IMA Research need #8: Developing methods to detect nanomaterials and determine exposure routes

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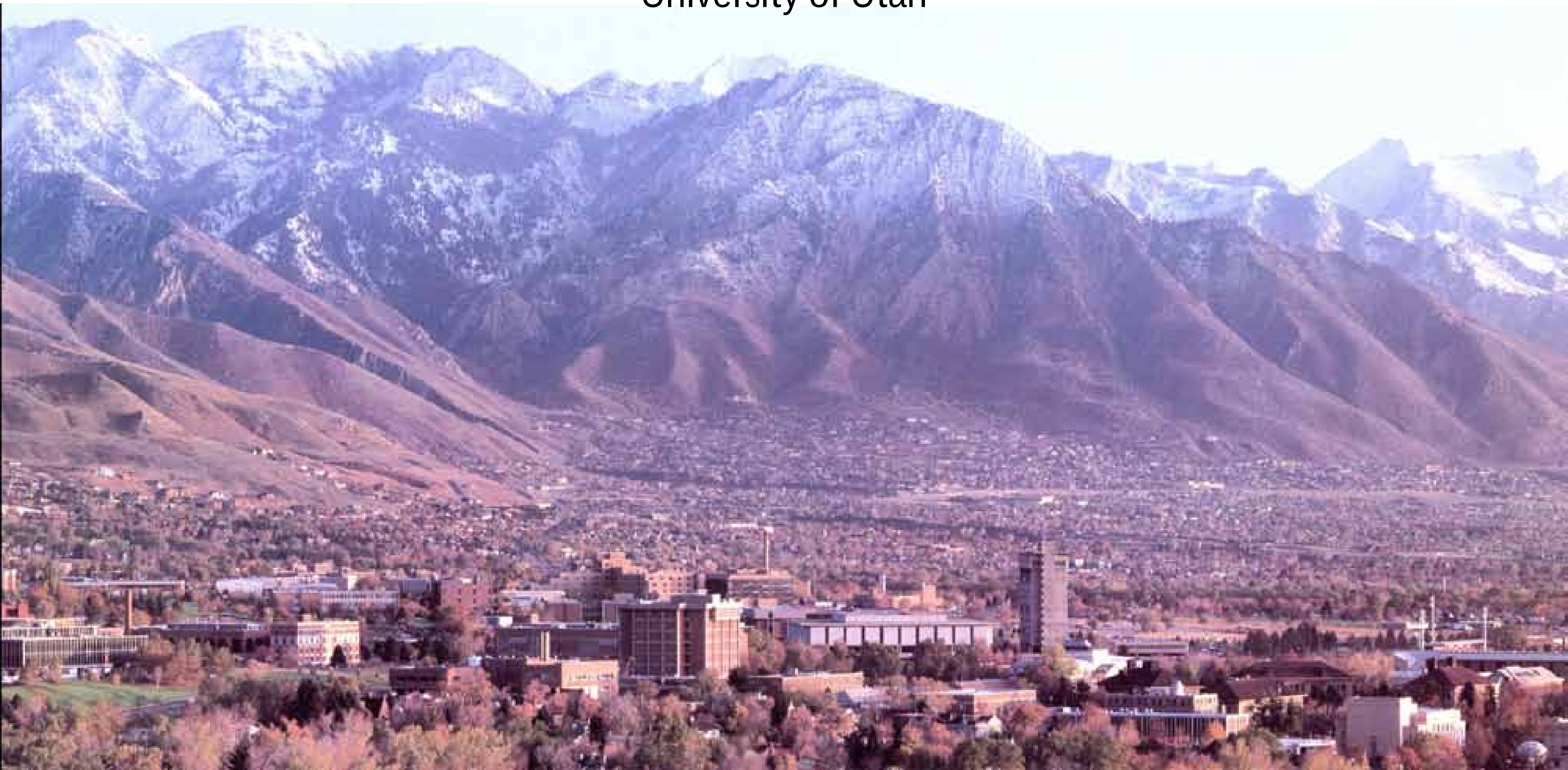


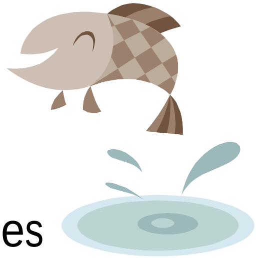
Case study: finding the cause

How would you go about identifying the one of potentially many nanomaterials in the air, soil, water, or organisms that could have caused this ecological catastrophe?

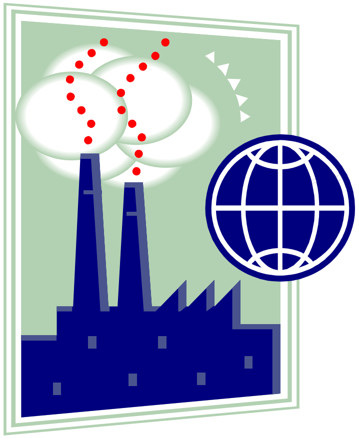
In affected populations, digest tissues and analyze to determine whether elevated concentrations of particular elements occur in these tissues

How would you find the nanoparticles, or their by-products, in the suite of natural and synthetic nanomaterials?

Need to refine techniques to:



1) Measure low concentrations in water and tissue
2) Distinguish engineered, natural, and incidental sources
3) Distinguish various sources within a class of engineered nanoparticles
4) Minimize sample disturbance so that the observation reflects the unperturbed environmental state

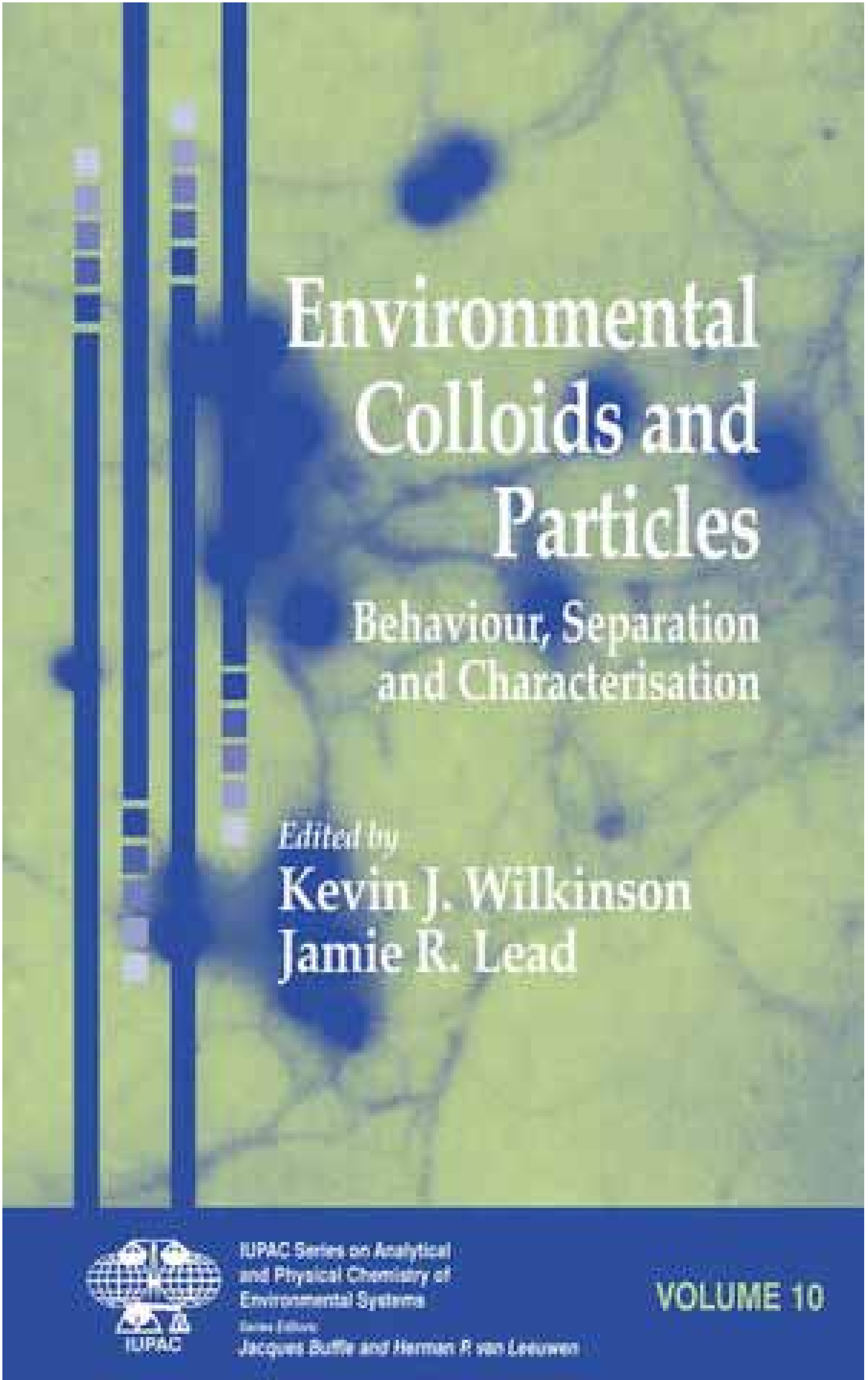


State of the Science – analytical methods:

Table 4. Nanoparticle properties and examples of analytical methods potentially suitable for their measurement.

Nanoparticle properties	Microscopy and related techniques	Chromatography and related techniques	Centrifugation and filtration techniques	Spectroscopic and related techniques	Other techniques
Aggregation	e.g. STEM, TEM, SEM, AFM. STM		e.g. ANUC	e.g. XRD, SANS	e.g. Zeta potential
Chemical composition	AEM, CFM			e.g. NMR, XPS, Auger, AES, AAS, MS, XRD, EBSD	
Mass concentration	AEM, CFM	√		√	e.g. Gravimetry, thermal analysis
Particle number concentration					e.g. Particle counter, CPC
Shape	e.g. STEM, TEM, SEM, AFM. STM	e.g. FlFFF-SLS, SedFFF-DLS	e.g. UC		
Size	e.g. STEM, TEM, SEM, AFM, STM	√			e.g. DMA
Size distribution	e.g. STEM, TEM, SEM, AFM, STM	e.g. FFF, HDC, SEC	e.g. CFF, UC, CFUF	e.g. SPMS, SAXS	e.g. UCPC, SMPS
Dissolution			Dialysis, CFUF		Voltammetry, diffusive gradients in thin films
Speciation		e.g. SEC-ICP-MS		e.g. XAFS, XRD	e.g. Titration
Structure	e.g. STEM, TEM, SEM, AFM, STM			e.g. XRD, SANS	
Surface area (& porosity)					e.g. BET
Surface charge		e.g. CE			e.g. Zeta potential
Surface chemistry	AEM, CFM			e.g. XPS, Auger, SERS	

From Tiede et al. (2008)



Environmental Colloids and Particles

Behaviour, Separation and Characterisation

Edited by

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IUPAC

IUPAC Series on Analytical and Physical Chemistry of Environmental Systems

Series Editors

Jacques Buffle and Herman P. van Leeuwen

VOLUME 10

State of the Science - continued:

Dynamic light scattering (DLS) and other common methods provide good results for monodisperse samples

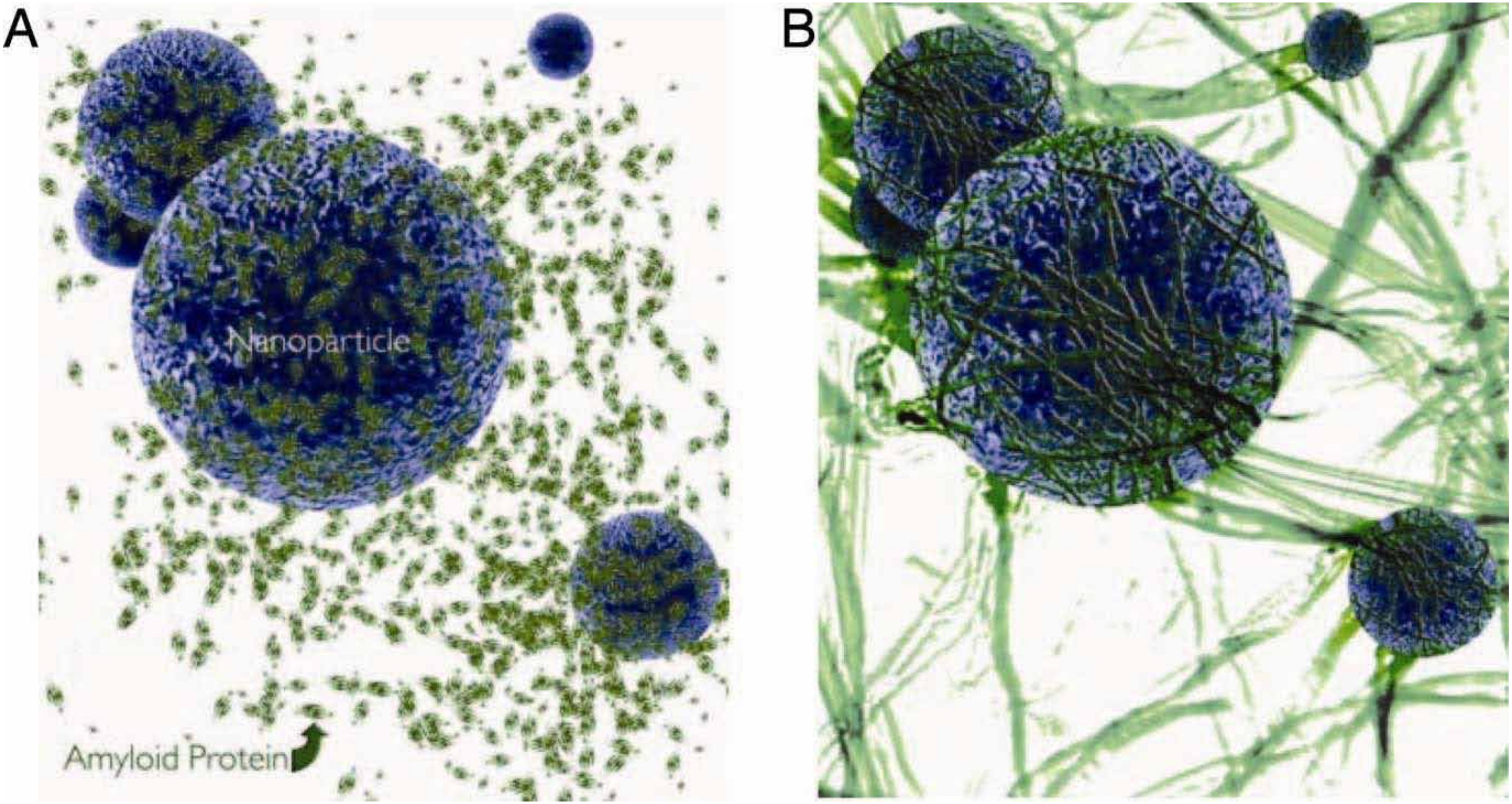
Nanopowders in clean water aggregate and become polydisperse

Nanoparticles in the environment end up bound with extracellular polymers and other natural organic matter

Also become bound with natural (e.g. clays, oxyhydroxides, sulfides) and incidental nanomaterials (soot)

May undergo oxidation, reduction, precipitation, dissolution in response to changes in geochemistry along their flowpath.

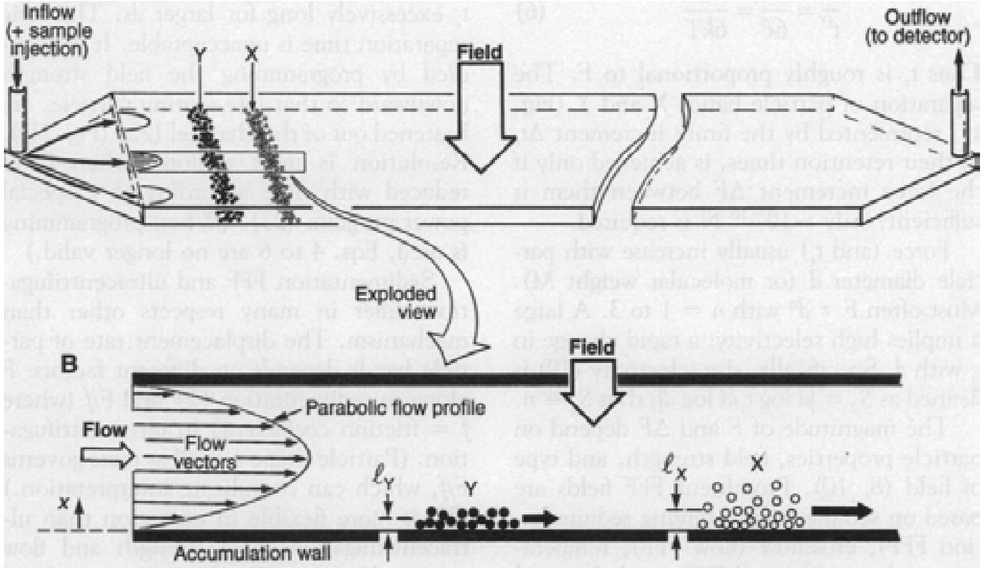
The resulting “clump” needs some separation to make the signals from the various detection methods useful.



http://cben.rice.edu/highlights.aspx

The same complications apply in tissue, likely to an even greater extent

State of the Science - continued:



Goal : Separation of polydispersed samples

Methods:

Field flow fractionation (FFF)

Cross-flow fields separate nanoparticles by size, charge, density, etc.
Low-invasive technique (only bounding membrane or surface)
Multiple field strategies (fluid drag, electrical, gravitational, thermal, acoustic)
Concerns: effect of carrier solution. Distribution represents in-situ?

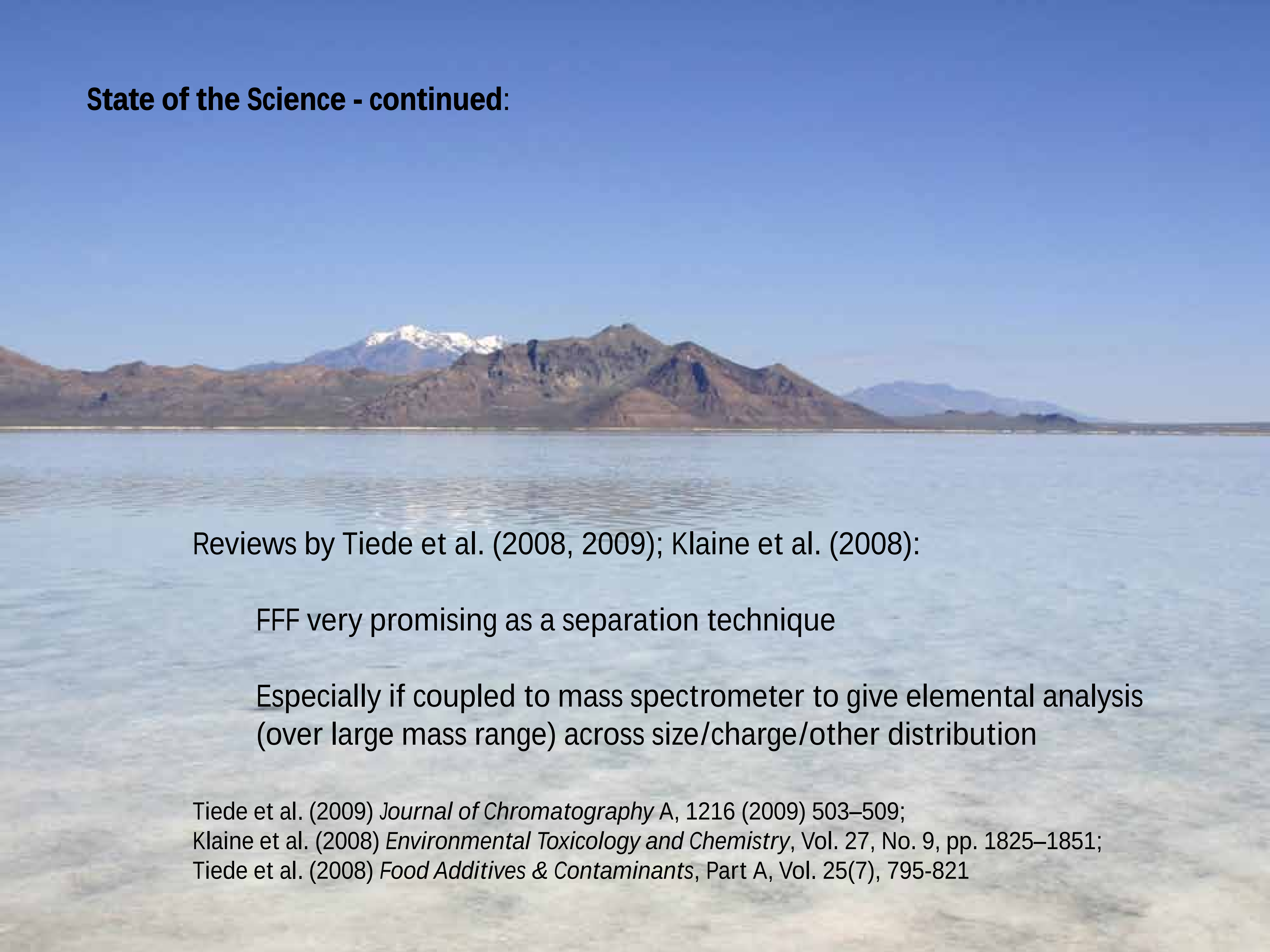
Size-exclusion chromatography (SEC)

Separate via hydrodynamic size in internally porous media
Concerns: low peak resolution, loss to media

Hydrodynamic chromatography (HDC)

Separate according to hydrodynamic size in solid sphere porous media
Concerns: low peak resolution

All of the above can be coupled to various detectors; e.g., UV, MS, etc.



State of the Science - continued:

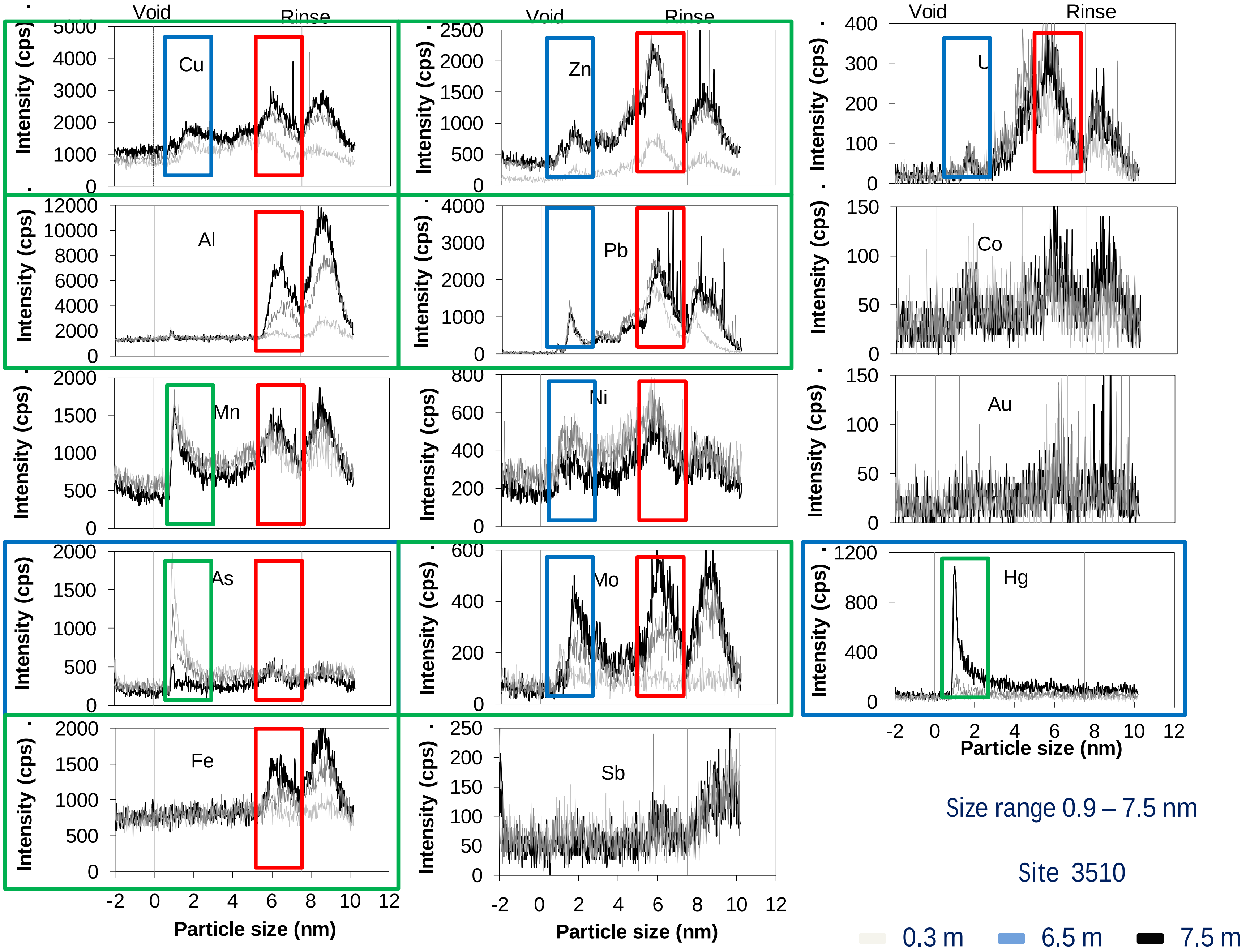
Reviews by Tiede et al. (2008, 2009); Klaine et al. (2008):

FFF very promising as a separation technique

Especially if coupled to mass spectrometer to give elemental analysis (over large mass range) across size/charge/other distribution

Tiede et al. (2009) *Journal of Chromatography* A, 1216 (2009) 503–509;
Klaine et al. (2008) *Environmental Toxicology and Chemistry*, Vol. 27, No. 9, pp. 1825–1851;
Tiede et al. (2008) *Food Additives & Contaminants*, Part A, Vol. 25(7), 795-821

many ~ 6 nm Some ~ 2 nm As, Hg dissolved? Fe,Cu,Zn,Pb,Mo Sulfides



Size range 0.9 – 7.5 nm

Site 3510

Diaz et al. (2009) *App. Geochem.*, doi:10.1016/j.apgeochem.2009.04.031.

NNI-EHS-Research-Strategy-2008:

“as there is a low number of projects [funded 2006] for determination of particle size, particularly in biological, environmental, and other complex media, efforts could be stronger in this area”

“the ability to accurately measure particle size is critical”

“detection in solid media (soil, solid waste streams) is not well addressed”

“IMA is supportive to the other four research categories”

The EHS priority research needs listed in table 3 (IMA needs) are:

- Develop methods to detect nanomaterials in biological matrices, the environment, and workplace.
    1) Evaluate the scope and suitability of technologies to quantify nanomaterials across biological media indicative of exposure.
    2) Develop common commercially available samplers for measuring mass concentrations of nanoparticles in air (indoor and outdoor).
    3) Develop instruments to measure nanomaterials in water
    4) Develop samplers for personal monitoring of nanomaterials and biomarkers indicative of exposure

Research Priorities On Target? Yes – but personally – I would focus this to:

- Investigation of success in separation into “primary” particle sizes
  - Carrier choice
    - Surfactants – how well do we break them apart?
    - Enzymes – digest organic matrix without dissolving nanoparticle
    - Allows sending samples to off-site laboratories?
    - The criterion is not to reflect the in-situ distribution (impossible?), but rather, to determine what’s in the “clump”.

- Determination of “fingerprints” of distinction among sources via elemental and isotopic signatures
  - Contaminant elements
  - Stable isotopes

- Development of robust methods for integration from larger volumes for monitoring low concentrations in water
  - SPLITT continuous binary separation
  - SPLITT in series
  - Integration via nanomembranes

Elemental signatures

Plata et al. (2008)

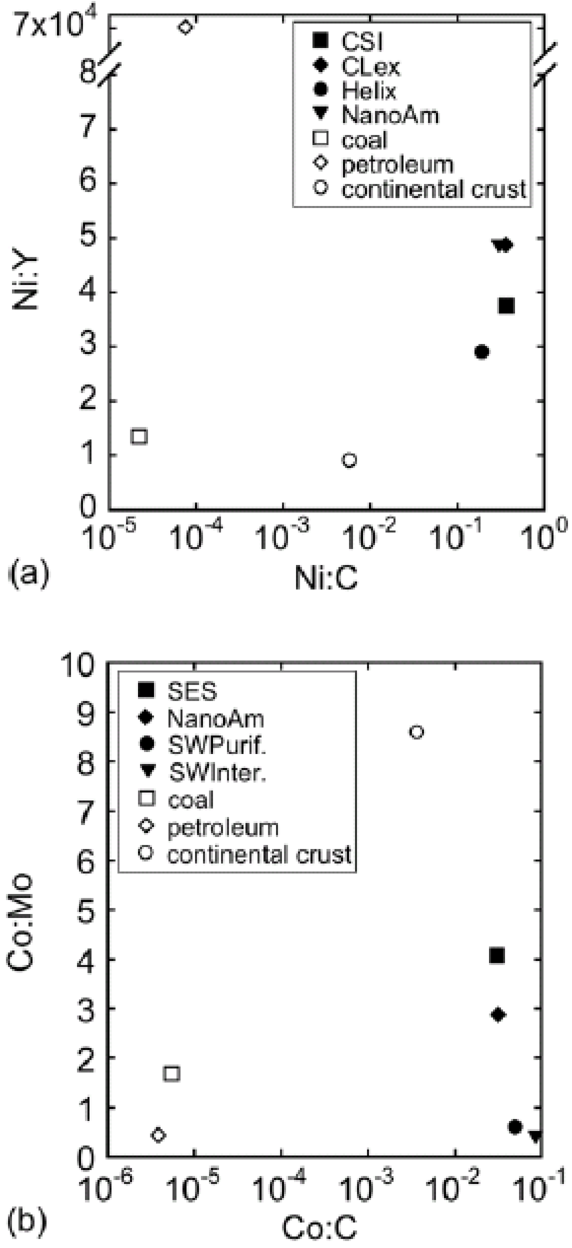
All available commercial SWCNT sources

All had “unexpected” trace metals

Ni:Y ratios showed distinct ranges for commercial SWCNTs (2.9 to 4.9)
relative to coal (1.3), petroleum (66 000), and continental crust (0.9)

Co:C ratios for commercial SWCNTs were relatively high (0.31 to 0.88)
relative to coal (5.6×10^{-6}), petroleum (4.0×10^{-6}), and continental crust (Co:C = 3.7×10^{-3}).

“… metal-to-carbon content of SWCNTs can be useful for tracing these emerging contaminants as they are released to the environment”.



Plata et al. (2009) *Nanotechnology* 19 185706
doi:10.1088/0957-4484/19/18/185706

Isotopic signatures

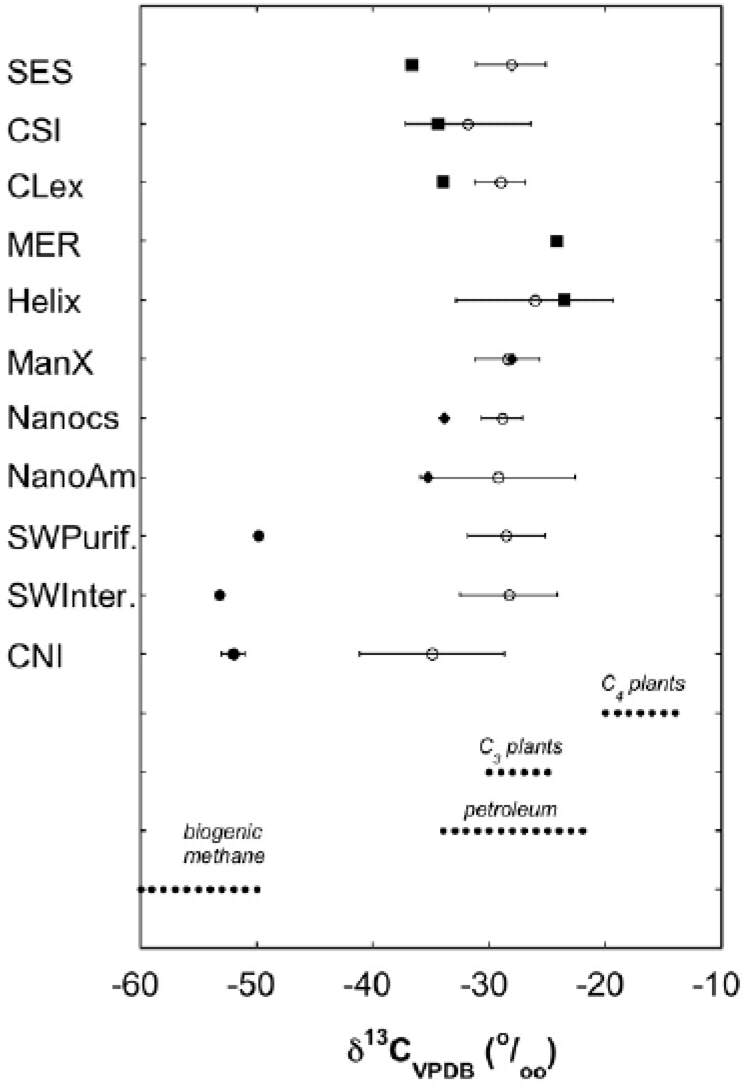
Plata et al. (2008)

SWCNTs manufactured by carbon monoxide chemical vapor deposition have distinct $d^{13}C$ (−51.7 to −49.8□‰) relative to other SWCNTs

Reflects ^{13}C-depleted feedstock

“... this unique isotopic signature may be a useful tracer of CO-SWCNTs and their metabolites in both laboratory and field studies”.

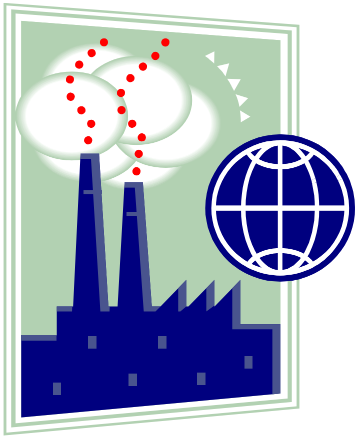
Distinct from the bulk isotopic content of marine seawater and sedimentary organic matter (−30 to −20 ‰)



SWCNTs Synthesized via:
arc-discharge (■), CVD (♦), CO-CVD (●)
Starting materials (•••)
Dichloromethane-extracted C (○)

Case study: preventing another disaster

- What biological and instrument methods could have been used to test all the nanomaterials produced by this company?
  - Characterize elemental and isotopic signatures associated with distributions (size, charge, etc.) in the product using FFF and MS methods.
- Are current paradigms for inorganic or organic chemicals suitable for use with nanomaterials?
  - Not in terms of current analyses used in environmental monitoring, which distinguish dissolved versus particulate with an arbitrary cutoff filter. Need to refine FFF and SPLITT methods coupled to MS methods to characterize distributions in size, charge, etc. across the range from nano to micro.



Which research needs should be addressed in the near- (< 5 years), medium- (5 – 10 years) and long-term (> 10 years)?

NNI-EHS-RS-2008 states (page 27):

Needed short term is the development of air samplers

Needed mid-term are technologies for monitoring nanomaterials in water.

My opinion: technologies for monitoring in water are needed in the near term. Developing this capability is critical to the other research needs, for example , other goals in IMA:

1) Understand the effect of surface function on mobility and transformations in water
2) Evaluate correlation of microscopic with other size-measurement techniques.
3) Evaluate or modify microscopic and mass spectrometric approaches for determination of shape and structure of nanomaterials
4) Explore methods beyond isothermal adsorption for nanomaterial surface area determinations.

These goals cannot be attained without robust methods to characterize nanoparticle size (charge, elemental) distributions in aqueous suspensions and tissues.

Thank You

State of the Science - microscopy-based techniques

Goals:

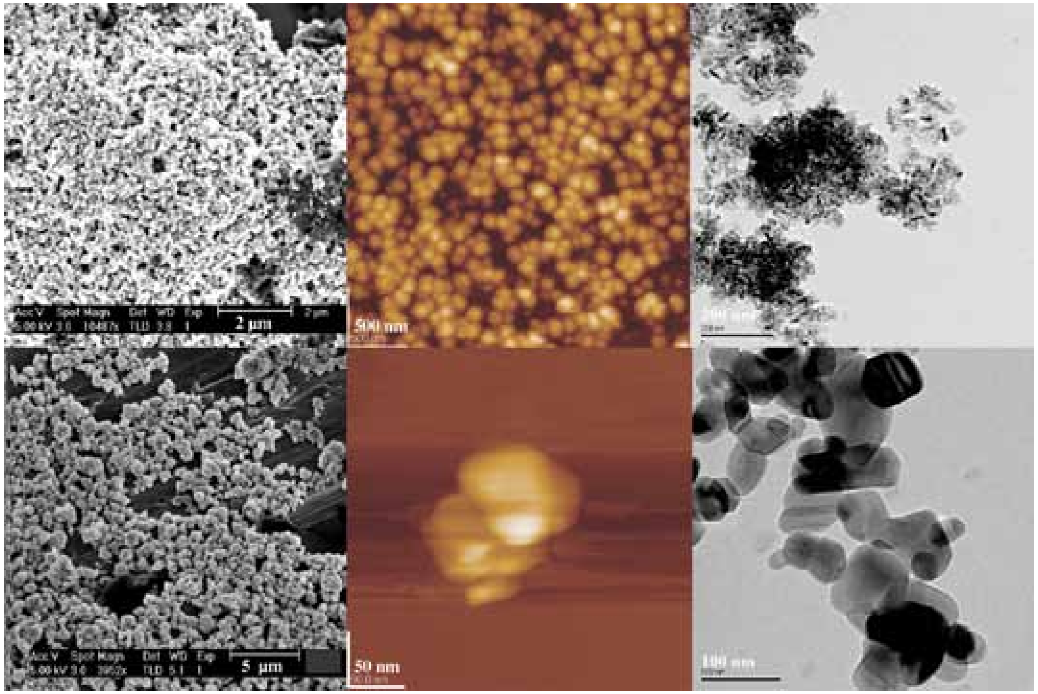
- Visual identification
- Aggregation, size, shape

Methods:

- Scanning electron microscopy (SEM)
- Transmission EM (TEM)
- Atomic force microscopy (AFM)
- Coupled to EDS gives elements

Concerns:

- Analysis-driven aggregation
- SEM and TEM under vacuum
- (some success in liquid via ESEM and others)
- AFM in solution
- Limited scale raises question of representativeness



Tiede et al. (2008), Detection and characterization of engineered nanoparticles in food and the environment, *Food Additives & Contaminants*, Part A, Vol. 25(7), 795-821

State of the Science (continued):

Ultracentrifugation, nanofiltration, cross-flow filtration
  Allows separation of solutes (e.g. < 1nm)
  Concerns: pore clogging.

Gel phase separation via voltammetry, diffusion gradients in thin films (DGT), diffusion equilibration in thin films, and the permeation liquid membrane method (PLM)
  Allows separation of very small sizes
  Concerns: sample is in gel or other medium

Isotopic signatures (continued)

Isotopic signatures have been used to study sources and transport of pollutants and the geochemical mechanisms operating in soil and groundwater systems.

Natural terrestrial d^{114}Cd/^{110}Cd range very low ~ 0.4 ‰
Anthropogenic d^{114}Cd/^{110}Cd shows large range
-0.64 ‰ (dust sample issued from a lead smelter)
+0.50 ‰ for NIST SRM 2711 (metal-rich soil)

Cloquet et al. (2005), *Geostandards and Geoanalytical Research*, v. 29, p. 95-106.