UNIVERSITY OF CALIFORNIA

UC CEIN Center for Environmental Implications of Nanotechnology

Behavior of nanoparticles in simple and natural aqueous matrices

Presented by Milka Montes

Collaborators: Arturo A. Keller, Hongtao Wang, Dongxu Zhou, Reginald Thio

University of California, Santa Barbara

Natural

- Volcanic ash
- Ocean spray
- Biogenic magnetite
- Protoctits, mollusks
- Mineral composites
- Ferritin (12.5 nm)
- Clouds

Anthropogenic

Incidental

- Combustion
- Sandblasting
- Mining
- Metal working
- Biomaterial degradation

Engineered

- CNTs
- Quantum dots
- Sunscreen Pigments
- Fullerenes
- Semiconductor wires

Photograph by Peter Greenfield, courtesy of Ohio State University

Photo courtesy the US Bureau of Land Management

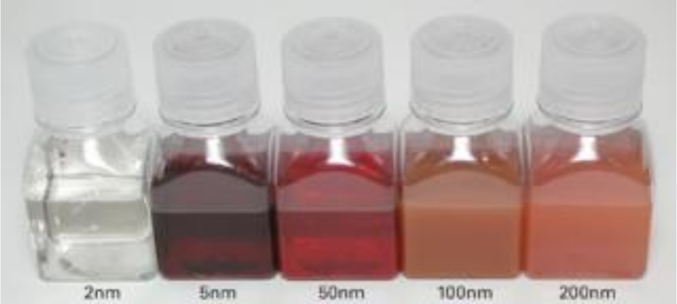
Colloidal Systems in Simple and Natural Aqueous Matrices

- Colloid dispersion
  - Thermodynamically unstable
  - Irreversible

- Association colloids (colloidal electrolytes)
  - Thermodynamically stable (at low concentration are stable, at high concentration form aggregates)

Factors leading to the formation of colloidal dispersions

- Brownian motion
- Depletion interactions
- Gravity
- Steric stabilization
- Electrostatic and van der Waals interactions



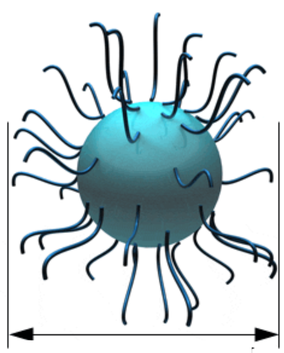
http://www.nanoopticalmaterials.com

Characterization of Colloids

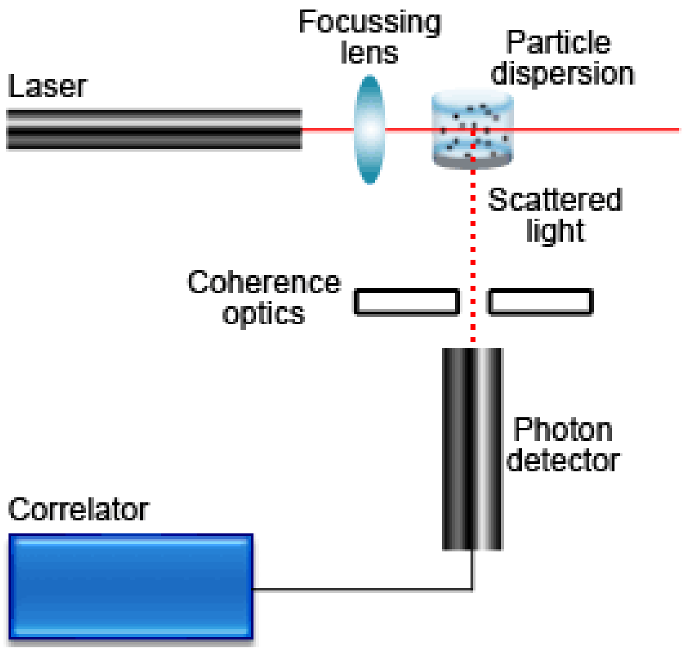
- Size
  - Dynamic light scattering (DLS)
  - Electron microscopy (TEM and SEM)
  - UV-Vis spectroscopy
- Charge
  - Zeta potential (Elecrophoretic mobility)
- Shape
  - Electron microscopy (TEM and SEM)
- Transport phenomena
  - Adhesion
  - Agglomeration
  - Aggregation
  - Deposition
- Dissolution

Size measurements

- Dynamic light scattering
- Based on Brownian motion of particles
- Uses Stokes-Einstein relationship



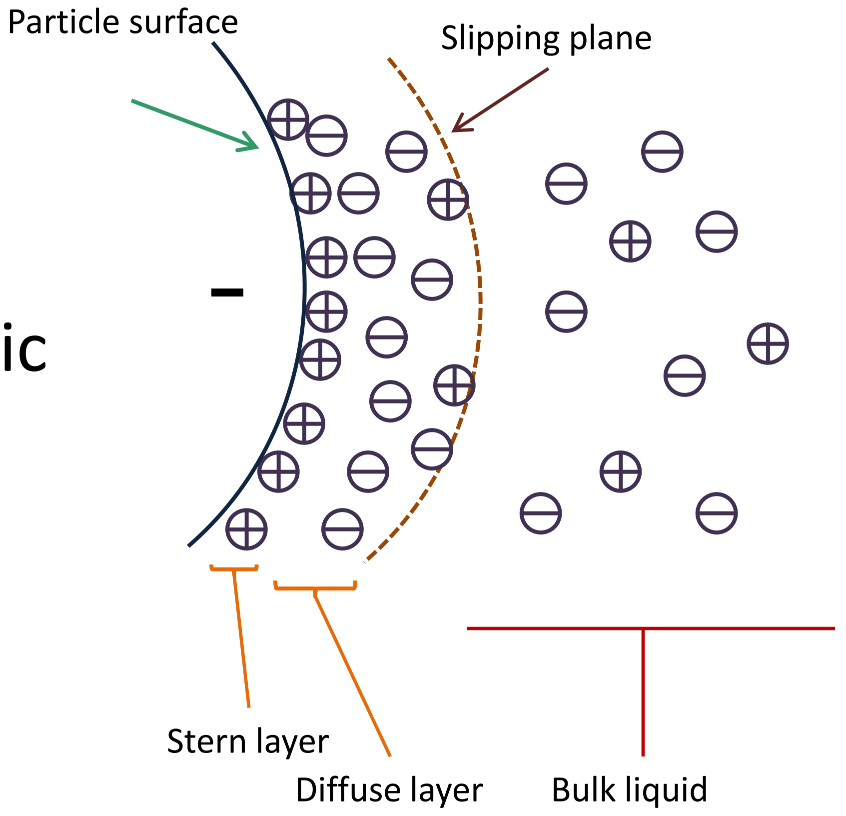
$$D = \frac{k_B T}{6\pi\,\eta\, r}$$



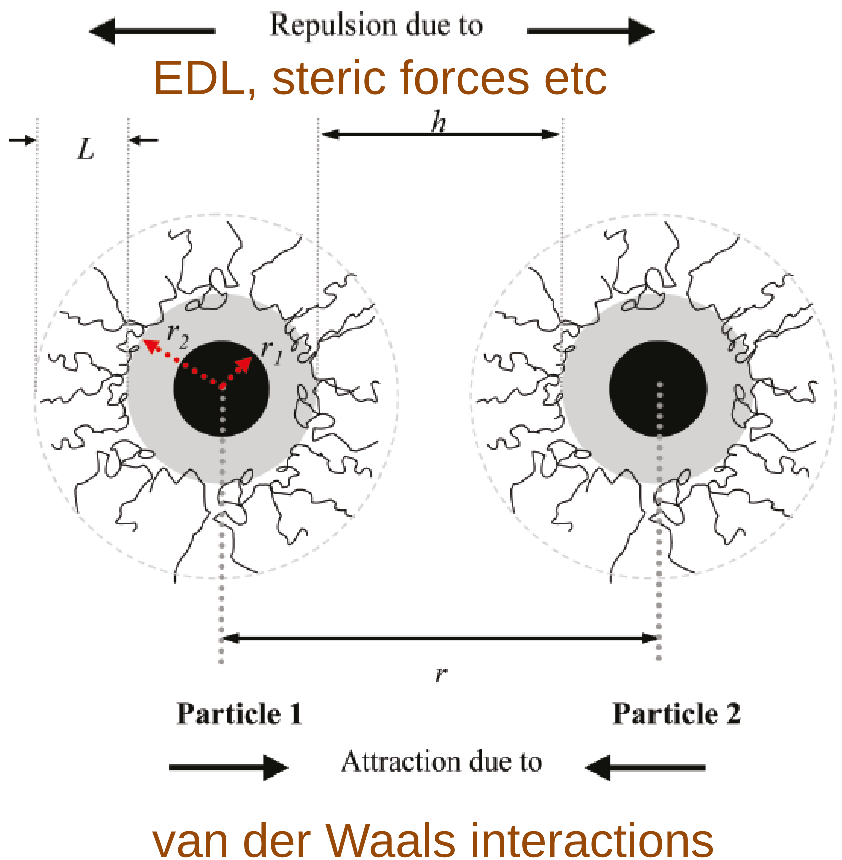
http://www.malvern.com

ζ- Potential measurements

- Reflects the effective charge on the nanoparticles
- Related to the electrostatic repulsion between particles
- Influenced by the nature and composition of the surrounding media



xDLVO theory



$$F_t = F_{vdW} + F_{edl} + F_s$$

DLVO ($F_{vdW} + F_{edl}$)

xDLVO (F_s)

*Adapted from Lim et al, *Langmuir*, 2009, 25, 13384

SRM Properties	Technique	Unit	TiO_2 Evonik 4168063098	CeO_2 Meliorum 121008	ZnO Meliorum 121008
Primary Size	TEM/SEM	nm	15-20	10-30	20-30
Particle Size in water	DLS	nm	194±7	231±16	205±14
Phase & Structure	XRD		81% anatase + 19% rutile	100% Ceria Cubic	100% Zincite Hexagonal
Shape/Morphology	TEM		Semi-spherical	Irregular	Spheroid
Surface Area	BET	$m^2 g^{-1}$	51.5	93.8	42.1
Isoelectric Point	ZetaPALS		6.5-6.6	7.5-7.8	8.4
EPM in 0.1 mM KCl	ZetaPALS	$m^2 V^{-1} s^{-1}$	3.11±0.12	2.52±0.39	1.73±0.11
Purity	TGA	wt.%	98.03	95.14	97.27
Moisture Content	TGA	wt.%	1.97	4.01	1.61
Acid Content	TGA	wt.%	0	0.85	1.12

Table courtesy of Ivy Ji

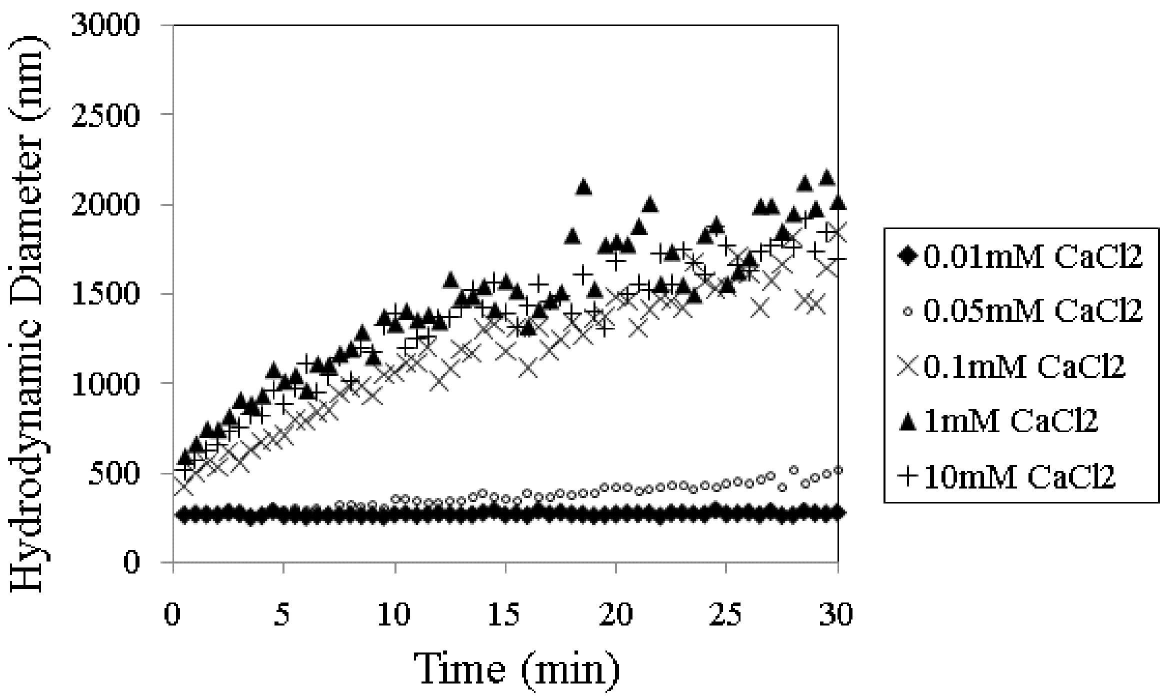
Significant parameters in the characterization of colloids

- Ionic strength (electrolytes present in solution)
- pH
- Particle size
- Particle surface charge
- Particle dissolution
- TOC (NOM)

Aspects affecting the characterization of nanoparticles in aqueous media

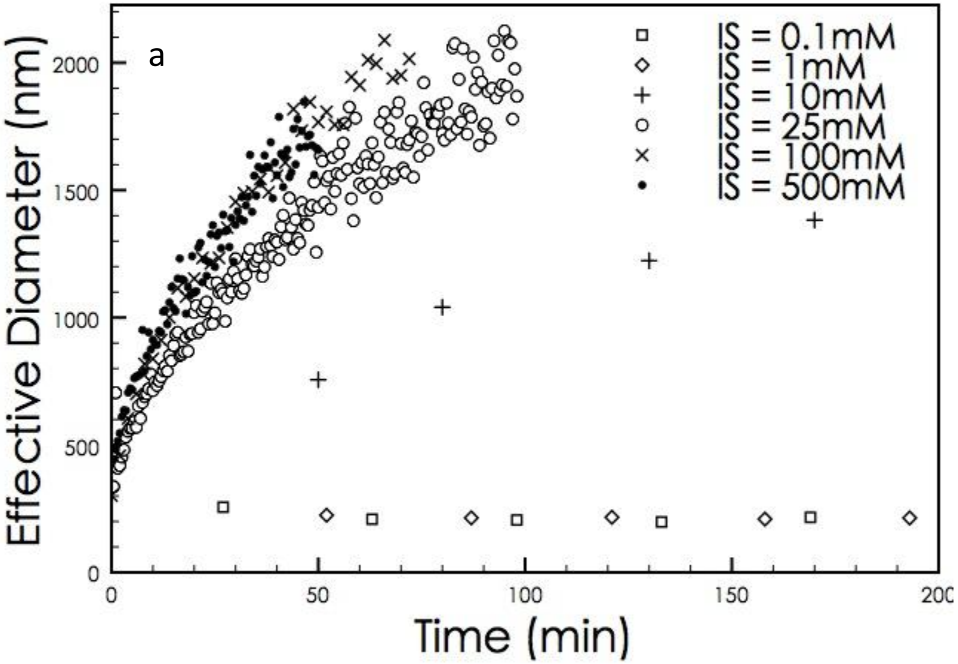
- Mobility
  - Physical transport
- Modification
  - Interactions with other constituents
- Effects on other molecules and contaminants
- Degradability
- Heterogeneity
  - Size, shape, composition

Aggregation of TiO_2 in DI



Rapid Aggregation with increasing hardness (Ca^{2+}); same with salinity (Na^{+})

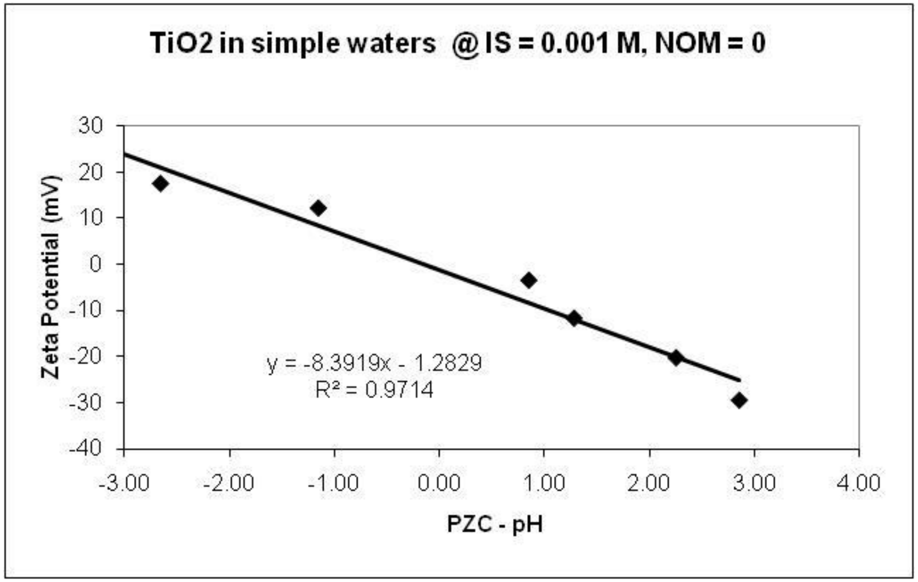
Aggregation of ZnO in DI

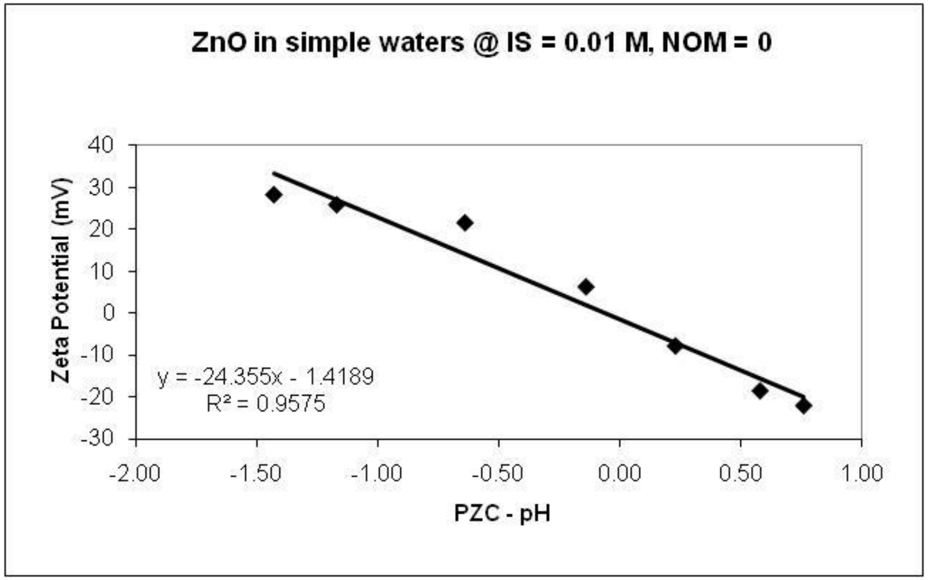


- Similar results for other metal oxides: rapid aggregation with increasing ionic strength (IS)

Zhou & Keller, Water Res. 2010

Charge on particle as function of pH

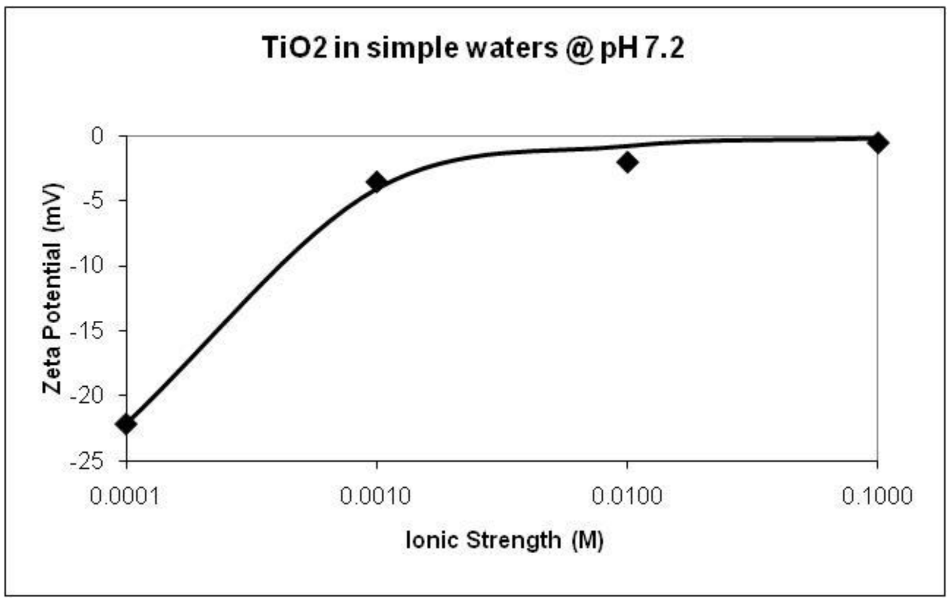


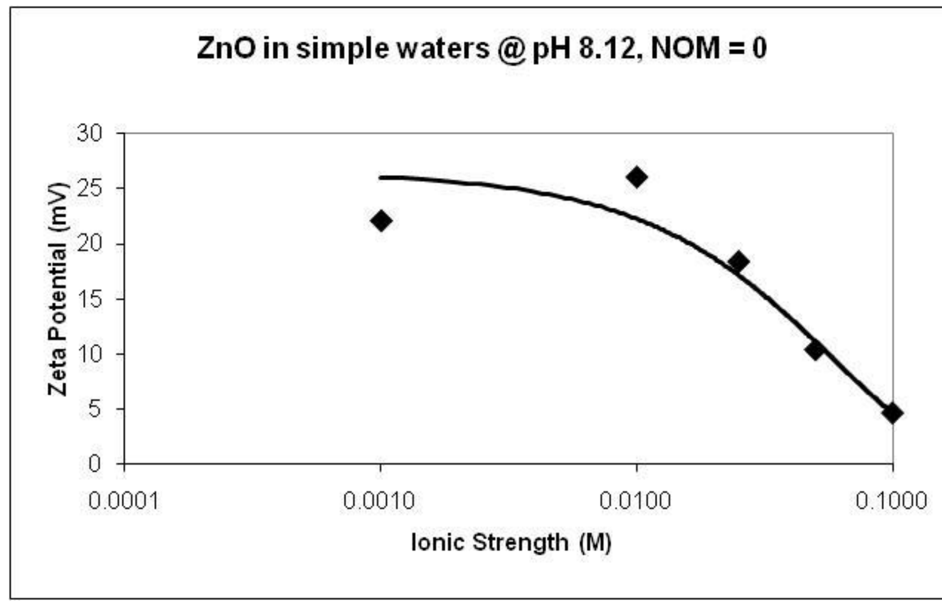


If particles very negative or very positive, they repel => little aggregation is expected

PZC = Point of Zero Charge; for TiO_2 @ pH 6.5, for ZnO @ pH 8.4

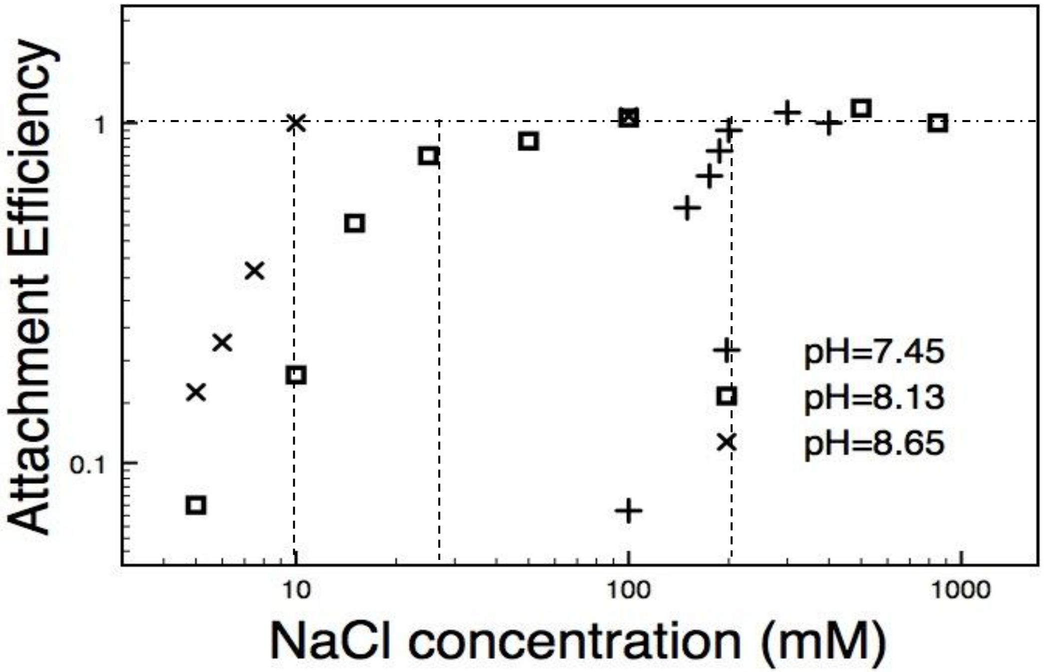
Charge on particle as function of IS





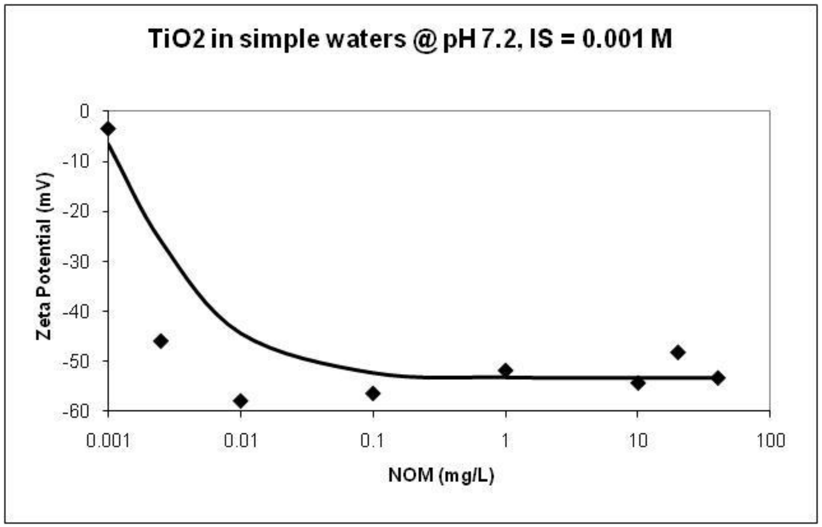
As salinity or hardness increases, the effective charge on the NP is reduced (screened)

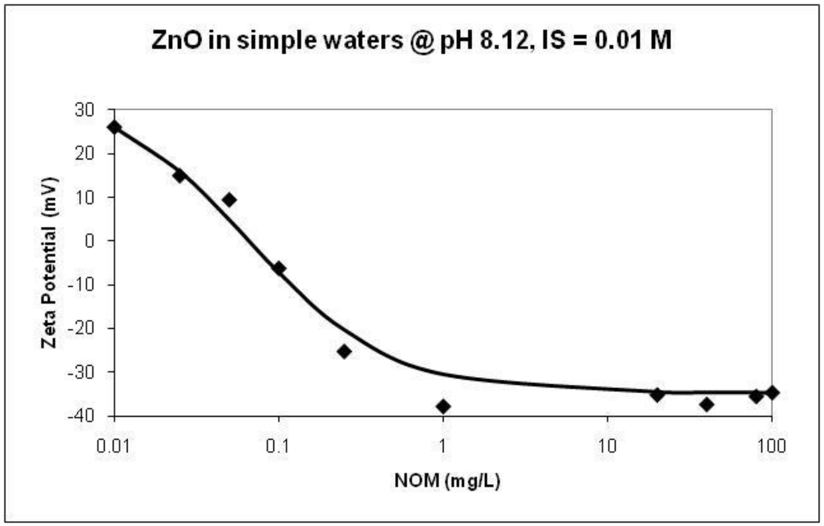
ZnO Nanoparticle Aggregation

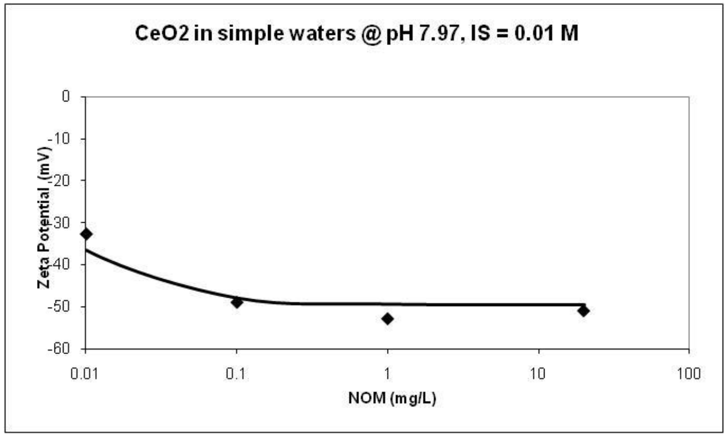


Attachment Efficiency measures “stickiness” of NPs at different conditions

Charge on particle as function of NOM

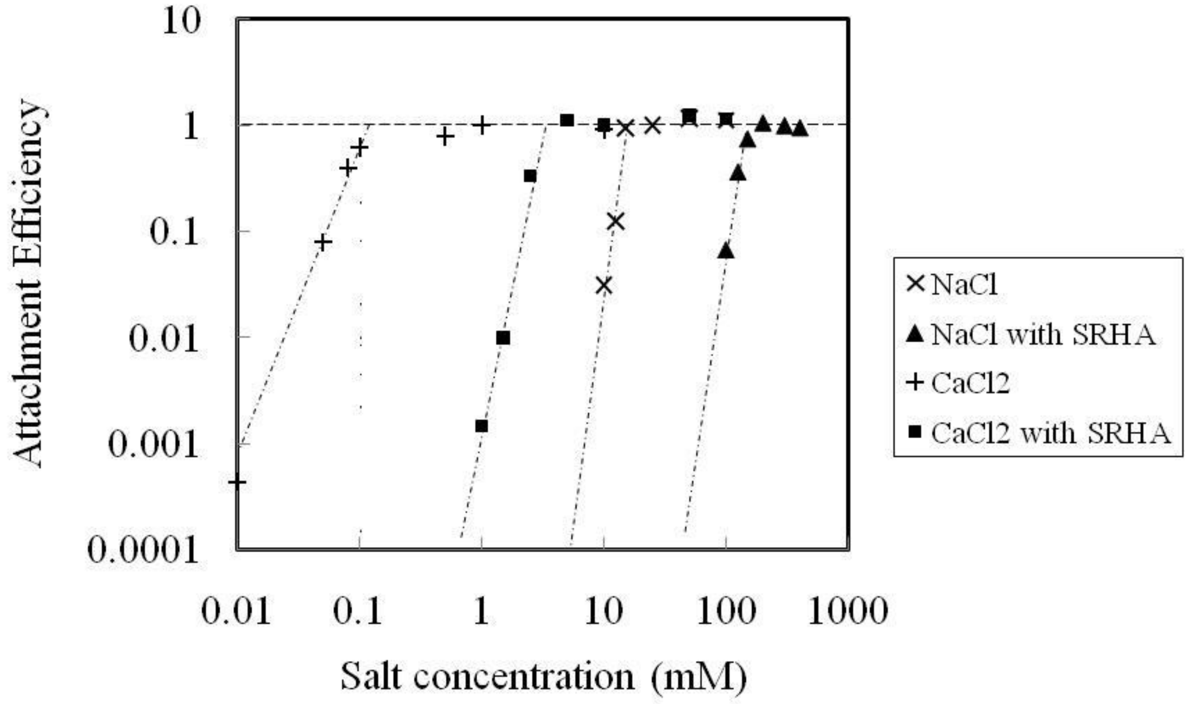






Increasing NOM makes particles more negative

TiO_2 NP-NP Attachment Efficiency shifted in the presence of NOM



SRHA = Suwannee River Humic acid, a common “reference” NOM

Physical stability of colloidal system

Brownian movement

↓

Collisions

Aggregation
(collection of particles into groups)

Stable system
(freely dispersed rebound particles)

Coagulation
- Particles are closely aggregated and difficult to redisperse
- Destructive and permanent

Flocculation
- Particles are loosely aggregated in open structures
- Reversible and temporary

Wide range of environmental media properties

Terrestrial

Micro arthropods

Protozoa

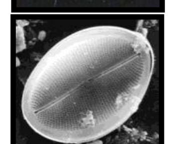
Bacteria

Freshwater

Predatory fish

Invertebrate grazers

Benthic algae

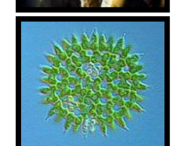


Marine

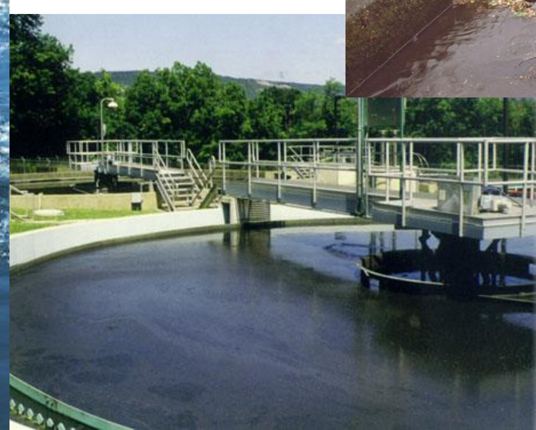
Predatory invertebrate

Invertebrate filter-feeders

Planktonic algae

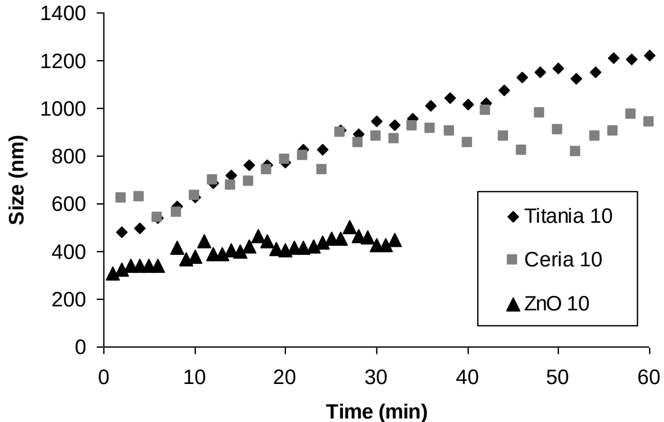


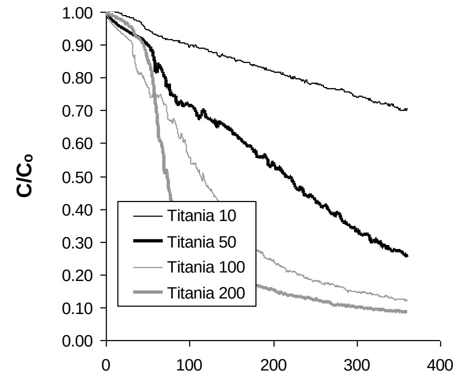
	Units	Seawater	Treated effluent	Stormwater	Mesocosm freshwater
pH	-	7.7	7.7	7.1	8.4
TOC	uM C	54.0	378.0	1564.0	5283.0
IS	eq.	0.71	0.032	0.010	0.007

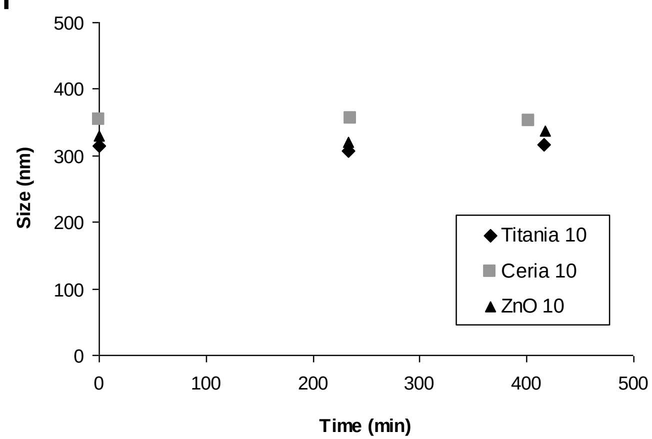
Sedimentation Rates

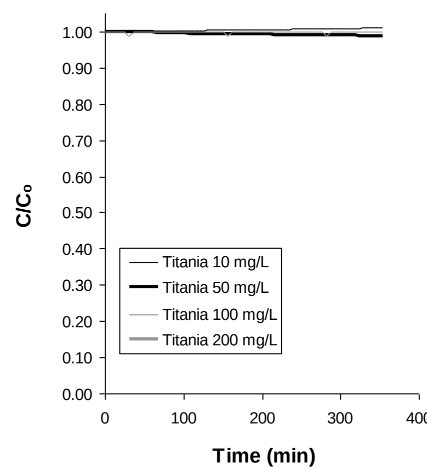
Seawater





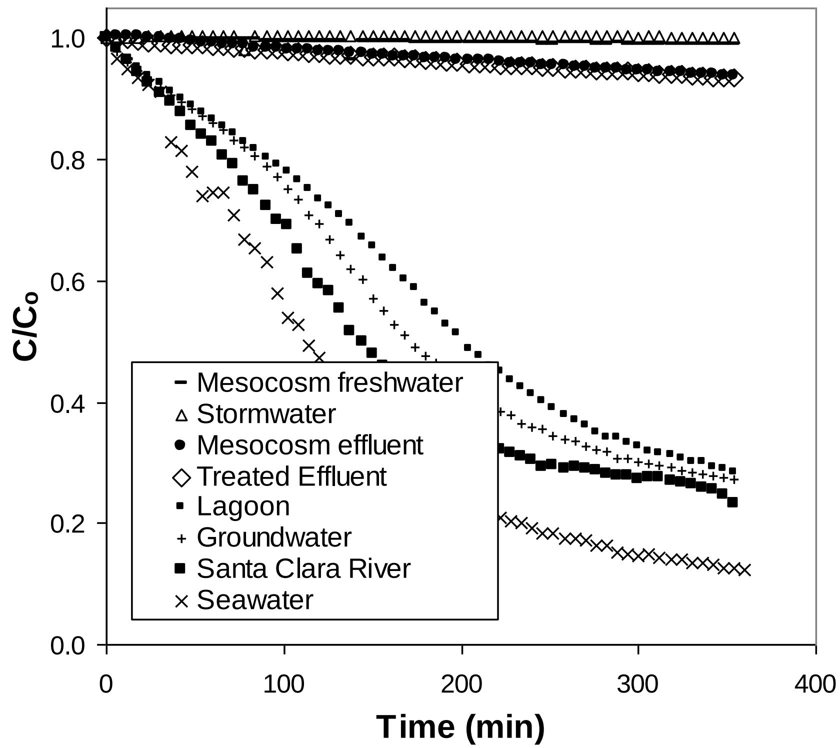
Freshwater





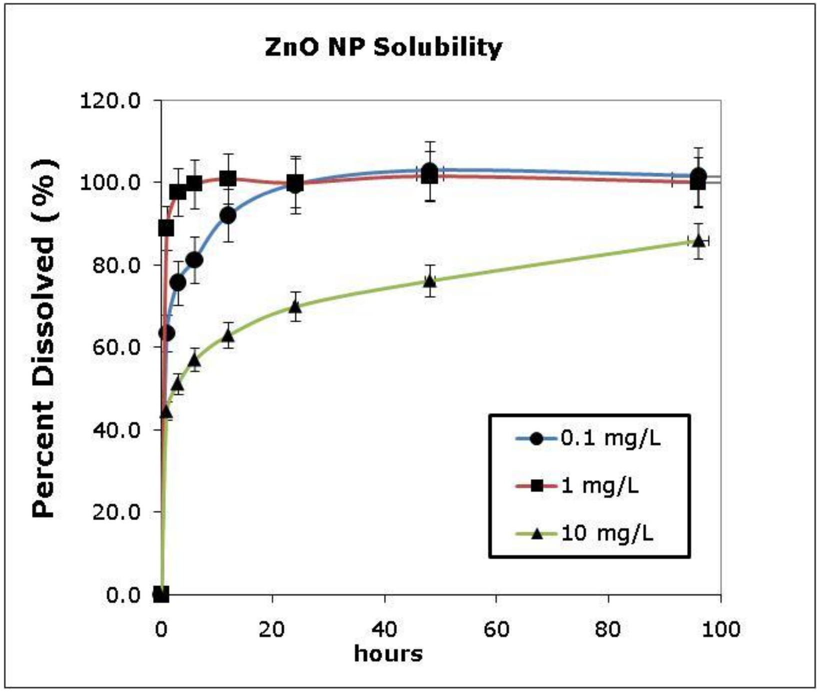
Keller et al., *ES&T 2010*

Sedimentation of ZnO



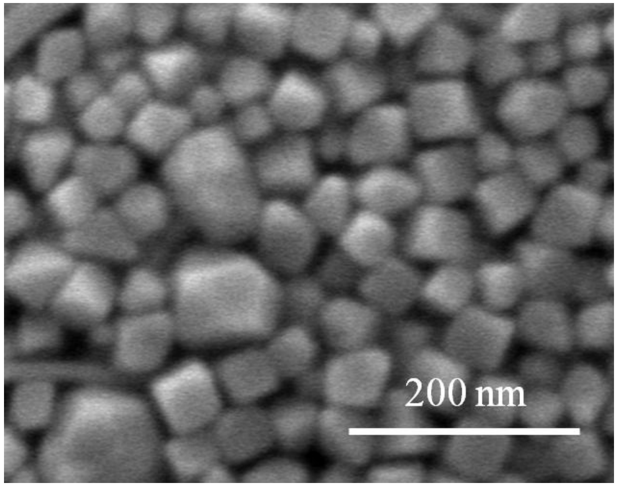
Keller et al., *ES&T 2010*

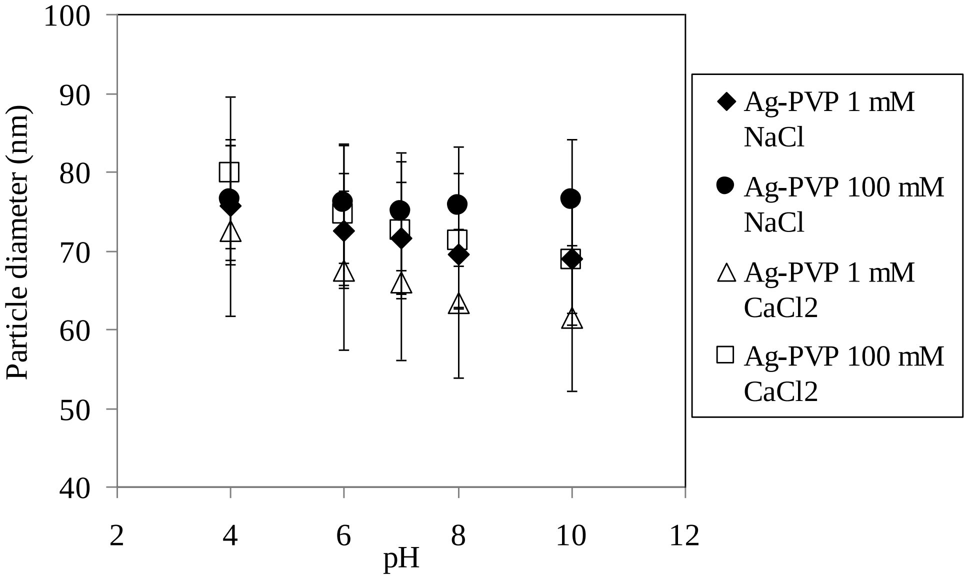
Dissolution of ZnO



ZnO and other metal and metal oxide NPs dissolve rapidly, liberating metal ions

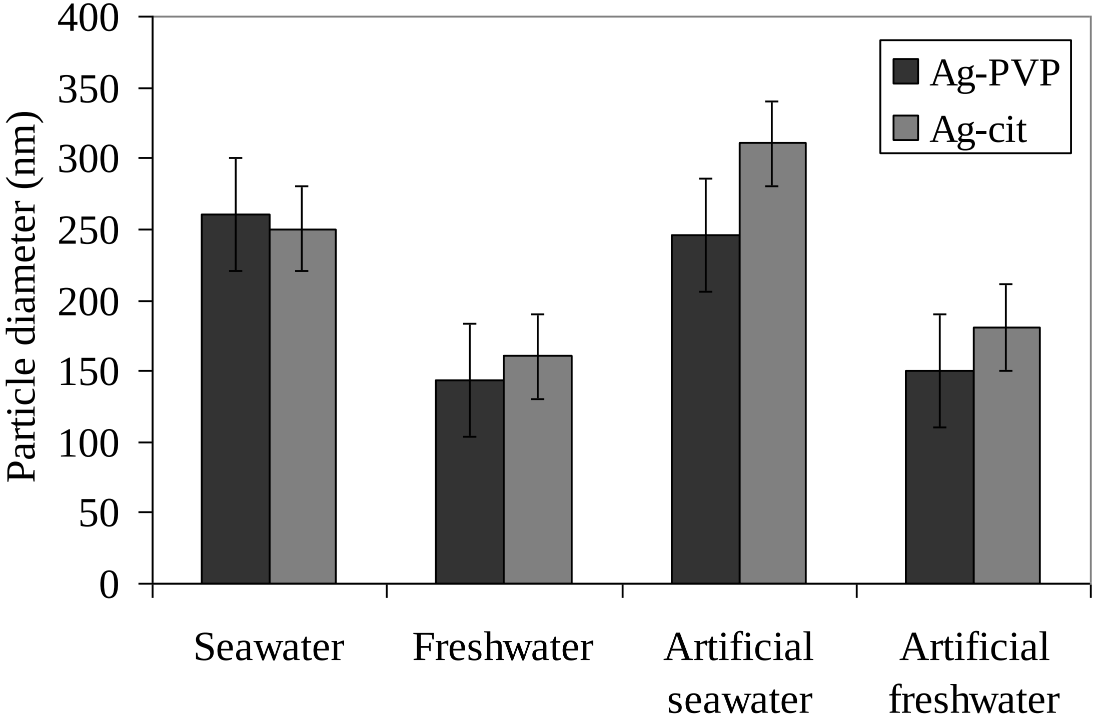
Silver (Ag) NPs Coated with PVP





NP diameter not a strong function of pH or IS due to coating

Ag NPs in real waters



Conclusions

- Aggregation & deposition in complex water matrices differs considerably from that in simple matrices
- NOM plays key role determining charge of metal oxide NPs, and thus their aggregation behavior
- Ionic Strength (IS) also plays important role, particularly increasing aggregation in hard (e.g. groundwater) or saline waters
- Dissolution is an important process for some metal and metal oxide NPs

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Questions?

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