



## Research paper

# Coagulation and sedimentation of gold nanoparticles and illite in model natural waters: Influence of initial particle concentration



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## ARTICLE INFO

## Article history:

Received 22 July 2016

Received in revised form 21 October 2016

Accepted 24 October 2016

Available online 27 October 2016

## Keywords:

Fate and transport nanoparticles

Model nanoparticles

Natural colloids

Natural water chemistry

## ABSTRACT

Gold nanoparticles (AuNP) possess unique characteristics that render them adequate for applications and also to be used as a model NP to evaluate the fate and behavior at low NP concentrations due to the ease of detection by modern analytical techniques. Moreover, AuNP may result in some negative effects in the environment and there is a necessity to predict their aquatic environmental concentrations by parameterizing the underlying transport and transformation processes. This study investigated the coagulation and sedimentation of 30 nm citrate-coated AuNP under enviro-mimicking conditions, i.e. model natural freshwaters (MNW) covering the range of European water chemistries relevant for colloids and NP (major ions, pH and dissolved organic matter) and artificial seawater (ASW). Firstly, the coagulation rates of AuNP at mg/L concentrations were evaluated using time-resolved dynamic light scattering which showed a decreased rate upon addition of Suwannee river natural organic matter (SRNOM) at low ionic strength (IS) but remained relatively high at high IS. Contrastingly, AuNP approaching environmental realistic concentrations (80 µg/L) in quiescent microcosms showed slow decline rates in all MNW and ASW regardless of the presence of SRNOM, as measured by nanoparticle tracking analysis and elemental Au spectrometry. When illite was added as model natural colloid the rates of decline of AuNP remained low as well. This is owing to limited collisions at low particle number concentrations. The results show that besides IS, pH, NOM concentration and type and the intrinsic surface charge of the particles, the particle number concentration and size distribution of both AuNP and natural colloids determine the extent of the large-scale fate of NP in aquatic environments.

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## 1. Introduction

The possibilities offered by the use of nanomaterials and nanoparticles (NP) in innovative products provide high expectations for enhanced technological development (Keller et al., 2013; Roco, 2011; Vance et al., 2015). Emission of NP into aquatic media has raised concern because of the different environmental interactions that can result in environmental effects for some specific NP (Ferry et al., 2009; Pokhrel et al., 2013; Ribeiro et al., 2014). Consequently, the risk assessment of possible NP releases into aquatic media needs to consider the relevant physical-chemical interactions with the receiving environments (Arvidsson et al., 2011; Lowry and Casman, 2009; Tiede et al., 2009; Wiesner et al., 2009). The exposure assessment must consider the strong relation between the NP intrinsic properties and the composition of the receiving environment which determine the exposure concentrations and bioavailable species of the NP

or their transformation products (Garcia-Negrete et al., 2013; Lowry et al., 2012; Nowack et al., 2012).

Once NP are present in the aquatic environment they will be subject to interactions with the surrounding media including electrolytes, dissolved gases, natural organic matter (NOM) and other natural particles (Buffle et al., 1998; Zhou et al., 2012) and they will be conditioned by physical forcing factors (e.g. hydrodynamic conditions, temperature). If the transformation processes lead to heavier and larger particles (e.g. via homo- or heterocoagulation) and hydrodynamic forces are negligible (i.e. laminar flow or stagnant conditions), particle sedimentation will be favored relative to diffusion or advection, respectively. Some studies have highlighted the relevance of heterocoagulation for the fate of NP in aquatic environments (Quik et al., 2012; Zhou et al., 2012) and soil environments (Cornelis et al., 2013). However, the processes of coagulation and sedimentation have not yet been investigated in a range of water chemistries representative of realistic aquatic environments. In addition, previous studies evaluating sedimentation rates of NP in natural and artificial waters have used NP concentrations above the expected environmental concentrations (Keller et al., 2010; Quik et al., 2014; Zhou et al., 2012). During experiments with relatively high particle number concentrations, not only the collision frequency

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and thus the coagulation rates of like and unlike particles are enhanced (see section 1 in the Supplementary information, SI), but also it neglects the importance of the ratio between NOM and particle concentration in more realistic scenarios (Gallego-Urrea et al., 2014b).

An experimental platform for evaluating sedimentation of aggregating NP was developed and tested in this work. A set of model natural waters (MNW) that encompasses the range of chemistries found in European freshwaters (Hammes et al., 2013) and one artificial seawater (ASW) were used as media. While experiments in natural waters have a higher relevance for a particular geographical location, artificial waters provide a more mechanistic overview of the processes in the environment with the physicochemical parameters being more easily controlled.

Gold NP (AuNP) were chosen as model particle to test this platform owing to their insolubility, high specific density, low background elemental concentrations and favorable scattering properties making them appropriate for fate investigations at concentrations as low as only approximately 10 times higher than environmentally expected (80 µg/L) (Tiede et al., 2009). Since AuNP do not dissolve at the conditions tested, there is no reduction of the original size nor an increase of dissolved ions in the medium (or possible newly formed particles due to complex formation). Their high specific density makes AuNP ideal for evaluating sedimentation of small particles. Their relative high scattering ability makes them easier to detect using single-particle methods at diluted concentrations (Gallego-Urrea et al., 2011). Additionally, the low background concentration of Au facilitates the detection using elemental analysis techniques like inductive coupled plasma mass spectrometry (ICP-MS). Moreover, AuNP have a strong potential to be used in many fields (Vance et al., 2015) and, therefore, it is one of the NP that has potential to become of environmental concern that requires prediction of their aquatic environmental concentrations by parameterizing the underlying transport and transformation processes (Lapresta-Fernández et al., 2012; Moreno-Garrido et al., 2015).

The aggregation and sedimentation rates of AuNP were tested with and without addition of previously characterized illite clay particles (Gallego-Urrea et al., 2014a) that were chosen as a model allochthonous colloid owing to its expected presence in natural waters usually coming from weathering of sedimentary rocks (Chanudet and Filella, 2006; Gallego-Urrea et al., 2014a; Hillier, 2001). Aggregation rates were measured using time-resolved dynamic light scattering (DLS) and aggregation and sedimentation were measured in mesocosms at lower AuNP concentrations using NTA and ICP-MS at a fixed depth. The objective of this study was to merge the relevance of experiments in natural waters and the controllable parameters of mechanistic studies to evaluate the dominant factors that regulate the fate of a model NP, i.e. AuNP, in European model natural waters, MNW, and artificial seawater, ASW.

## 2. Experimental

### 2.1. AuNP and illite dispersions

The citric acid coated AuNP dispersion used in this work was synthesized by the Chemistry Department of the University of Alberta in Edmonton, Canada. Details of the synthesis method can be found elsewhere (Liu et al., 2012a). The stock concentration was 40 mg/L. The size of AuNP was characterized by dynamic light scattering (DLS) performed on a Malvern Zetasizer ZS (Malvern instruments Ltd., Worcestershire, UK) and nanoparticle tracking analysis, NTA, done on a NanoSight LM10 (NanoSight Ltd., Amesbury, UK) giving average hydrodynamic diameters close to 30 nm. Observe that hydrodynamic diameters from DLS were corrected in order to ignore the effects of the rotational diffusion coefficient which generates a fraction of small particles in the particle size distribution (PSD) (Khlebtsov and Khlebtsov, 2011).

The illite stock dispersion was prepared following the procedure described in Gallego-Urrea et al. (2014a). Briefly, 10 g of powder obtained from the source clay mineral repository at the University of Missouri-Columbia, Columbia, MO, USA (Clay Minerals Society and Organisation for Economic Co-operation Development, 1979) was mixed with different concentrations of concentrated NaCl solutions to replace all  $\text{Ca}^{2+}$  ions from the clay, followed by ultrasonication. The resulting suspension was then centrifuged at 2800g for 8 min to remove particles with Stokes diameters (Gallego-Urrea, 2013) above 400 nm. This solution contained 6.5 g/L of illite with average hydrodynamic diameter of 190 nm determined with DLS (Gallego-Urrea et al., 2014a). The aspect ratio of the illite suspension was investigated in detail in a previous work, showing that the most numerous particles had an average size of  $206 \pm 96$  nm in the major axis and  $10.2 \pm 7.8$  nm in thickness (Gallego-Urrea et al., 2014a).

### 2.2. Particle number concentrations

The chosen illite mass concentration (650 µg/L) was chosen based on typical measured number concentrations of natural NP found in other studies ( $10^8$  to  $10^{11}$  particles per mL) (Gallego-Urrea et al., 2010). This concentration is relatively low compared to typical total suspended solid (TSS) measurements in surface waters (1–15,000 mg/L) (Chapman, 1996). However, the composition of illite particles with sedimentation diameters below 400 nm (see Gallego-Urrea et al., 2014a for details) is not comparable to that of the TSS that are usually measured using the burned filter “cake”. Most of the mass of this cake comprises very large material (usually larger than 0.45 µm) and thus does not necessarily mean more available surface for heterocoagulation as fewer particles are available for the same mass compared to small particles. Nevertheless, collisions may be enhanced in natural waters due to a large volume fraction and the presence of turbulence leading to significant differential-settling and orthokinetic flocculation as well as the influence of other material constituents of the TSS. The measurement in turbid natural waters is very relevant but adds another level of complexity that does not allow the identification of the mechanisms and materials involved in the coagulation and sedimentation processes. The level of complexity applied here is valid for specific cases with an amount of illite in the colloidal fraction.

### 2.3. Aquatic media

Six synthesized European MNW were prepared following the procedure described by Hammes et al. (2013) and summarized in section 2 in the SI. Briefly, the salts were added and mixed thoroughly in 25 L of MQ water, the solution was left overnight for equilibration with atmospheric gases and the pH was adjusted with NaOH and HCl when required, reaching the MNW compositions shown in Table 1. The use of buffers was avoided in order to evade possible interactions with the surface of the NP and the pH was monitored whenever possible. In experiments with illite, the dispersion was added to the MNW to reach a

**Table 1**

Composition of the model natural waters (MNW) as prepared. Ionic strength (IS) and electrolyte concentrations are in mM.

Parameters	I	II	III	IV	V	VI
pH	7.01	6.20	7.29	8.15	8.01	8.02
Ionic strength	0.247	0.430	2.60	3.16	6.47	16.5
$\text{HCO}_3^-$	0.076	0.186	0.732	0.515	1.237	3.260
$\text{Cl}^-$	0.026	0.106	0.527	0.166	0.716	5.121
$\text{NO}_3^-$	0.002	0.009	0.197	0.072	0.330	0.478
$\text{K}^+$	0.007	0.015	0.085	0.029	0.086	0.282
$\text{Na}^+$	0.049	0.131	0.557	0.228	0.696	2.977
$\text{Mg}^{2+}$	0.017	0.033	0.179	0.180	0.380	1.917
$\text{Ca}^{2+}$	0.044	0.094	0.507	0.549	1.512	2.845
$\text{SO}_4^{2-}$	0.022	0.018	0.227	0.347	0.901	1.894
SRNOM, mg/L	1.84	12.48	11.05	1.75	4.6	8.63

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