

# Interactions between engineered nanoparticles in aquatic systems: Roles of engineered capping agents and natural organic matter



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## Introduction

### Motivation:

The development, manufacture, and use of engineered nanoparticles (NPs) is increasing rapidly.<sup>1</sup> As such, there is a need to better understand the environmental implications of these novel materials, including their transformations in the environment.<sup>2</sup> As with natural colloids, interactions with natural organic matter (NOM) are likely to strongly influence environmental behavior. Existing studies have often focused only on a single NOM isolate at one representative concentration. In this work, we aim to more systematically investigate the influence of NOM type and concentration on NP colloid stability.

### Hypothesis:

Different NOM fractions and NOM from different sources will have distinct effects on NP colloidal stability. Behavior will correlate with NOM **properties** and **concentration**.

### Objective:

- Quantify the rates of gold nanoparticle aggregation in the presence and absence of several NOM isolates at varying concentrations

## Materials and Methods

### Nanoparticles:

Citrate-stabilized gold NPs (NanoXact) were purchased from Nanocomposix, Inc. NP core size as measured by TEM was  $12.0 \pm 1.3$  nm (1 SD). Hydrodynamic diameter as measured by dynamic light scattering was  $20.2 \pm 3.1$  nm (95% CI)

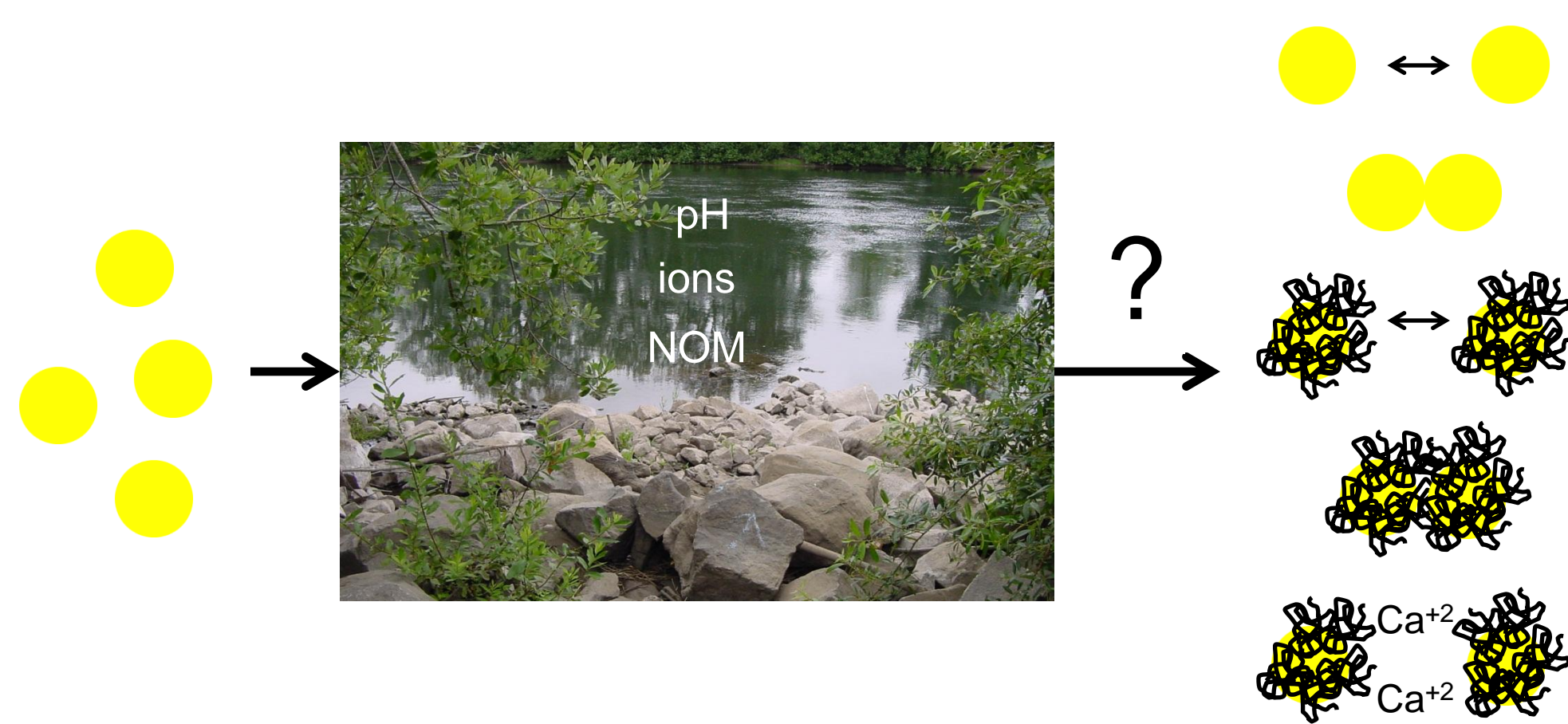
### Natural Organic Matter:

Four NOM fractions were purchased from the International Humic Substances Society (IHSS)

- Suwannee River NOM (SRNOM)
- Suwannee River Humic Acid (SRHA)
- Suwannee River Fulvic Acid (SRFA)
- Poly Lake Fulvic Acid (PLFA)

### Dynamic Light Scattering:

Initial aggregation rates were quantified using time-resolved dynamic light scattering (Brookhaven 90 Plus) and attachment efficiencies were calculated following established procedures.<sup>3</sup>



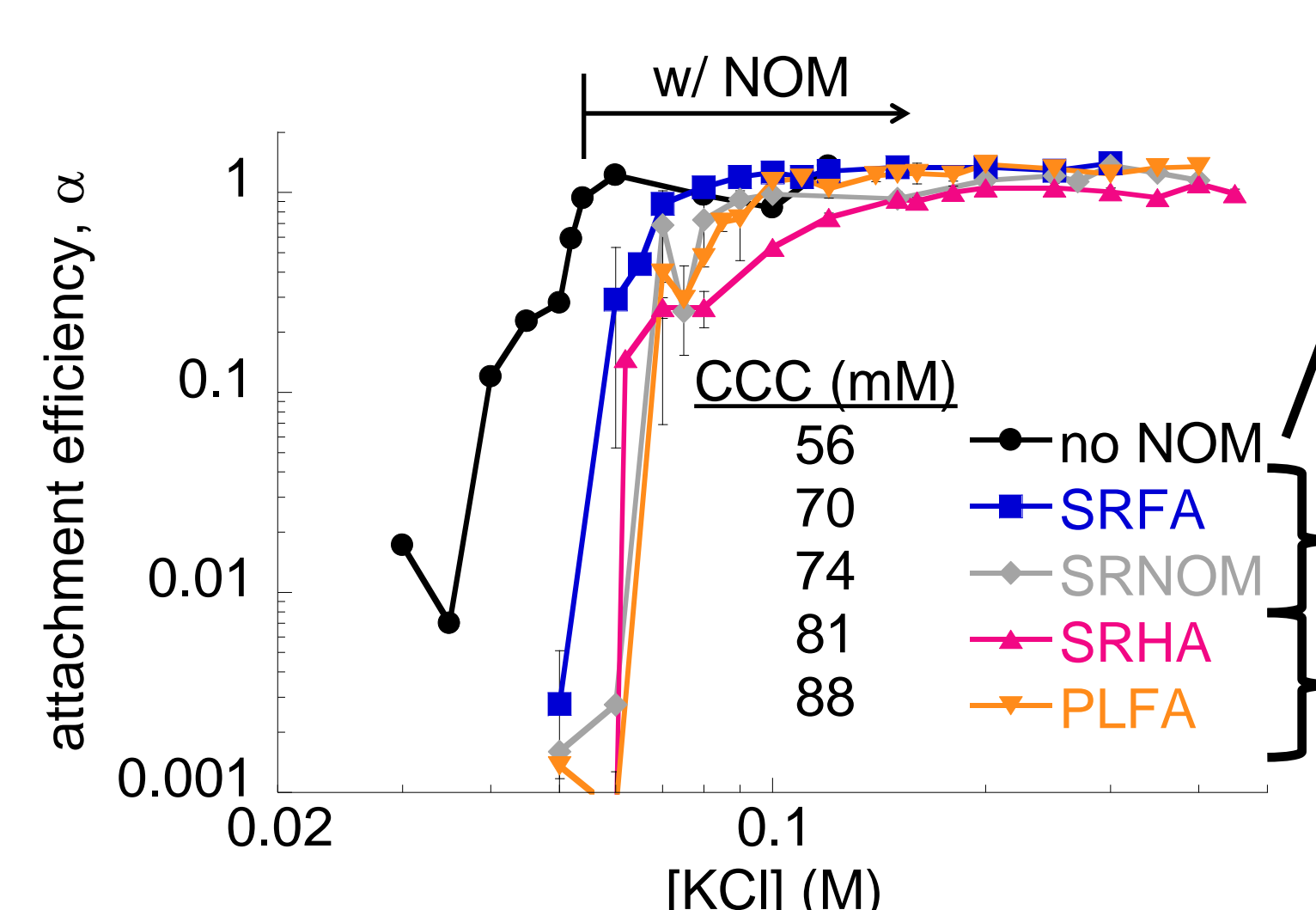
## Results

### Effect of NOM Type:

#### Experimental Conditions:

Citrate AuNPs = 1 mg/L as Au  
NOM = 1 mg/L as DOC  
pH = 6.0  
KCl = 30-600 mM

#### NOM stabilizes citrate AuNPs



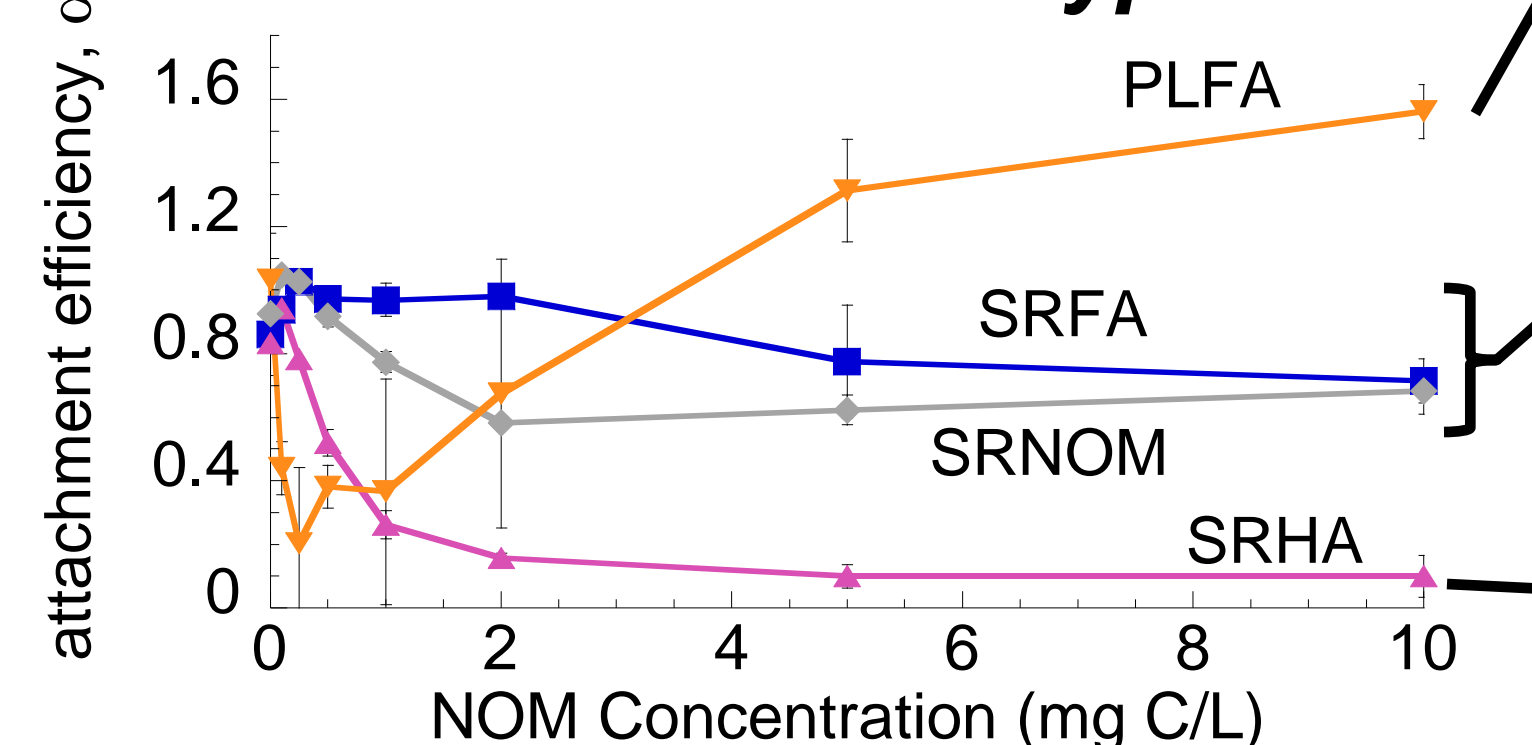
**Figure 1.** Attachment efficiencies of AuNPs in the presence of the four NOM isolates as a function of ionic strength (KCl). Critical coagulation concentrations (CCC) for AuNPs in each NOM isolate are shown in the inset table.

### Effect of NOM Concentration:

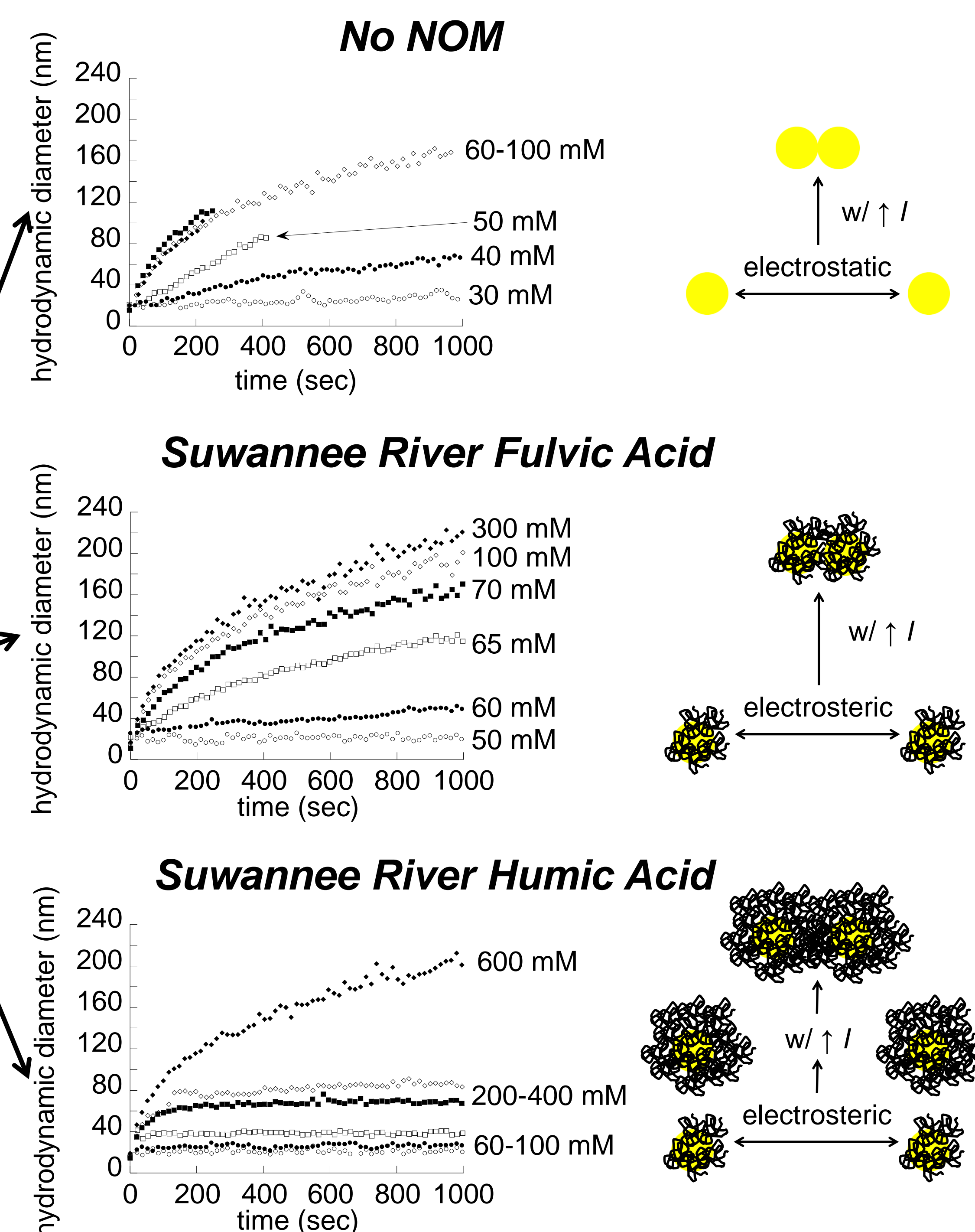
#### Experimental Conditions:

Citrate AuNPs = 1 mg/L as Au  
NOM = 0-10 mg/L as DOC  
pH = 6.0  
KCl = 80 mM

#### Concentration Effects vary with NOM Type

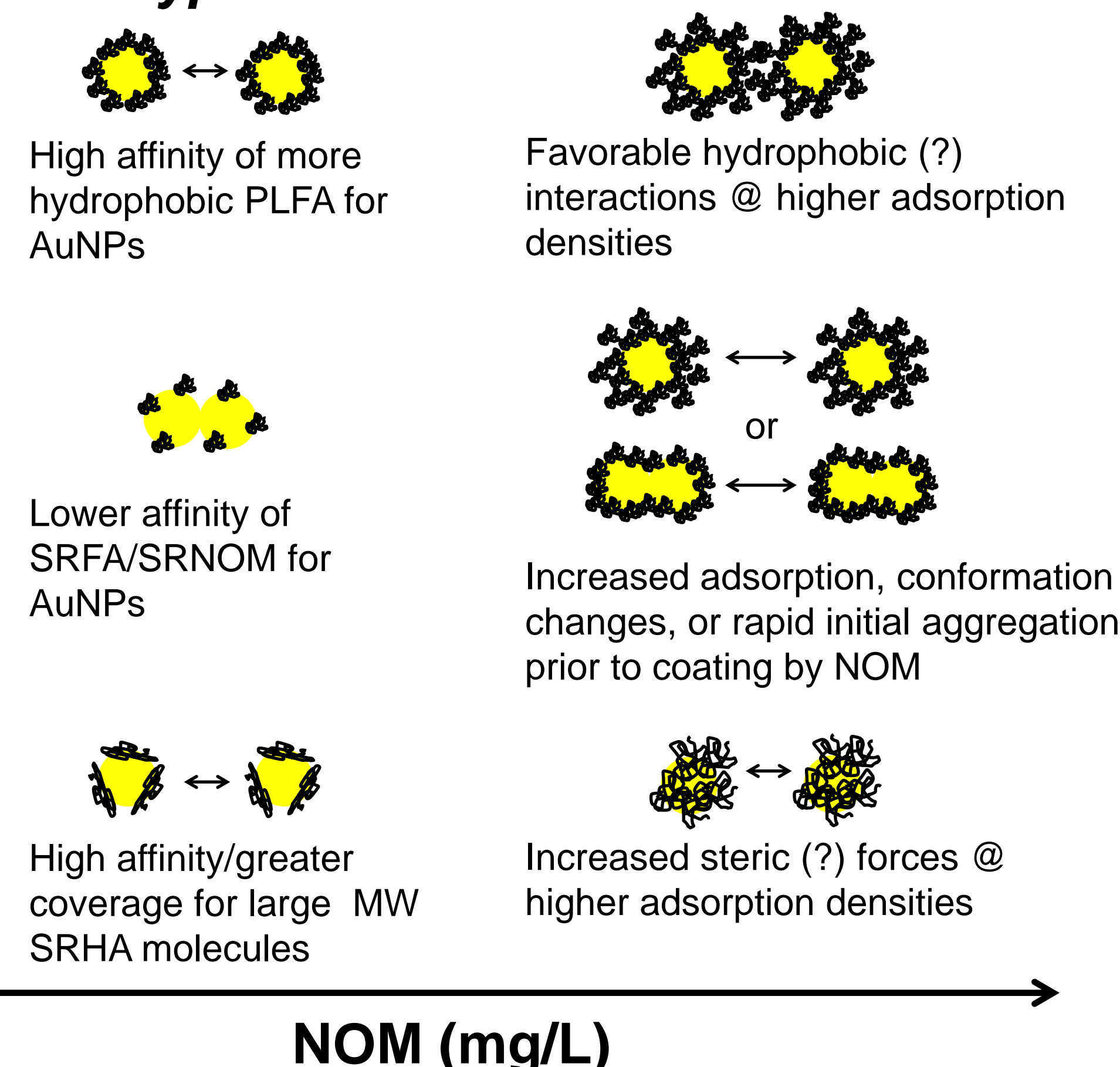


**Figure 2.** Attachment efficiencies of AuNPs in the presence of 0-10 mg C/L of four different NOM isolates in 80 mM KCl.



**Figure 3.** Aggregation of cit-AuNPs in the presence of NOM isolates and KCl as quantified by time-resolved dynamic light scattering.

### Hypothesized Mechanisms



## Conclusions

Clearly, both the **type** and **concentration** of NOM, along with the ionic strength of the system are important factors in determining AuNP colloidal stability. Specific conclusions include the following:

- At low to moderate NOM concentrations, all four NOM fractions stabilize citrate-capped AuNPs
- Larger molecular weight (SRHA) and more hydrophobic (PLFA) NOM provide greater stability
- Elevated ionic strength induces increased NOM adsorption and/or conformational changes
- Steric interactions likely play a role in the stability of NOM-coated AuNPs, but electrostatics remain important
- At  $I = 80$  mM,  $<0.5$  mg C/L as SRHA or PLFA are required to stabilize AuNPs, while  $> 2$  mg C/L as SRFA is required.
- Behavior of SRNOM-coated AuNPs lies between that of SRFA and SRHA, but closer to SRFA behavior

## Ongoing Work

- Mechanism of NOM-NP Interaction
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- Different capping agents and NOM fractions
  - Development of structure-property relationships
  - Influence of coatings on heteroaggregation of AuNPs with natural colloids

## Acknowledgements

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## References

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- Lowry et al. (2012) *Environmental Science and Technology*. 46 (13) p. 6893-6899.
- Nason et al. (2012) *Journal of Environmental Monitoring*. 14, p. 1885-1892.