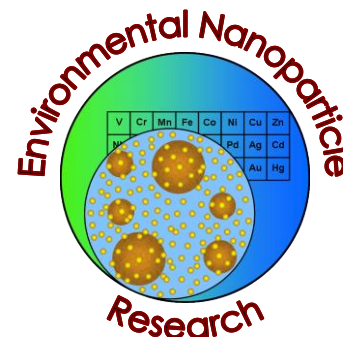# Analysis of the adsorption of environmentally relevant macromolecules on TiO2 NP and the effects on dispersion stability, agglomeration and sedimentation rates.

Julián Gallego-Urrea, Jenny Perez Holmberg, Aldina Bijedic, Caroline M. Jonsson, Martin Hassellöv

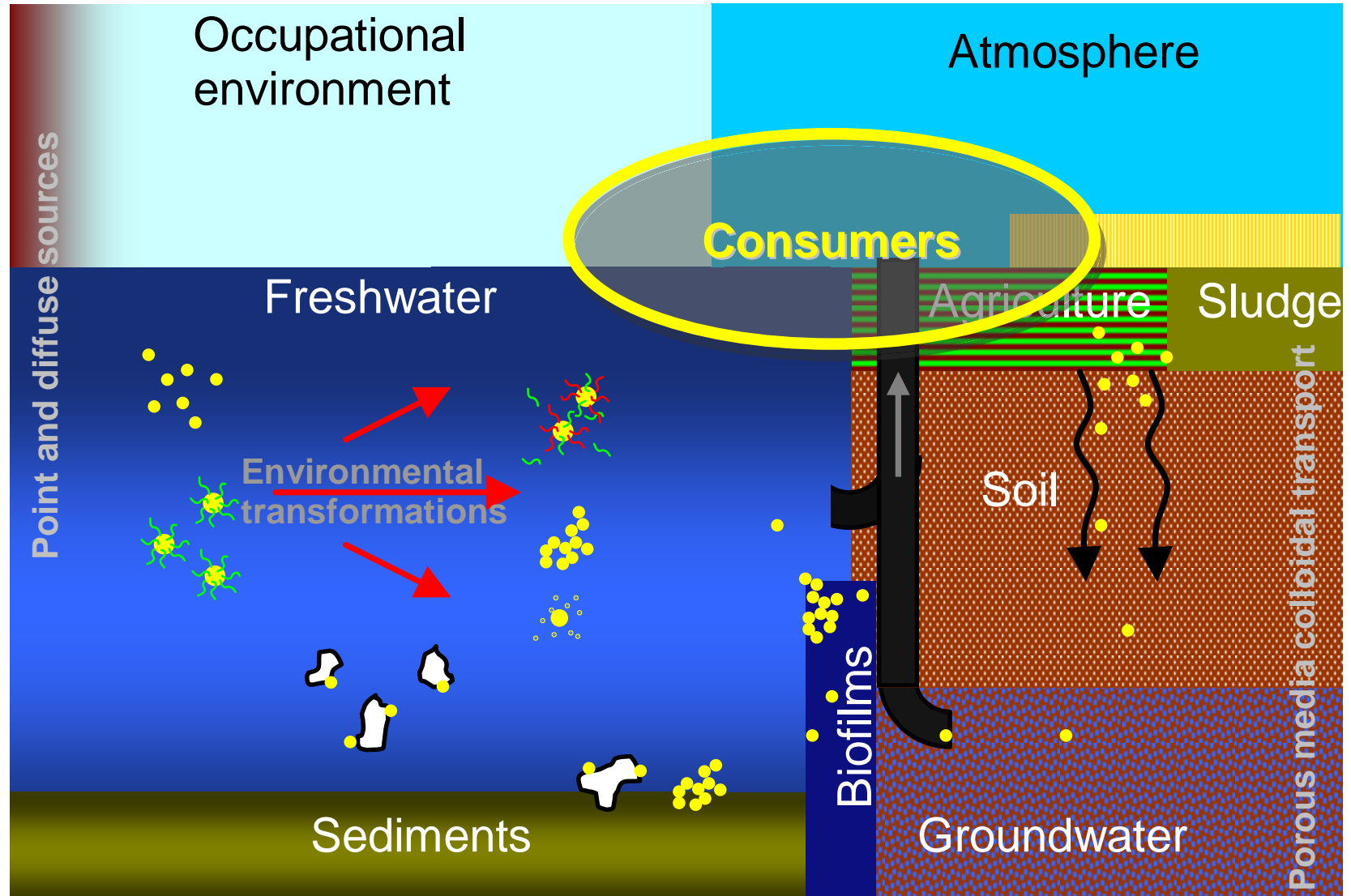Environmental nanochemistry research group

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Fate and transport processes

Exposure assessment.
fate and transport: case study TiO2

Modeling environmental transformation and transport

Classical: Simplifications building on chemical equilibrium concepts and phys-chem properties of a chemical

- (vapor pressure, water solubility etc)

For nanoparticles: not applicable

- NP behavior builds on physical forces between particles
- Not in thermodynamic equilibrium
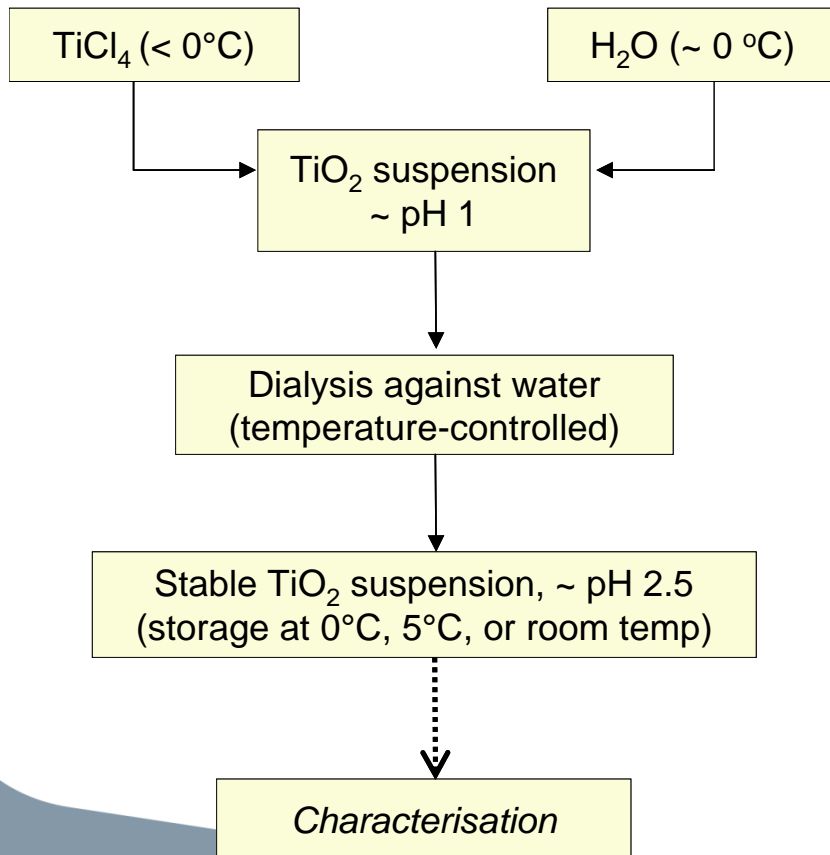
New concepts and studies necessary

Wet-chemical synthesis of TiO_2
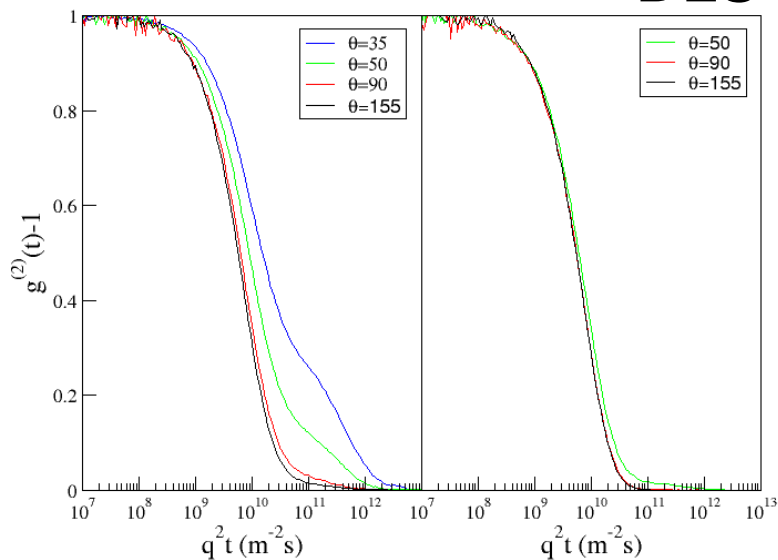Responsible: J. Perez-Holmberg

Low temperature controlled hydrolysis of $TiCl_4$

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4H^+ + 4Cl^-$$

No surfactants; goal: to obtain clean surfaces

$TiCl_4$ (< 0°C)		H_2O (~ 0 °C)

TiO_2 suspension
~ pH 1

Dialysis against water
(temperature-controlled)

Stable TiO_2 suspension, ~ pH 2.5
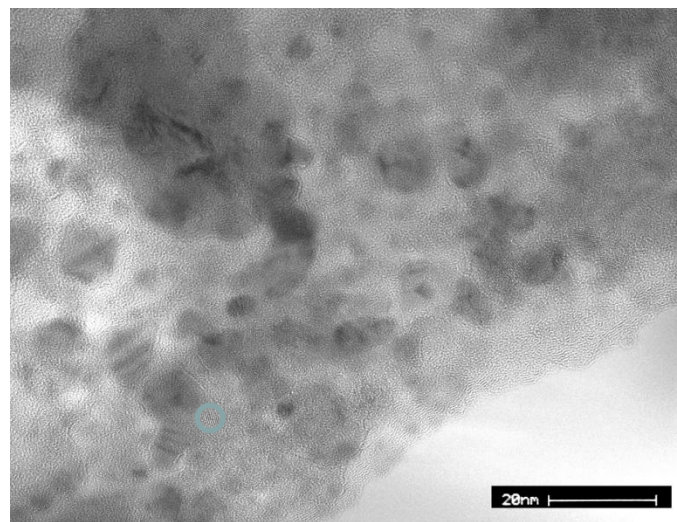(storage at 0°C, 5°C, or room temp)
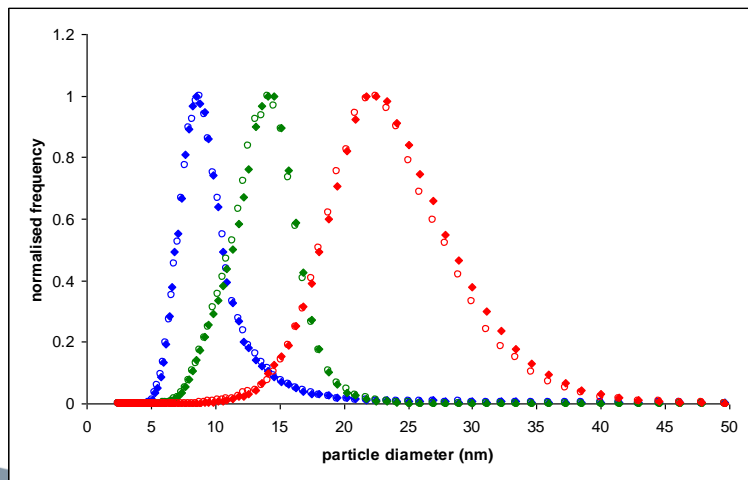
Characterisation
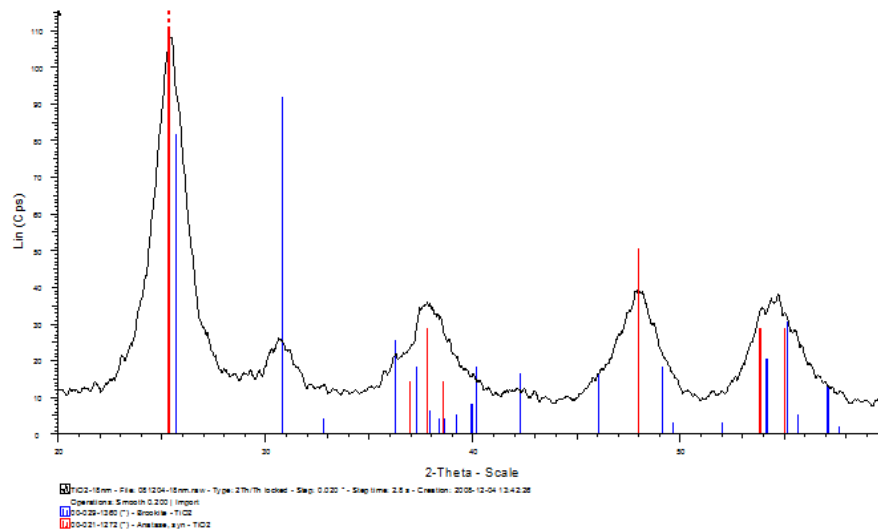
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Characterisation

DLS

XRD
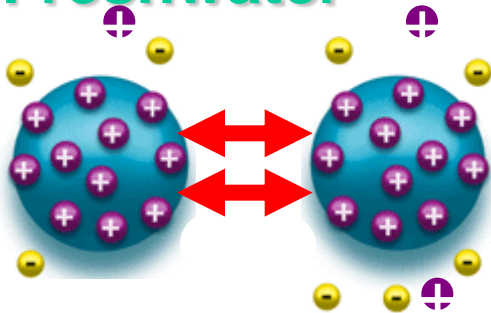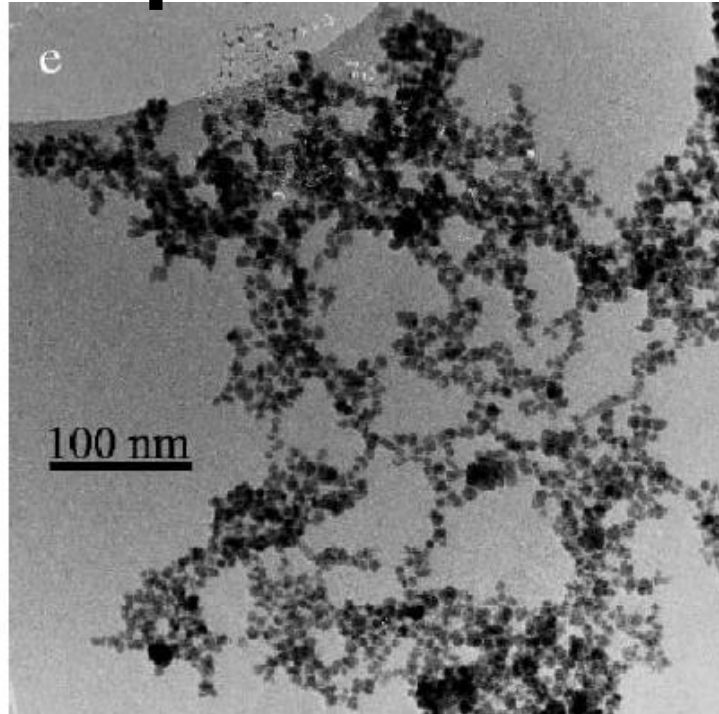

ES-SMPS

TEM

Agglomeration or Stabilisation of colloidal nanoparticles

Freshwater

Seawater

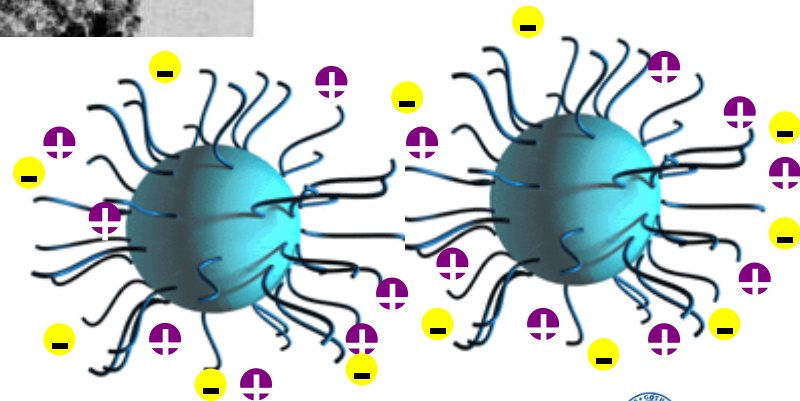Electrostatic stabilization

100 nm

Steric stabilisation

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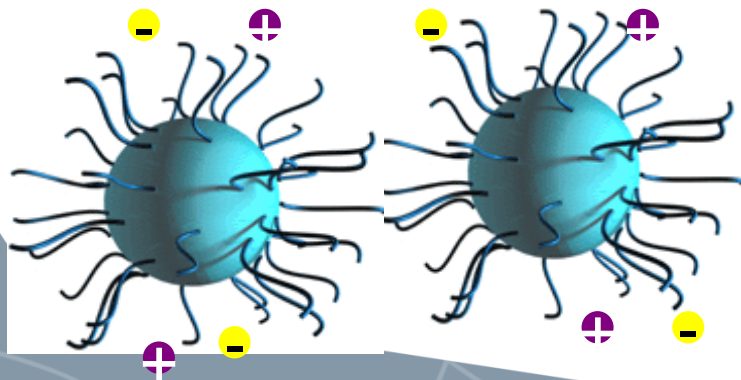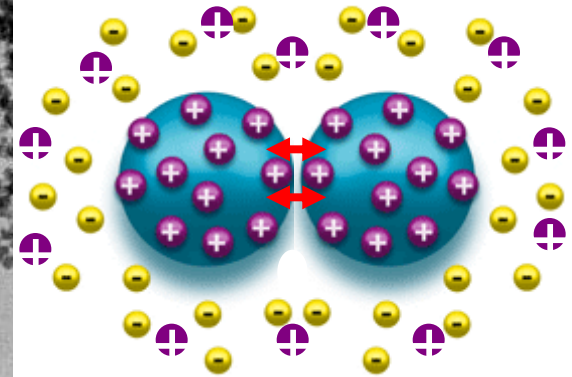
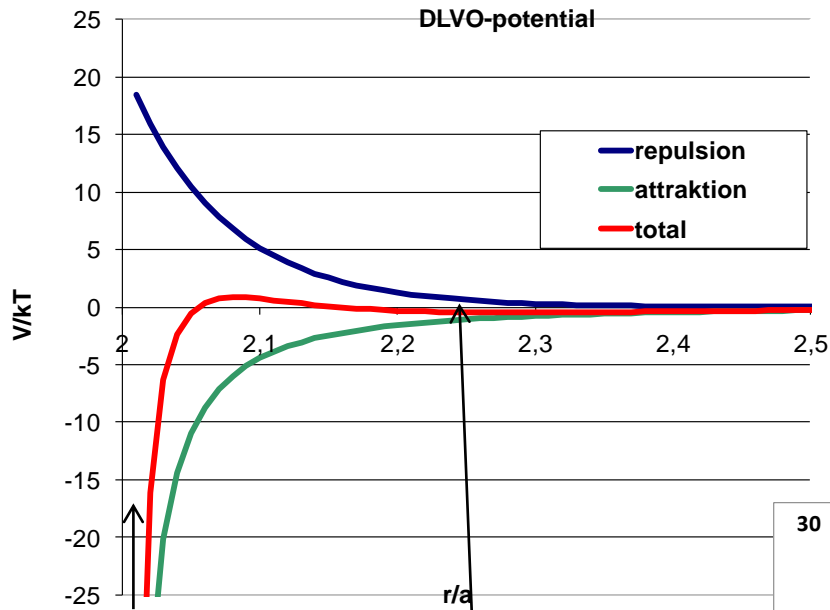# Double layer theory and DLVO

Primary minimum

Secondary minimum

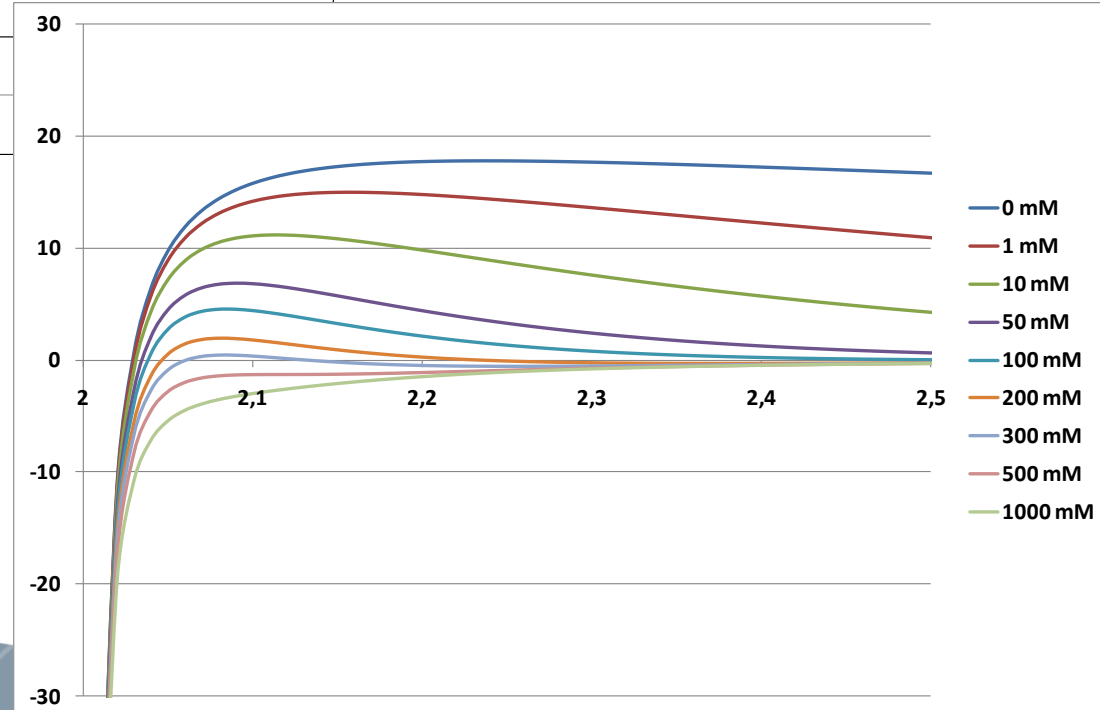Electrostatic stabilization:

$$V_T = V_R - V_A$$

radius= 8 nm

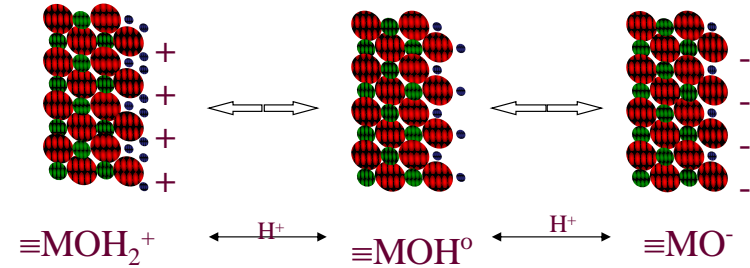A= 3.70E-20 J Hamaker constant

C_NaCl= 270 mM 1-1 salt

Surf. Pot.= 50 mV

Interfacial phenomena

Protonation of surface functional groups, pH dependancies on surface charge

Surface charge, potential, the electric double layer

The stagnant hydration layer, zeta potential at the hydrodynamic slipping plane

Surface complexation

Size-dependencies?

$\equiv MOH_2^+$ $\xleftrightarrow{H^+}$ $\equiv MOH^o$ $\xleftrightarrow{H^+}$ $\equiv MO^-$

Stern-Gouy-Chapman model of the electrical double layer

Stern layer   diffuse layer   bulk solution

Ψ
Ψ_s
ζ
Ψ_s/e

x_s $1/\kappa$ x

Slipping Plane

Charged Particle

Diffuse Double Layer

Condensed Counterions

Stern Layer

Surface potential
Stern potential
Zeta potential

mV

Distance from surface
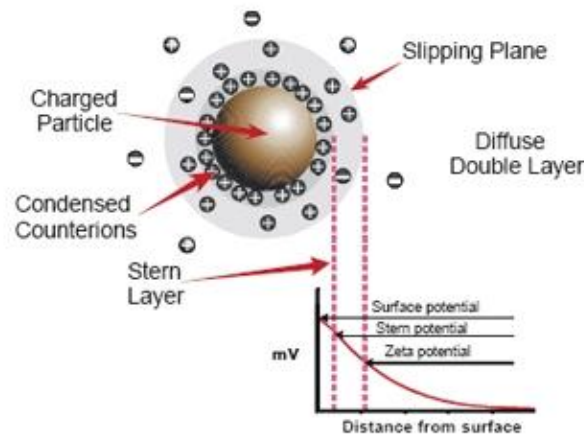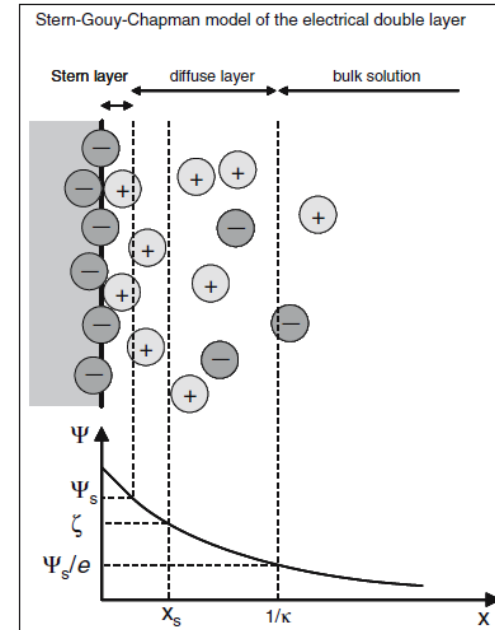
Change in pH of TiO2 NP

- Fast addition of concentrated NaOH

  - Sizes between 40 – 60 nm

NP at low pH positively charged

NP and aggregate with a new hydrodynamic diameter at high pH are negatively charged. Presence of ions that can screen the NP.

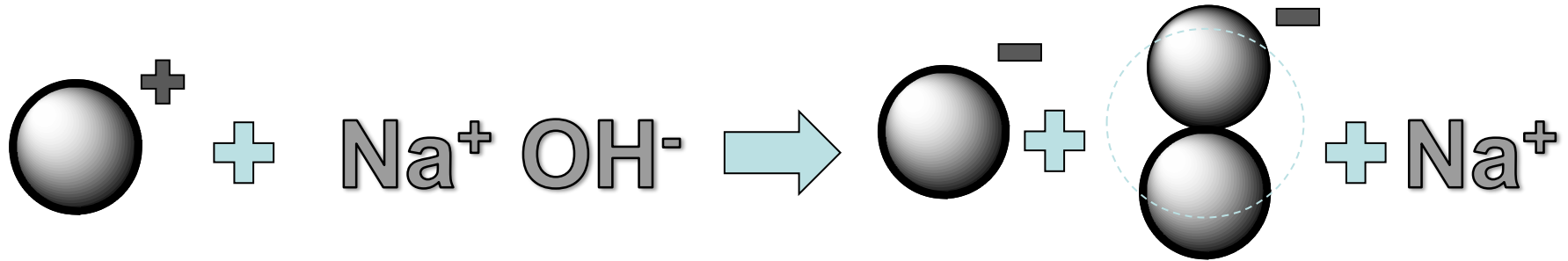$$\equiv TiOH_2^+ \quad \xrightleftharpoons[-H^+]{+H^+} \quad \equiv TiOH \quad \xrightleftharpoons[-H^+]{+H^+} \quad \equiv TiO^-$$
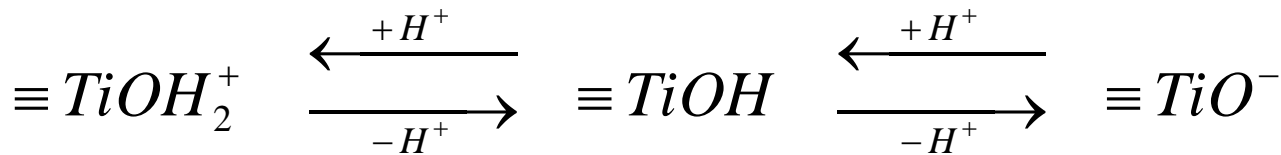
Schematic representation of the surface charge change of TiO_2 NP at different solution pH.

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Colloidal forces in particle deposition and aggregation
Petosa et al. ES&T 2010

- Derjaguin-Landau-Verwey-Overbeek (DLVO) theory:

- VT = VR + VA

  - Repulsion due to Van der Waals (VDW) interactions. Function of Hamaker constants which describe the interaction between pairs of atoms located between two surfaces.

  - Attraction due to the overlap of the diffuse electrical double layer (EDL).

- Non - DLVO interactions

  - Steric interactions (adsorbed layers of different substances)

  - Magnetic forces for Fe-based nanomaterials.

  - Hydration forces: biomolecules, hydrophilic material or functional groups at the surface that have bounded water molecules increases the repulsive interaction.

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Colloidal forces in particle deposition and aggregation
Petosa et al. ES&T 2010

- Unique features at the nanoscale particle interactions:

  - High influence of geochemical heterogeneities (patches)

  - Low energy barrier leading to aggregation in the primary minimum. When changes in pH or IS occur then there is less release than with larger particles.

  - Negligible secondary energy minimum (particles larger than 0.5 um usually attach at secondary minimum at natural conditions; NP may not follow this pattern leading to more mobility)

  - Interaction energies equations have been deduced under assumptions that migth not be valid for NP.

Mechanisms for particle collisions
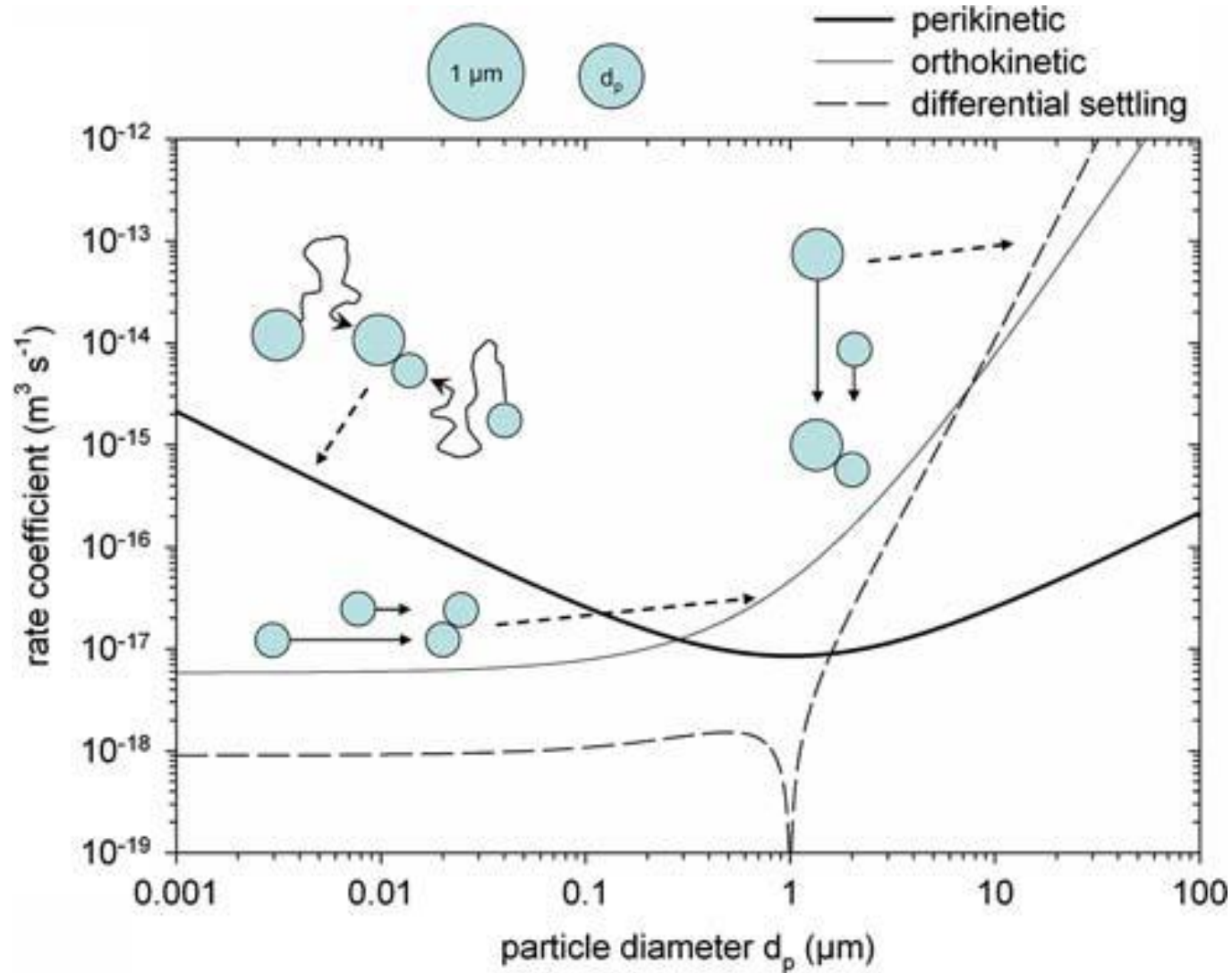
Mechanisms for particle collisions

- Brownian motion is predominant at NP level.

- Aggregation induced with electrolytes:

  - Unfavorable aggregation (slow): reaction limited; stability ratio (W) or attachment efficiency ($\alpha=1/W$)

  - Favorable (fast): diffusion limited; Critical coagulation concentration, CCC. Schulze-Hardy rule:

    - If ζ large, then CCC is proportional to z^{-6}

    - If ζ small, then CCC is proportional to z^{-2}

    - Z is zeta potential and z is counter-ion valence

Mechanisms for particle collisions

- Experimental approach:

- Aggregation rates during the early stage of aggregation (dupplet formation) measured by dynamic ligth scattering (DLS) can be expressed as (Chen, Mylon and Elimelech, ES&T, 2006):
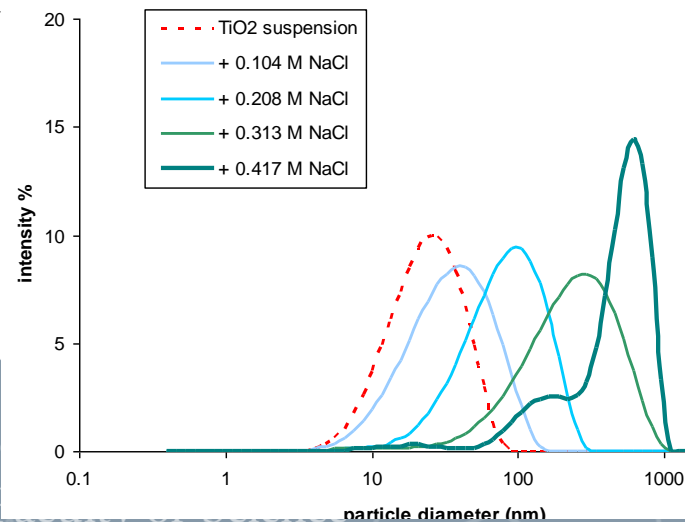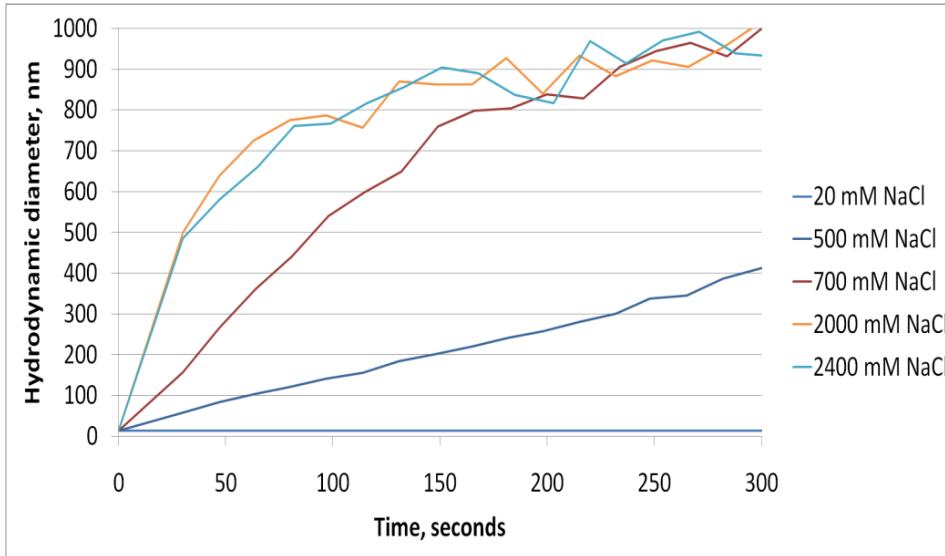
$$\left(\frac{dR_H}{dt}\right)_{t\to 0} \propto k_{11} \cdot N_0$$

- Where R_H is the hydrodynamic radius of the particles, N_0 is the initial particle concentration and k_{11} is the aggregation rate constant.

NP aggregation studies
Responsible: J. Gallego

Determining attachment efficiency, α:

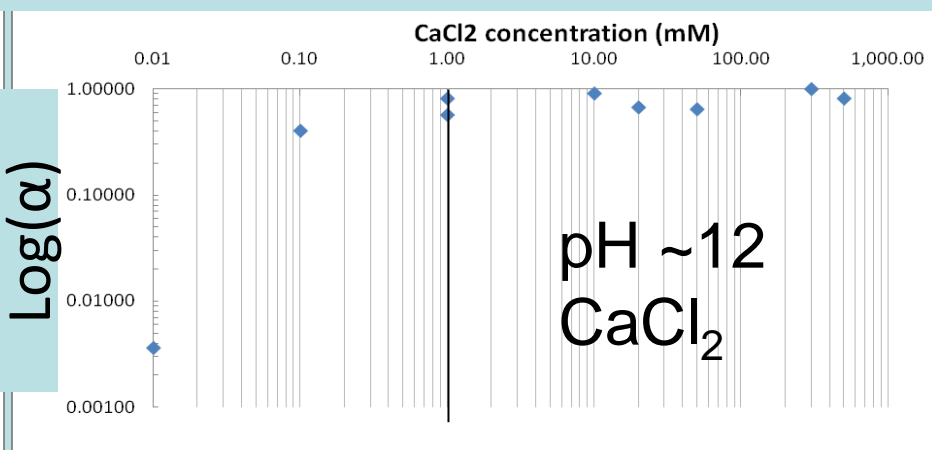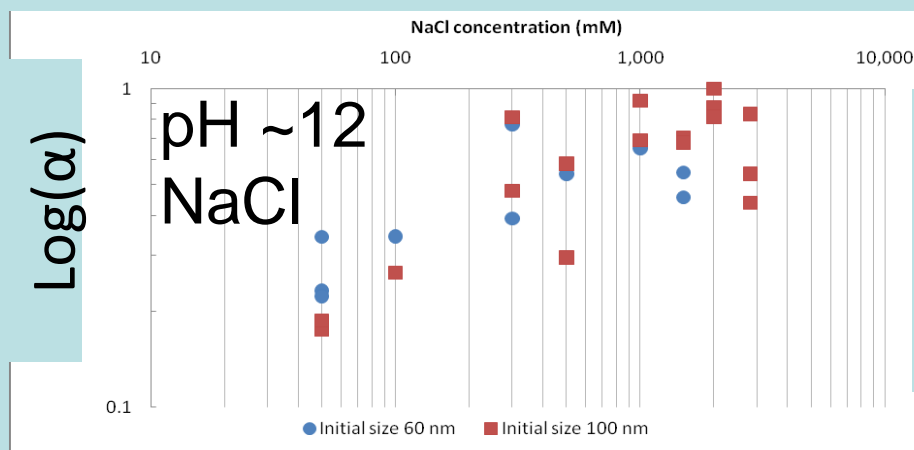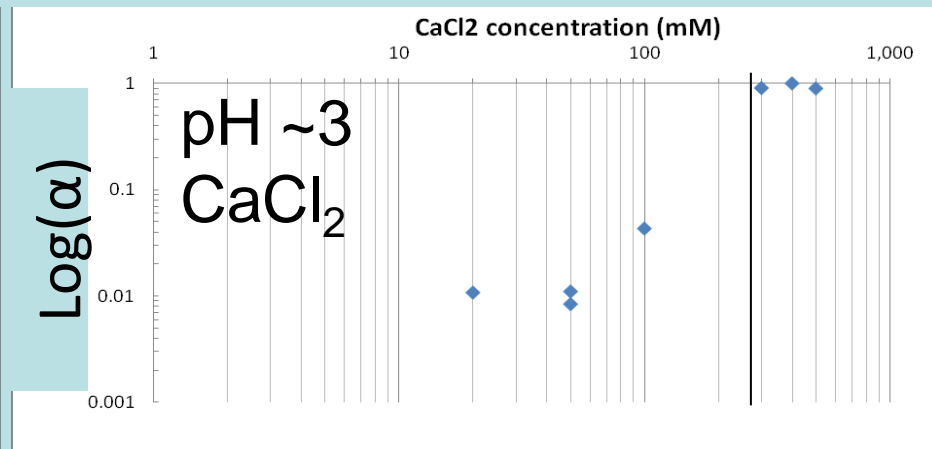$$k \propto \frac{1}{N_0} \left(\frac{d(R_h(t))}{dt} \right)_{t \to 0}$$

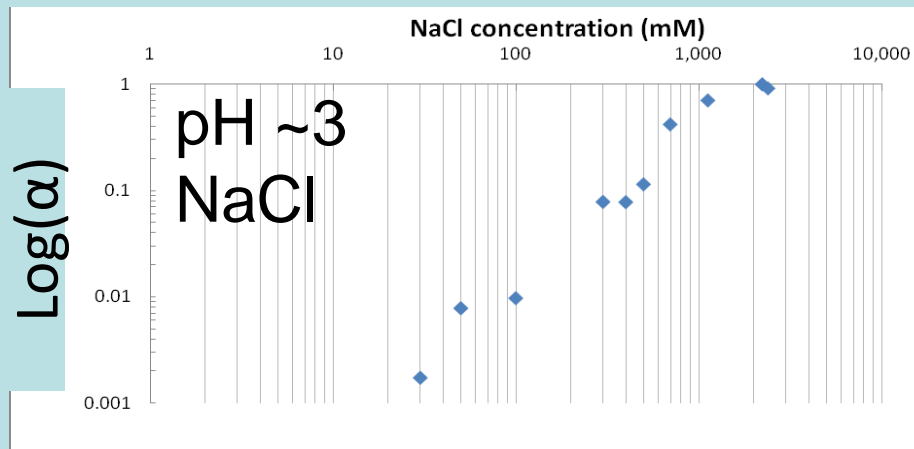$$\alpha = \frac{\left(\dfrac{d(R_h(t))}{dt} \right)_{t \to 0}}{\left(\dfrac{d(R_h(t))}{dt} \right)_{t \to 0, \, fav}}$$

α: fraction of collissions that lead to attachement

NP aggregation theory

Critical coagulation concentration, CCC:

Stabilization by Natural Organic Matter (NOM) and model molecules

NOM:

Isolated Humic acid (HA), Fulvic acid (FA) and Sodium Alginate (Alg).
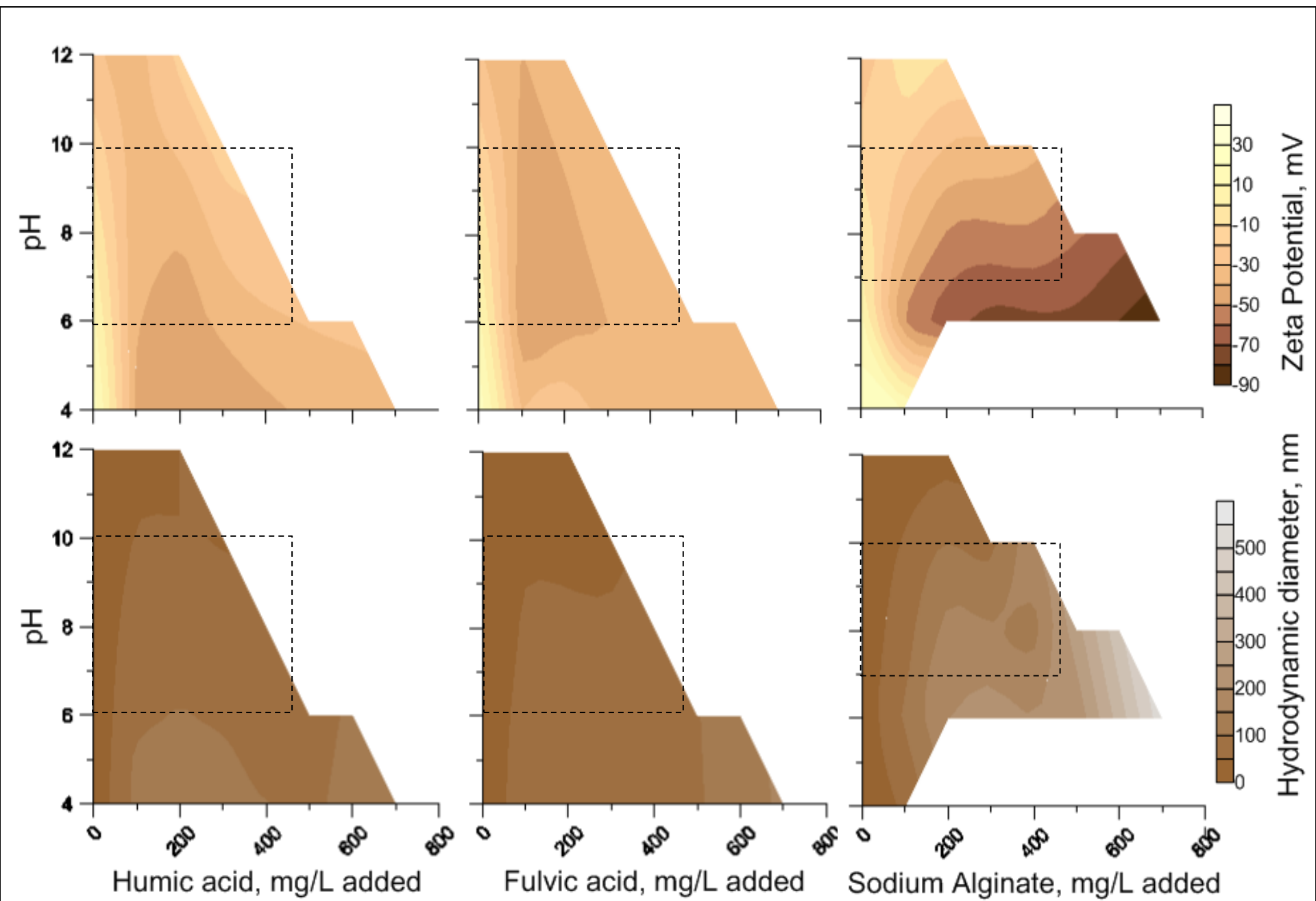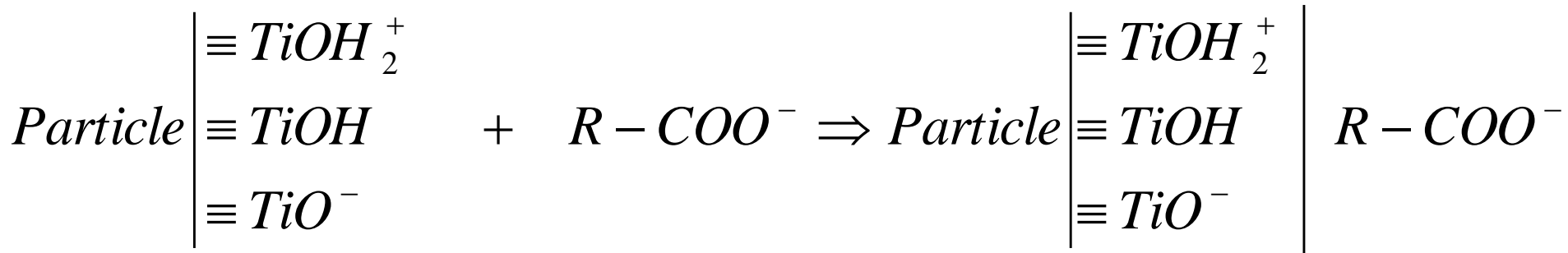
Advantages:

Standard material

Natural conditions

Disadvantages:

Poor for explaining molecular mechanisms

NOM sorption on TiO2 NP:

Natural Organic Matter (NOM) and model molecules

$$Particle \begin{vmatrix} \equiv TiOH_2^+ \\ \equiv TiOH \\ \equiv TiO^- \end{vmatrix} + R-COO^- \Rightarrow Particle \begin{vmatrix} \equiv TiOH_2^+ \\ \equiv TiOH \\ \equiv TiO^- \end{vmatrix} R-COO^-$$

Schematic representation of the adsorption of macromolecules to the available sites of TiO_2 NP; the sorption mechanism can be either surface complexation with the carboxylic, phenolic, or hydroxyl groups on the NOM or with hydrophobic interactions. Since NOM macromolecules are polyelectrolytes with low pK_a, even if only one or few groups on each molecules complex the mineral surface then the remaining charged groups provide the particle with a net negative charge.

Beckett, R. and N. P. Le (1990). "The role or organic matter and ionic composition in determining the surface charge of suspended particles in natural waters." Colloids and Surfaces 44: 35-49.
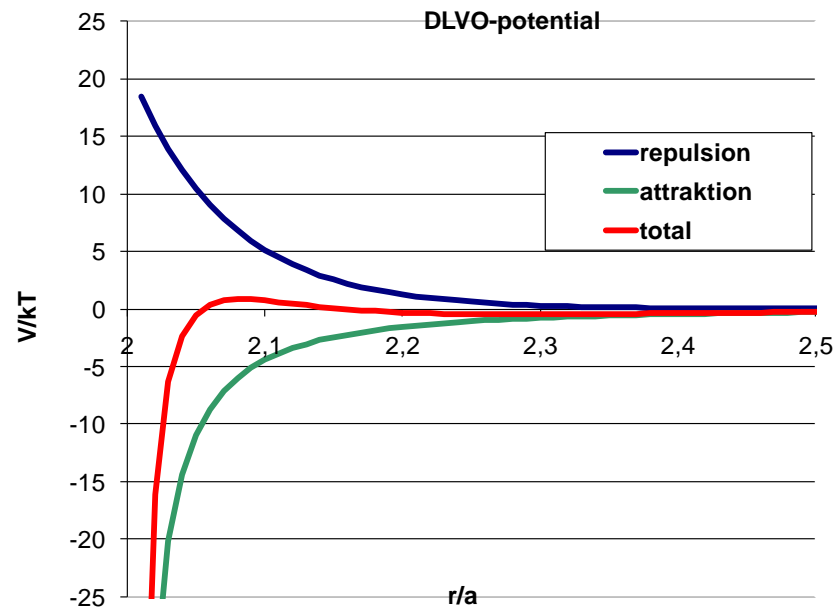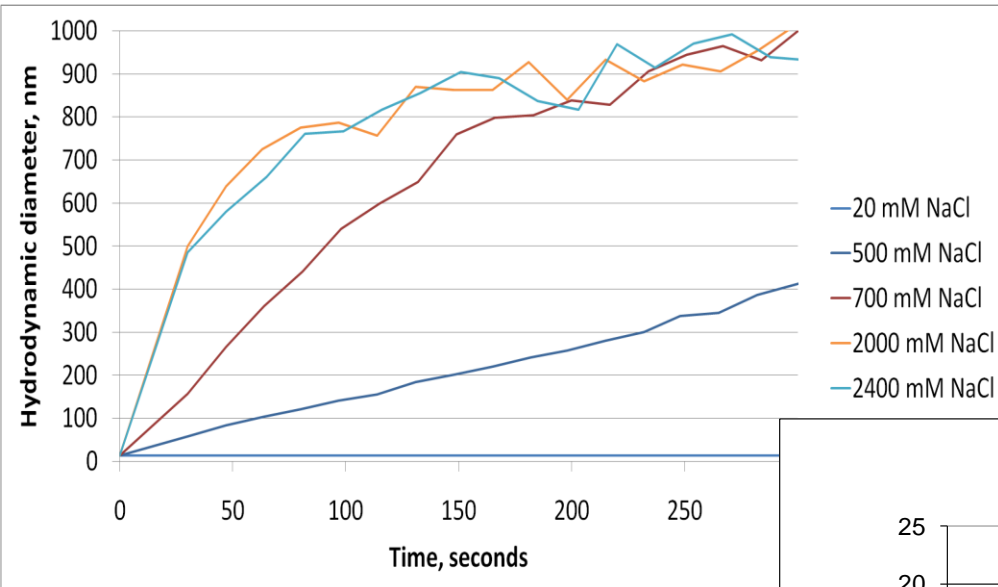
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NP aggregation theory
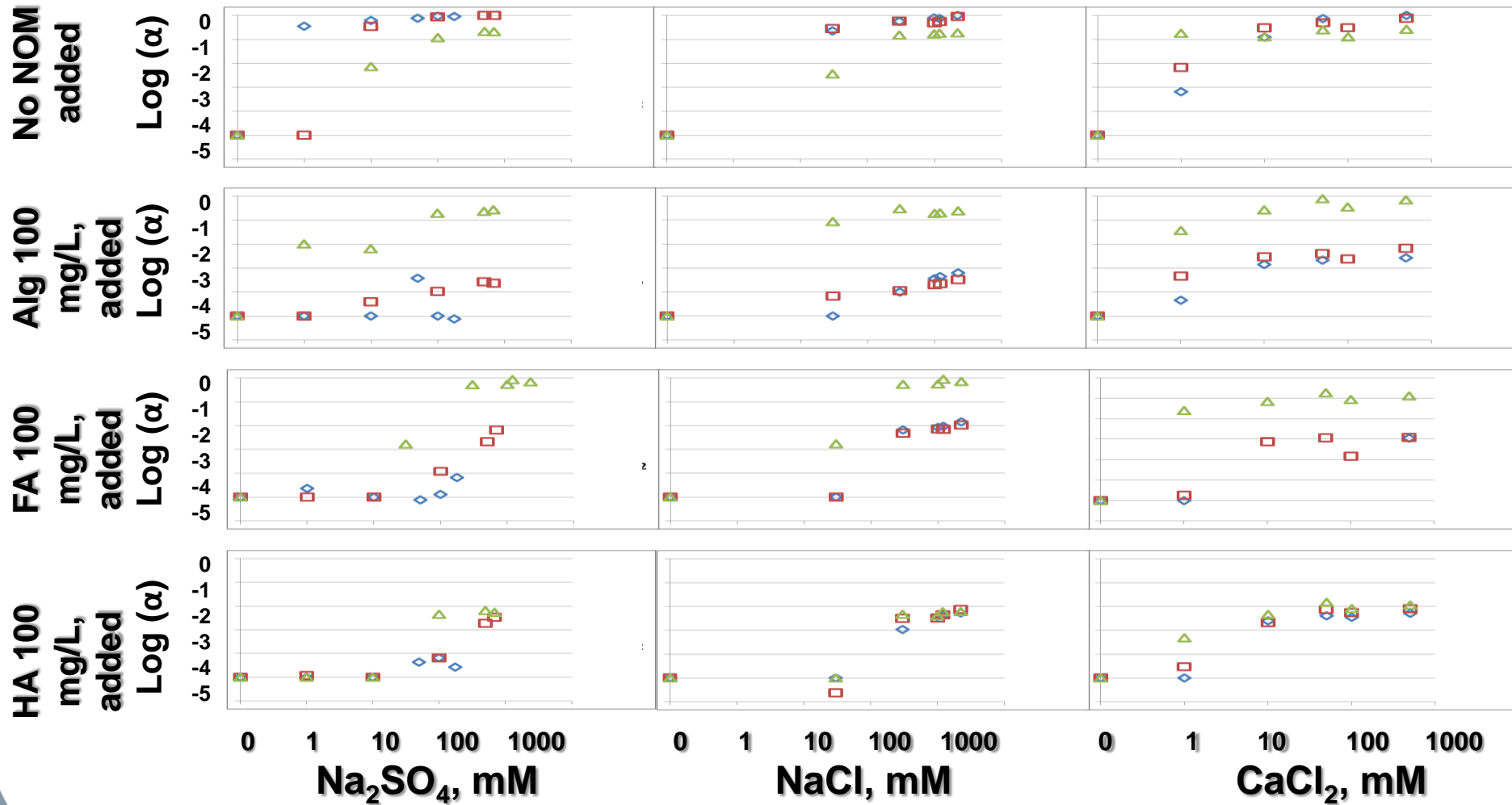
Experiments vs modelling

- Attachment efficiency, α

Towards a kinetic exposure assessment model

Temperature
Radii
pH
Point of zero charge
Hamaker constant
Ion valence
Ion concentration

Density
Radii
Viscosity

$$\frac{dn_j}{dt} = \frac{1}{2} \sum_{i=1}^{i=j-1} \alpha_{i,j-i} K_{i,j-i} n_i n_{j-i} - n_j \sum_{i=1}^{i=\infty} \alpha_{j,i} K_{j,i} n_i - \frac{v_s}{d} j^{\beta} n_j + I_j$$

Change in concen-
tration

Formation
through
agglomeration

Reduction
through
agglomeration

Sedi-
mentation

Inflow

Temperature
Radii
Viscosity

Challenges in Exposure Modeling of Nanoparticles in Aquatic Environments.
RICKARD ARVIDSSON, SVERKER MOLANDER, BJÖRN A. SANDÉN AND
MARTIN HASSELLÖV. Human and Environmental Risk Assessment. 2010 (in
press)

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Example of model output
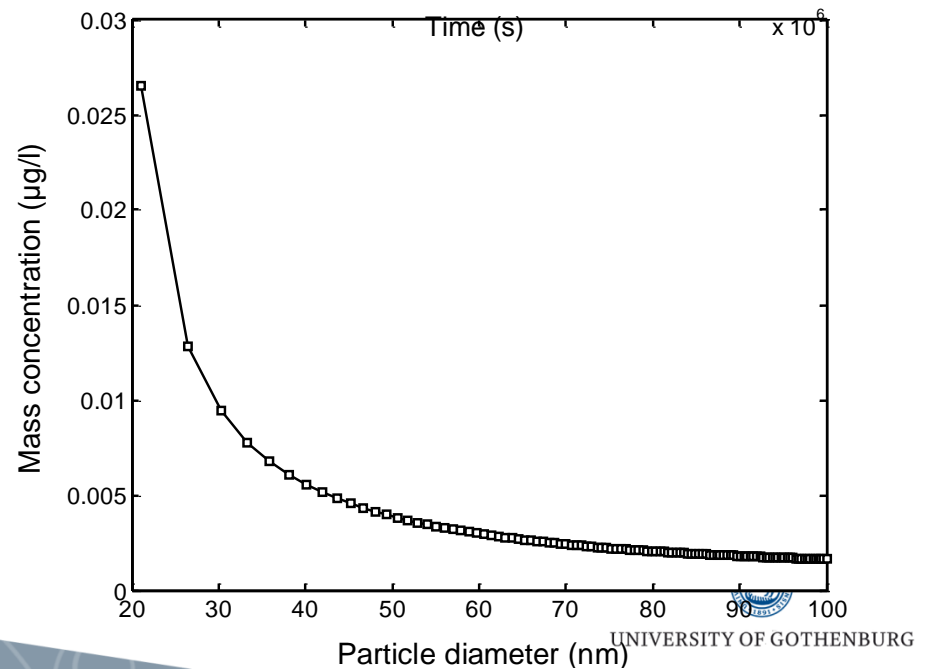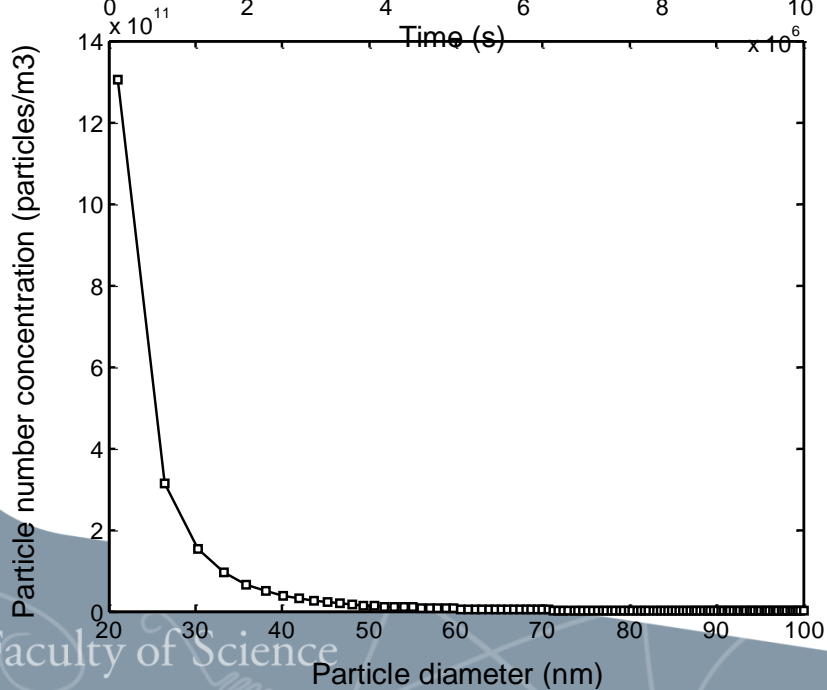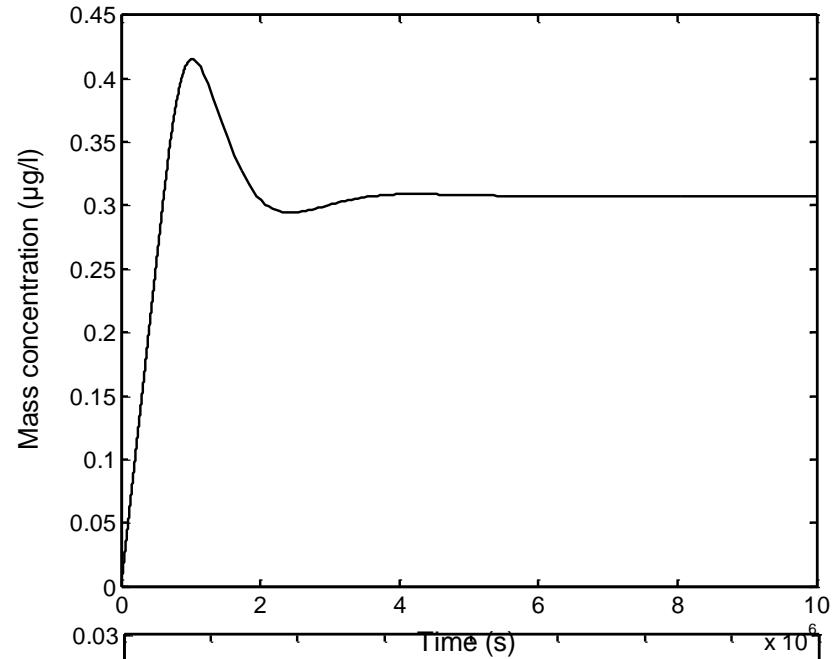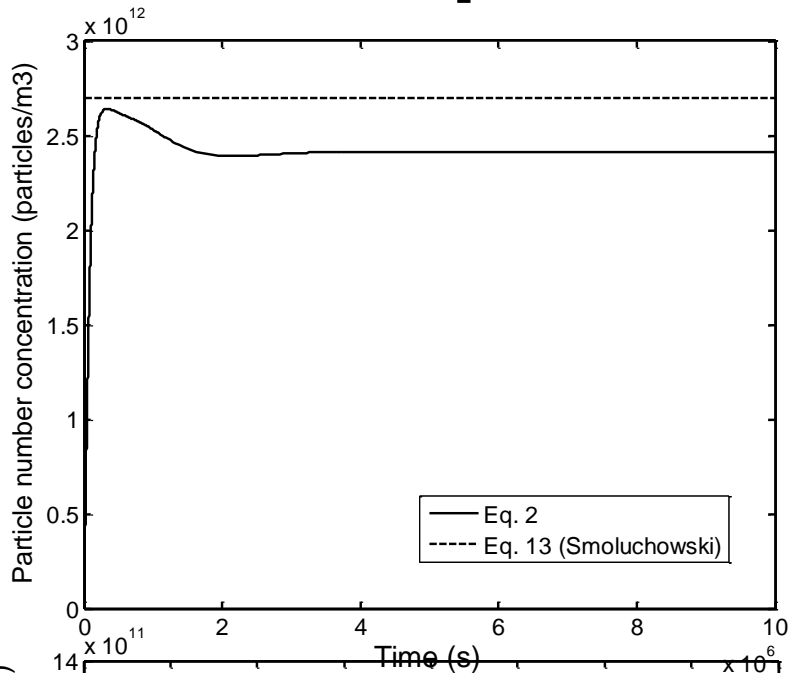
Natural Organic Matter (NOM) model molecules

Responsible: C. Jonsson

- Hydroxy-benzoic acids as molecular proxies of NOM:

  - Good for explaining molecular mechanisms

  - Bridging the molecular level with the macromolecular binding and the natural behaviour.

Methods

Surface properties (surface charging, pH_{PZC}, acid/base properties):
Potentiometric titrations
NOM adsorption:
Adsorption experiments (sorbed vs. non-sorbed)

As a function of:
Particle size
pH
Ionic strength (salinity)
Ligand-to-solid ratio

Other characterization methods:
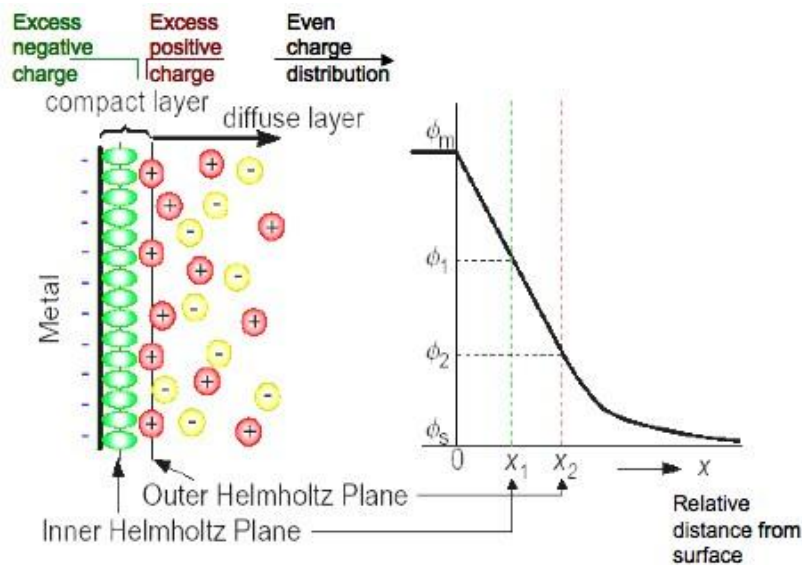
DLS, XRD, BET, TEM, ES-DMA etc.

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Surface Complexation Modeling

CD-MUSIC (Charge Distribution-MUltiSIte Complexation) **model**

Hiemstra T., Van Riemsdijk W.H., Bolt G.H., 1989, *JCIS,* 133
Hiemstra T., Van Riemsdijk W.H., 1996, *JCIS,* 179, 488

Electrical Double Layer

Model Input:

Particle specific parameters (surface area, capacitance, site density, etc)
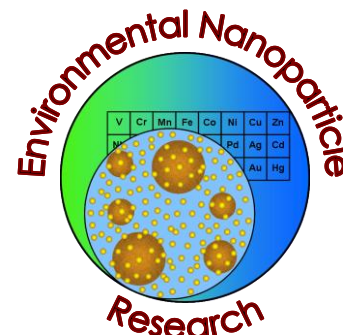Adsorption and titration data at varying pH, ionic strengths, concentrations

Model output:
Surface charge of nanoparticles
Size-dependent speciation as a function of environmental conditions
Predictive adsorption characteristics and resulting effect on particle behavior

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Analysis of the adsorption of environmentally relevant macromolecules on TiO2 NP and the effects on dispersion stability, agglomeration and sedimentation rates.

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