Sources of Nanomaterials in Drinking Waters

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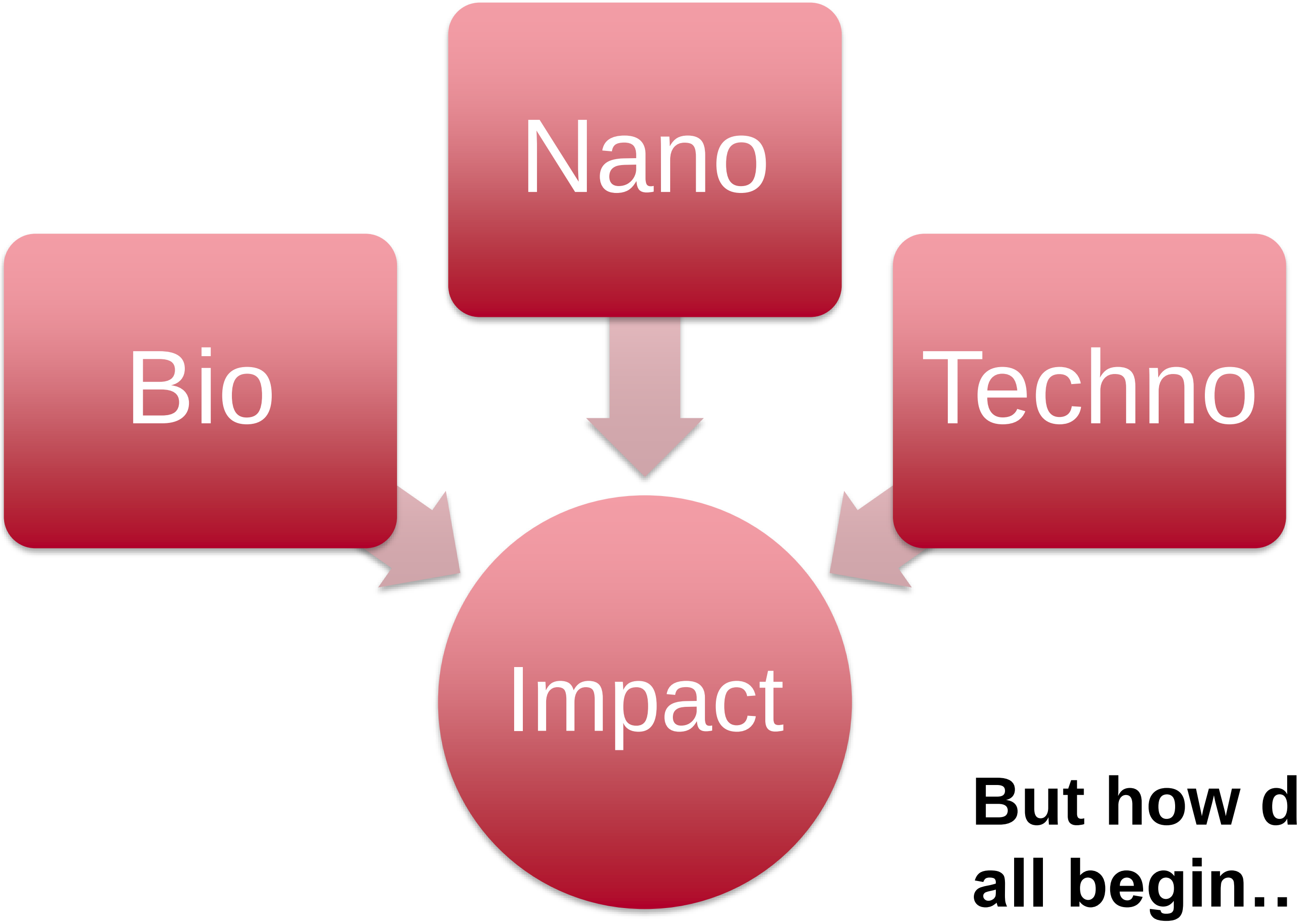
Nanosystems Engineering Research Center for
Nanotechnology-Enabled Water Treatment

Pedro Alvarez Exemplifies the Bio-Nano-Convergence



Nano

Bio

Techno

Impact

But how did it all begin…

Like bacteria
he emerged from hot springs

…Is fueled by organic substrates

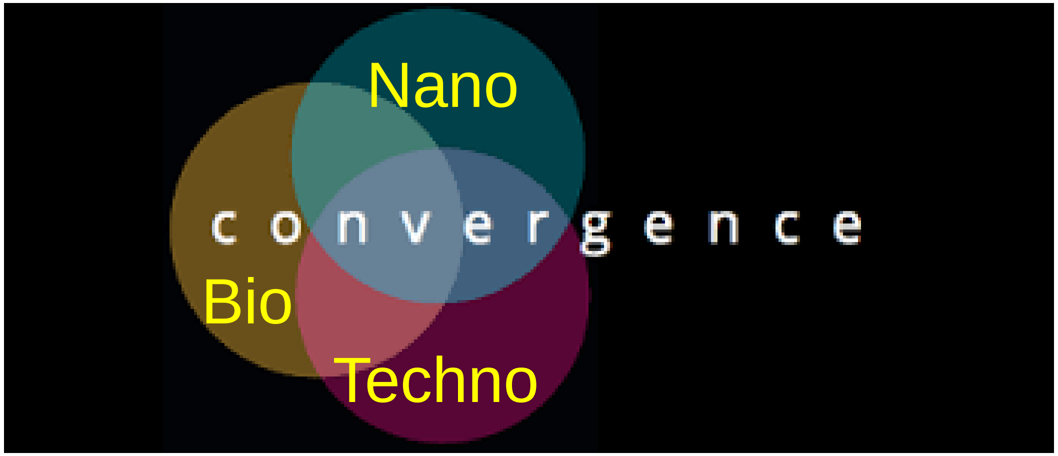
He colonizes with other prominent types of bacteria & roams the earth…

… Understanding how Life and Nanotechnology Interact…

… and facilitates high impact interdisciplinary science at convergence of bio- & nano-technology

Environmental Science & Technology

…And he is always wearing a smile!

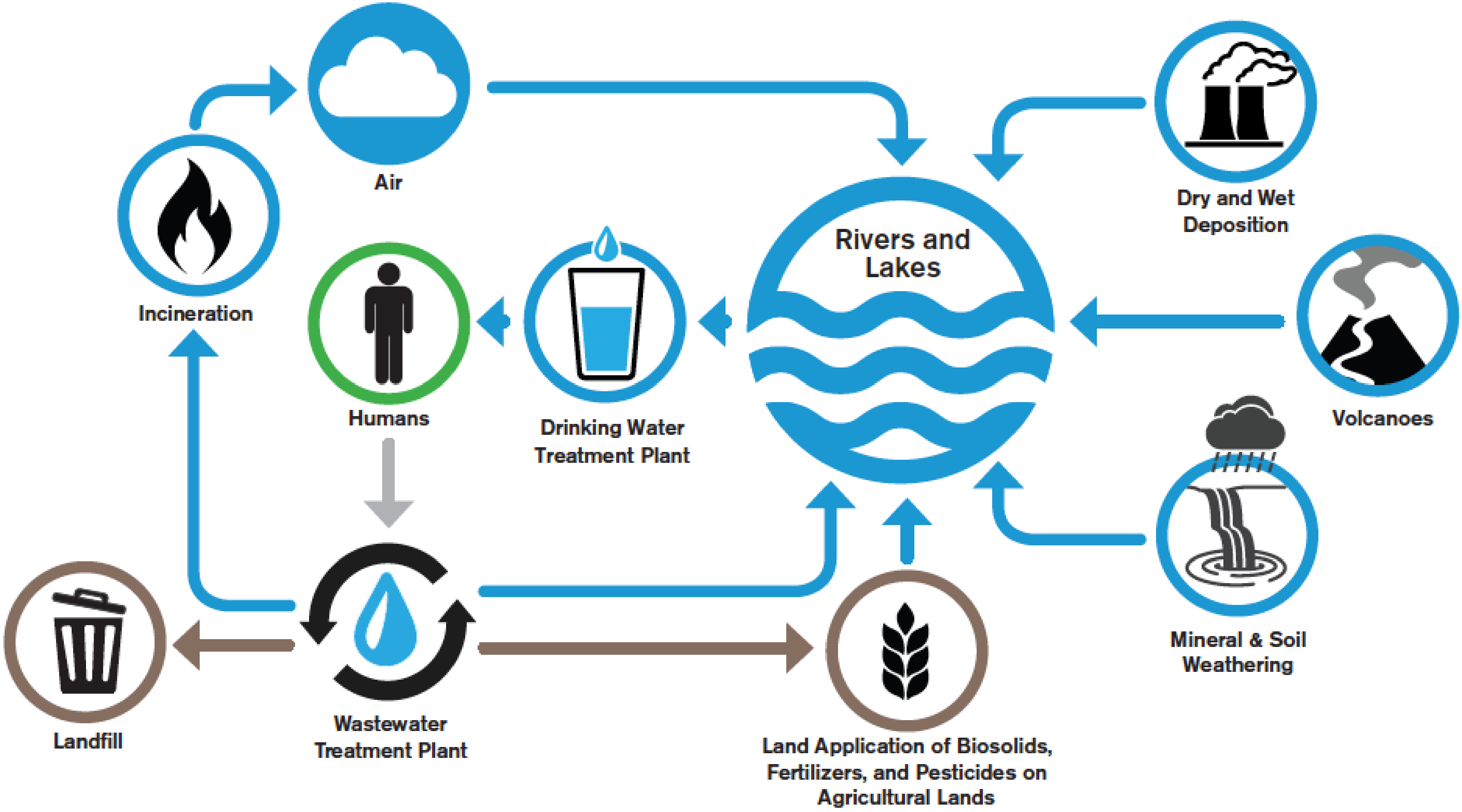


Sources of Nanomaterials in Drinking Waters

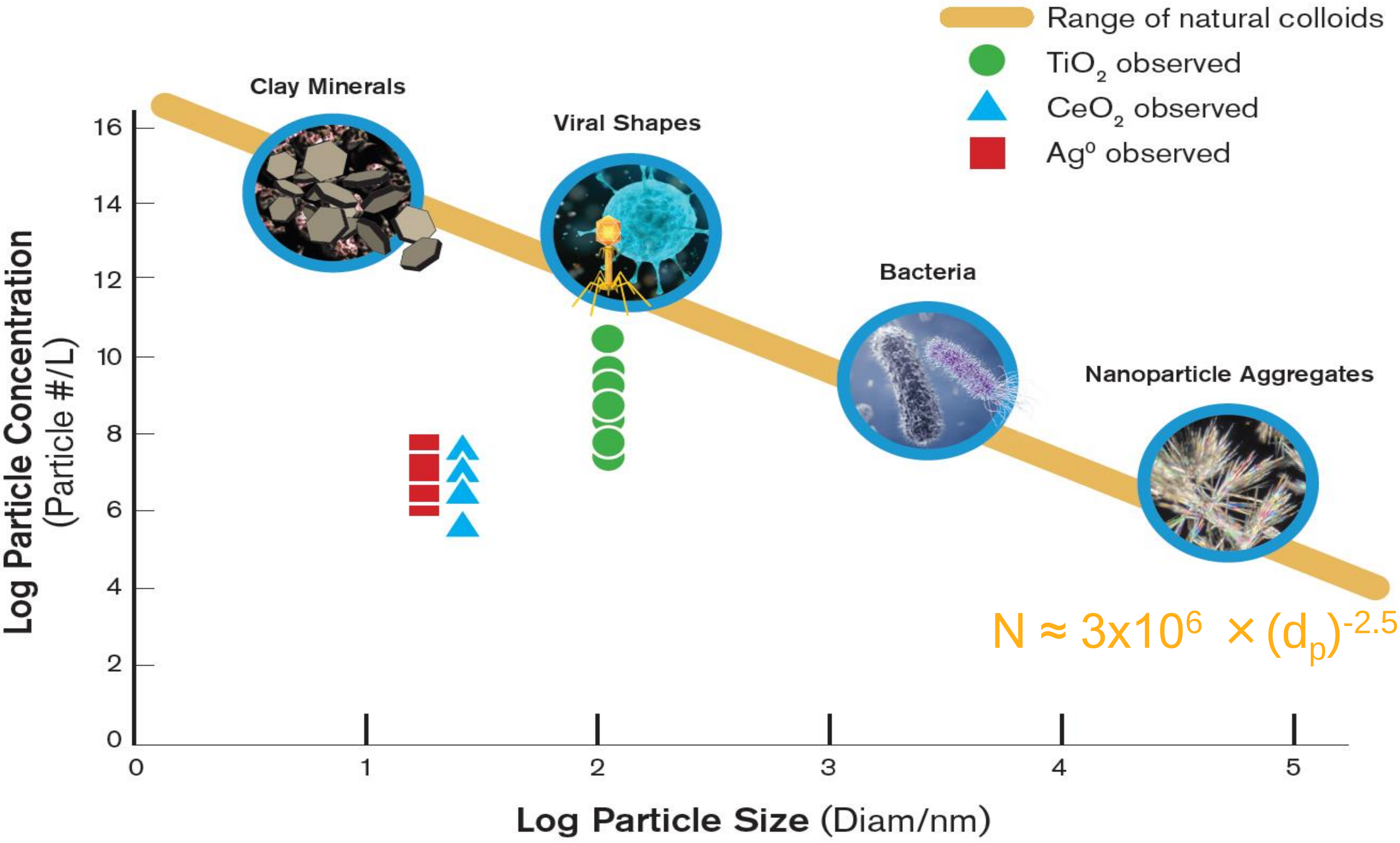
Do we know the levels or origins of nanomaterials in drinking water sources or tap water?

Could or should we be measuring nanomaterials in tap water?

Potential Sources of Natural, Incidental and Engineering NMs into water supplies

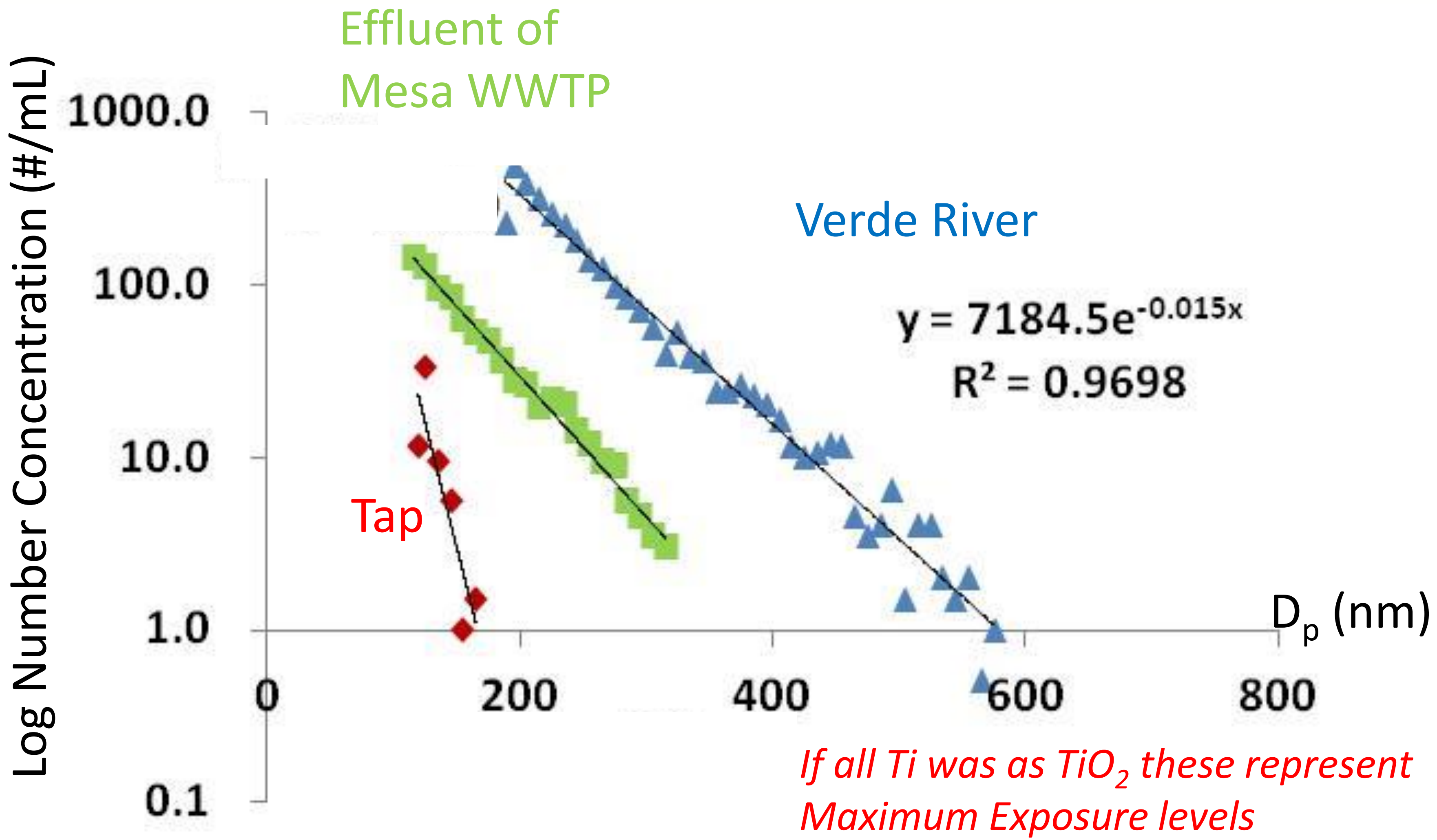


Particle size distributions across many water types follow Pareto's Law



$N \approx 3x10^6 \times (d_p)^{-2.5}$

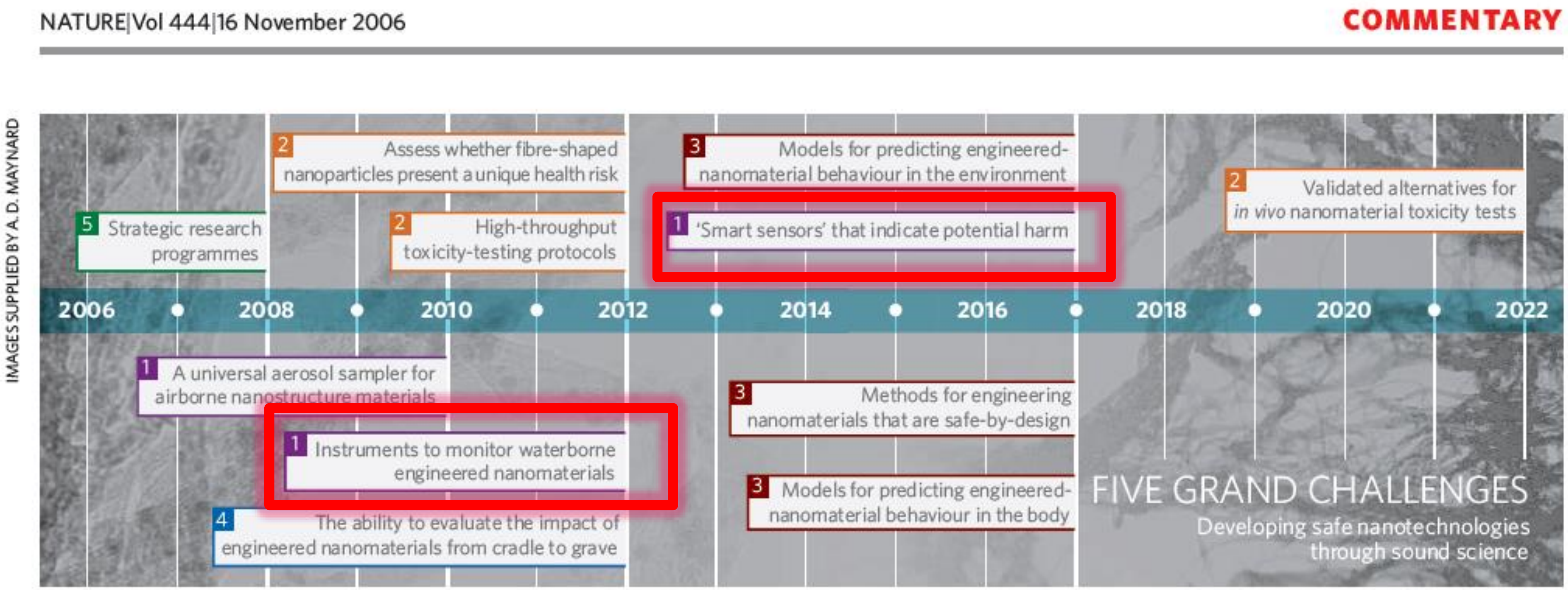
Pareto's Law Distributions of **Equivalent TiO_2** # Concentrations



If all Ti was as TiO_2 these represent Maximum Exposure levels

Reference: Total # natural 10 nm particles is ~ 10^9/mL

Nanomaterial Measurement Methods



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COMMENTARY

IMAGES SUPPLIED BY A. D. MAYNARD

5 Strategic research programmes

1 A universal aerosol sampler for airborne nanostructure materials

2 Assess whether fibre-shaped nanoparticles present a unique health risk

2 High-throughput toxicity-testing protocols

1 Instruments to monitor waterborne engineered nanomaterials

4 The ability to evaluate the impact of engineered nanomaterials from cradle to grave

3 Models for predicting engineered-nanomaterial behaviour in the environment

1 'Smart sensors' that indicate potential harm

3 Methods for engineering nanomaterials that are safe-by-design

3 Models for predicting engineered-nanomaterial behaviour in the body

2 Validated alternatives for *in vivo* nanomaterial toxicity tests

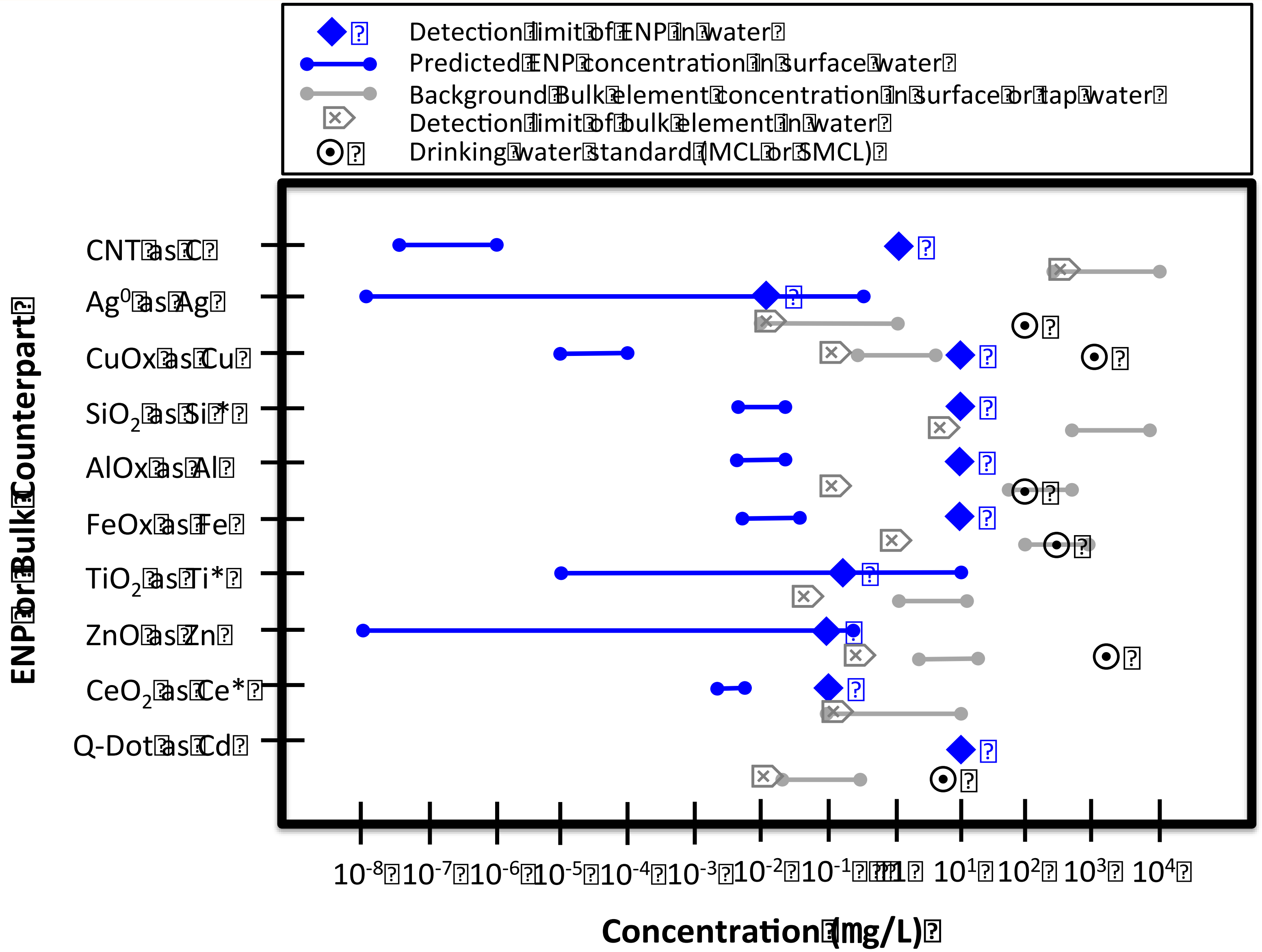
FIVE GRAND CHALLENGES

Developing safe nanotechnologies through sound science

- Colorimetry
- Fluorescence
- Electrochemical
- Light scattering or particle tracking
- Electron microscopy
- **Single particle ICP-MS (*ICP*-TOF-MS)**

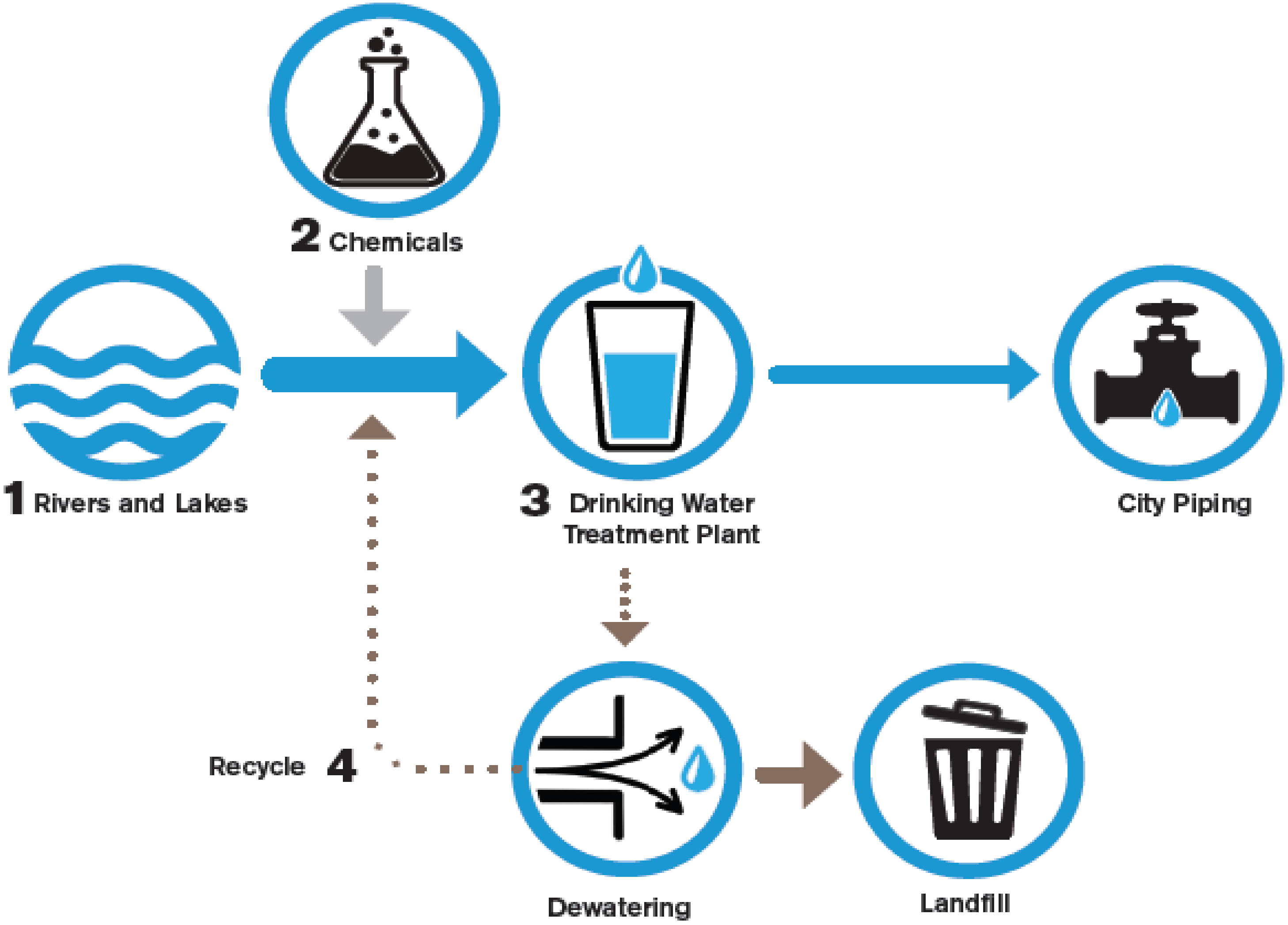
Suitability for drinking waters
&
expected NP Concentrations?

Comparison of ENP predicted surface water concentrations, background bulk concentrations, detection limits and drinking water standards (* Element has not MCL or SMCL in drinking water)

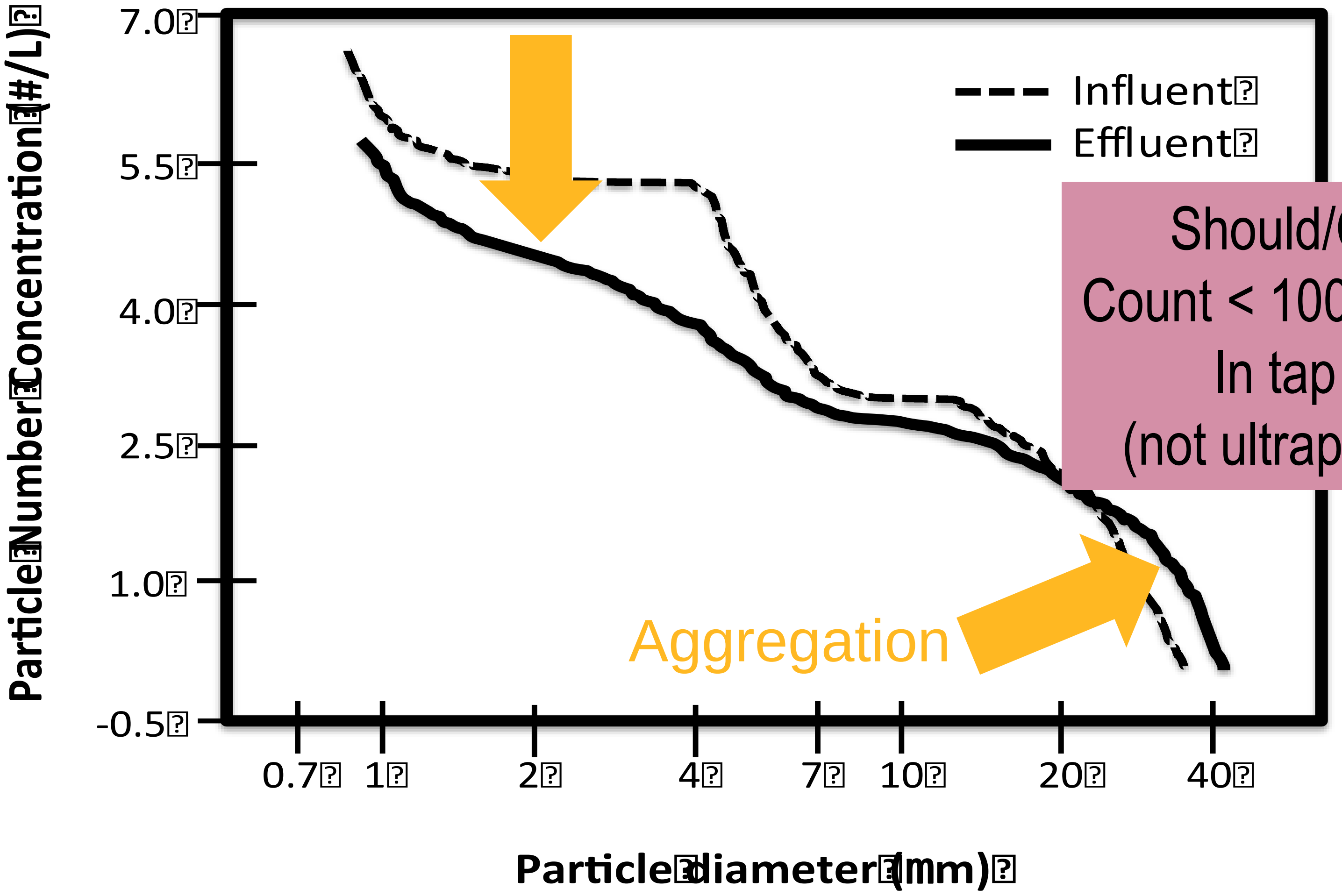


Adapted from Good et al., JAWWA 2016

Water Treatment Can Remove *nano-* and *micron*-sized particles



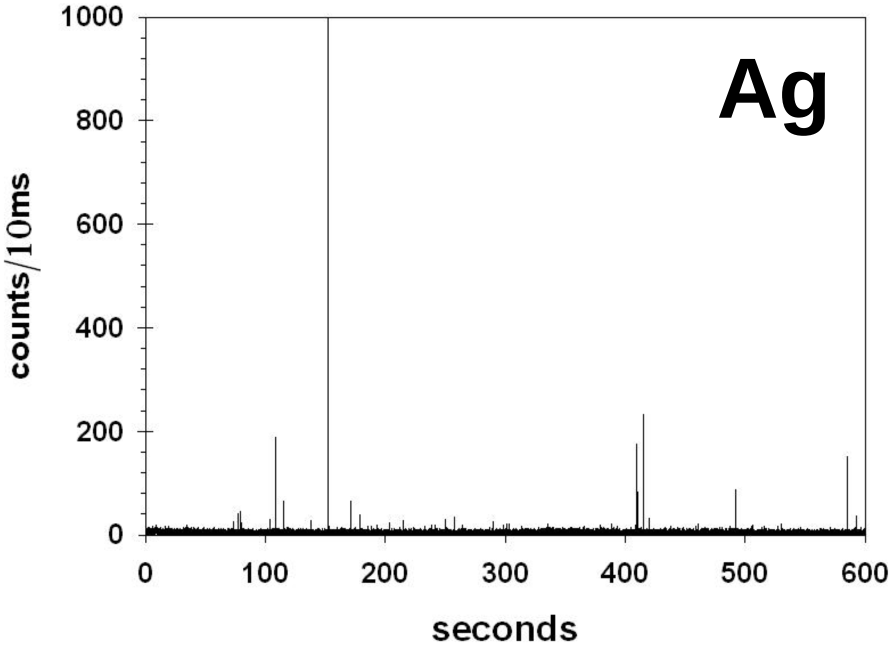
WTPs can monitor *micron* sized particles during treatment



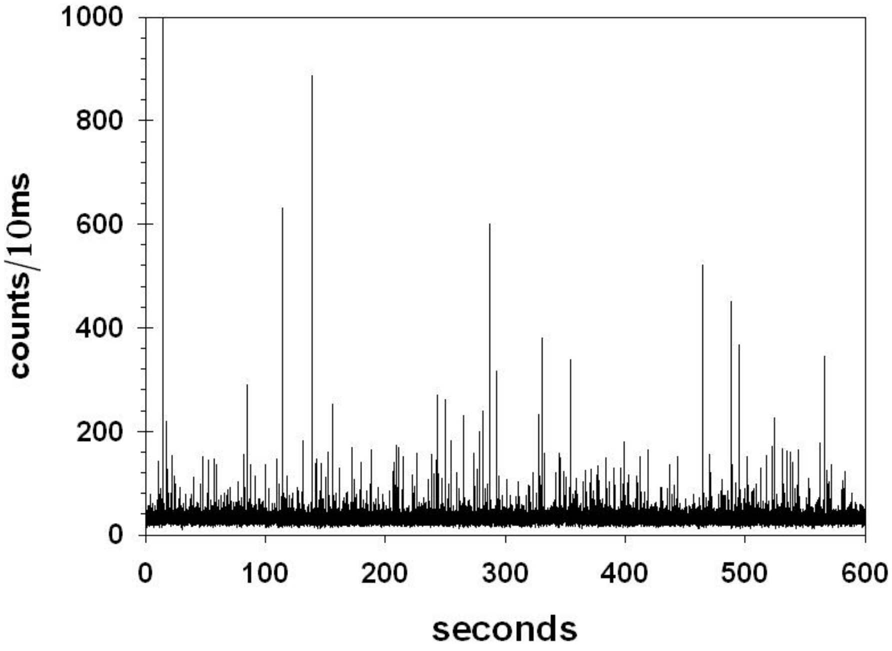
Should/Could we
Count < 100 nm particles
In tap water?
(not ultrapure water..)

spICP-MS Time-resolved data of ^{49}Ti, ^{140}Ce and ^{107}Ag for Verde River and tap water

Verde River

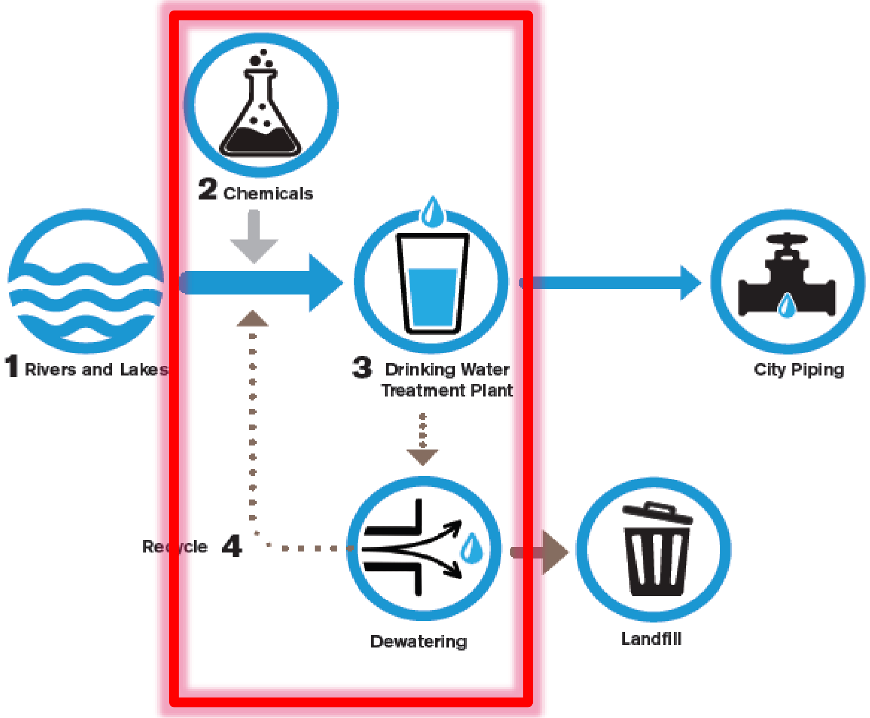


Tap Water

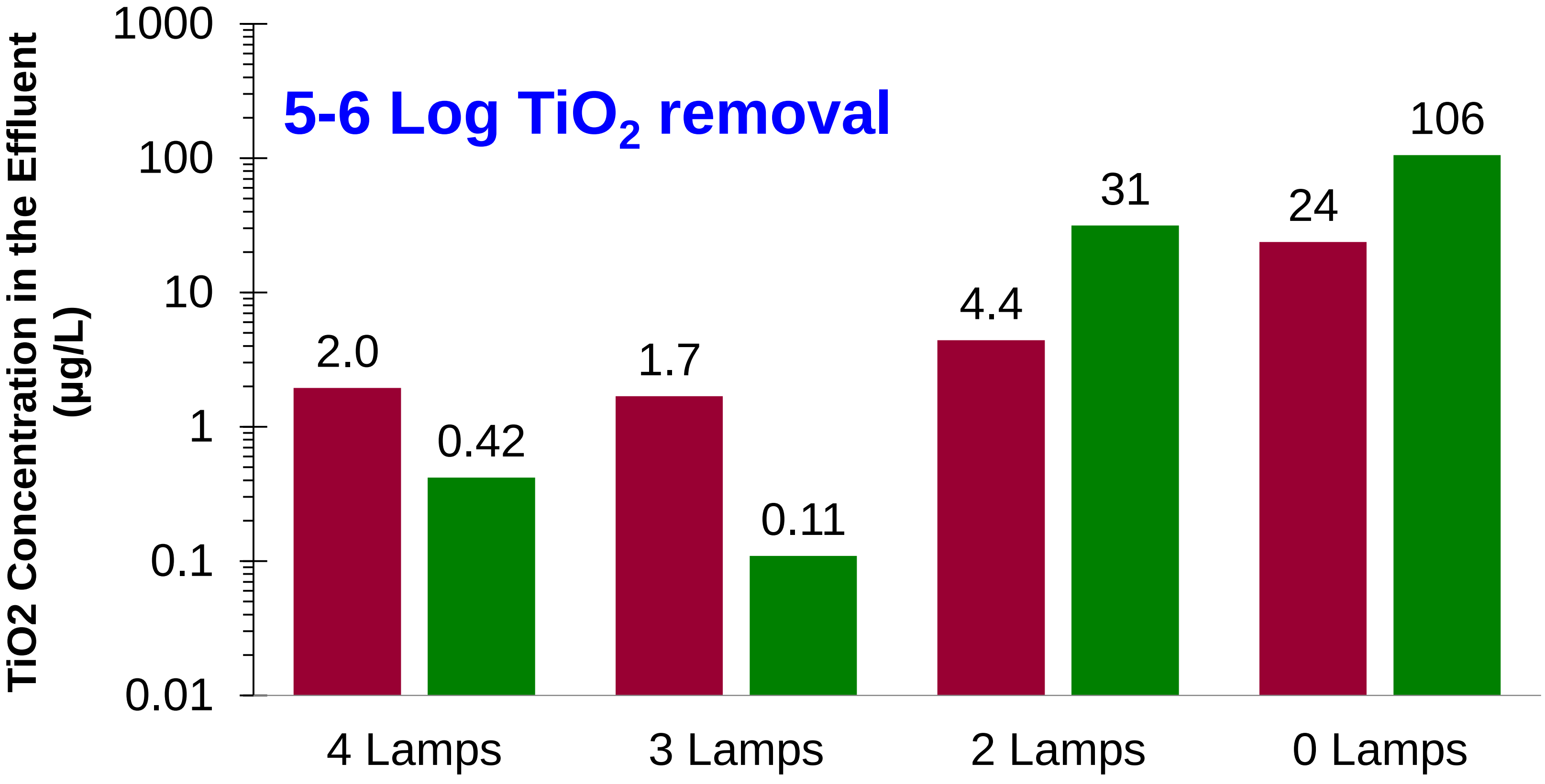


Water Treatment Processes as *Sources* of Nanoparticles

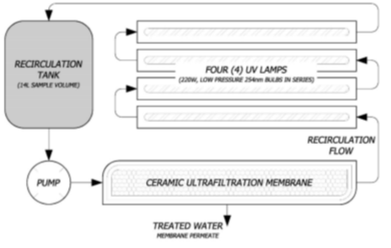
- Nano-enabled sorbents
- Nano-enabled catalysts
- Nano-enabled membranes



Freely dispersed NMs require separation

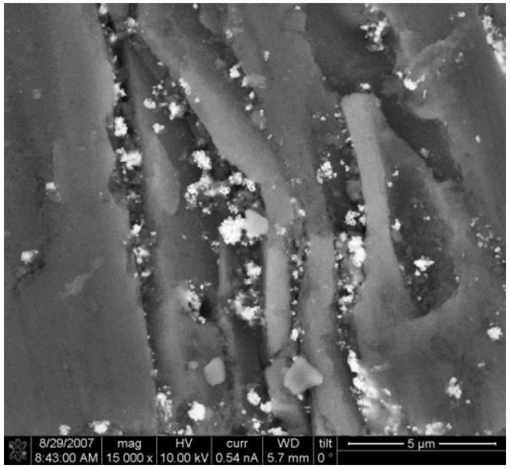


🟥 TiO2 dosage=0.1 g/L; Cr(IV)=500ppb; Dechlorinated Tap Water
🟩 TiO2 dosage=0.1 g/L; Cr(IV)=500ppb; Buffered DI Water



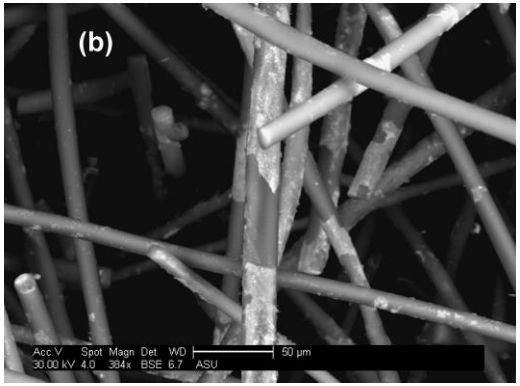
Attaching or embedding NMs reduces need for filtration systems

Nanoparticles on Macroscale Scaffolding

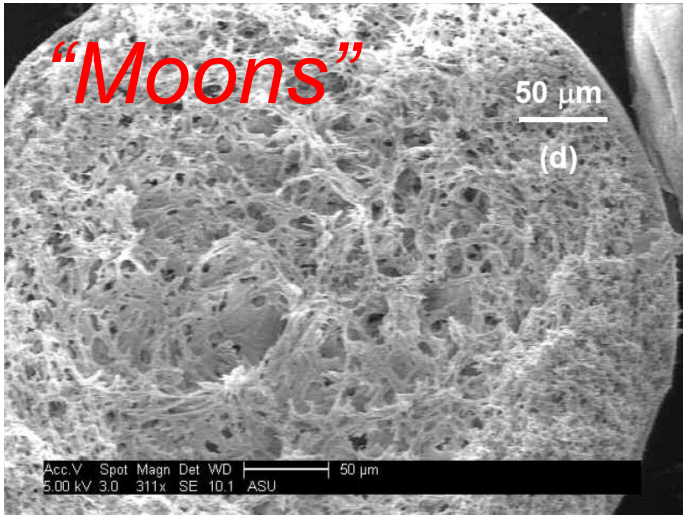


GAC

AC Fibers

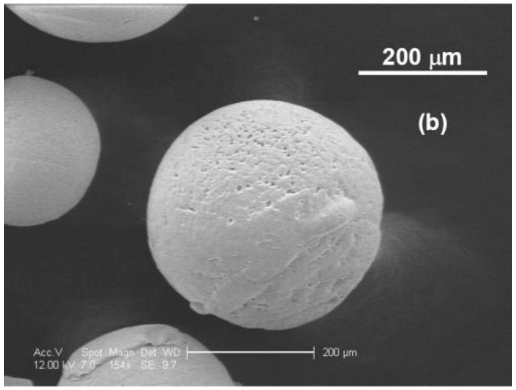


Electrospun fibers



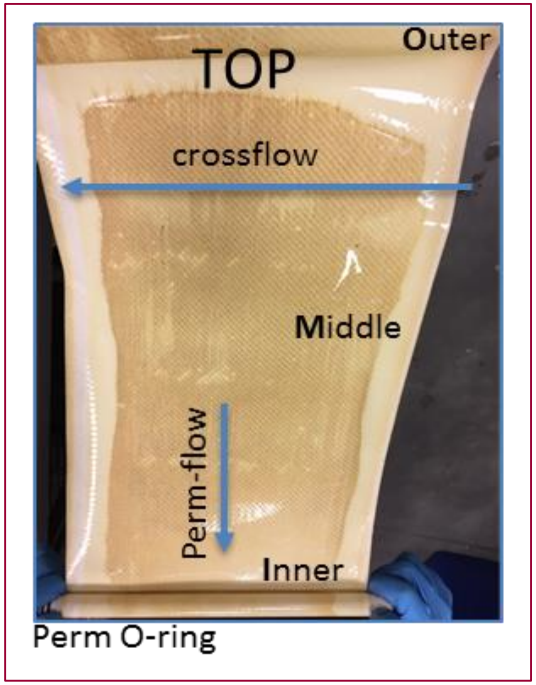
"Moons"

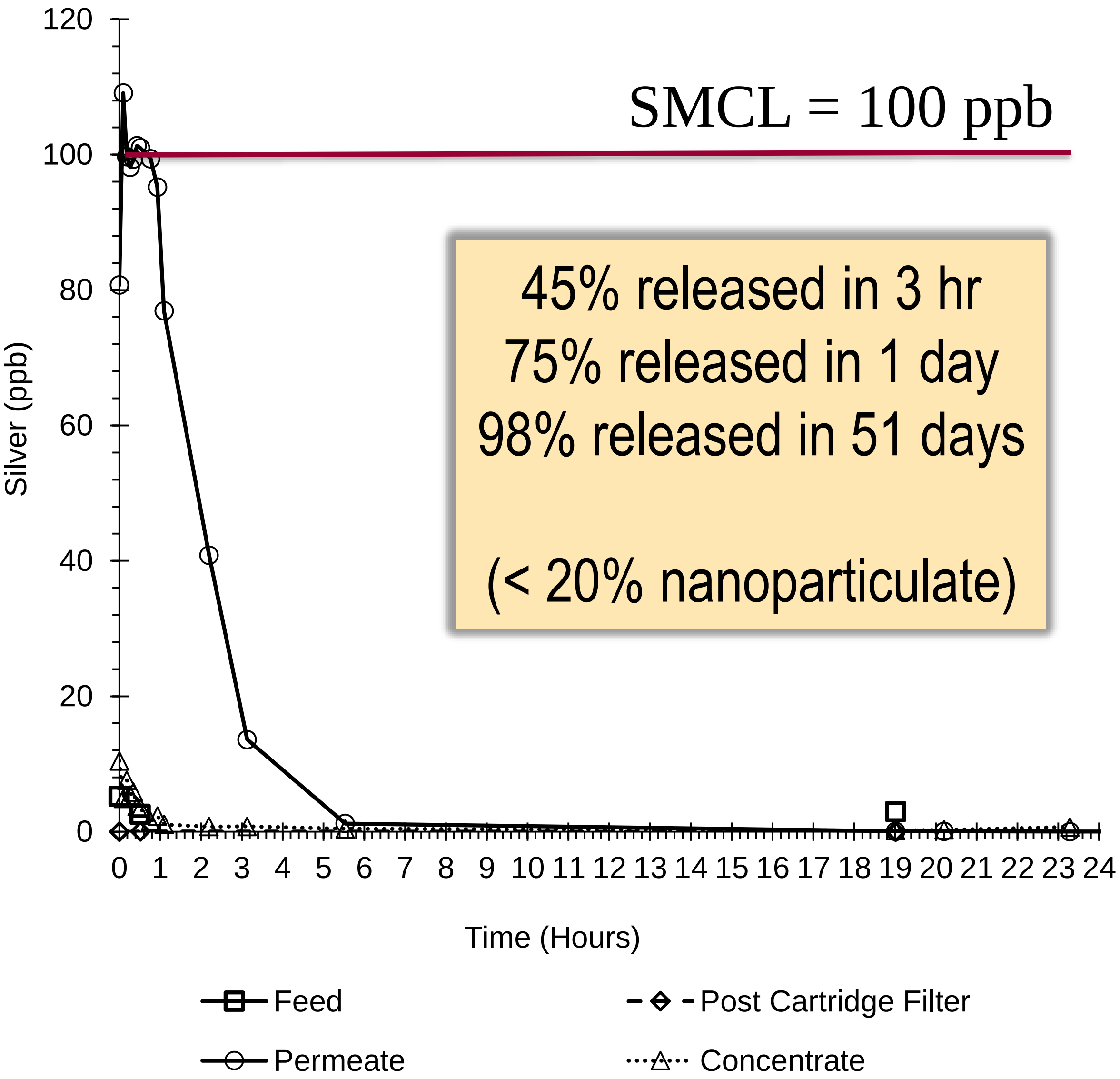
Ion exchange beads



Nano-Enabled Membranes Can Leach NMs?

Nano-Ag (2 $\mu g/cm^2$)
POU RO Membranes

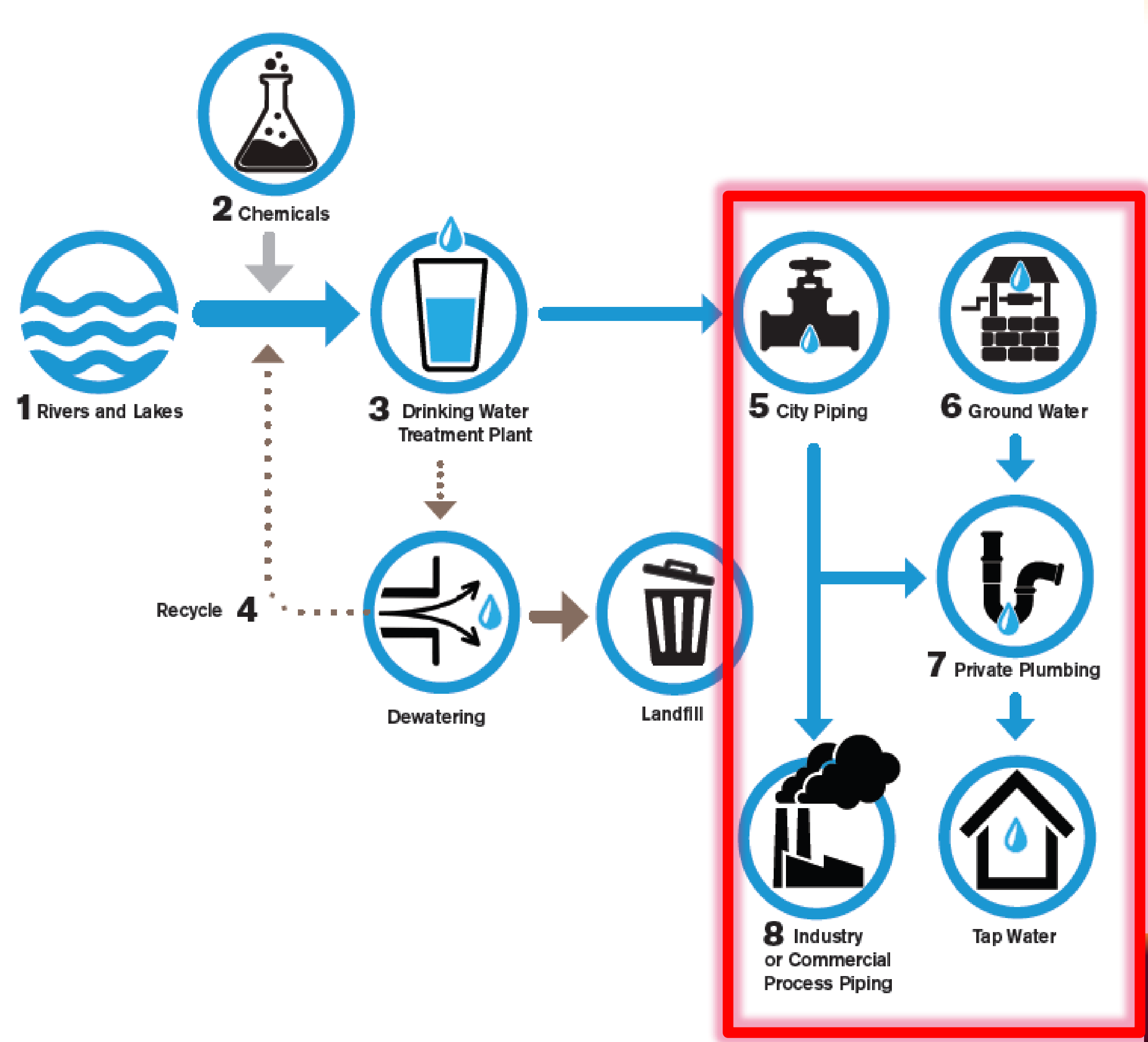




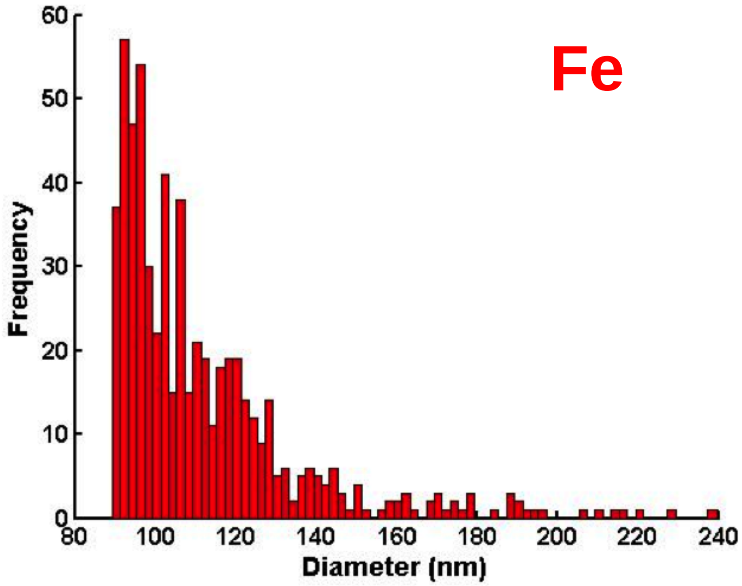
45% released in 3 hr
75% released in 1 day
98% released in 51 days

(< 20% nanoparticulate)

Other sources of NPs into Tap Water



spICP-MS on Tap water can detect NPs




- [161011 SP CuO tap DI :- Needs Recalculating!]

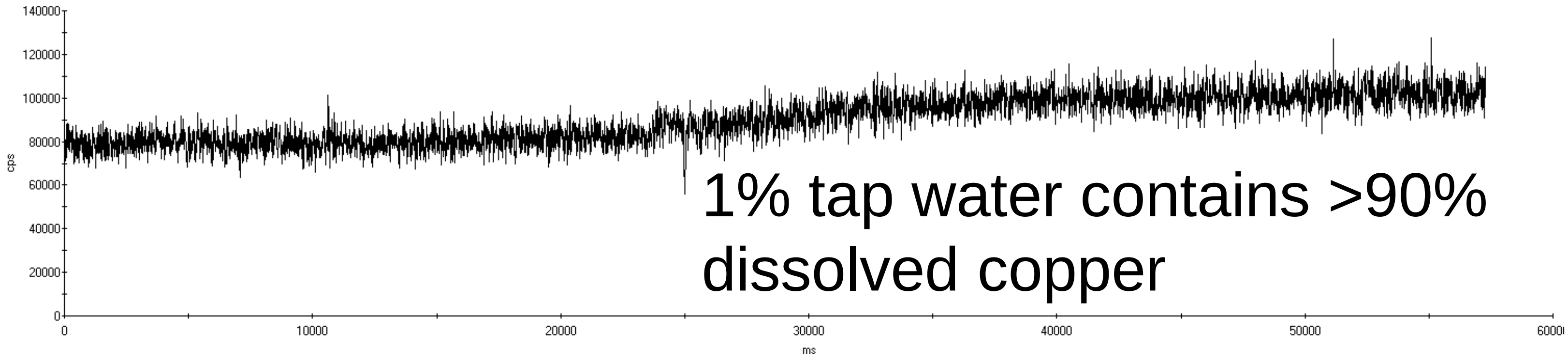
.0 bar Fwd.: 0 W | Ref.: 0 W | Load: 45 | Tune: 186 | Exp.: 1.5 x10+1 mbar | Ana.: 6.2 x10-8 mbar | Speed 1000 Hz | Load: 0.96 A

Vacuum ready | BTP | P QD

65Cu
- Blank
- HNO3
- 100 ppt Cu diss
- 500 ppt Cu diss
- 1 ppb Cu diss
- 2 ppb Cu diss
- BLK
- BLK

	Label	Start Time	End Time
✳			

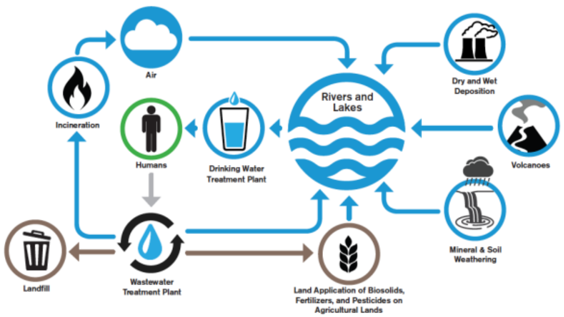
1 ppb spike CuO in nanopure water

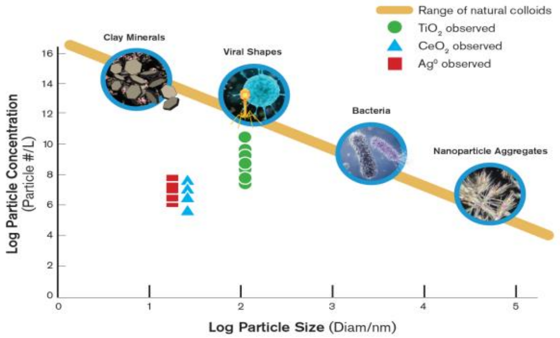


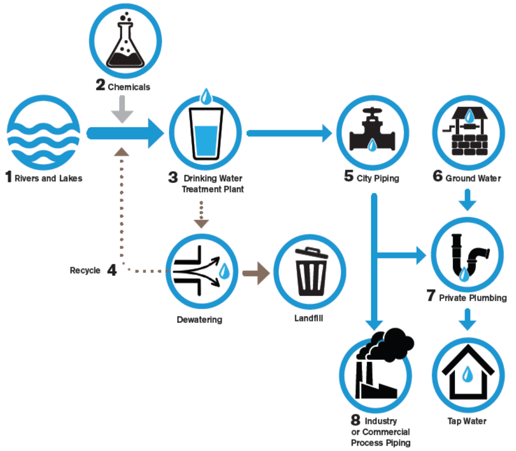
1% tap water contains >90% dissolved copper

Summary

- Nanoparticles exist in source and tap waters
- Detection strategy
  - Element specific
  - # counting
  - Both?
- National NP Reconnaissance could generate baseline data
- Nano-enabled devices
  - Long-term operation & monitoring of required
  - What is an acceptable NP release level into tap water for regulated vs non-regulated elements?







Acknowledgements

Contributors:

- ASU: Ariel Atkinson, Pierre Herckes, Arjun Venkatesan, Yuqiang Bi, Sean Zimmerman, Bingru Han
- John Fortner, Michael Wong, Julie Zimmerman, Jorge Gardea-Torresdey, James Ranville
- NSF Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment

…And he is always wearing a smile!

Engineered NPs likely represent a small fraction of all NPs

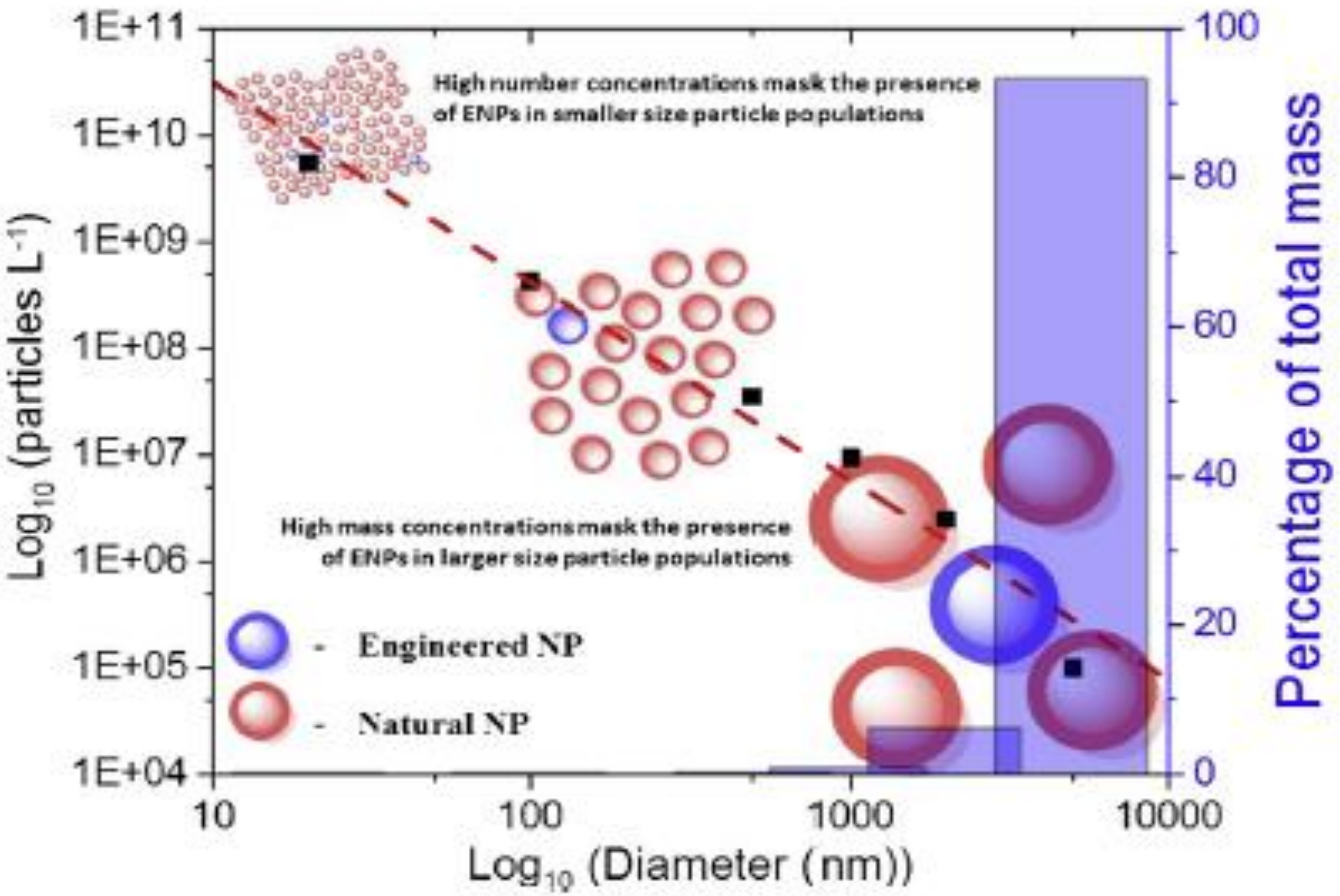
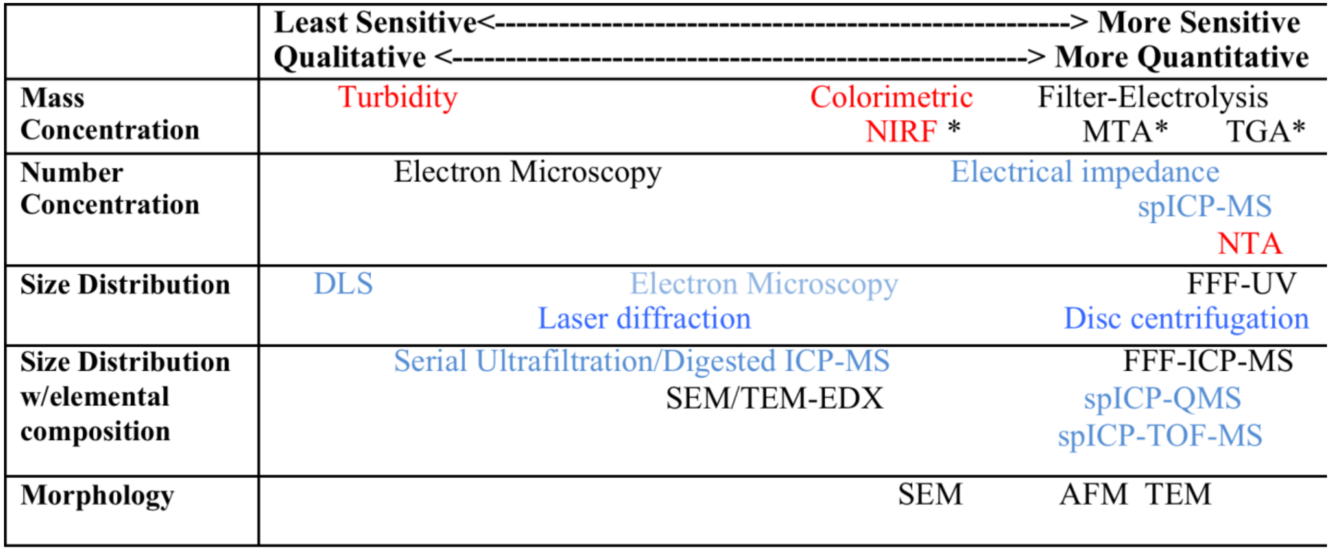


FIGURE 7 Considerations for PSDs when examining particles in natural waters. *Data from Harris (1977)*[94].

Ranville and Montano

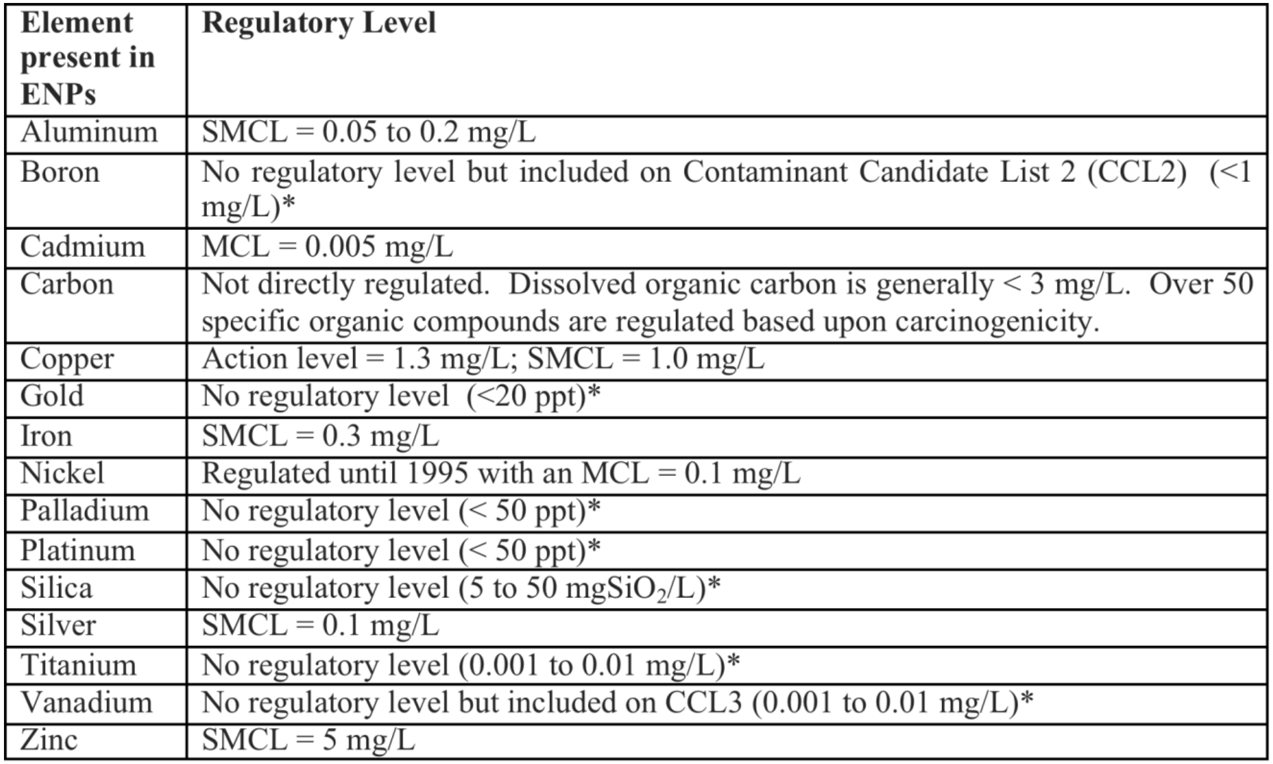
Capability of commonly accessible methodology to characterize and quantify engineered NPs in natural water samples. Text color codes for analysis speed of water samples (#/day): >50 ; 10-50 ; <10.



	Least Sensitive<--> More Sensitive Qualitative <--> More Quantitative
Mass Concentration	Turbidity Colorimetric Filter-Electrolysis NIRF * MTA* TGA*
Number Concentration	Electron Microscopy Electrical impedance spICP-MS NTA
Size Distribution	DLS Electron Microscopy FFF-UV Laser diffraction Disc centrifugation
Size Distribution w/elemental composition	Serial Ultrafiltration/Digested ICP-MS FFF-ICP-MS SEM/TEM-EDX spICP-QMS spICP-TOF-MS
Morphology	SEM AFM TEM

*For carbon analysis only: NIRF=Near Infrared Fluorescence; MTA=Microwave thermal analysis; TGA=thermogravimetric analysis; ICP-MS=Inductively coupled plama-mass spectrometry; spICP-MS=single particle ICP-MS (Q-quadrupole, TOF-Time of flight); DLS=Dynamic Light Scattering; FFF=field flow fractionation; SEM/TEM/EDX=scanning electron microscopy/transmission electron microscopy/energy-dispersive Xray analysis; AFM=atomic force microscopy; NIRF=near-infrared fluorescence spectroscopy

Regulatory implications for elements commonly used in engineered nanoparticles (* provides commonly-occurring range in surface waters for non-regulated elements as a comparison)



Element present in ENPs	Regulatory Level
Aluminum	SMCL = 0.05 to 0.2 mg/L
Boron	No regulatory level but included on Contaminant Candidate List 2 (CCL2) (<1 mg/L)*
Cadmium	MCL = 0.005 mg/L
Carbon	Not directly regulated. Dissolved organic carbon is generally < 3 mg/L. Over 50 specific organic compounds are regulated based upon carcinogenicity.
Copper	Action level = 1.3 mg/L; SMCL = 1.0 mg/L
Gold	No regulatory level (<20 ppt)*
Iron	SMCL = 0.3 mg/L
Nickel	Regulated until 1995 with an MCL = 0.1 mg/L
Palladium	No regulatory level (< 50 ppt)*
Platinum	No regulatory level (< 50 ppt)*
Silica	No regulatory level (5 to 50 mgSiO_2/L)*
Silver	SMCL = 0.1 mg/L
Titanium	No regulatory level (0.001 to 0.01 mg/L)*
Vanadium	No regulatory level but included on CCL3 (0.001 to 0.01 mg/L)*
Zinc	SMCL = 5 mg/L

Key Considerations	**Potential strategies**	**Example metrics**
1. Material Selection	Incorporate earth-abundant elements and trade-offs versus rare earth elements or toxic metals; prefer GRAS materials if possible	Upper continental crust wt% abundance of elements in ENP; MCL, SMCL or LC50 of element associated with ingestion
2. Material Structure/Property and Function and Hazard Interdependence	Structure-property-function-hazard design guidance plots have been developed to guide rational selection and design of materials	Life cycle DALY cost versus life cycle DALY benefit (e.g., nano-enabled drug delivery) Life cycle energy consumed versus life cycle energy saved (e.g., nano-enabled batteries)
3. ENP Synthesis Route	Low energy self-assembly of biologically based ENPs, rather than high energy content of some ENPs (e.g., CNTs); wet synthesis instead of powder or aerosol production to minimize worker exposure and maximize ENP yield on device	Embedded energy (kJ/kgENP) or virtual water (m^3/kgENP) required to produce ENP Yield of on-spec ENP
4. ENP Incorporation into device	Strategy to incorporate nano-structures into macro-scale devices (e.g., tethering, enmeshing) without losing unique nano-scale property	Relative % surface or net wt% loading of ENP in device Loss of efficiency in pollutant removal between slurry and surface attached ENP (e.g., electrical energy per order (EEO) removal (kWhr/m^3); specific membrane flux; adsorption density (μg/g sorbent))
5. ENP Detection	Ensure quantitative ENP analytical methods exist on-line or off-line during device development	Obtain minimum detection limits at least one order of magnitude below MCL, SMCL or other health-based standard or element Estimate health based concentration guideline for pristine and transformed ENP from literature or studies
6. End-of-life consideration	Design for recycling or non-toxic classification for disposal	Percentage composition or recycled products Metal loading (e.g., As) after long-term use

Thesis Objectives

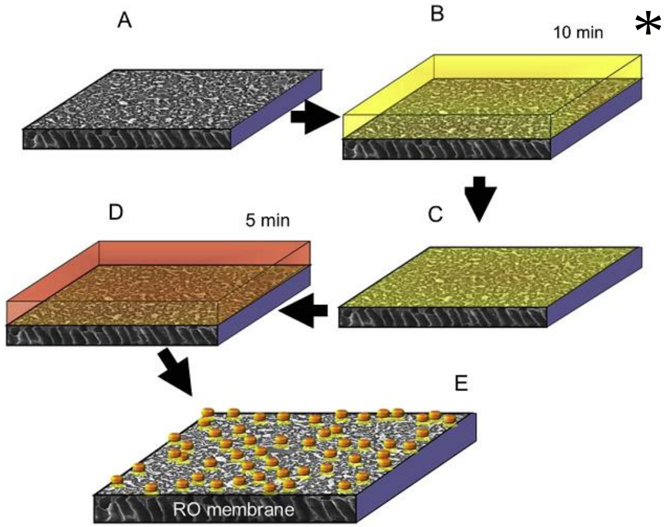
- Develop a extreme leaching test method — water jet test, compare the water jet method with the batch test, dead-end filtration, and cross-flow filtration

- Determine the Ag leaching amount and percentage for every leaching tests

- Compare the four different leaching test results, coming up with which leaching test
  - —has the highest Ag leaching
  - —is the easiest to replicate
  - —is the most cost-effective

- Develop standard protocols for standard silver composite membrane leaching tests

Membrane Preparation

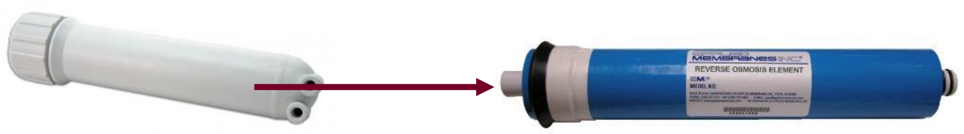


1. Rinse the membrane with 3mM $AgNO_3$ solution 10 minutes, then discard the solution and left a thin layer on the top;

2. Rinse the membrane with 3mM $NaBH_4$ solution for 5 minutes, then discard it;

3. Rinse the membrane with Nanopure water for 10 seconds

Spiral Wound



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* Ben-Sasson, M.; Lu, X. L.; Bar-Zeev, E.; Zodrow, K. R.; Nejati, S.; Qi, G. G.; Giannelis, E. P.;

Four Test Solutions

Methodology

NSF/ANSI-61

Nano-pure Water
(about pH 5)

pH5 (with Cl^-)

1 mM $MgCl_2$

2.5 mM NaH_2PO_4

pH10

2.5 Mm $Na_2B_4O_7$

5mM NaOH

pH5 (without Cl^-)

1 mM $MgSO_4$

2.5 mM NaH_2PO_4

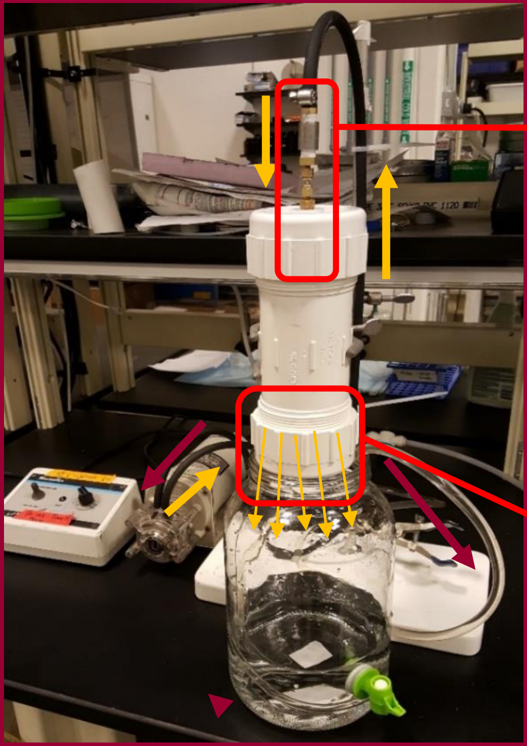
Cl^- may influence Ag^+ leaching, change to SO_4^{2+}

$$K_{sp,AgCl} = 1.6 \text{ x } 10^{-10}$$

Leaching Test — Water Jet

Methodology

- Water Jet
- Batch Test
- Cross-flow
- Dead-end



Water Jet Set-up

Water jet

Water jet outlet **D = 1.19 mm**

Flow rate up to **1.1L/min**

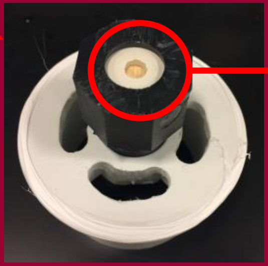
Water velocity up to **16.5 m/s**

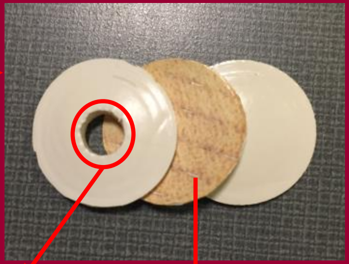
Water flow pressure **up to 20 psi**

Membrane size **D = 18 mm**

Exposing area **D = 6.35 mm (1/4”)**

Fixed between two rubber gaskets





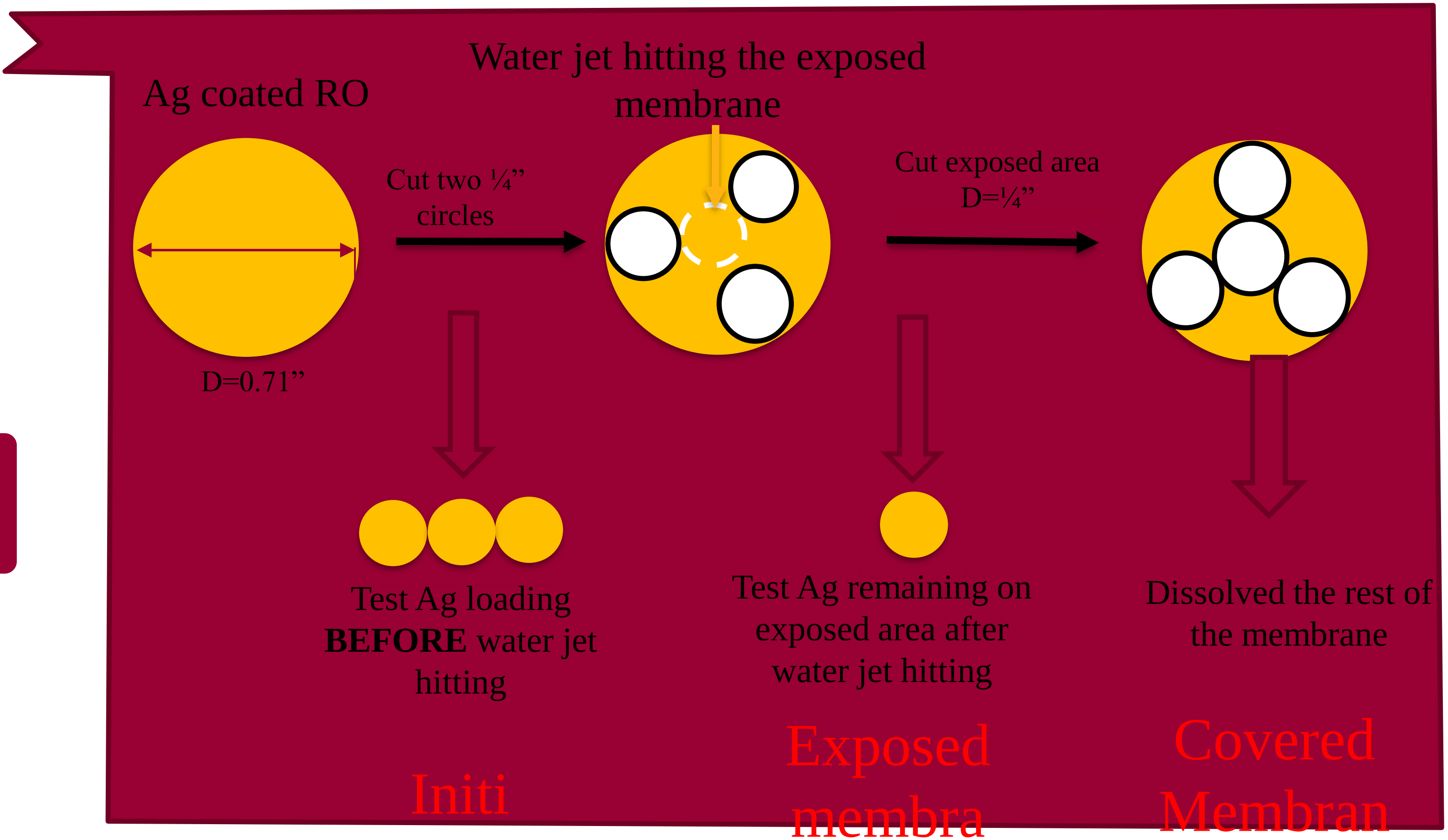
Exposing area

Membrane

Leaching Test — Water Jet

Methodology

- Water Jet
- Batch Test
- Cross-flow
- Dead-end



Ag coated RO

D=0.71”

Cut two ¼” circles

Water jet hitting the exposed membrane

Cut exposed area D=¼”

Test Ag loading **BEFORE** water jet hitting

Test Ag remaining on exposed area after water jet hitting

Dissolved the rest of the membrane

Initial

Exposed membrane

Covered Membrane

Leaching Test — Batch Test

Methodology

Water Jet

Batch Test

Cross-flow

Dead-end

Shaking for 3 days

Change the extraction solution every 24 hours

40 mL Extraction solution

+

4.9 cm^2 2.0 cm^2 0.44 cm^2

Study the influence of sa/vol on silver leaching

Leaching Test — Cross-flow

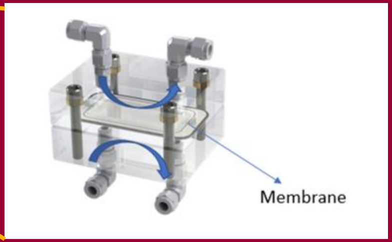
Methodology

Water Jet

Batch Test

Cross-flow

Dead-end



Samples were taken both for concentrate and permeate during the 50h

Pressure: 90 psi
Feed flow rate: 1.8 GPM
Permeate Flux: 20~40 L/hr/m^2
Operation time: 50 hrs
Solution volume: 23 L
(all the solution was recirculated in the system)

Leaching Test — Dead-end

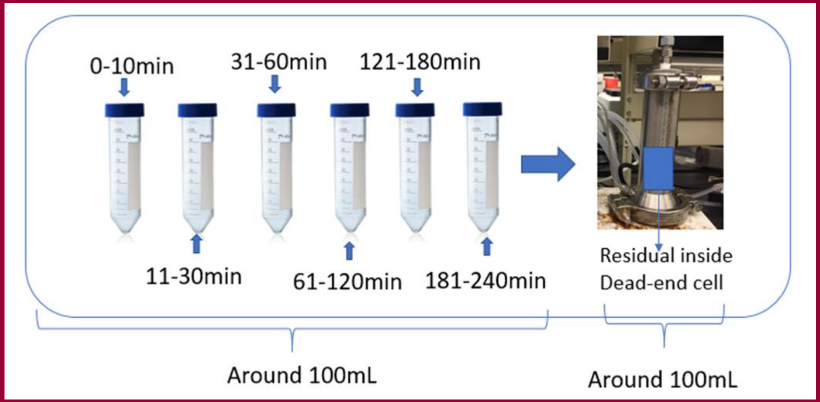
Methodology

Water Jet

Batch Test

Cross-flow

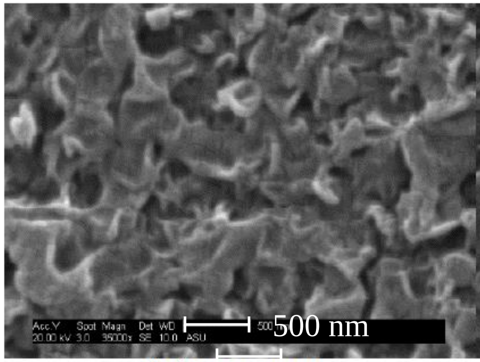
Dead-end



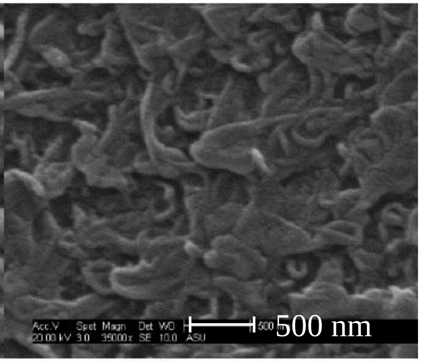
Operation pressure: 90 psi
Extraction water volume: 200 mL
Operation time: 4 hours

SEM Images of RO with/without Silver Impregnation

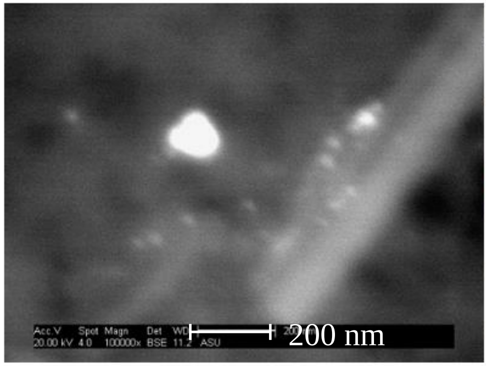
Results



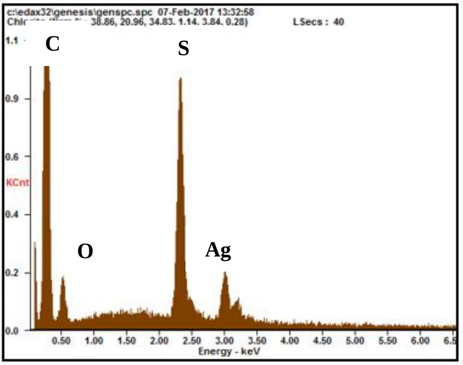
A (Pristine RO)



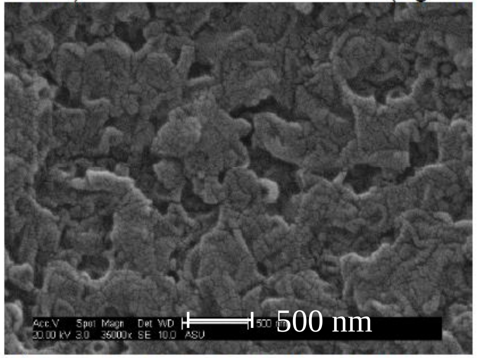
B (Ag Coated RO)



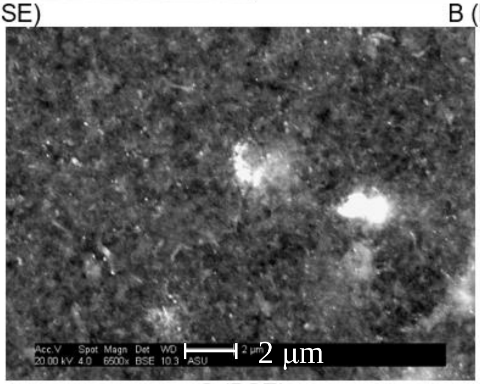
A (BSE)



B (EDX)



C (Ag coated RO after I hour water jet wash)



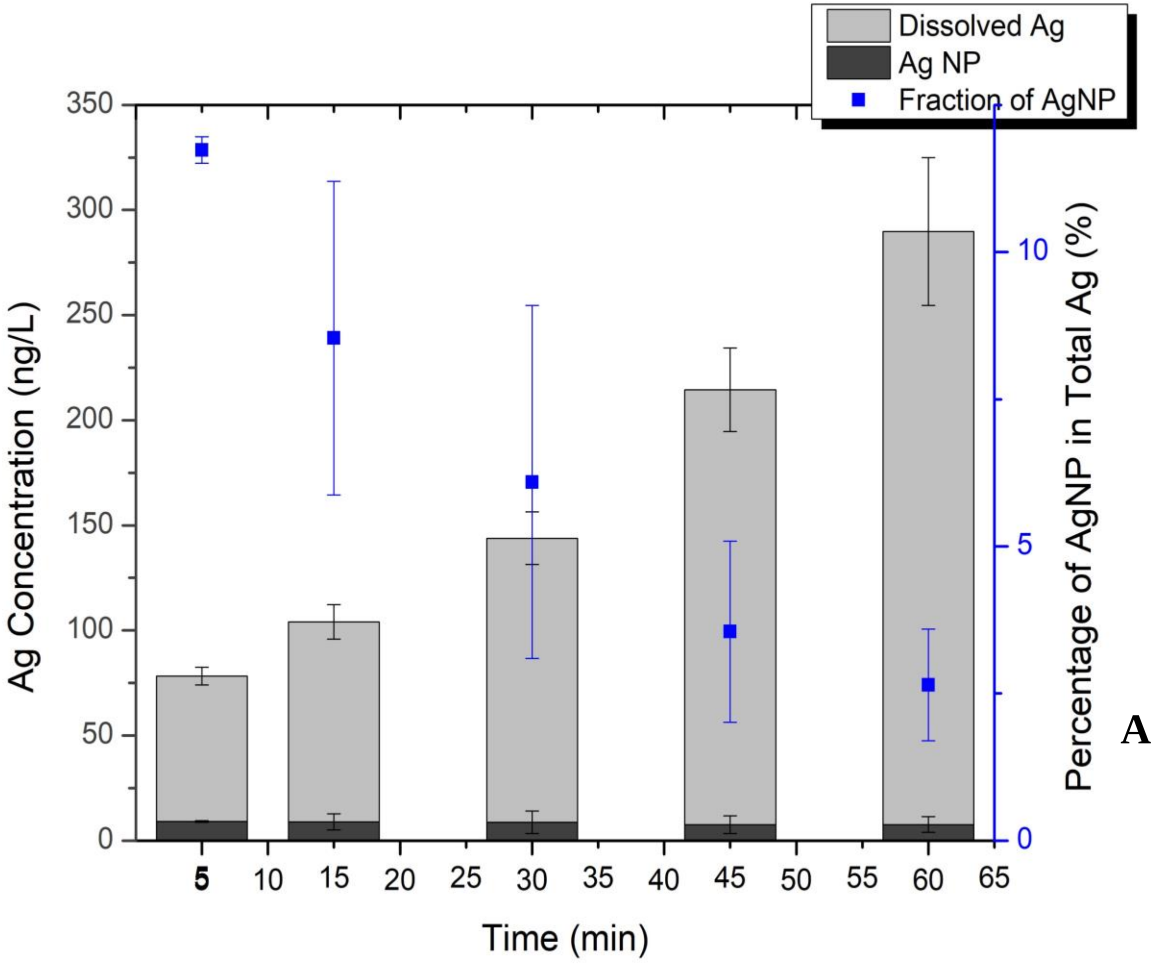
C (BSE)

- The average silver loading on the membrane is **2.0 ± 0.51 µg/cm^2**
- Lower than the Ag loading (2 - 4 µg/cm^2) reported by Ben-

* Ben-Sasson, M.; Lu, X. L.; Bar-Zeev, E.; Zodrow, K. R.; Nejati, S.; Qi, G. G.; Giannelis, E. P.;

Water Jet — Ag Leaching Trend

Results



Ag remaining in the exposed area +
Ag remaining in the covered area +
Ag released to water

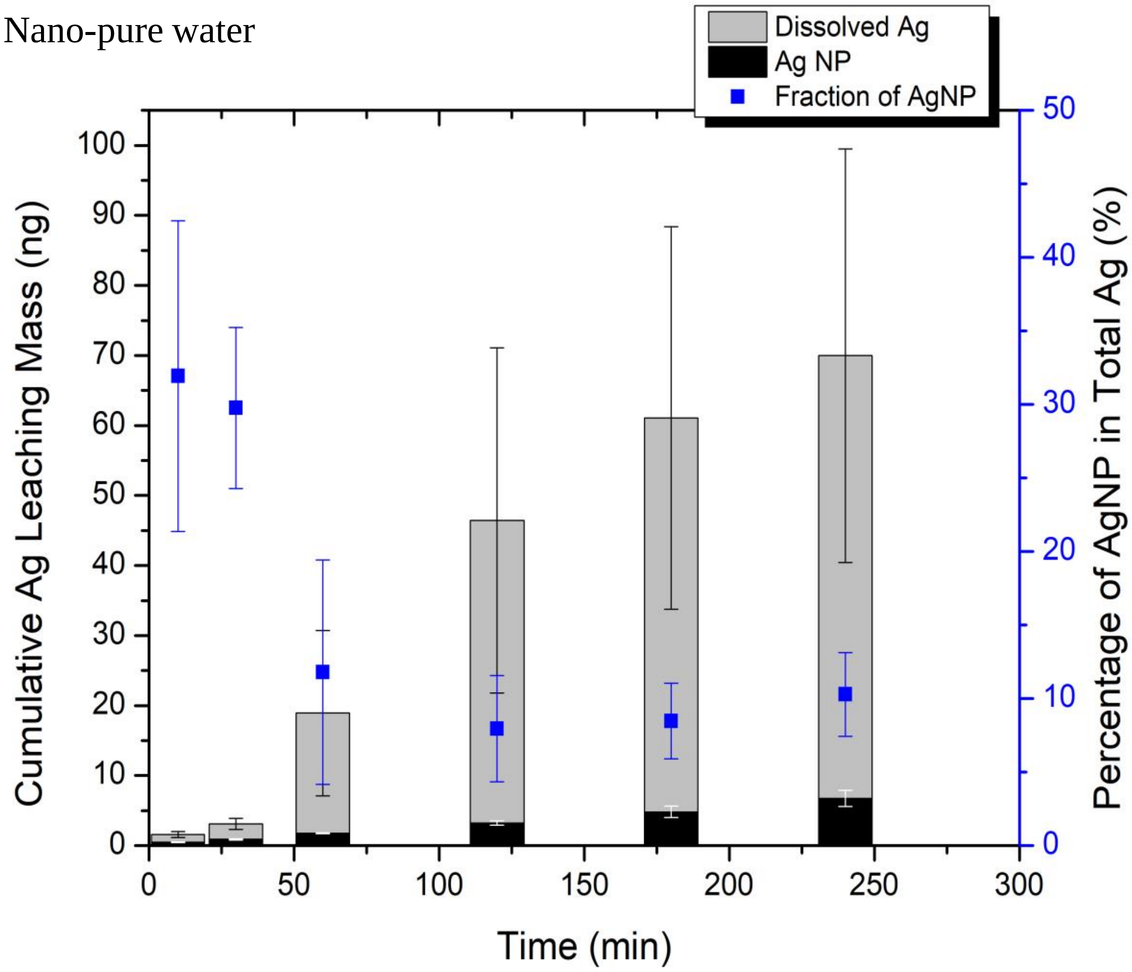
Ag Total measured (ug)	Ag Initial Loading (ug)	Mass Balance (%)
5.4 ± 0.22	6.0 ± 0.93	93 ± 13
5.9 ± 0.64	6.2 ± 0.76	95 ± 1.0
6.0 ± 0.22	6.7 ± 1.4	91 ± 14
3.7 ± 0.58	4.1 [illegible] 0.7[illegible]	89 ± 6.0

Acceptable Mass Balance 100± 25%

- Ag loading on the membrane has a variance of ± 25%
- Ag attached at the experiment set-up may have influence on mass balance

Dead-end — Ag Ions vs. Ag NP in Filtrate

Results

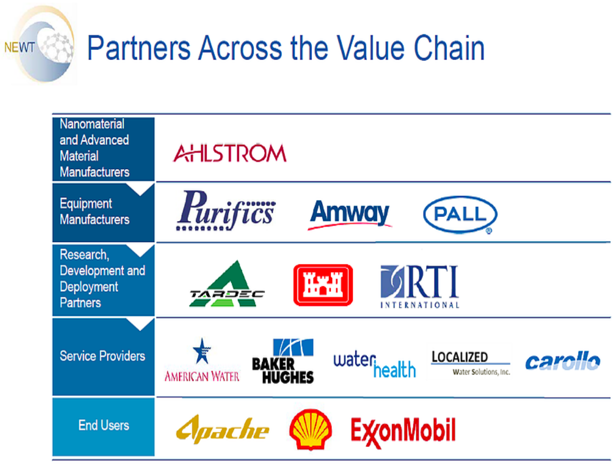


Nano-pure water

- Both AgNP and Ag ions are increased during the dead-end filtration
- The silver concentration in the filtrate area all below 2 ppb;
- The silver concentration in the concentrate are around 5 ppb

Clean Water Grand Challenge

- **Engineering Research Centers (ERC)**
  - ERCs operate at the **interface between** the **discovery**-driven culture of science and the **innovation**-driven culture of engineering
  - 2015 launched NSF Nanosystems ECR on **N**ano-**E**nabled **W**ater **T**reatment (NEWT)
- **NEWT VISION**
  - Enable access to treated water almost anywhere in the world, by developing transformative and off-grid modular treatment systems empowered by nanotechnology that protect human lives and support sustainable development.
  - **Focus on Two Applications**
    - Off-grid humanitarian, emergency-response and rural **drinking water** treatment systems
    - Industrial **wastewater reuse** in remote sites (e.g., O&G)



NEWT Partners Across the Value Chain

Nanomaterial and Advanced Material Manufacturers	AHLSTROM
Equipment Manufacturers	Purifics Amway PALL
Research, Development and Deployment Partners	TARDEC RTI INTERNATIONAL
Service Providers	AMERICAN WATER BAKER HUGHES waterhealth LOCALIZED Water Solutions, Inc. carollo
End Users	Apache ExxonMobil

NSF

RICE ASU UTEP Yale

Over Arching Science Questions

- How can we use novel nano-properties for water purification?
- How can nano-materials be embedded into scaffolding without loosing their functionality?
- What “activation” modalities can be employed to replace use of chemicals?
- What safety concerns exist around nano-enabled water technologies?

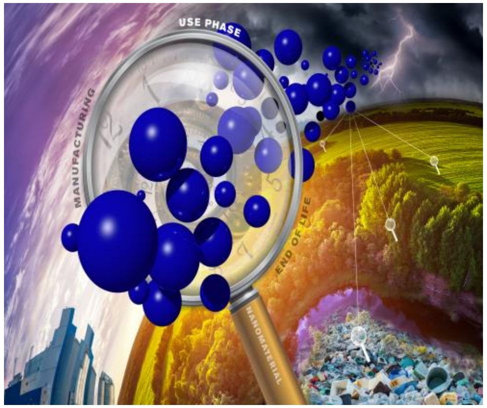
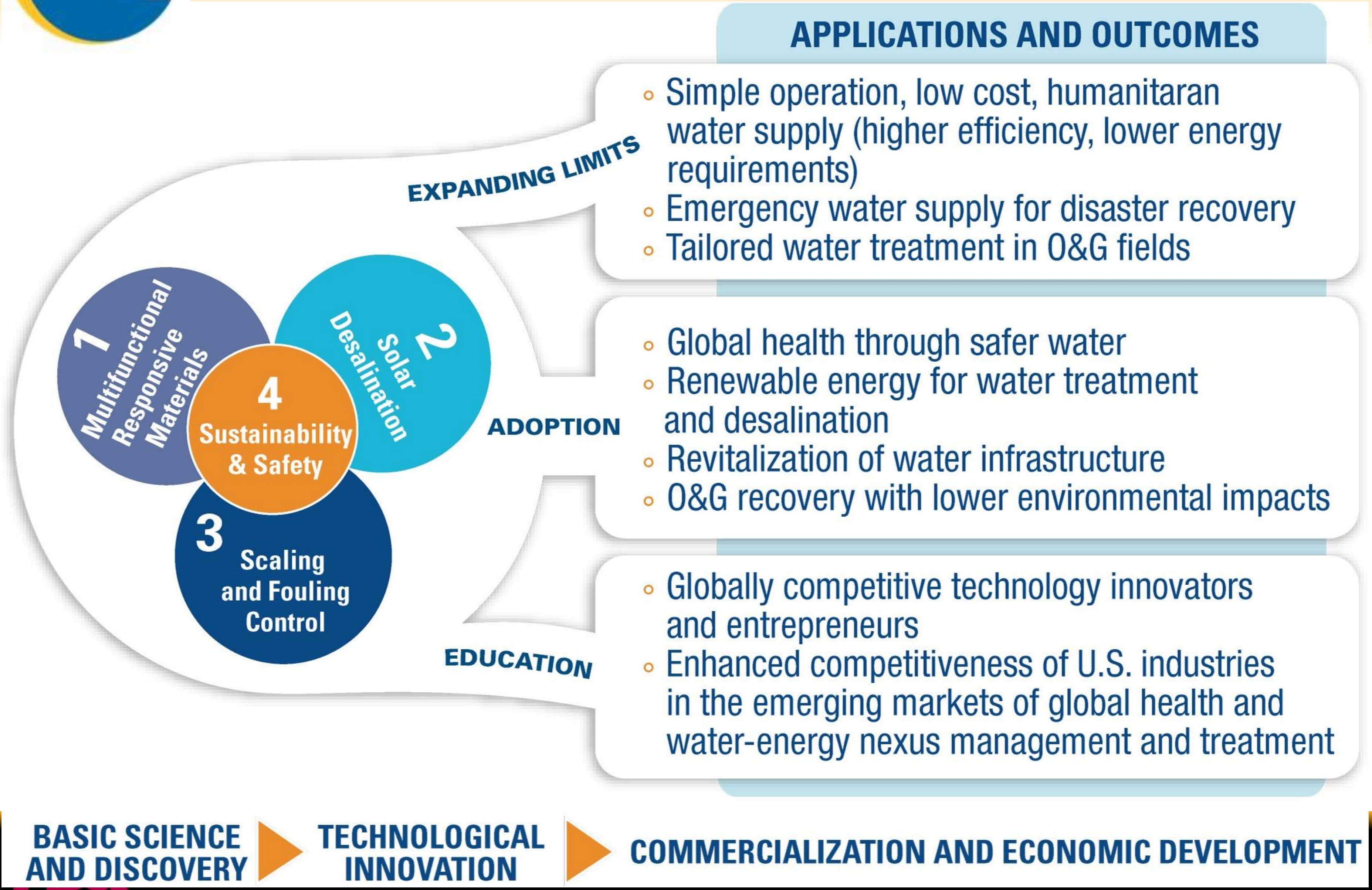


Image Credit: M. Northrop/ASU

Operational Vision & Outcomes



1 Multifunctional Responsive Materials

2 Solar Desalination

3 Scaling and Fouling Control

4 Sustainability & Safety

APPLICATIONS AND OUTCOMES

EXPANDING LIMITS

- Simple operation, low cost, humanitaran water supply (higher efficiency, lower energy requirements)
- Emergency water supply for disaster recovery
- Tailored water treatment in O&G fields

ADOPTION

- Global health through safer water
- Renewable energy for water treatment and desalination
- Revitalization of water infrastructure
- O&G recovery with lower environmental impacts

EDUCATION

- Globally competitive technology innovators and entrepreneurs
- Enhanced competitiveness of U.S. industries in the emerging markets of global health and water-energy nexus management and treatment

BASIC SCIENCE AND DISCOVERY ▶ **TECHNOLOGICAL INNOVATION** ▶ **COMMERCIALIZATION AND ECONOMIC DEVELOPMENT**