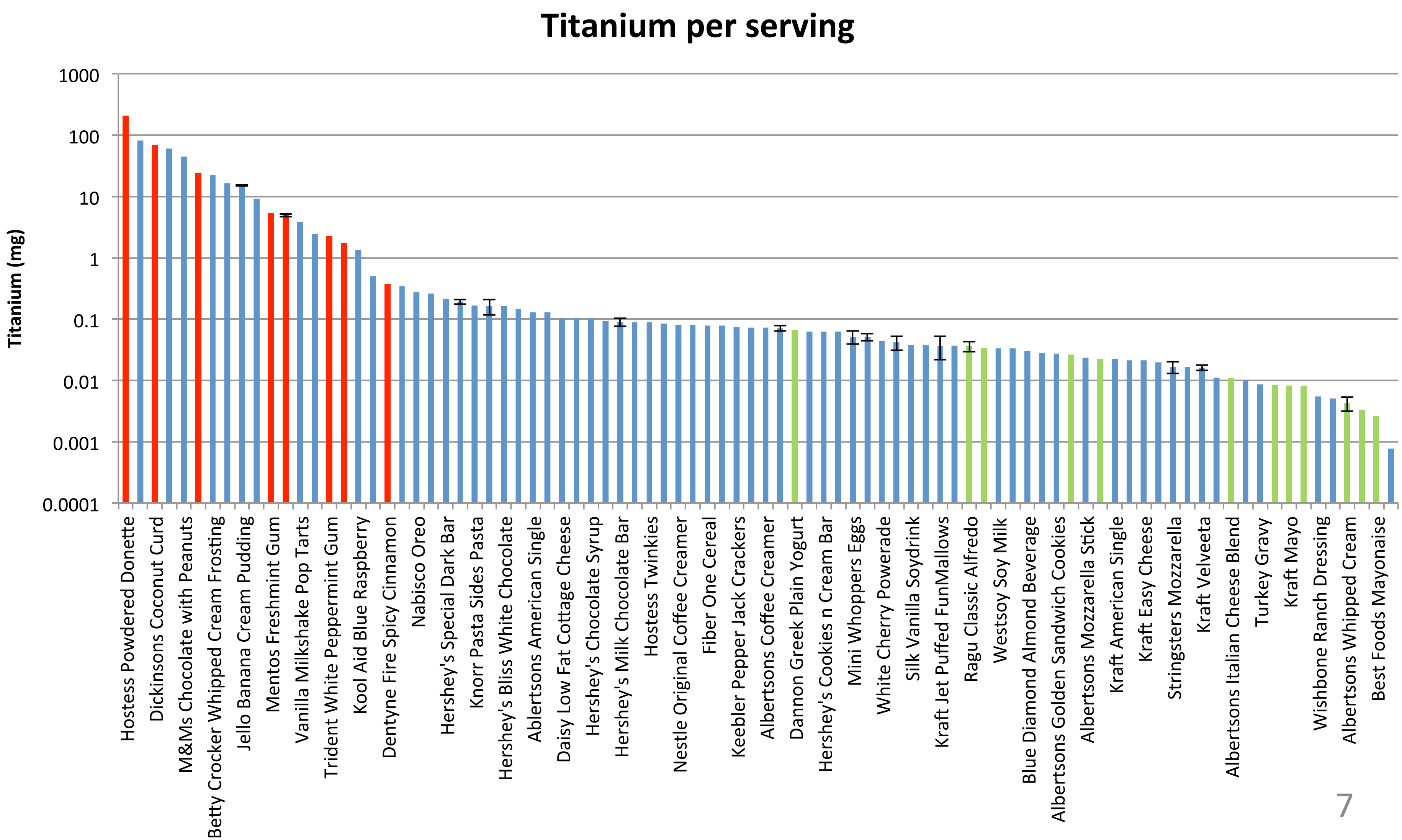
ENMs come in all shapes and sizes



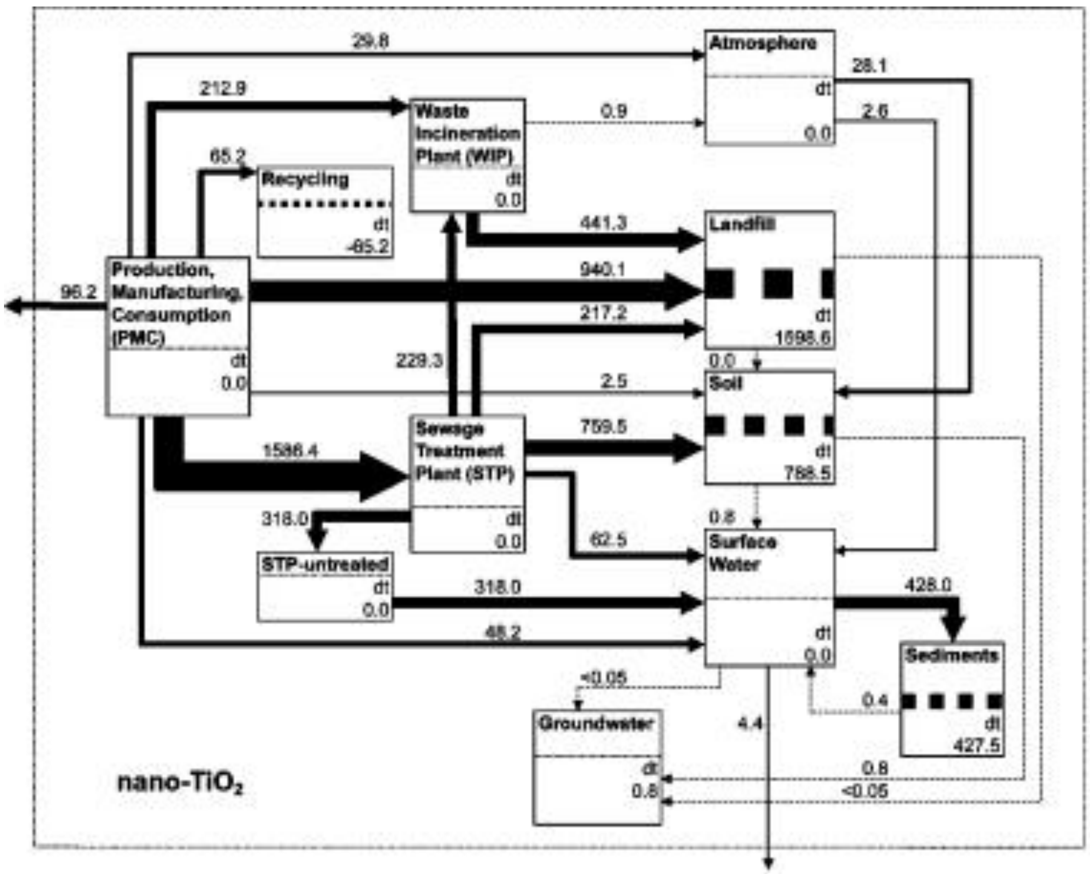
Titanium in Food



Titanium In Common Foods



“Society” is a source of engineered nanomaterials



Modeled Environmental Concentrations of Engineered Nanomaterials (TiO_2, ZnO, Ag, CNT Fullerenes) for Different Regions

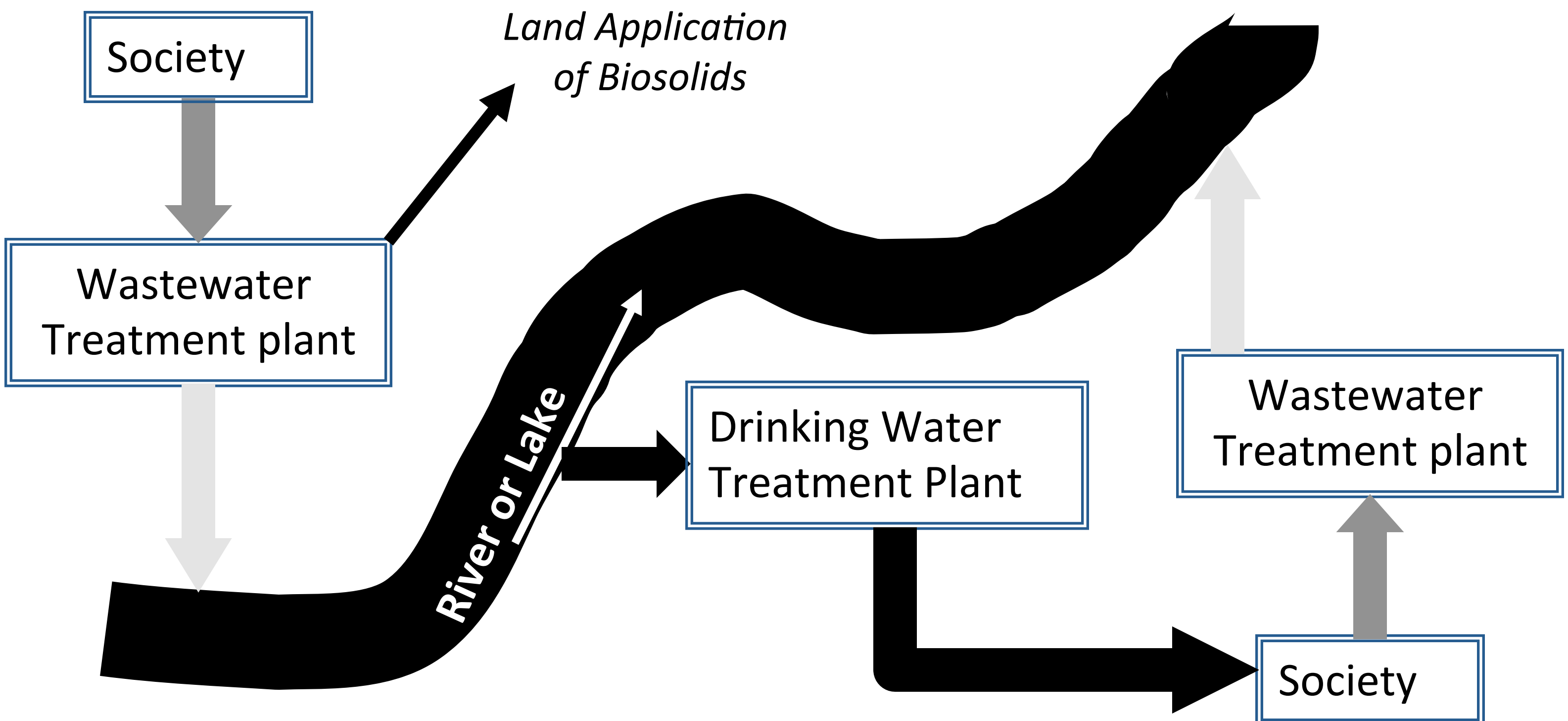
FADRI GOTTSCHALK,†,‡
TOBIAS SONDERER,†
ROLAND W. SCHOLZ,‡ AND
BERND NOWACK*,†

- Nanomaterials most likely to occur:

  TiO_2 > ZnO > Ag > CNT > fullerene

Framework for Fate of Nanoparticles in Engineered Systems

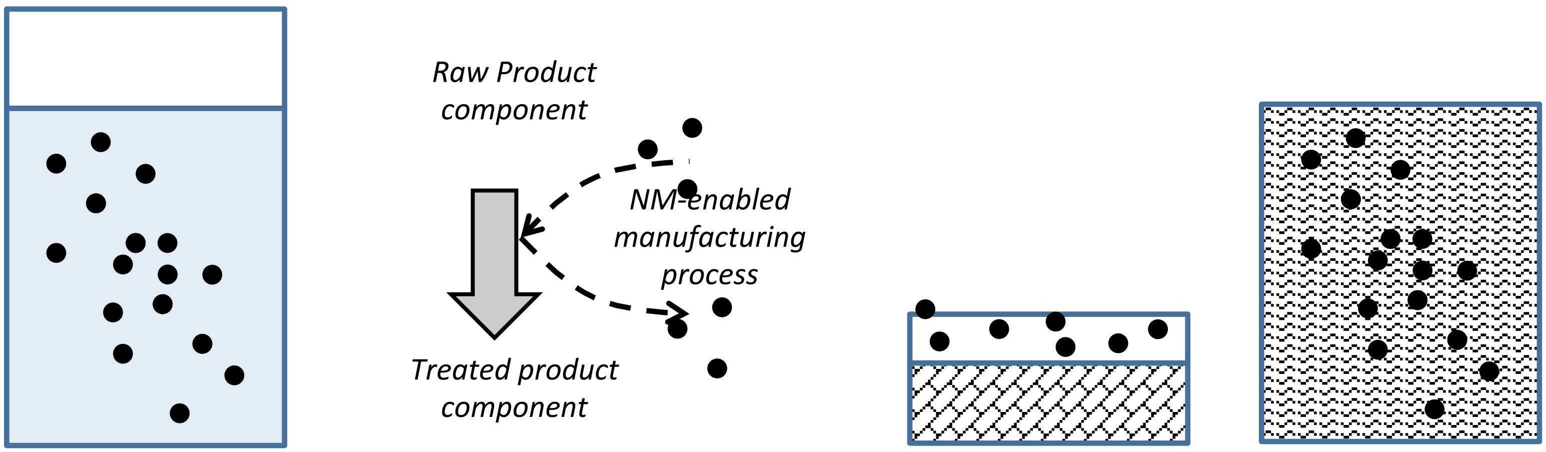
Sewer Systems Emerge as very important



>75% of the US population is served by centralized wastewater treatment facilities

Not Everyone Lives Upstream

Life cycle of nanoparticles varies for different Product Lines



NMs dispersed in fluid, gel, creme

Industrial processing using NMs

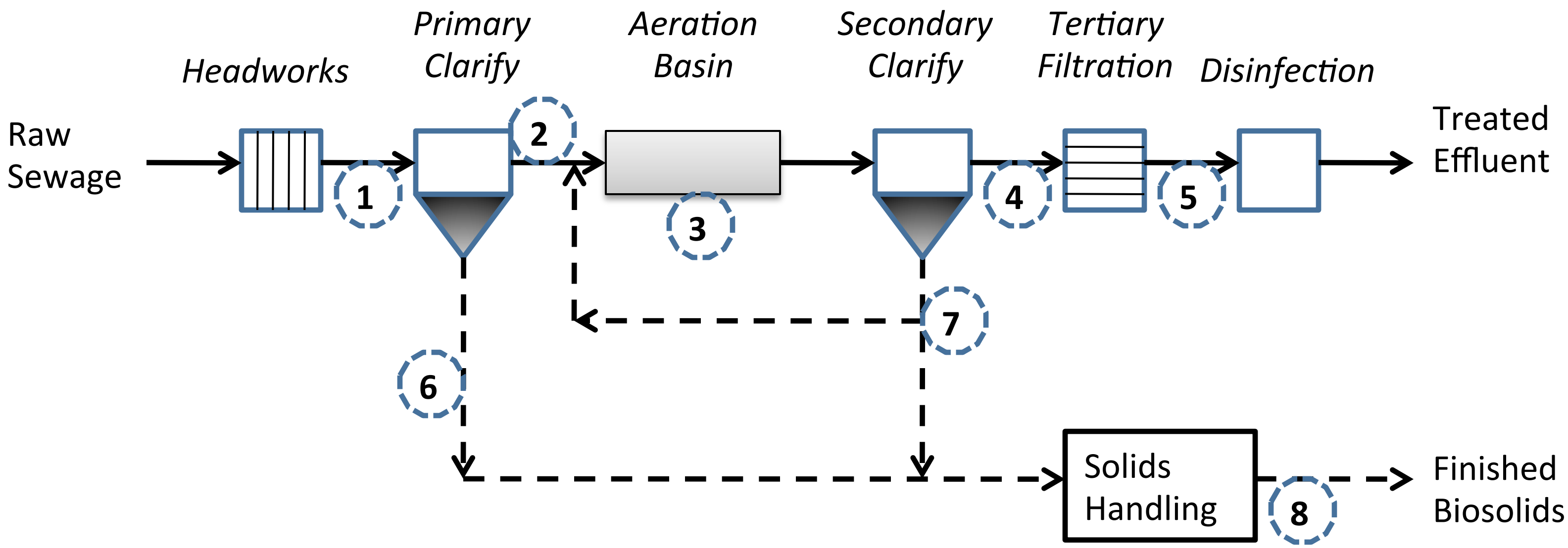
NMs Attached to surfaces (fabrics, plastics, etc)

NMs embedded in polymers or other composites

Discharge to sewer likely

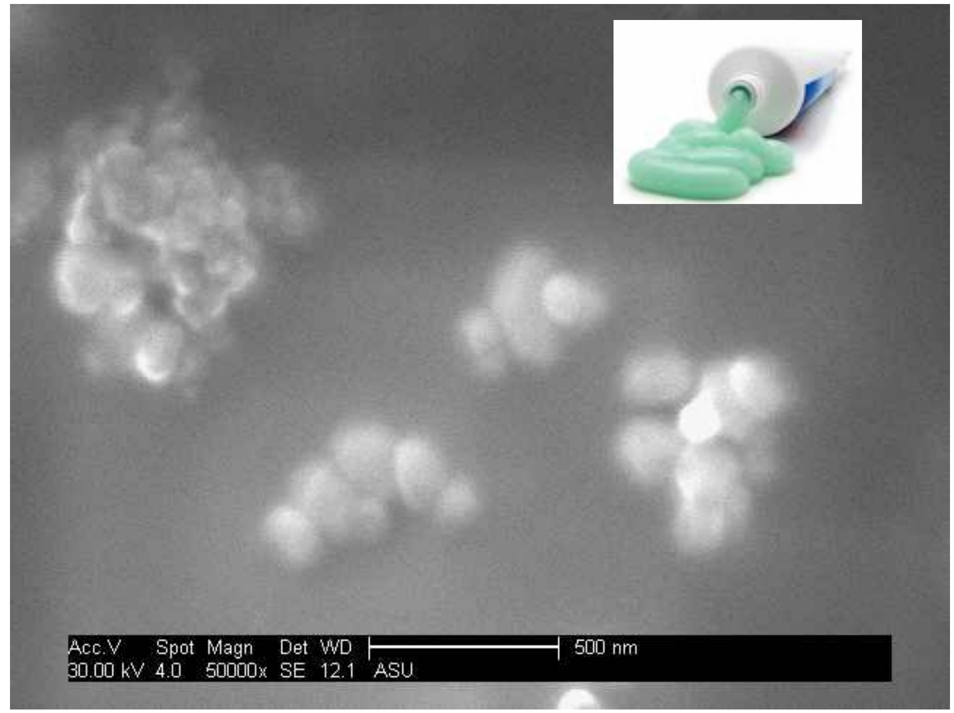
Discharge to landfill likely

Nanomaterial Sampling and Removal at Full-Scale Wastewater Treatment Plants



Case Study around Titanium Dioxide

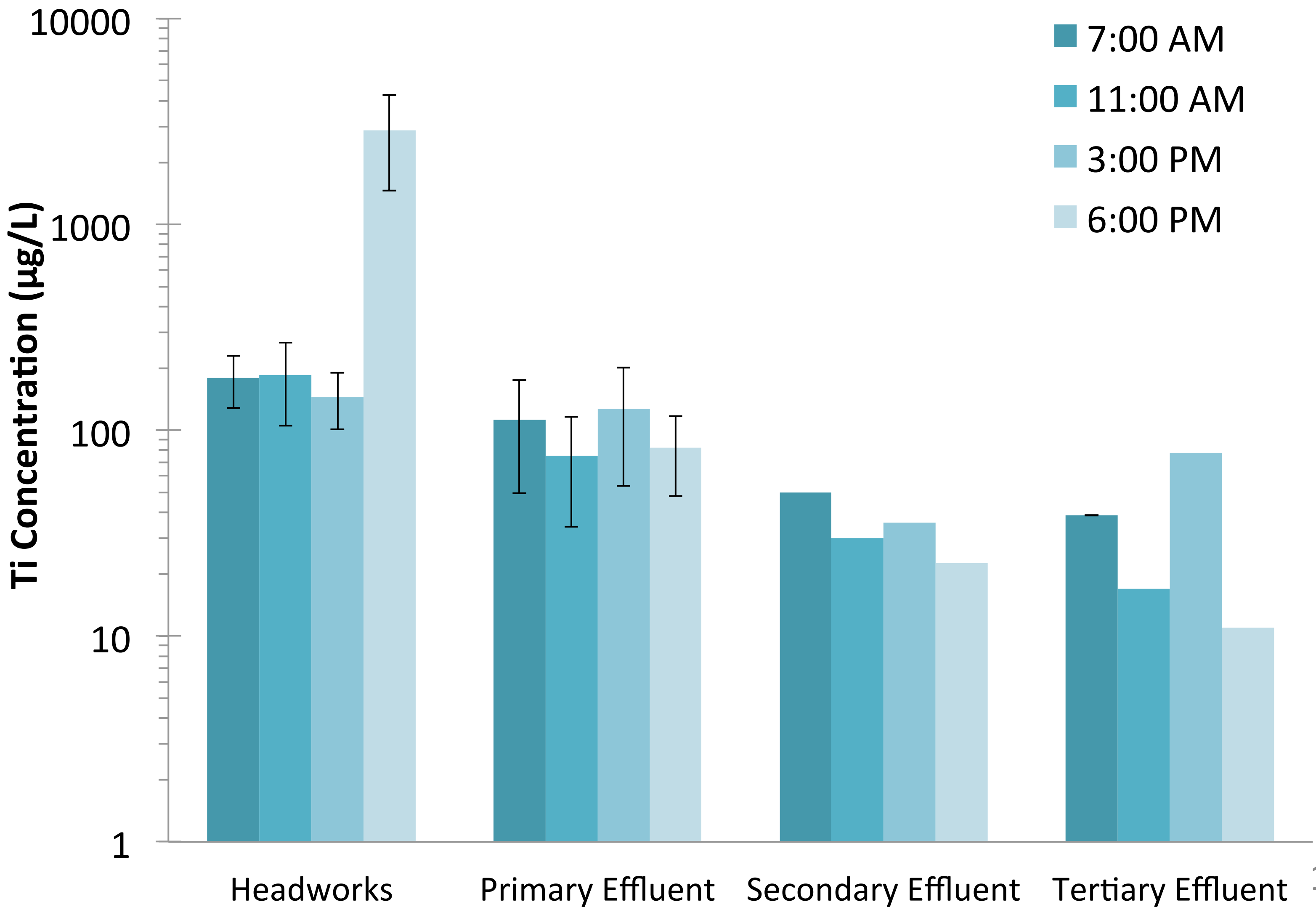
- Size distribution
- Surface coatings
- Zeta potential
- Optical properties
- Shape or aspect ratio
- Unit of measure: mass, surface area, volume, number concentrations



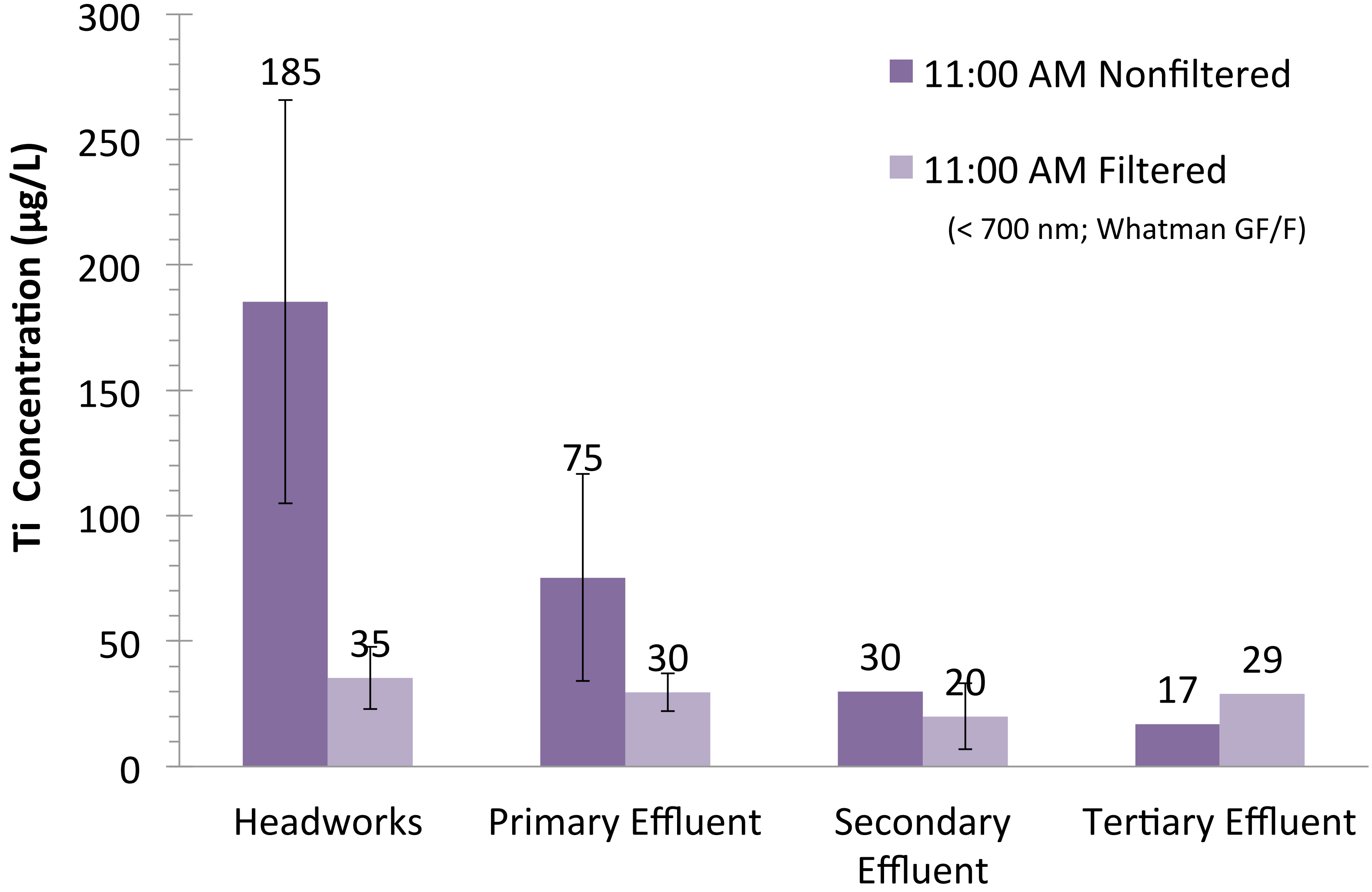
TiO_2 in Toothpaste

Seeing is believing when it comes to Nano

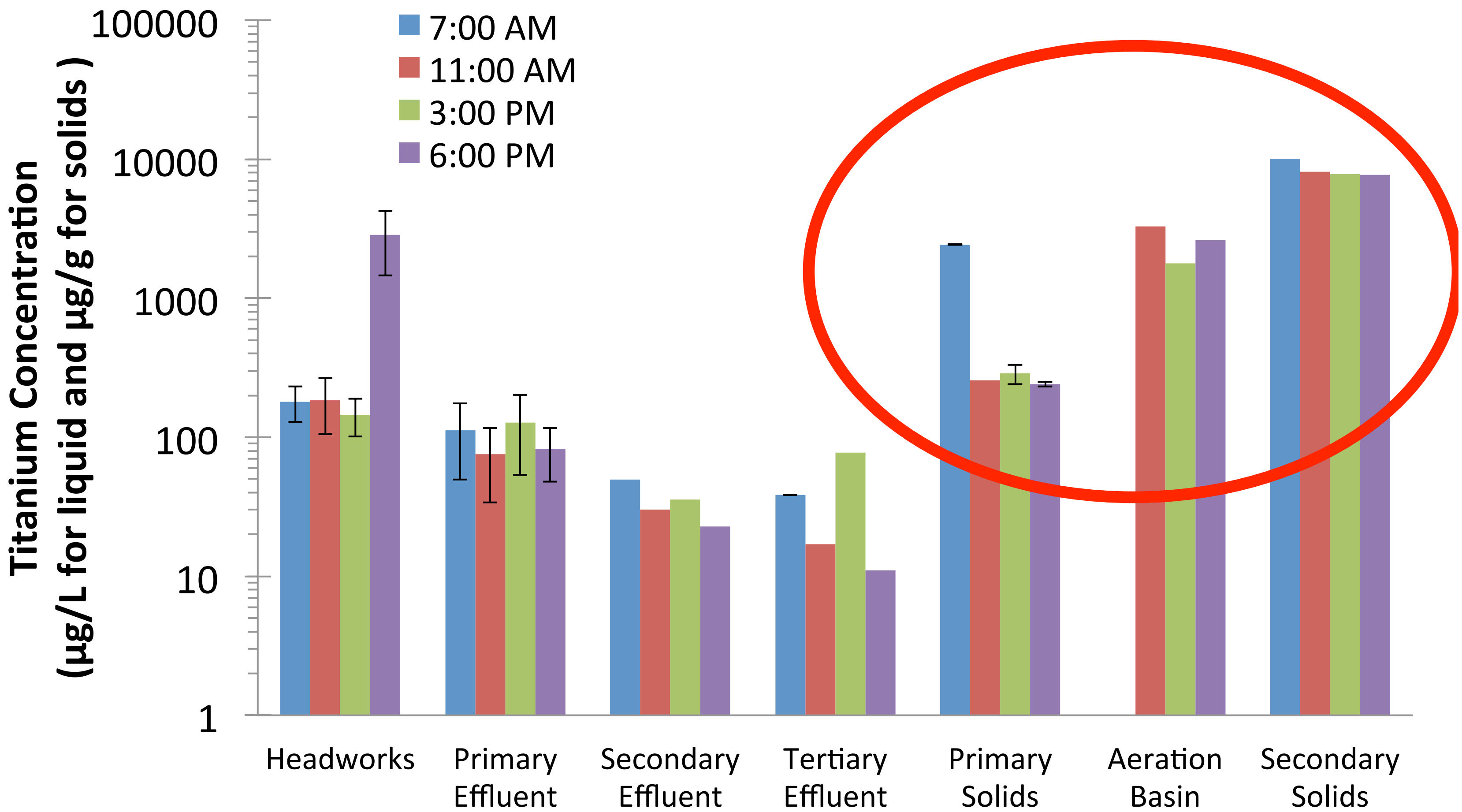
Ti Concentrations across WWTP



Size Fractionation of Titanium



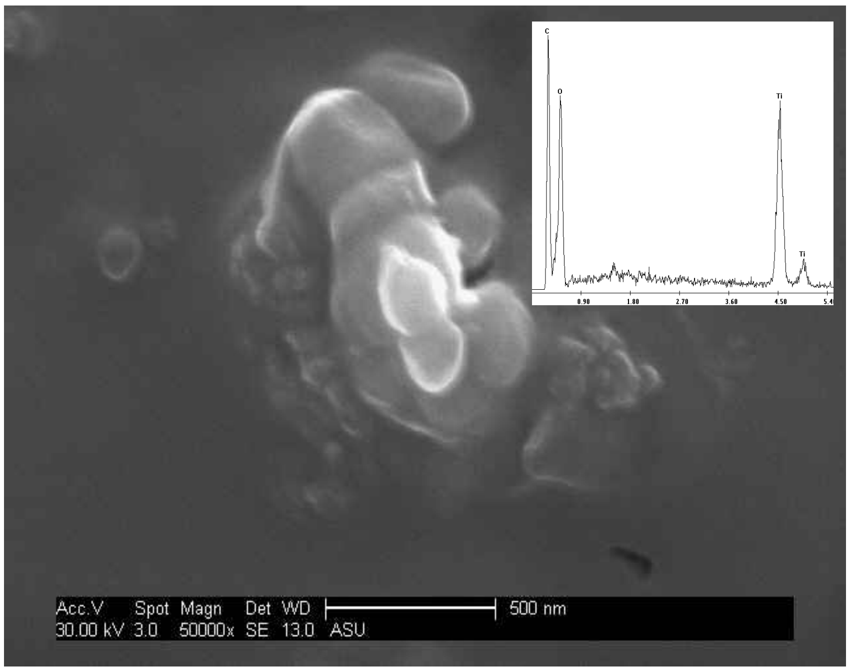
Titanium removed from water accumulates in biosolids



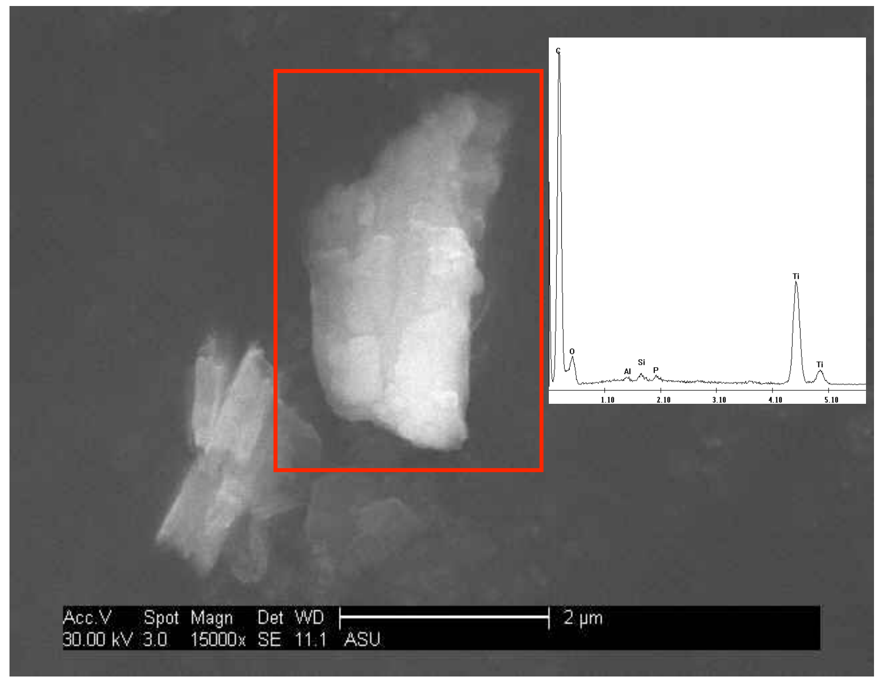
Kiser et al., ES&T (2009)

>90% removal in coming titanium

TiO_2 in biosolids
"Seeing is Believing"



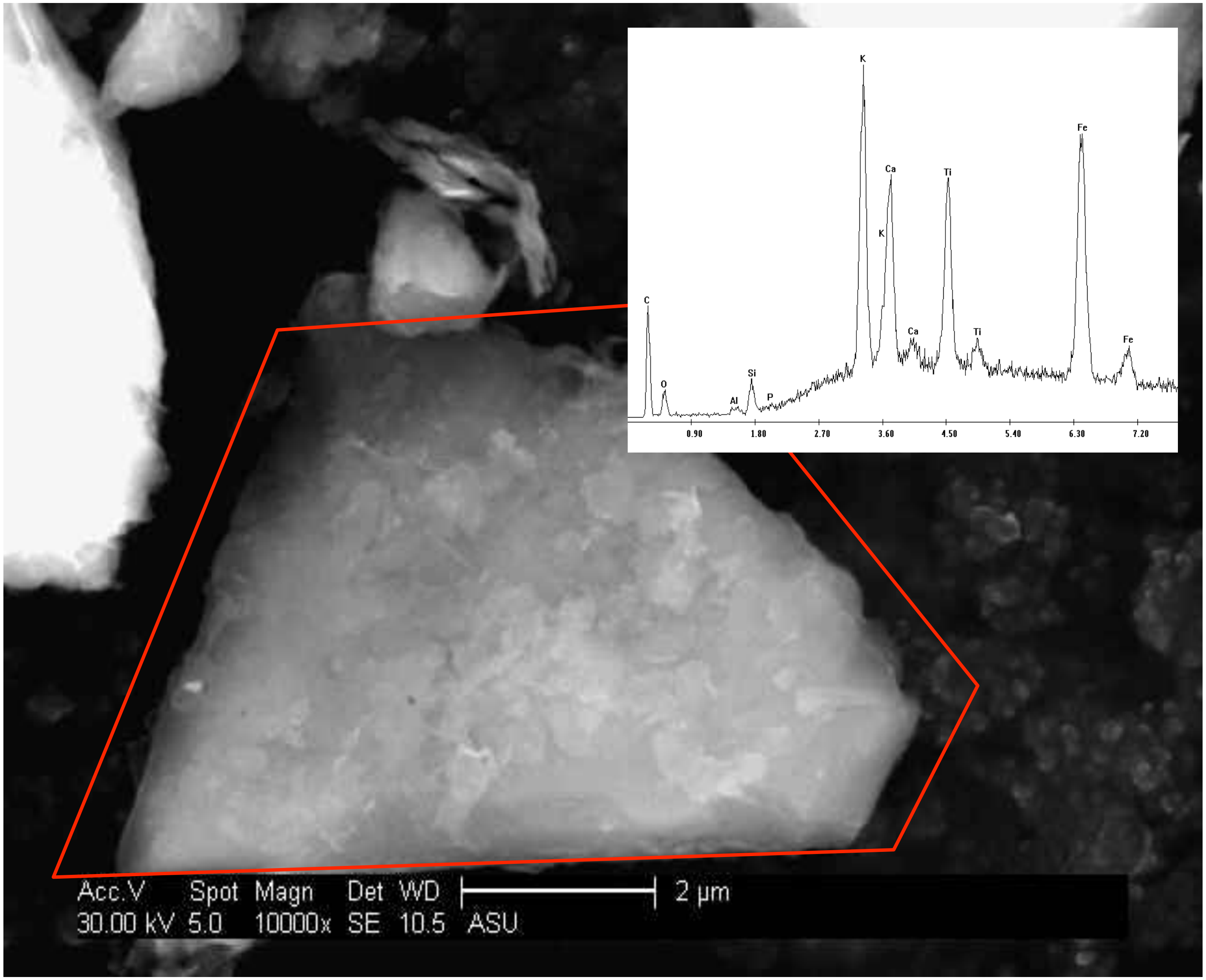
Nano-Scale TiO_2



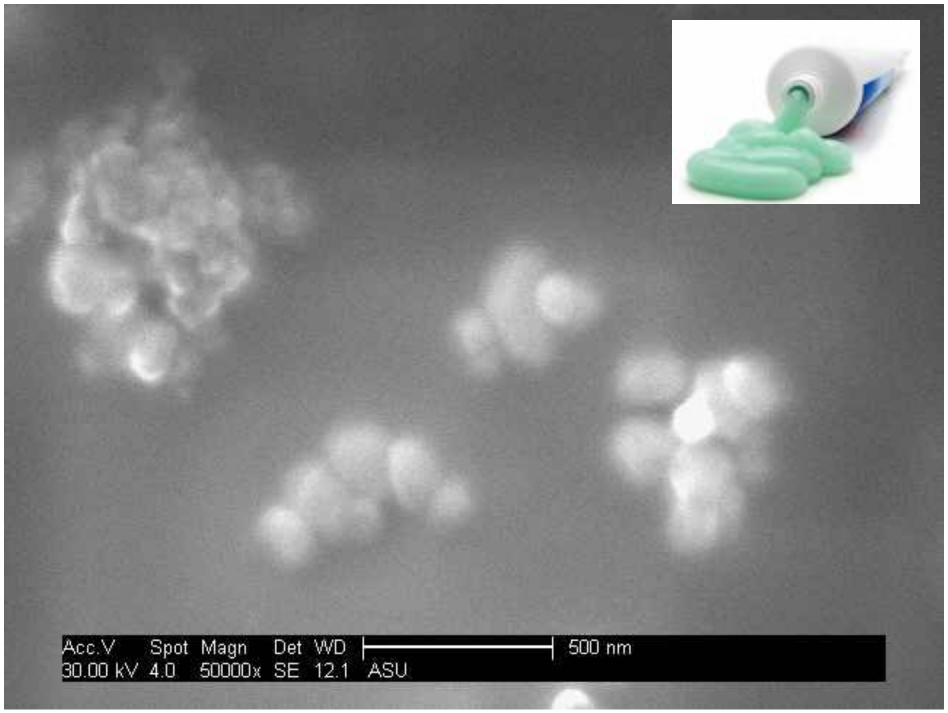
Micro-Scale TiO_2

Oxidized away biosolids in organics with hydrogen peroxide H_2O_2 does not affect titanium dioxide

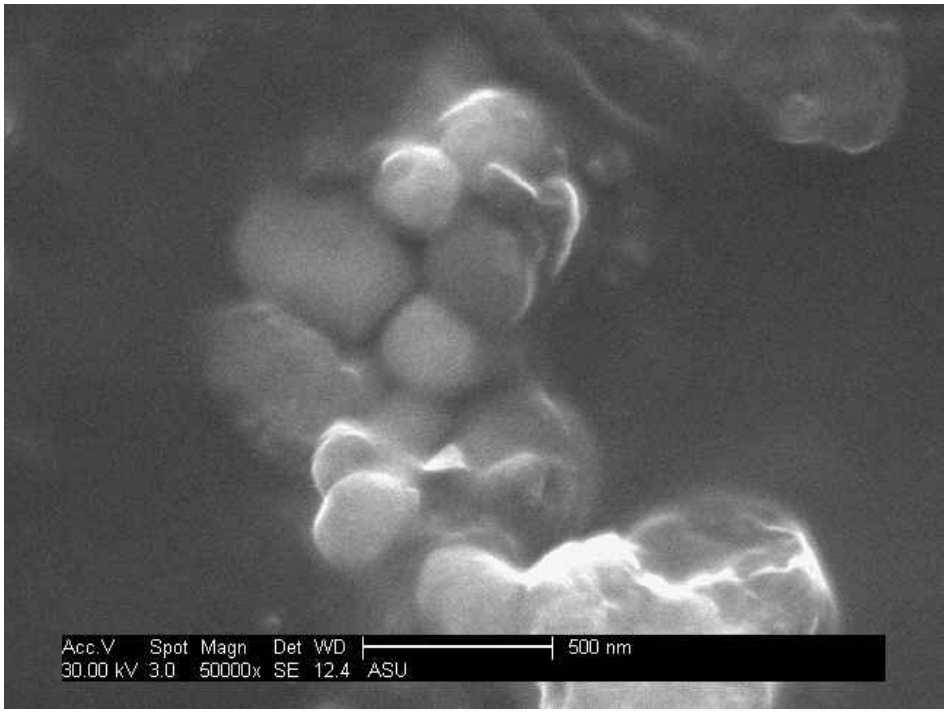
Titanium in soil particles are not pure TiO_2



TiO_2 in commercial products are similar to TiO_2 extracted from biosolids



TiO_2 in Toothpaste



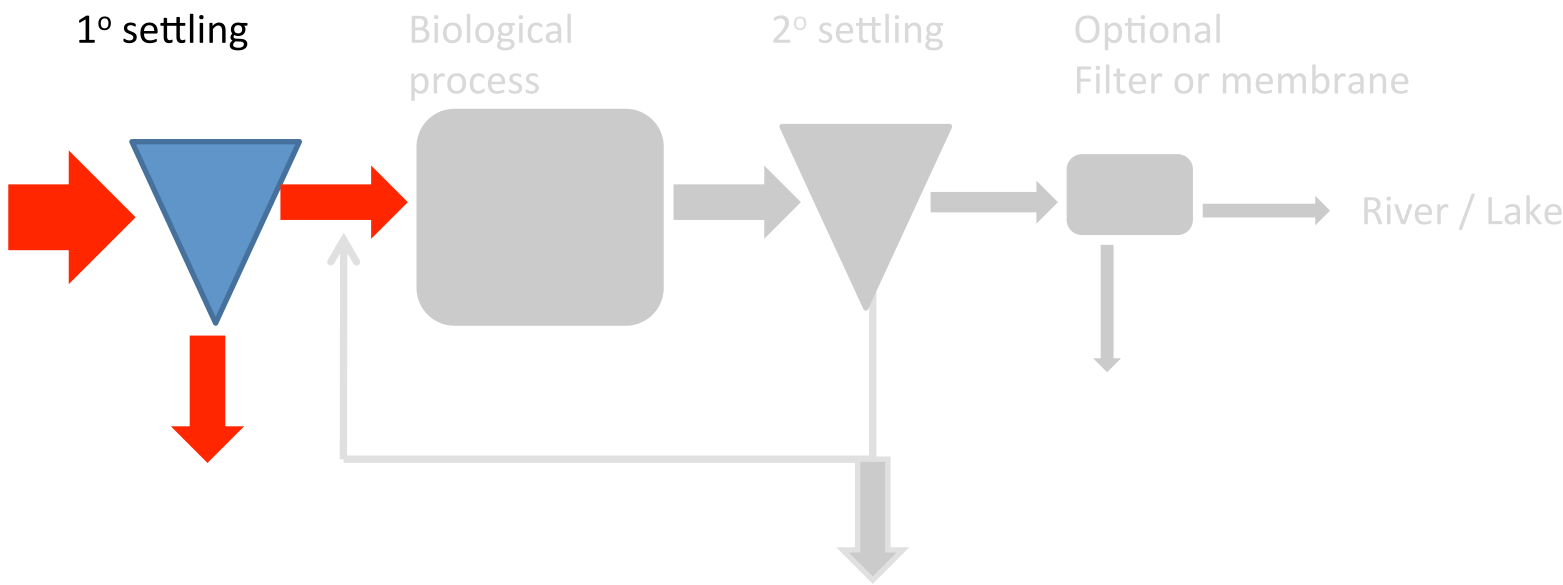
TiO_2 in Biosolids

Titanium Removal at other WWTPs in Arizona

- Effluent Ti concentrations are similar to LCA model predictions
- Membrane bioreactors have very low effluent Ti

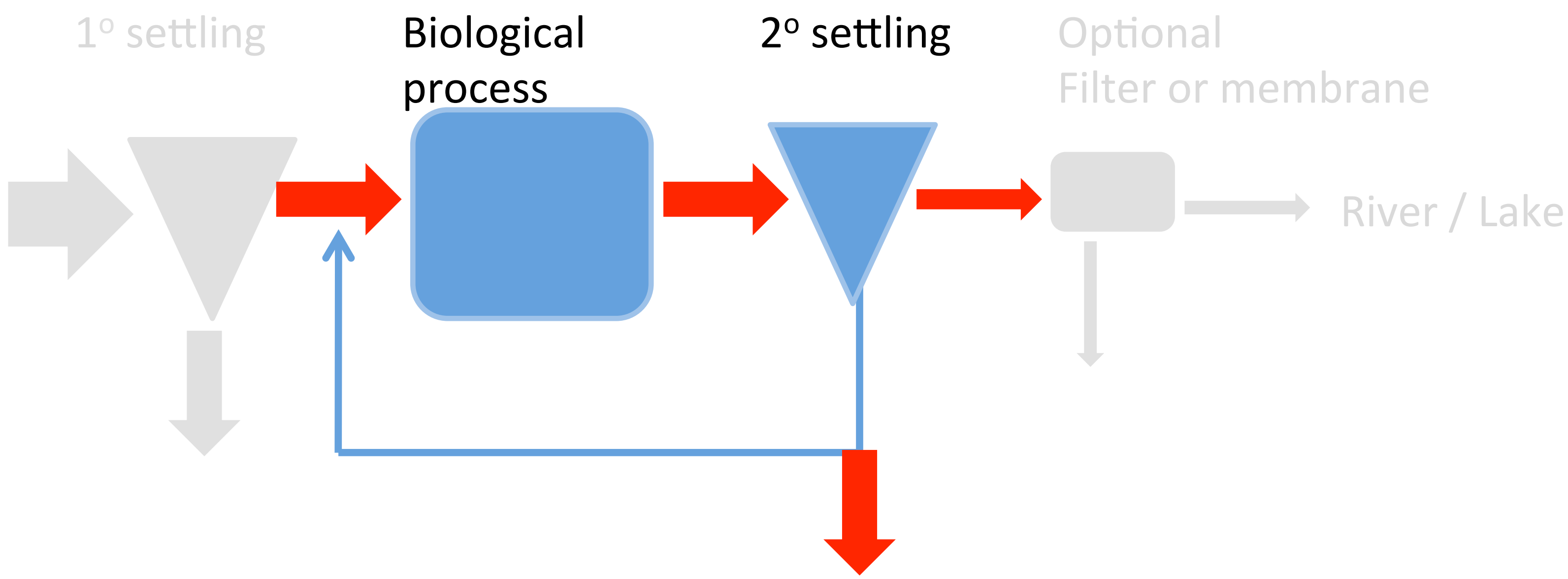
Different Facilities	Titanium Content of water (ugTi/L)	
	Headworks	Effluent
Activated sludge	615	5
Act. Sludge + filter	180	7
Activated sludge	363	3
Activated sludge	141	2
Activated sludge	581	18
Activated sludge		8
Activated sludge	233	2
Trickling filter	549	13
MBR	310	1
MBR	422	4
Average	377	6

Primary Settling



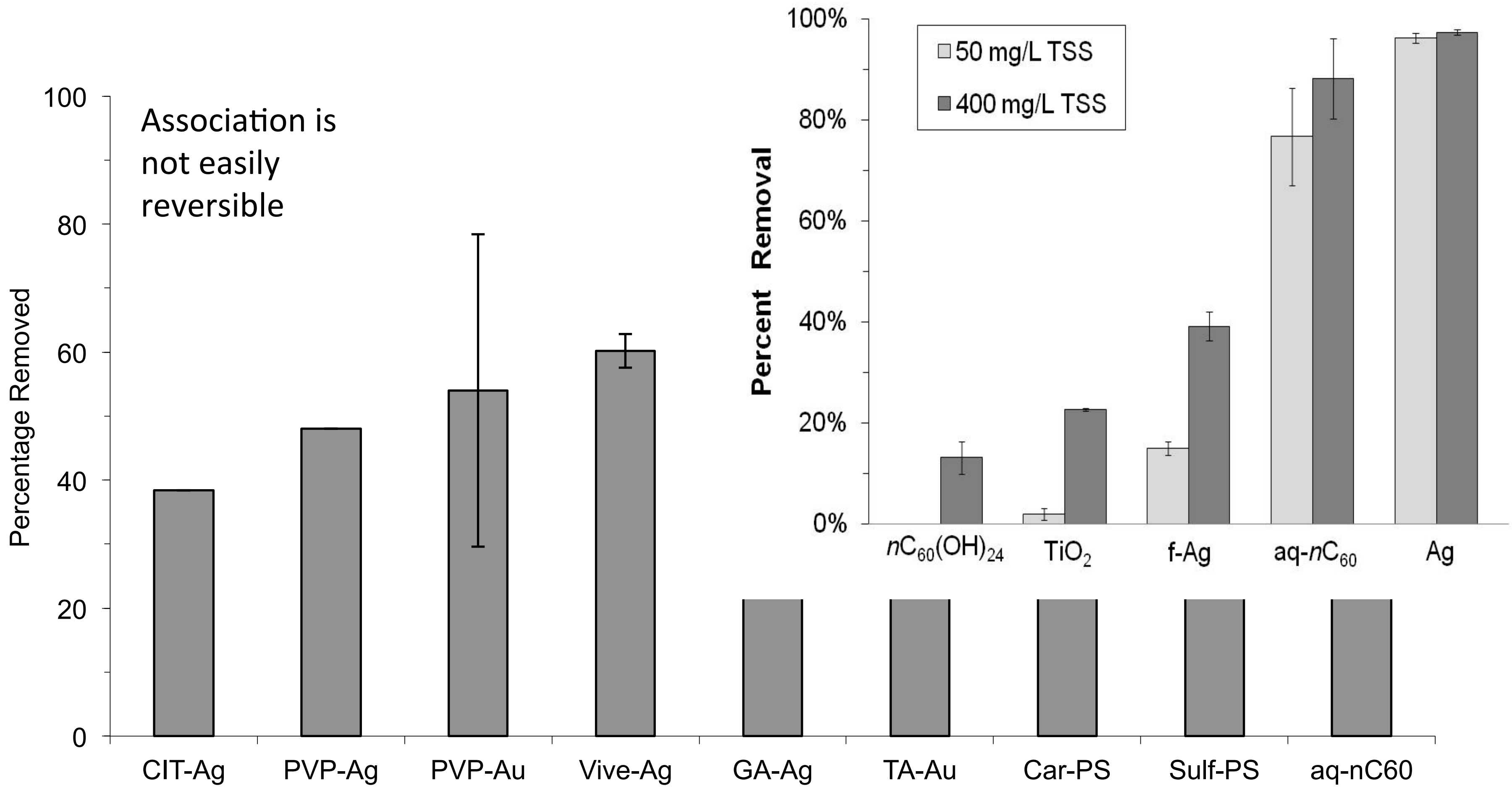
Removal of nanomaterials that are aggregated to clays, bacteria or other solids > 20 um in size

Biological Treatment



Removal of nanomaterials occurs when they interact with biofilms or biosolids

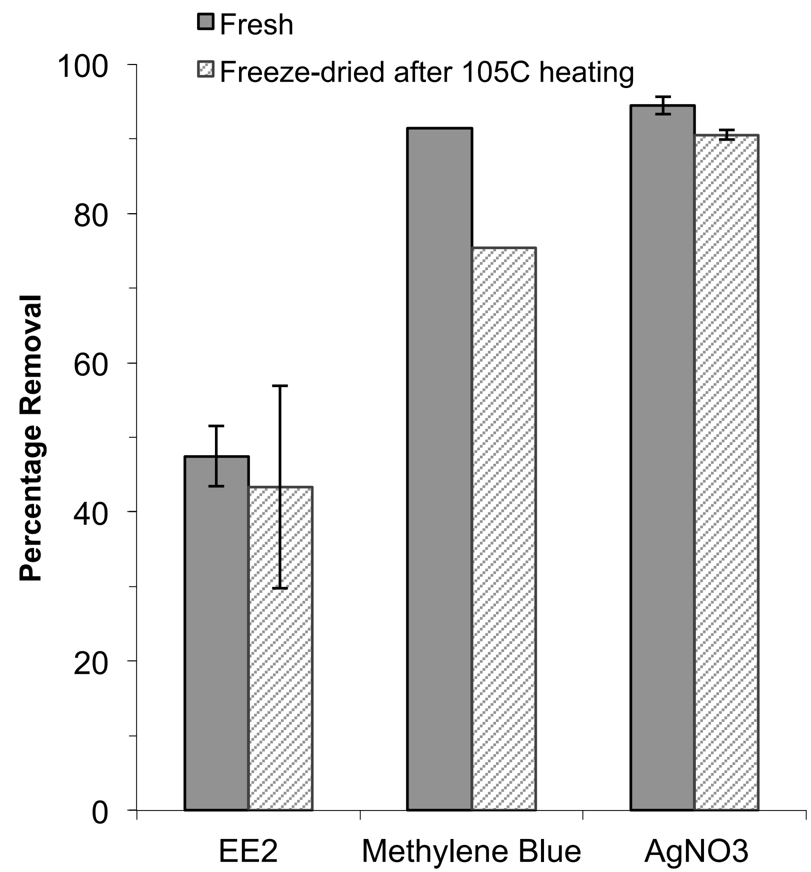
Nanomaterial Interaction with Wastewater biosolids



Kiser et al (2012); Kiser et al., WR, 2010

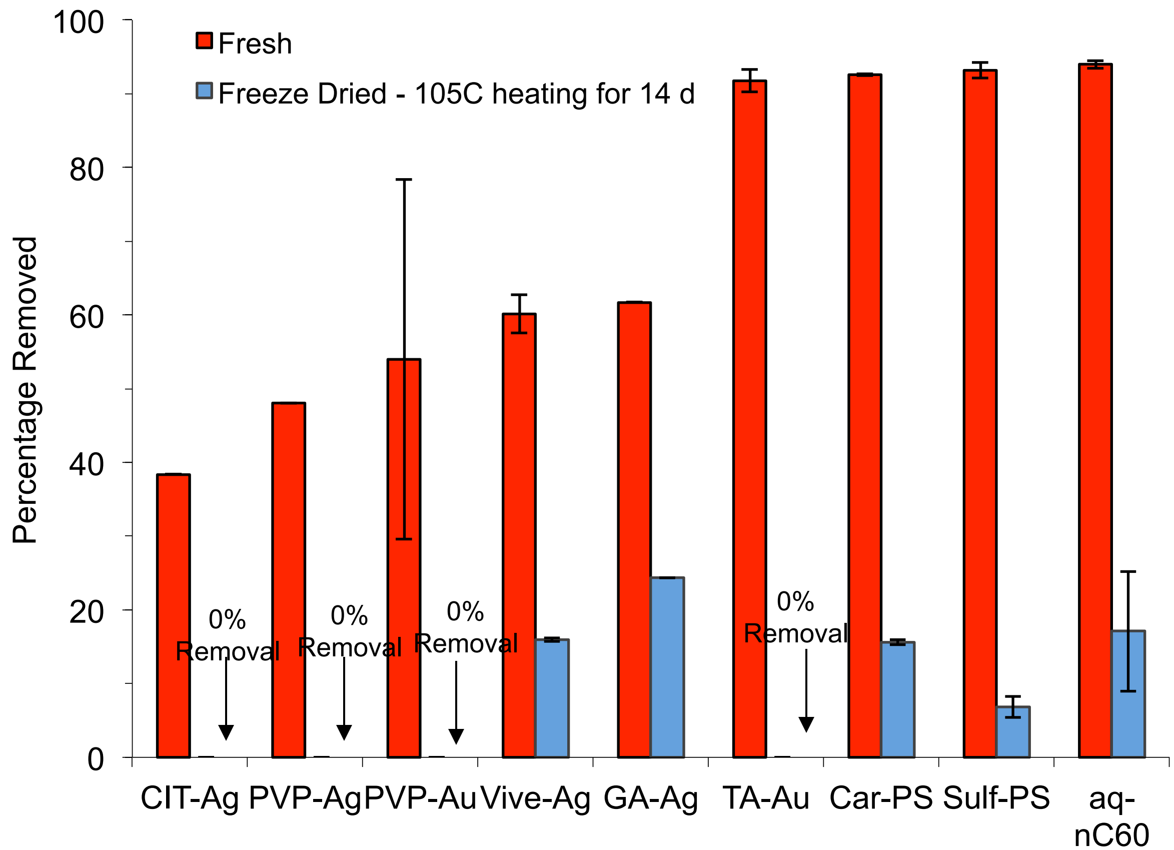
Standard Batch Methods

- 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



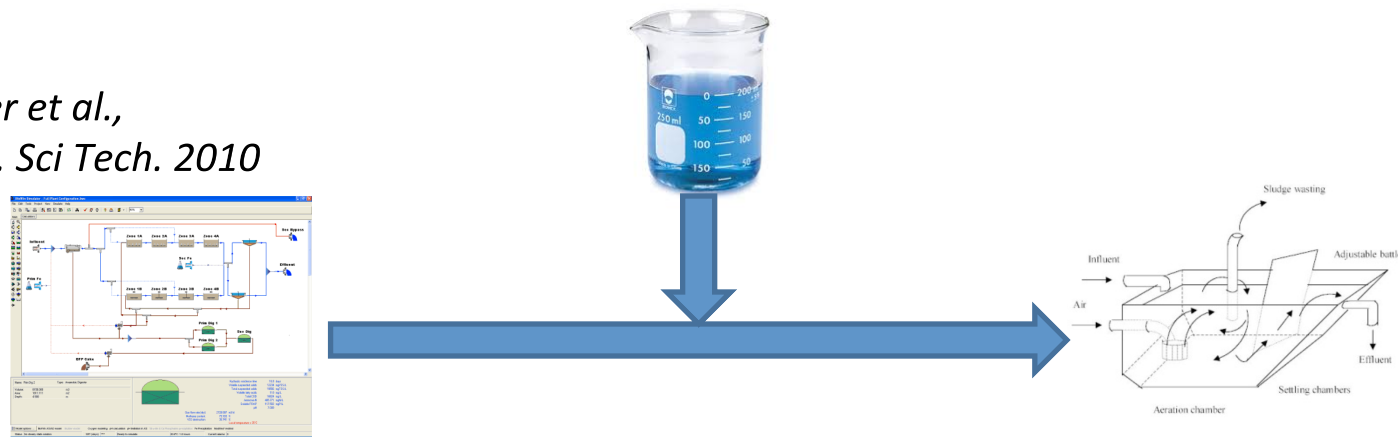
Does OPTT Test work for NPs?

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



Modeling NP Removal

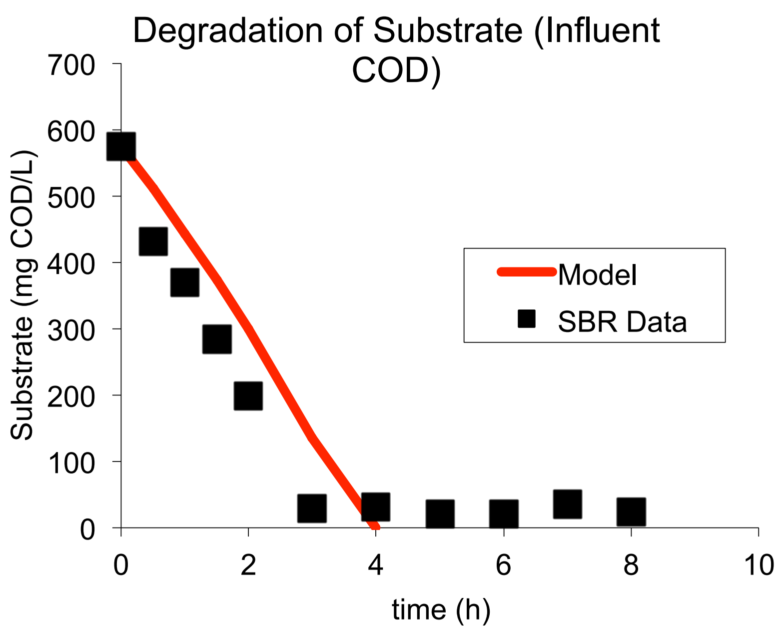
Kiser et al.,
Sep. Sci Tech. 2010

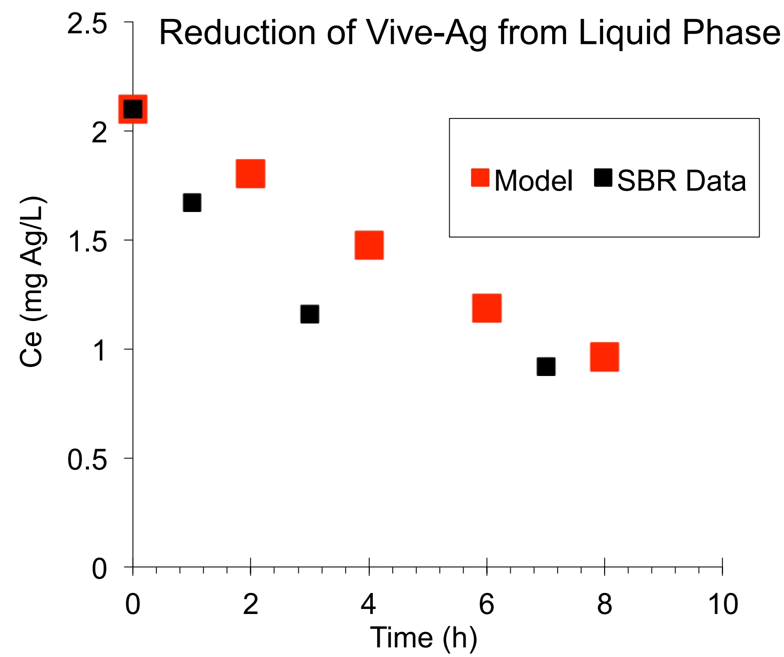


Hypothesis: Batch NP sorption experiments linked with dynamic bacterial growth models and reactor models can predict nanomaterial removal

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



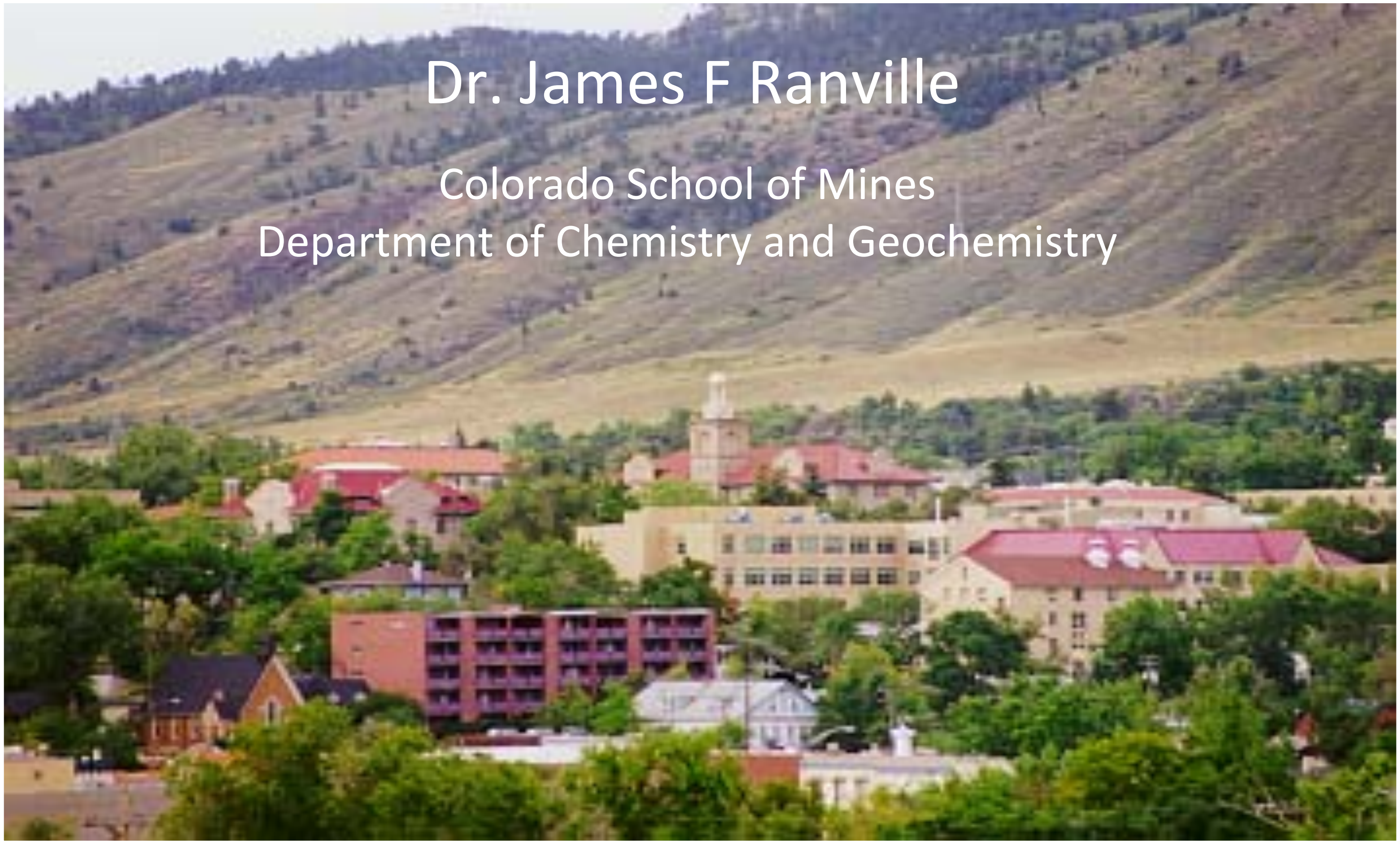


Conclusion: Preliminary confirmation exists that we can go from batch experiments to simulations of continuous flow performance. Difference in NP effluent concentration probably related to NP association with non-settlable colloids

Part 1- Summary

- Nanomaterials will enter sewage systems
- Potential discharge "guidelines" in the future for industries
- Nanomaterials interact with wastewater biomass
- Drying biomass looses critical lipid structures and releases soluble surfactants which decrease nanoparticle removal
- Existing batch sorption method (OPPTS) not valid for nanoparticles
- Biosolids disposal options (~50% land applied; 35% landfilled; 15% incernated)
- Nanoparticles are present in wastewater effluents today
- Analytical methods are needed to detect the amount and size of engineered nanoparticles in water

New Developments in Nanometrology for Metal-containing NPs



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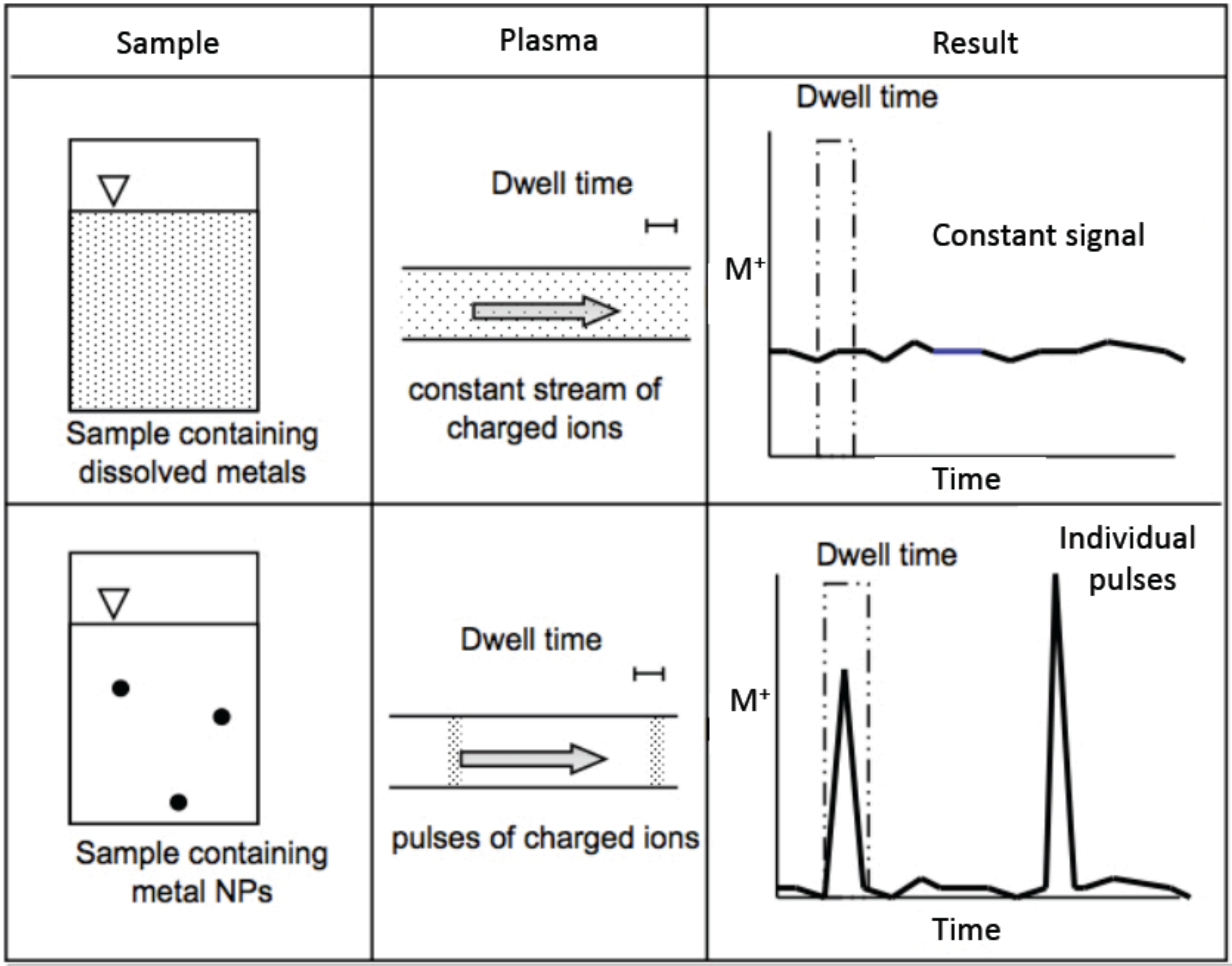
Featured Methodologies

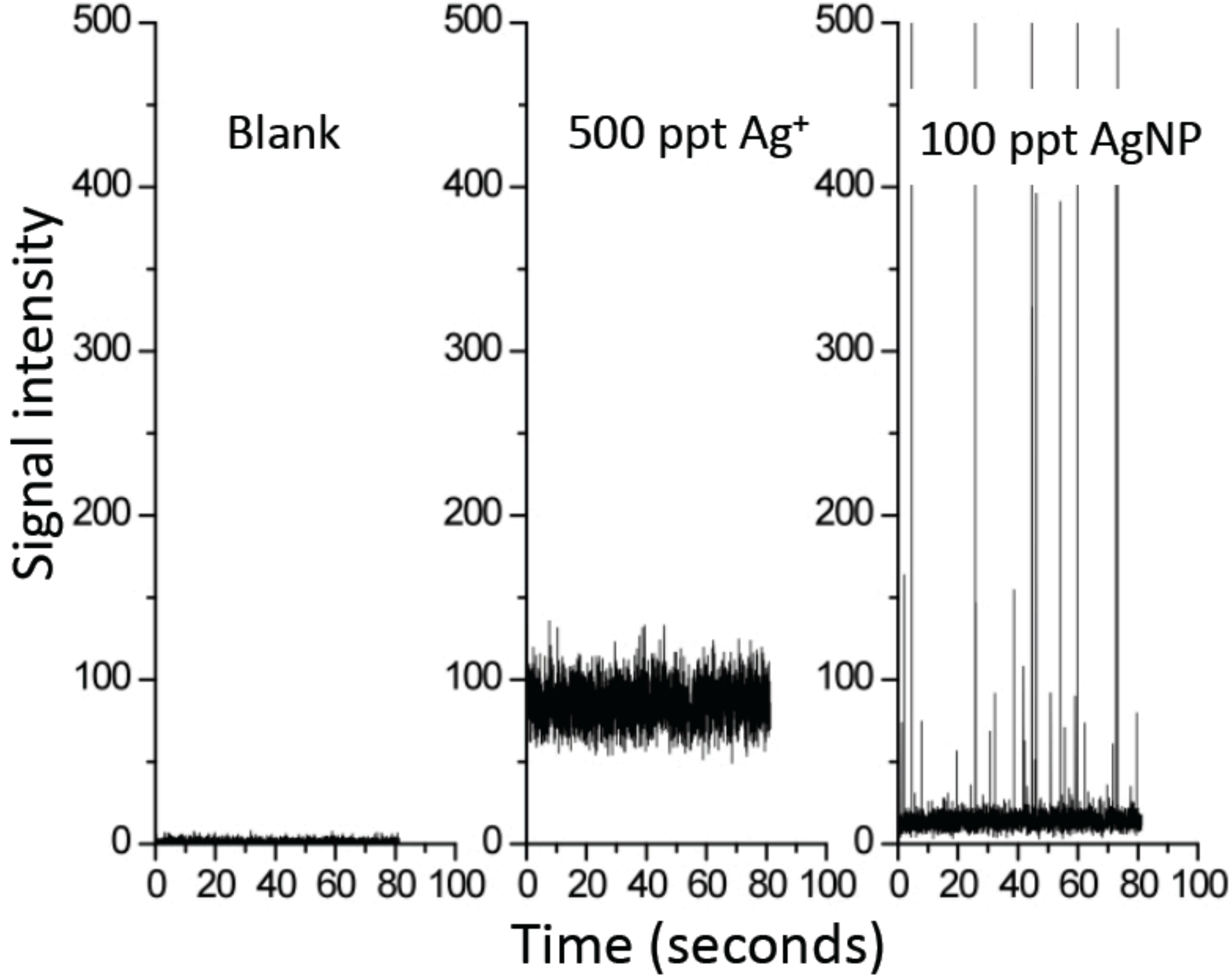
- **Particle Counting by ICP-MS (Sp ICP-MS)**
  - **Provides number, size, and composition data for particles as small as 20 nm at ng/L (environmentally relevant) levels**
- **Hyphenated Methods**
  - **Field Flow Fractionation-ICPMS**
  - **Hydrodynamic Chromatography-ICPMS**
  - **Seperation technique for nanoparticles as small as 2-3 nm, gives hydrodynamic diameter. Coupling to ICP-MS provides element specificity**
- **These methods are improvements because they are:**
  - **Quantitative (number and/or mass concentrations)**
  - **Potentially NP Specific (depends on elements of interest)**
  - **Have low detection limits**

Element Specific Particle Counting: Sp ICP-MS



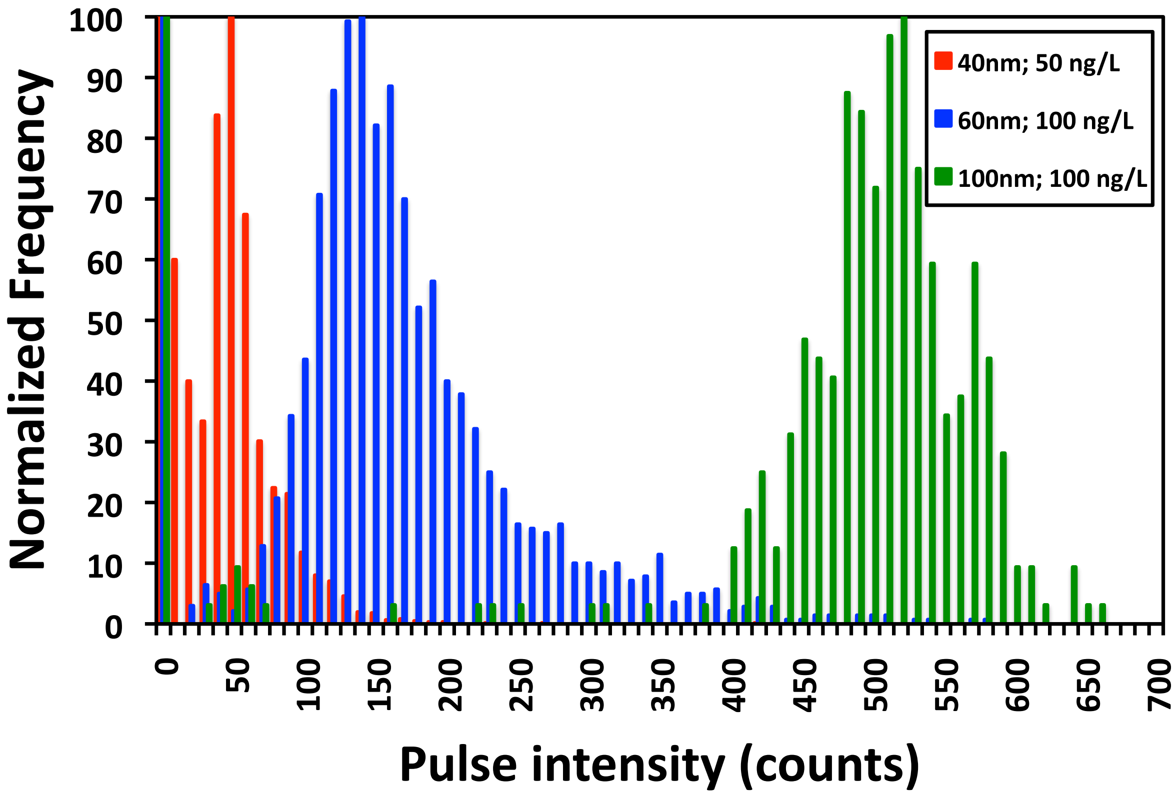
Mitrano et al, ET&C, Jan 2012

Element Specific Particle Counting: Sp ICP-MS



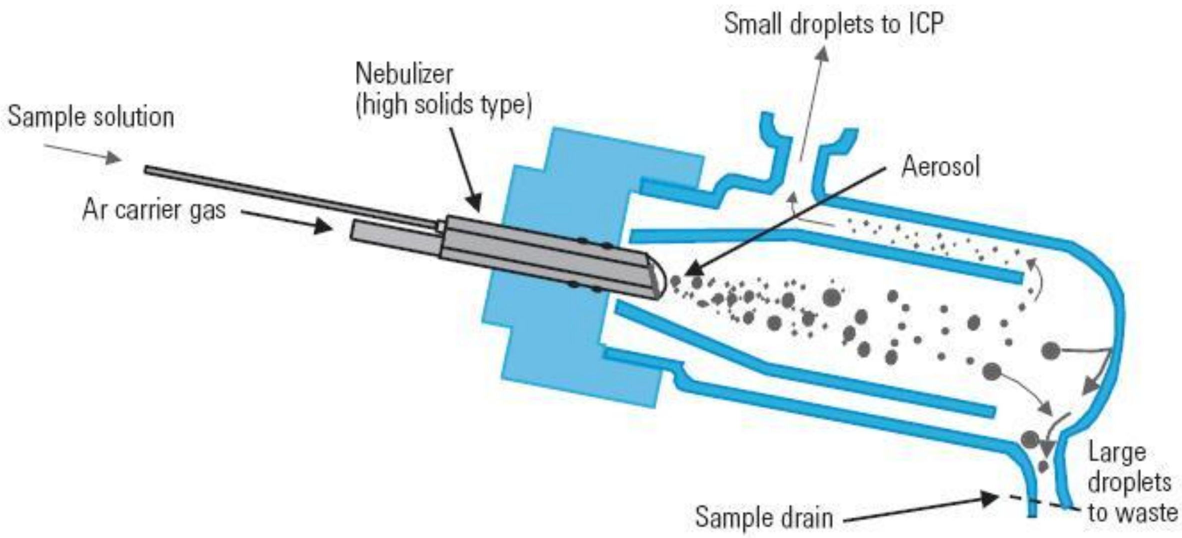
Mitrano et al, ET&C, Jan 2012

Binned Intensity vs size: Ag Nancomposix

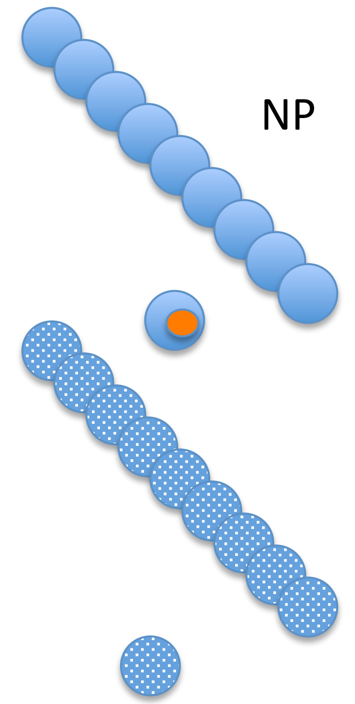


- Data collected at 10 msec per dwell
- Can plot intensity versus size to create sizing curve for NPs for which monodisperse standards exist

Sizing NPs: Efficiency of spray chamber



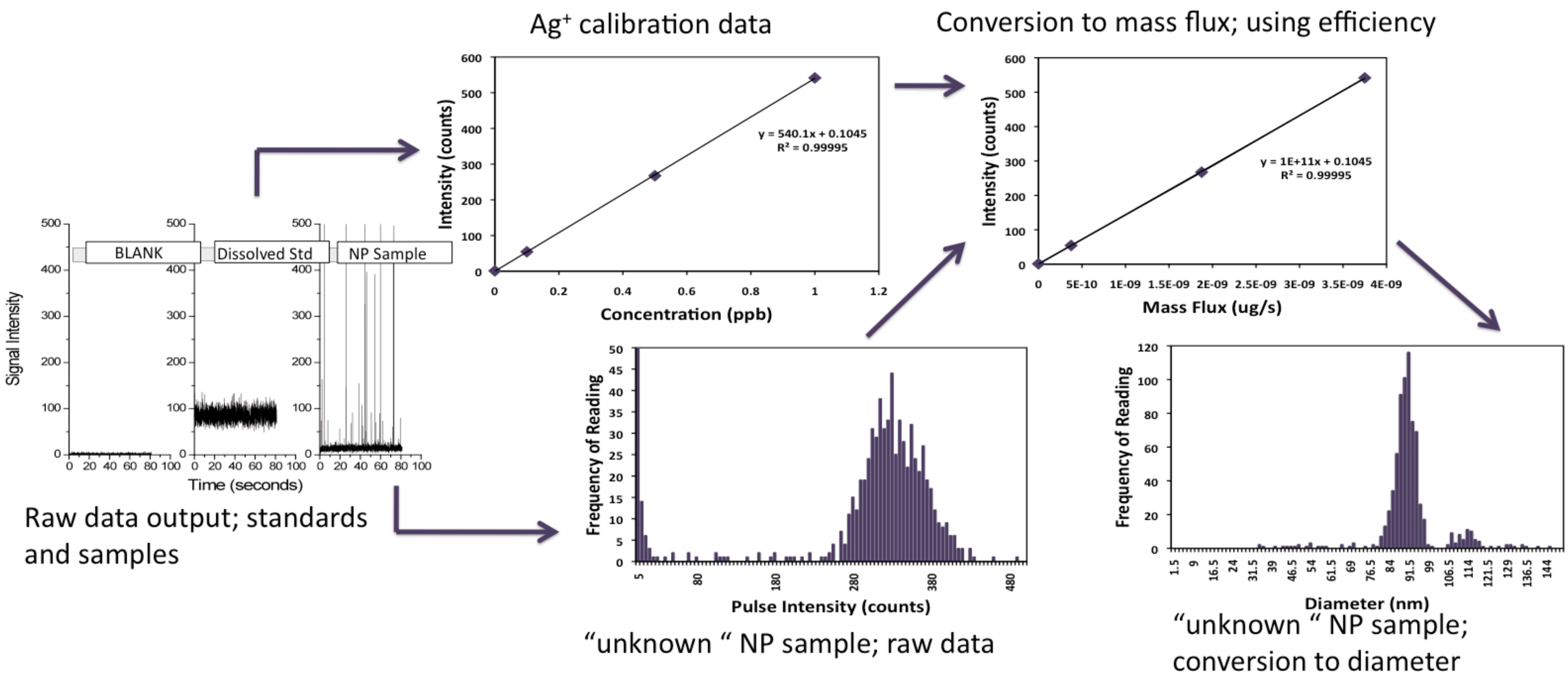
www.agilent.com



- Entire mass of atoms in a NP enter the plasma
- But only < 10 % of liquid droplets enter plasma
- Need to know mass of atoms in dissolved standard that actually enter plasma (transport efficiency)

Complete procedure for sizing

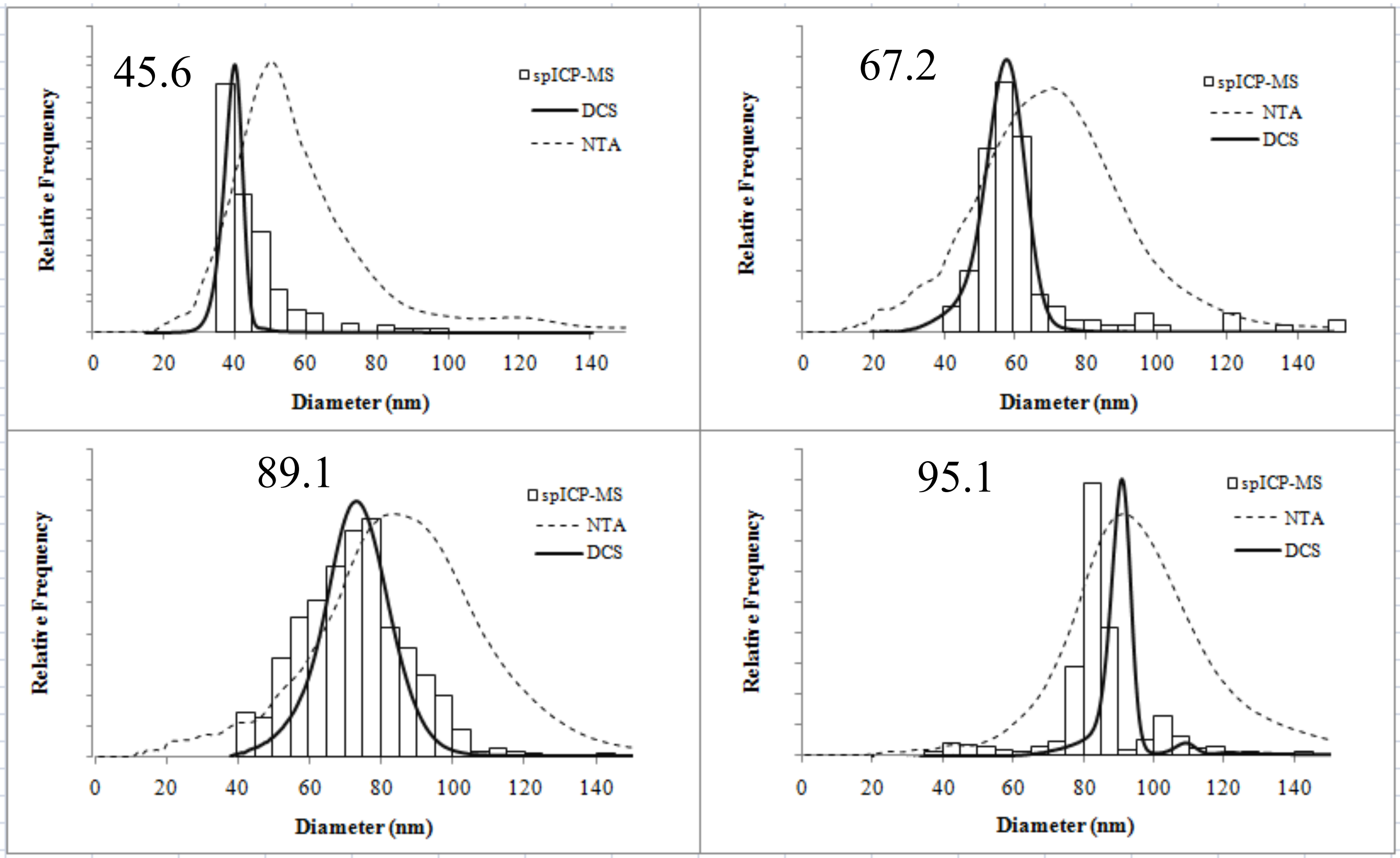
- Need a monodisperse “NP standard” (Au)
- Compare measured # to computed # to obtain efficiency
- Do not need NP standards for all NPs



Pace et al. 2011, Analytical Chem, 83, 9361-9369

Sizing NPs: Method Comparison

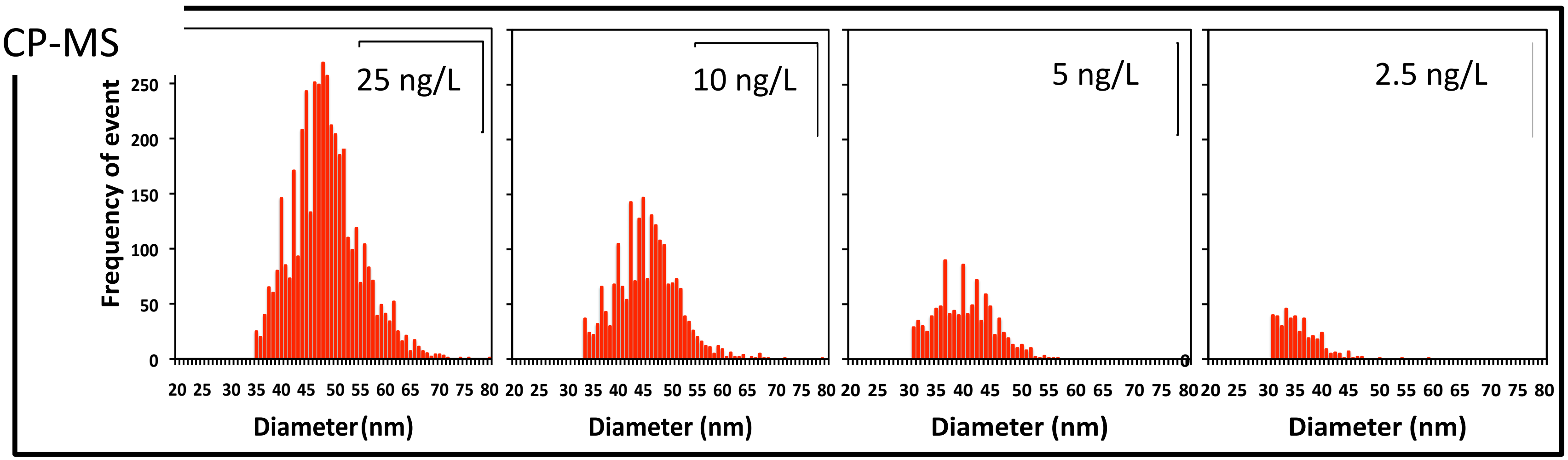
Monodisperse Ag sized using Au NP standard



Sp ICP-MS Compared to Disc Centrifuge (DCS) and Nanotracking Analysis (NTA)

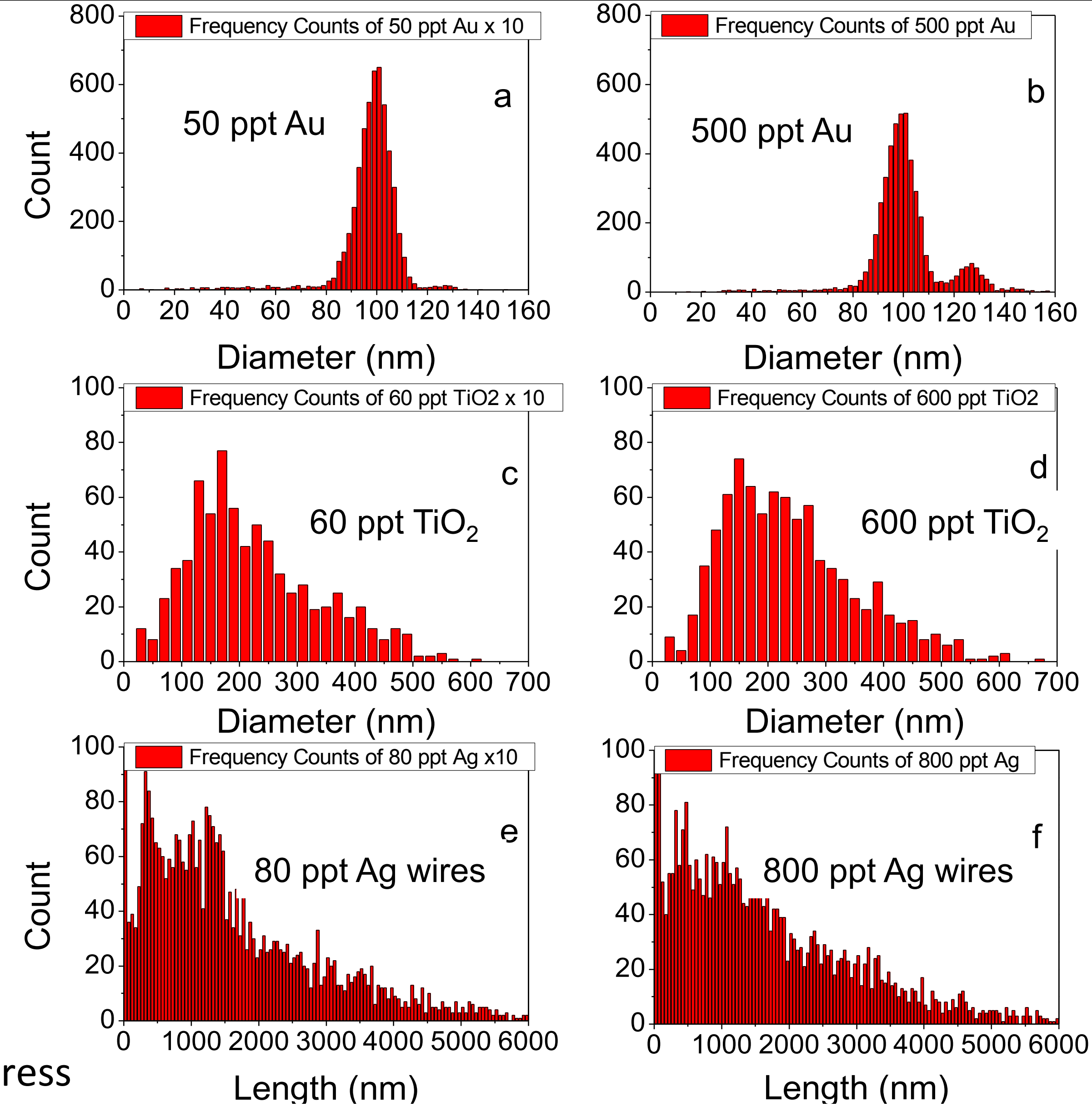
Concentration DL: 40 nmAg Nancomposix

SP-ICP-MS



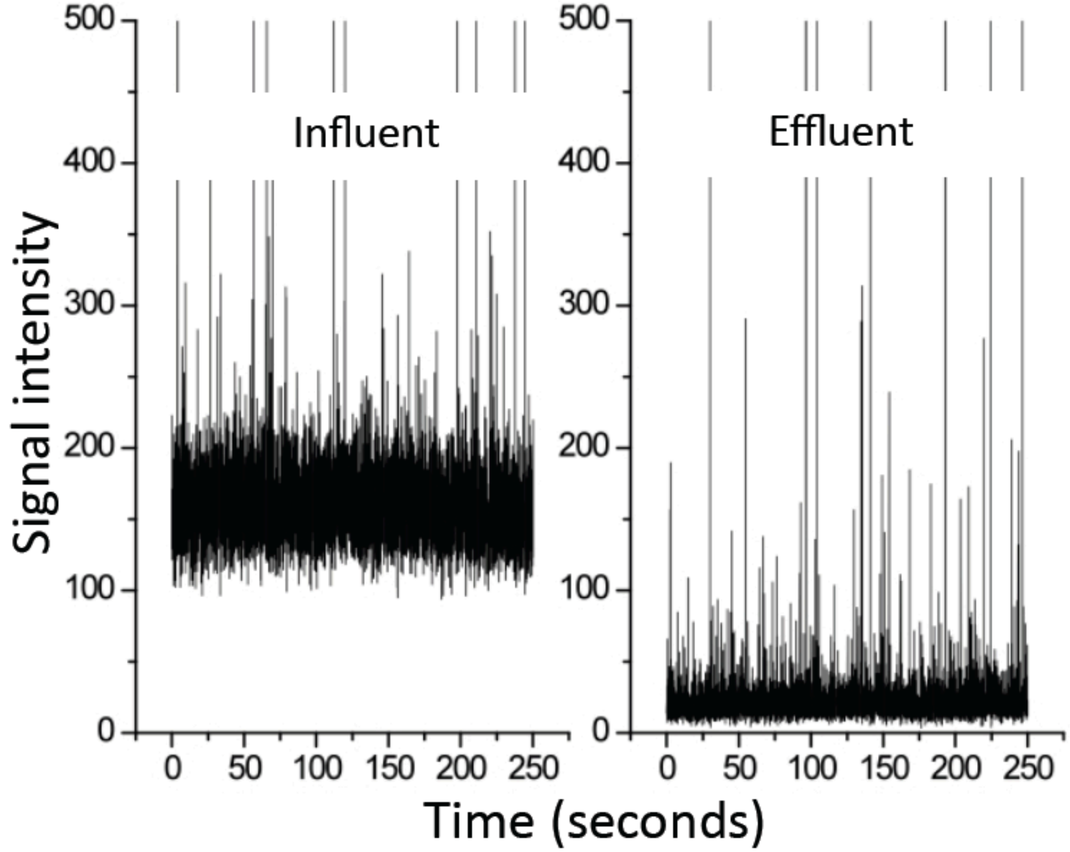
- Data collected at 10 msec per dwell
- Concentration range on the order to 5 -500 ppt

Sizing various NPs



Reed et al, JAAS in press

Environmental Detection: WWTP

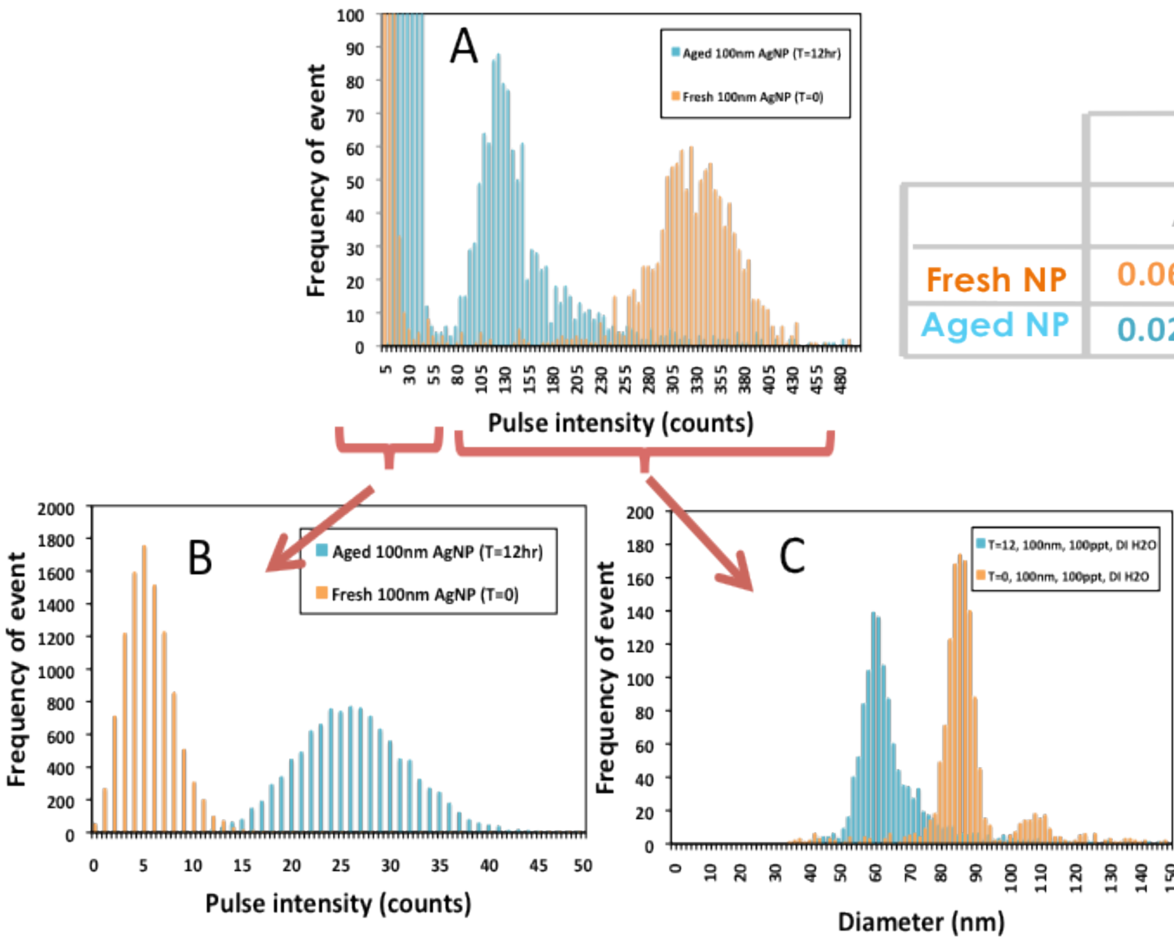


- Influent: 520 ng/L dissolved Ag, 200 ng/L Ag NP
- Effluent: 60 ng/L dissolved Ag, 100 ng/L Ag NP
- Form of Ag NP unknown

Mitrano et al, ET&C, Jan 2012

Application to EHS studies

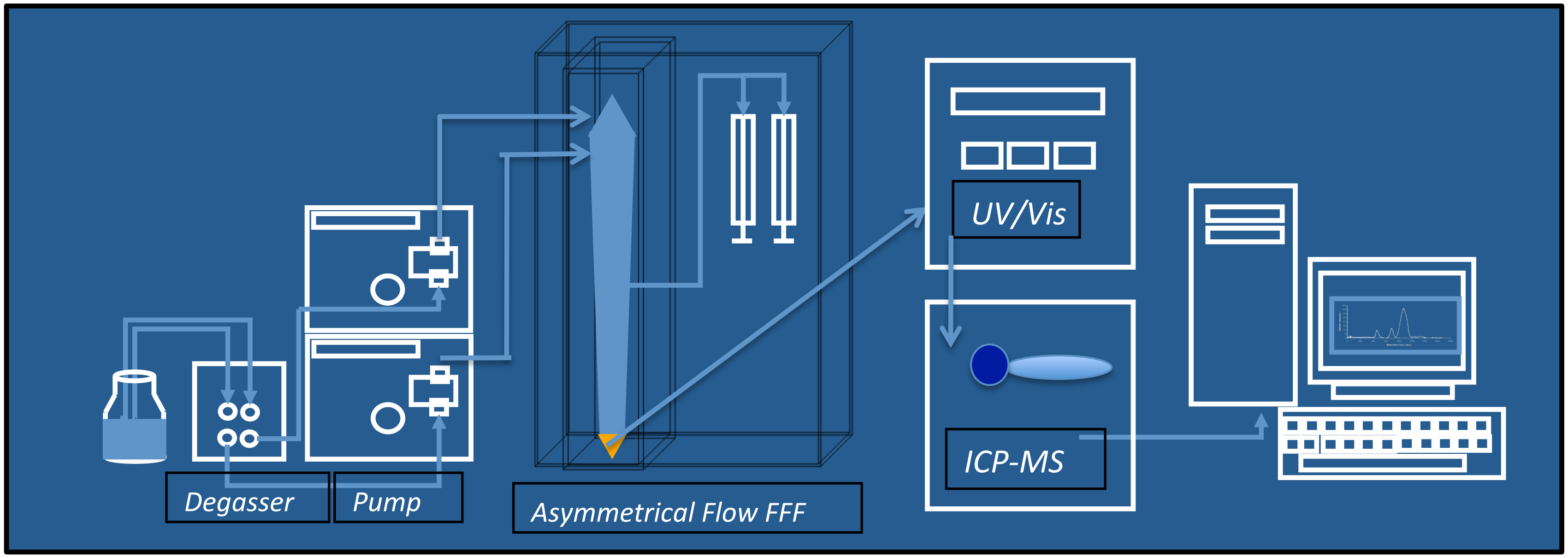
Differentiating dissolved and NP metals: Ag NP dissolution

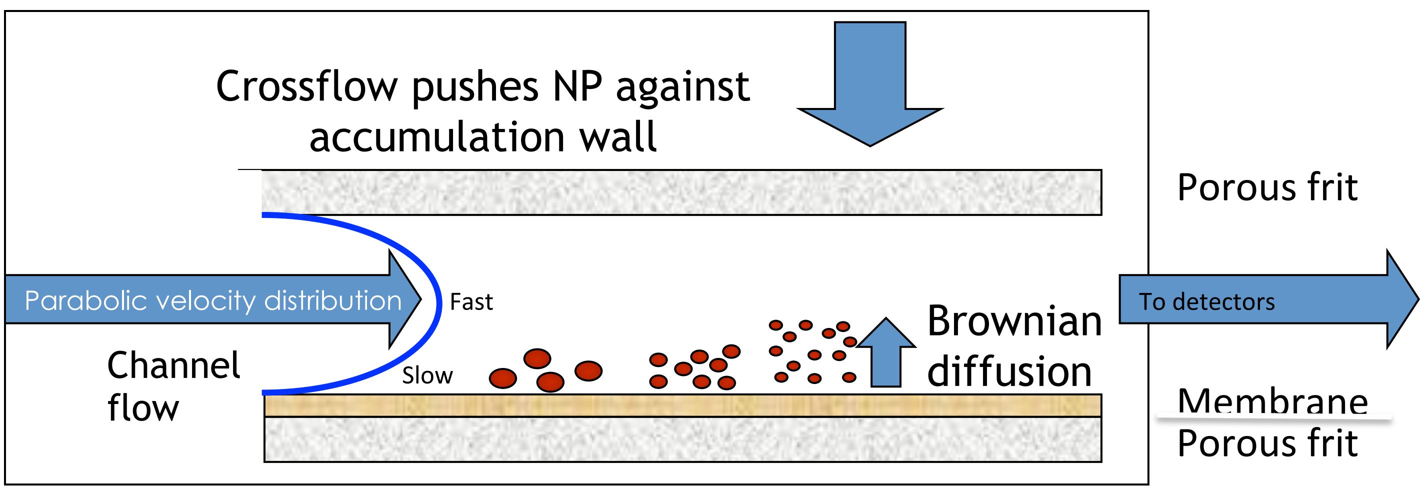


	Concentration (µg/L)		
	AgNP	Ag^+	Total Ag
Fresh NP	0.067 ± 0.005	0.002 ± 0.001	0.069 ± 0.006
Aged NP	0.025 ± 0.004	0.041 ± 0.005	0.066 ± 0.006

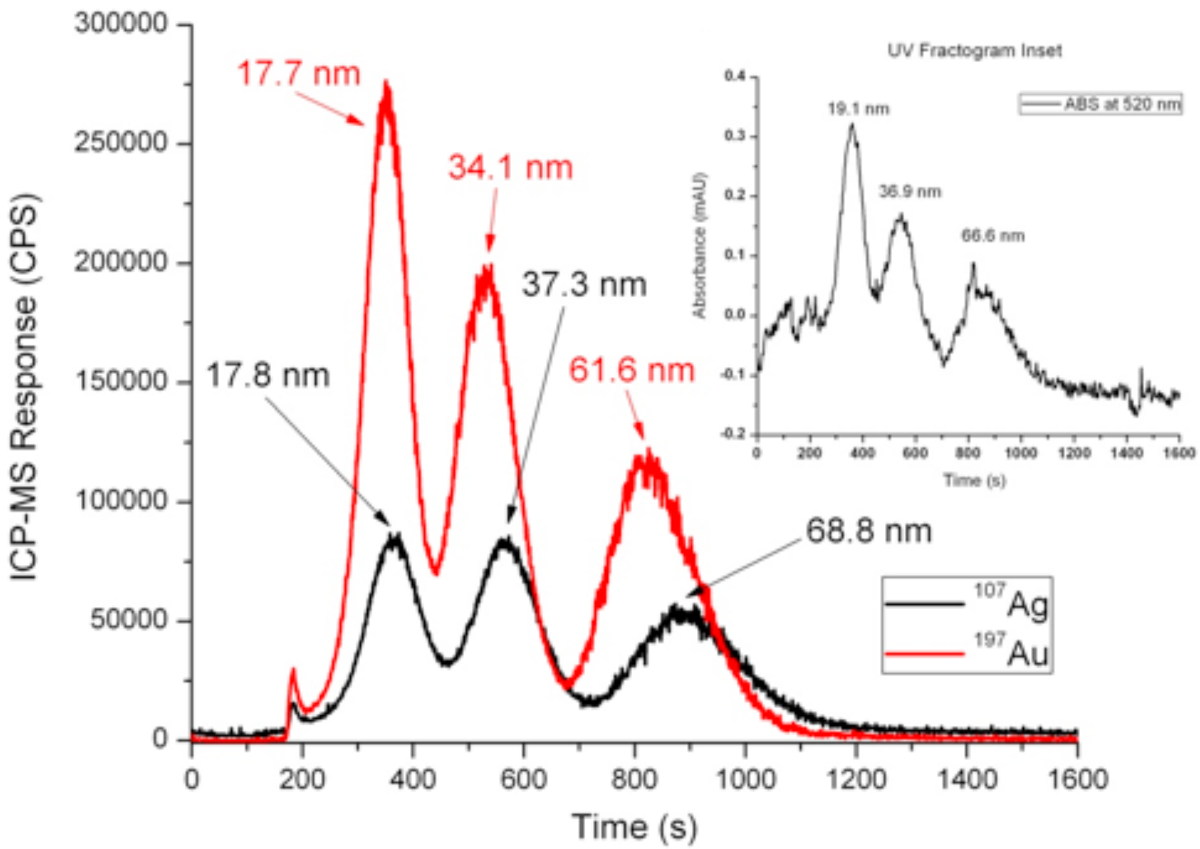
Filtration or centrifugation not needed to measure dissolved and NP elements

NP Characterization:AF4-ICP-MS



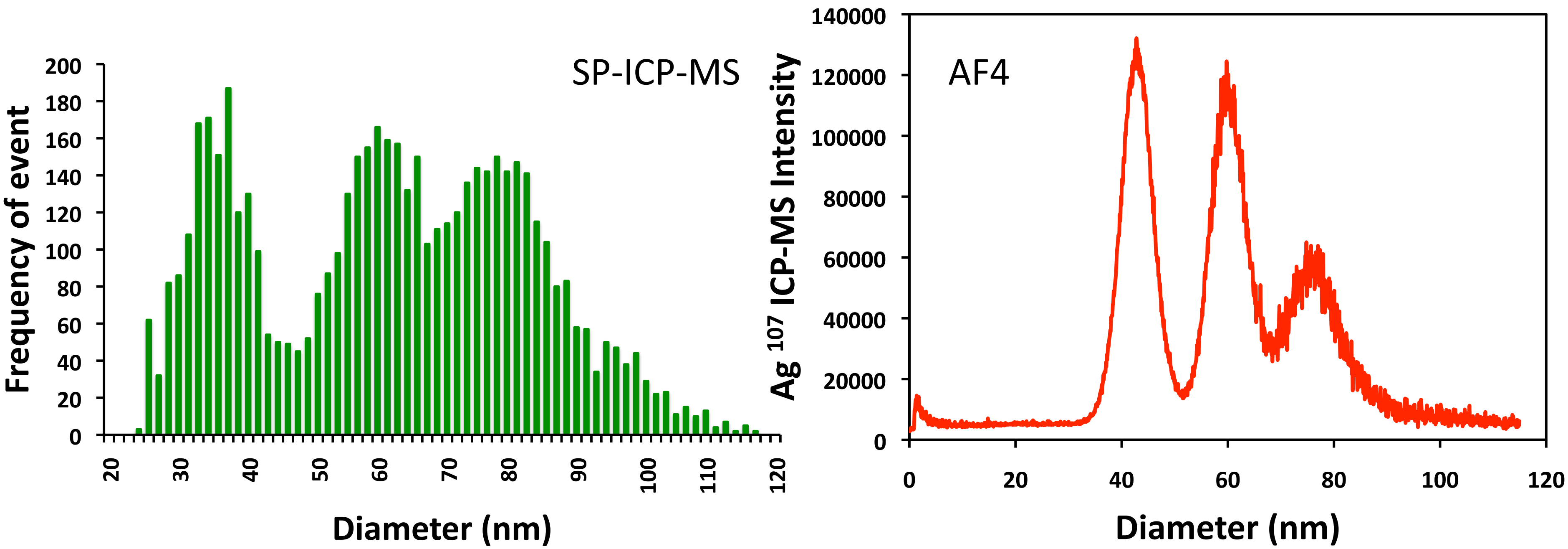


Multi-Element Specificity of AF4-ICP-MS



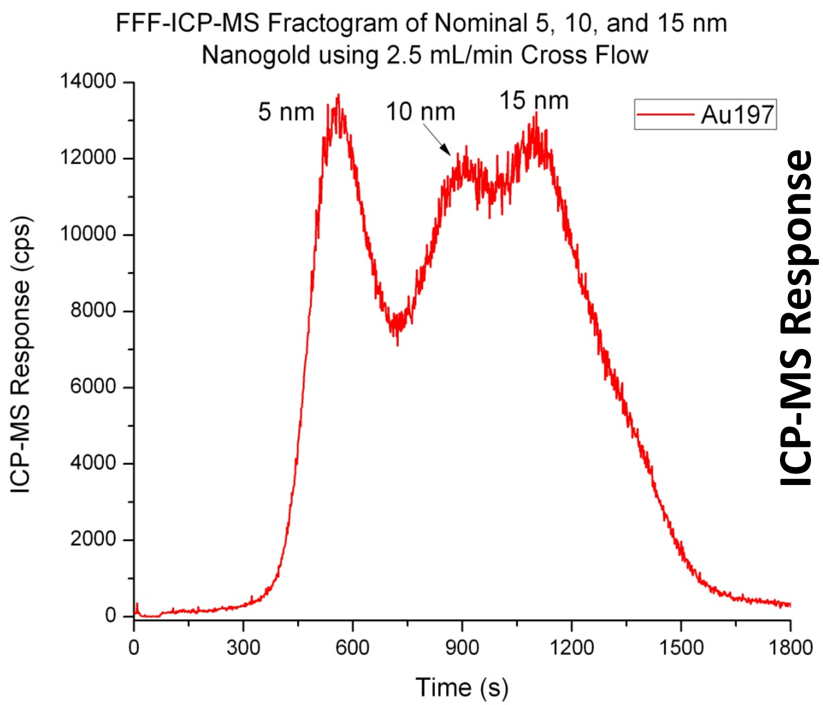
Ag Mixture Resolution: SP-ICP-MS and AF4

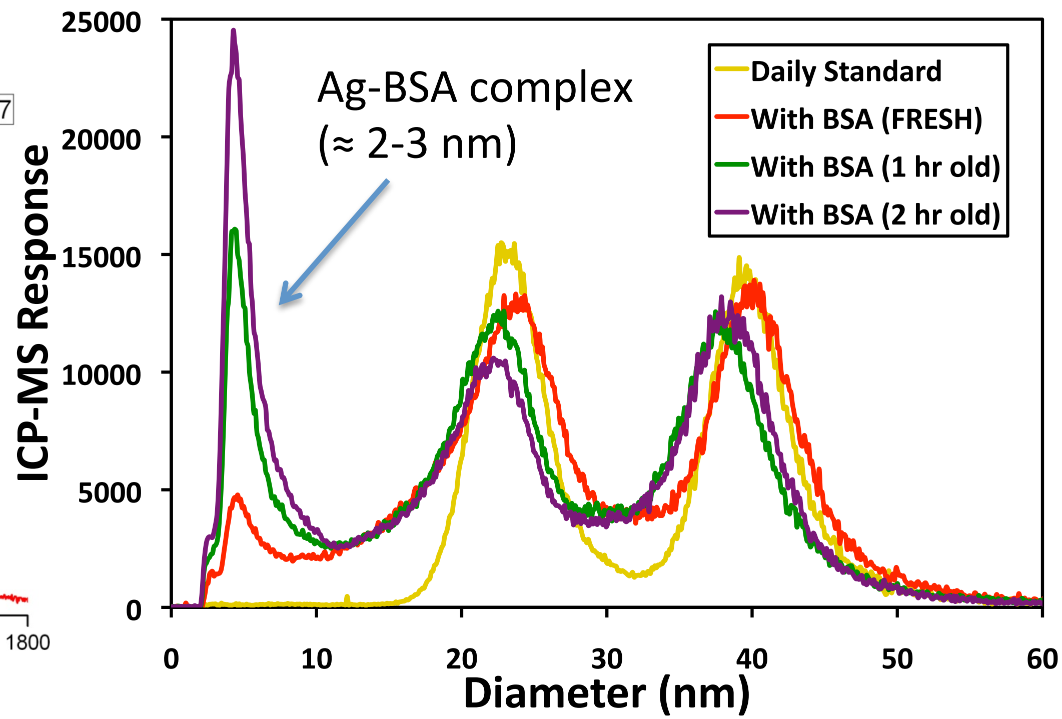
- Ag Nanocomposix: 40, 60, and 80 nm



NexION 300 Q

Minimum detectable size (AF4-ICP-MS)

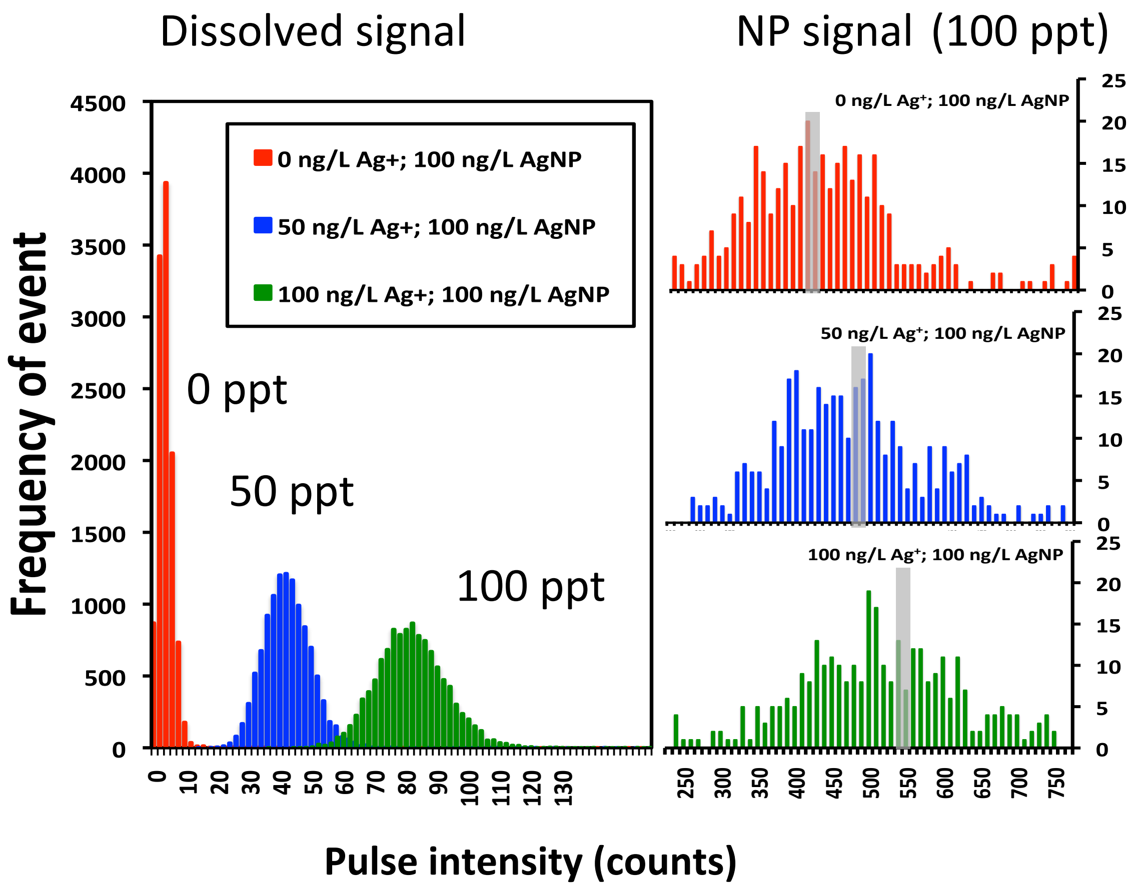




FFF:

- Depends on field strength (cross-flow for AF4, rpm for SdFFF)

Detection of dissolved elements



SP-ICP-MS

- Dissolved species lost through membrane in AF4

Method Summary

- AF4
  - Pros
    - Very good Resolution
    - Multielement detection
    - Small size detection limit
  - Cons
    - Long Runs
    - Poor Recovery
    - Dissolved not detected
- SP-ICP-MS
  - Pros
    - Good Resolution
    - Lowest concentration detection limit (ppt)
    - "Dissolved" analysis
  - Cons
    - High size detection limit (>20 nm)
    - Single element detection
    - Narrow concentration range (serial dilutions)

General Conclusions

- SP-ICP-MS is effective for detection of NPs at part-per-trillion concentrations
- Sizing of NPs is possible, although smaller NPs may be lost to background
- Possible to examine dissolution and aggregation

- AF4-ICP-MS provides a characterization tool that has:
    - element specificity allowing analysis of chemically heterogeneous NPs at ppb levels
    - high size resolution that allows analysis of polydisperse samples
    - Separation capabilities to sizes as small as 3-5 nm