Hydrodynamic Chromatography for Studying Interactions between Colloids and Dissolved Organic Matter in the Environment

by

Allan Philippe (MSc.)

from Creil, France

Accepted dissertation thesis for the partial fulfilment of the requirements for a

Doctor of Natural Sciences

Fachbereich 7: Natur- und Umweltwissenschaften

Universität Koblenz-Landau

Thesis examiners:

Prof. Dr. Gabriele E. Schaumann, Universität Koblenz-Landau, Germany

PD. Dr. Thomas Baumann, Technische Universität München, Germany

Prof. Dr. Torsten C. Schmidt, Universität Duisburg, Germany

Date of the oral examination: 29th April 2015

Declaration

I hereby declare that I autonomously conducted the work presented in this Ph.D thesis entitled "Hydrodynamic Chromatography for Studying Interactions between Colloids and Dissolved Organic Matter in the Environment". All used assistances and involved contributors are clearly declared. This thesis has never been submitted elsewhere for an exam, as thesis or for evaluation in a similar context; to any department of this university or any scientific institution. I am aware that a violation of the aforementioned conditions can have legal consequences.

Landau in der Pfalz,
_____

Place, Date   Signature

The following parts of this thesis are published:

Chapter 2: the literature was reviewed by A. Philippe. Both authors contributed to the writing of the article.
Philippe, A., Schaumann, G.E., (2014) *Interactions of Dissolved Organic Matter with Natural and Engineered Inorganic Colloids: a review*. Environmental Science & Technology 48(16) 8946-8962.

Chapter 4: A. Philippe conceived, designed and conducted the experiments. Both authors contributed to the writing of the article.
Philippe, A., Schaumann, G.E., (2014) *Evaluation of Hydrodynamic Chromatography Coupled with UV-Visible, Fluorescence and Inductively Coupled Plasma Mass Spectrometry Detectors for Sizing and Quantifying Colloids in Environmental Media*. PLoS ONE 9(2) e90559.

Chapter 5: A. Philippe conceived and designed the experiments. The experiments were conducted by the first and second authors. The data analysis was conducted by the first, second and third authors. First and last authors contributed to the writing of the article.
Philippe, A., Gangloff M., Rakcheev D., Schaumann, G.E., (2014) Philippe, A., Schaumann, G.E., (2014) *Evaluation of Hydrodynamic Chromatography Coupled with Inductively Coupled Plasma Mass Spectrometry Detector for Analysis of Colloids in Environmental Media-Effects of Colloid Composition, Coating and Shape*. Analytical Methods 6(21) 8722-8728.

Chapter 6: A. Philippe conceived and designed the experiments. The experiments were conducted by the first and second authors. The data analysis was conducted by the first and second authors. All authors contributed to the writing of the article.
Rakcheev, D., Philippe, A., Schaumann, G.E., (2013) *Hydrodynamic Chromatography Coupled with Single Particle-Inductively Coupled Plasma Mass Spectrometry for Investigating Nanoparticles Agglomerates*. Analytical Chemistry 85(22) 10643-10647.

In addition, A. Philippe contributed to the following publications:
Chenal, M., Rieger, J., Philippe, A., Bouteiller, L., (2014) *High Yield Preparation of All-Organic Raspberry-like Particles by Heterocoagulation via Hydrogen Bonding Interaction*. Polymer 55 3516-3524.
A. Philippe carried out the HDC and zeta-potential measurements.

Metreveli, G., Philippe, A. and Schaumann, G. E. (2014) *Disaggregation of silver nanoparticle homoaggregates in a river water matrix*. Science of The Total Environment, in press, doi:10.1016/j.scitotenv.2014.11.058.
A. Philippe carried out the HDC measurements and contributed to the writing of the article.

Acknowledgements

Á Flo et Patrick…

Table of contents

Abstract

Engineered nanoparticles are emerging pollutants. Their increasing use in commercial products suggests a similar increase of their concentrations in the environment. Studying the fate of engineered colloids in the environment is highly challenging due to the complexity of their possible interactions with the main actors present in aquatic systems. Solution chemistry is one of the most central aspects. In particular, the interactions with dissolved organic matter (DOM) and with natural colloids are still weakly understood. The aim of this work was to further develop the dedicated analytical methods required for investigating the fate of engineered colloids in environmental media as influenced by DOM.

Reviewing the literature on DOM interactions with inorganic colloids revealed that a systematic characterization of both colloids and DOM, although essential, lacks in most studies and that further investigations on the fractionation of DOM on the surface of engineered colloids is needed. Another knowledge gap concerns the effects of DOM on the dynamic structure of colloid agglomerates. For this question, analytical techniques dedicated to the characterization of agglomerates in environmental media at low concentrations are required. Such techniques should remain accurate at low concentrations, be specific, widely matrix independent and free of artefact due to sample preparation.

Unfortunately, none of the currently available techniques (microscopy, light scattering based methods, separation techniques etc.) fulfills these requirements. However, a compromise was found with hydrodynamic chromatography coupled to inductively coupled plasma mass spectrometry (HDC-ICP-MS). This method has the potential to size inorganic particles in complex media in concentration ranges below ppb and is element specific; however, its limitations were not systematically explored. In this work, the potential of this method has been further explored. The simple size separation mechanism ensures a high flexibility of the elution parameters and universal calibration can be accurately applied to particles of different compositions and surface chemistries. The most important limitations of the method are its low size resolution and the effect of the particle shape on the retention factor. The implementation of HDC coupled to single particle ICP-MS (HDC-SP-ICP-MS) offers new possibilities for the recognition of particle shape and hence the differentiation between primary particles and homoagglomerates. Therefore, this coupling technique is highly attractive for monitoring the effects of DOM on the stability of colloids in complex media.

The versatility of HDC-ICP-MS is demonstrated by its successful applications to diverse samples. In particular, it has been used to investigate the stability of citrate stabilized silver colloids in reconstituted natural water in the presence of different types of natural organic matter. These particles were stable for at least one hour independently of the type of DOM used and the pH, in accordance with a coauthored publication addressing the stability of silver colloids in the River Rhine. Direct monitoring of DOM adsorption on colloids was not possible using UV and fluorescence detectors. Preliminary attempts to investigate the adsorption mechanism of humic acids on silver colloids using fluorescence spectroscopy suggest that fluorescent molecules are not adsorbed on silver particles. Several solutions for overcoming the encountered difficulties in the analysis of DOM interactions are proposed and the numerous perspectives offered by further developments and applications of HDC-(SP)-ICP-MS in environmental sciences are discussed in detail.

Zusammenfassung

Synthetische Nanopartikel sind neuartige Schadstoffe. Aufgrund ihrer häufigeren Anwendung wird sich ihre Konzentration in der Umwelt in Zukunft voraussichtlich stark erhöhen. Die Untersuchung des Schicksals von synthetischen Kolloiden in der Umwelt erweist sich als schwierig, bedingt durch deren mögliche komplexe Wechselwirkungen mit den Bestandteilen aquatischer Systeme. Eine zentrale Rolle spielt hierbei die Lösungschemie. Insbesondere die Wechselwirkungen mit gelösten organischen Stoffen (DOM) sind bisher wenig verstanden. Das Ziel dieser Arbeit bestand darin, angepasste analytische Methoden zu entwickeln, um die Effekte von DOM auf das Schicksal synthetische Kolloide in der Umwelt zu untersuchen.

Eine Literaturrecherche über die Wechselwirkungen den DOM mit anorganischen Kolloiden hat ergeben, dass es einen Mangel an systematischen Charakterisierungen von Kolloiden und DOM in den meisten Studien gibt, obwohl diese wesentlich wäre. Des Weiteren wäre die Erforschung der Fraktionierung von DOM auf Kolloiden bedeutend sowie die Untersuchungen der Effekte von DOM auf die dynamische Struktur von Agglomeraten. Für die Charakterisierung von niedrigkonzentrierten Agglomeraten in Umweltmedien werden passende analytische Techniken benötigt. Solche Techniken müssen genau, spezifisch, artefaktfrei (minimale Probenvorbereitung) und matrixunabhängig bei niedrigen Konzentrationen sein.

Keine der üblichen Methoden (Mikroskopie, Lichtstreuungsmethode, Trenntechnicken) erfüllt alle diese Voraussetzungen. Jedoch stellt die Hydrodynamische Chromatographie gekoppelt mit Massenspektrometrie mit induktiv gekoppeltem Plasma (HDC-ICP-MS) einen vielversprechenden Kompromiss dar. Mit dieser Methode kann die Größe von anorganischen Partikeln in komplexen Medien und in Konzentrationsbereichen unter ppb elementspezifisch gemessen werden. Allerdings wurden die Begrenzungen der Methode nicht systematisch untersucht. Während dieser Doktorarbeit wurde das Potenzial dieser Methode weiter untersucht. Der einfache Trennmechanismus ermöglicht einen großen Spielraum für die Elutionsparameter und eine universelle Kalibrierung kann für Partikel mit unterschiedlicher Zusammensetzung und unterschiedlicher Oberflächenchemie angewendet werden. Eine schwache Auflösung der Partikelgröße sowie die Effekte der Partikelform auf den Retentionsfaktor stellen die wichtigsten Begrenzungen der Methode dar.

Die Anwendung von HDC gekoppelt mit Einzelpartikel ICP-MS (HDC-SP-ICP-MS) bietet neue Möglichkeiten für die Partikelformerkennung und die Differenzierung zwischen primären Partikeln und Homoagglomeraten. Diese Kopplungstechnik ist deswegen hochattraktiv, um Effekte von DOM auf der Stabilität von Kolloiden zu untersuchen.

Die Vielseitigkeit der HDC-ICP-MS konnte durch verschiedene erfolgreiche Anwendungen hervorgehoben werden. Insbesondere wurde sie genutzt, um die Stabilität von zitrat-stabilisierte Silberkolloiden in synthetischem Flusswasser unter Anwesenheit verschiedener Typen DOM zu untersuchen. Diese Partikel waren mehr als eine Stunde stabil unabhängig von pH und vom Typ der DOM. Dieses Ergebnis deckt sich mit den Ergebnissen einer parallel publizierten Studie über die Stabilität von Silberkolloiden in Rheinwasser. Die direkte Untersuchung von DOM-Adsorption auf Kolloiden war mit UV- und Fluoreszenzdetektoren nicht möglich. Vorversuche wiesen darauf hin, dass die fluoreszierenden Huminsäuremoleküle auf Silberkolloiden nicht adsorbieren. Lösungen für die verbleibenden Schwierigkeiten in der Analyse der Wechselwirkungen der DOM werden vorgeschlagen und die vielfältigen Entwicklungs- und Anwendungserspektiven von HDC-(SP)-ICP-MS in den Umweltwissenschaften werden im Detail diskutiert.

List of Abbreviations

AF4: asymmetrical flow-field flow fractionation
AFM: atomic force microscopy
AUC: analytical ultracentrifugation
BSA: bovine serum albumin
CC: Coulter counter
CCC: critical coagulation concentration
CE: capillary electrophoresis
DOM: dissolved organic matter
DLS: dynamic light scattering
DLVO: Derjaguin Landau Verwey Overbeek
DR: differential refractometer
EDX: energy dispersive X-ray spectroscopy
EM: electron microscopy
EPR: electron paramagnetic resonance
ESI: electrospray ionization
EXAFS: extended X-ray adsorption fine structure
FLD: fluorescence detector
HA: humic acids
HDC: hydrodynamic chromatography
HPLC: high performance liquid chromatography
ICP-OES/MS: inductively coupled plasma optical emission spectroscopy/mass spectrometry
IR: infrared
LIBD: laser induced breakdown detection
MALDI: matrix-assisted laser desorption/ionization
MALS: multi-angle light scattering
MS: mass spectrometry
NTA: nanoparticle tracking analysis
NMR: nuclear magnetic resonance
SEC: size exclusion chromatography
Sed-FFF: sedimentation field flow fractionation
SP-ICP-MS: single particle inductively coupled plasma mass spectrometry
SRHA: Suwannee River humic acids
TOF: time of flight
UHR-MS: ultra-high resolution mass spectrometry
UVD: ultraviolet detector
VISC: differential viscosimetry
XRD: X-ray diffraction

Chapter 1

Introduction and objectives

Table of contents

1   Nanoparticles and colloids in the environment

1.1   On definition and physical meaning

It is traditional to recall the definition of nanoparticles at the beginning of books or theses addressing nanomaterials. This is not always due to a lack of imagination during the writing of the introduction. Indeed, the definition of nanomaterial is still matter of debate. Without entering the details of this discussion, which were comprehensively reviewed elsewhere (Lövestam et al., 2010), it is important to explain that the definition of nanomaterial is not based on a scientific need but on the necessity to regulate the use of emerging materials with unique properties.

In October 2011 the European Commission published official recommendations for the definition of nanomaterial (Commission, 2011). Those recommendations are based on several years of debate which involved international scientific experts. The recommended definition is the following (Definition of a nanomaterial, n.d.):

"A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.
In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50 % may be replaced by a threshold between 1 and 50 %.
By derogation from the above, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials."

At present, the definition of the European Commission seems to be widely accepted. The focus on size gave a strong impulse for further developments of sizing techniques since a harmonized size measurement method still must be developed (Commission, 2011). From the point of view of the regulation authorities, this definition may be a good compromise.

From the scientific perspective however, this recommendation can be criticized for being based solely on the size of the constituent particles of a material and not on its physical properties (Maynard, 2011). Indeed, size may not be the best descriptor for identifying the safety and environmental risk of some nanomaterials (Maynard, 2011). There is hence a risk that some products may be considered as bulk material although they content a small portion of highly toxic nanomaterial (e.g. vermiculite used in construction) (Maynard, 2011). This definition also ignores the specificity of each material by reducing the problem of the risk assessment to the determination of the size. Furthermore, there are plenty of publications demonstrating that specific physical and biological properties become observable only below a certain size threshold. Published recommendations based on literature data concerning this so-called "nano-effect" suggest that specific physical or chemical properties due the size do not appear above 30 nm in size (Auffan et al., 2009). The 100 nm threshold is thus purely arbitrary, as recognized by the European Commission itself (Commission, 2011):

"An upper limit of 100 nm is commonly used by general consensus, but there is no scientific evidence to support the appropriateness of this value."

For regulation purposes, which should consider the realistic risk represented by a product, a definition based on a set of selected physical properties, including e.g. human toxicity, would be more meaningful (Maynard, 2011).

In the last decade, the term "nanoparticle" has been more and more used in environmental sciences for referring to engineered colloids and the term "colloids" for dispersed particles of natural origin. This use may be confusing, since synthetic colloids may not be nanoparticles in the sense of the European Commission (e.g. large polymers) and nanoparticles are commonly found in nature (Wigginton, Haus and Hochella Jr, 2007). In addition, it is sometimes highly challenging to distinguish between natural and engineered nanoparticles, since there is no standard method for that purpose.

In order to avoid the use of the term "nanoparticle" which is obviously matter of confusion and more related to marketing than to science, the term "colloid" will be preferred through this thesis and its related publications. The latter term is also convenient, since its definition is based on a clear, easily observable property: the dispersability of the particles. The retained definition for colloids follows the traditional one, which can be found in text books (Hunter, 2001) and which defines colloids as particles, molecules or molecular assemblies small and light enough to remain dispersed in their medium. For all cases where the term "nanoparticle" will be used, this term will refer to the definition recommended by the European Commission.

Following the same set of recommendations, agglomerates or aggregates will be also considered as "nanomaterial" (Commission, 2011). Unfortunately, the terms "aggregates" and "agglomerates" were also matter of debate as they are often misused in scientific publications. Currently, the term "aggregate" is used to denote any type of structure formed by attachment of small particles to each other. This use contradicts several textbook definitions referring to "aggregate" only for irreversibly attached primary particles, while "agglomerate" refers to reversible attachment (Nichols et al., 2002). However, it is difficult to estimate the strength of attachment for a specific type of particle in practice. Furthermore, the nature of the attachment changes with the conditions. For instance, agglomerates of silver particles may become aggregates if chlorine is added into the solution (Li, Lenhart and Walker, 2010).

In order to avoid confusion when referring to agglomerates or aggregates, published recommendations will be followed in this thesis (Nichols et al., 2002). In this work, the term "agglomerate" will be used to denote any structure formed from single particles (similar or not) attached to each other if no further information on its structure is known. When agglomerates are formed by a molecular bridging mechanism, they will be denoted as "flocs". Agglomerates which can release single particles or even completely break under the effect of shear (stirring, ultrasounds, etc.) or surfactants will be denoted as "soft agglomerates", while "hard agglomerates" will denote agglomerates formed in a way that the agglomeration is irreversible. The term "aggregates" will be reserved for a structure formed of particles grown together. This choice was not consequently followed in the published chapters due to the contradicting point of view of one reviewer about this definition. Based on these clear and unambiguous definitions the nature and origin of natural or artificial colloids will be presented with the concerns and the questions associated to them.

1.2   Natural inorganic colloids in freshwaters

Natural colloids are fascinating for themselves as they play a fundamental, but only partly understood, role in the environment. Although organic colloids are also a crucial part of the ecosystem, we will focus on inorganic colloids in this work, since the science and the analytical

techniques required for both types of colloids differ fundamentally. As shown in the chapter 2, natural organic matter and pollutants can adsorb onto colloid influencing the fate of both colloids and sorbate. Therefore, natural colloids are crucial links of the element cycling. In addition, they are highly challenging analytes as they show high diversity in composition, shape and structure. They constitute a natural colloidal background, which makes the detection of specific colloids such as engineered nanoparticles especially difficult. Several reviews and books address natural colloids (Wigginton, Haus and Hochella Jr, 2007; Wilkinson and Lead, 2007). This section aims to give an overview on the diversity of natural colloids and to give some keys to understand the analytical challenges encountered during the analysis of engineered colloids.

The main source of natural colloids is weathering (Wilkinson and Lead, 2007). Typically, colloid minerals can detach from soil (e.g. during rain fall) or be produced by mechanical forces through glacial erosion in glacial lake or river (Wilkinson and Lead, 2007). For instance, aluminosilicates and quartz originate from weathering (Wilkinson and Lead, 2007). Such colloids have often very irregular shape. Another source of colloids is the precipitation of insoluble salts. Once nuclei are formed different growth mechanisms can occur and lead to diverse morphologies. Crystal growth, Ostwald ripening and aggregation are possible mechanisms for mineral growth under environmental conditions (Wigginton, Haus and Hochella Jr, 2007). Examples of natural colloids formed from insoluble salts are iron and manganese oxides in surface waters (Wigginton, Haus and Hochella Jr, 2007) and calcite in lake and ocean (Wilkinson and Lead, 2007). Iron oxides and metal sulphides precipitate in anoxic waters (Wilkinson and Lead, 2007).

Microorganisms directly or indirectly synthesize colloids. Some species of bacteria, called magnetosoms, have organelles containing magnetite colloids (Bazylinski and Frankel, 2004). Other species reduce dissolved metals in order to gain energy. Their activities produce sometimes particulate waste containing the respective metal in the form of oxides or sulphides. For instance, the main source of particulate manganese oxides is thought to be of bacterial origin (Tebo et al., 2004) and bacteria can also produce iron sulphides (Watson et al., 2000) and uraninite (UO_2) (Wigginton, Haus and Hochella Jr, 2007) colloids.

Aluminosilicates are the most abundant colloids in aquatic systems and can be found in most rivers and lakes around the world (Wilkinson and Lead, 2007). Their structure and composition are diverse with plate-shape or irregular particle shape. This complex shape has for consequence an anisotropic surface charge distribution (Furukawa et al., 2009). Thus, clay minerals form agglomerates with complex morphology which depends on the solution conditions. The sorption and ion exchange properties of aluminosilicates make them attractive for the industry.

Iron oxides are often formed by precipitation of $Fe^{(III)}$ and by bacteria (Wilkinson and Lead, 2007). These different origins explain the high diversity observed in the structure of iron oxides found in the environment. For instance, hematite, goethite (α-FeOOH), lepidocrotite (γ-FeOOH), maghemite (α-Fe_2O_3), magnetite (Fe_3O_4) and ferrihydrite were observed in surface waters (Wilkinson and Lead, 2007). Some iron oxides such as ferrihydrites are metastable and undergo chemical reactions, phase changes and recrystallization throughout their lifetime (Wilkinson and Lead, 2007). Iron oxides can be found in most rivers and lake where they interact strongly with bacteria (Bonneville et al., 2006; Neal et al., 2005). For instance, systematic characterization of iron oxides was done in the Amazon River (Allard et al., 2004) and in a fresh water lake (Tipping and Ohnstad, 1984).

Manganese oxides have been identified in eutrophic lake, in the Black Sea and in the Baltic Sea for instance (Wilkinson and Lead, 2007). The biogeochemical cycle of manganese is essentially controlled by biological processes involving redox reactions with dissolved $Mn^{(II)}$ and insoluble $Mn^{(III, IV)}$ oxyhydroxydes (Tebo et al., 2004).

More related to human activities, some pollutants may undergo chemical and morphological changes leading to the formation of colloids. For instance, mining activities may also result in the release of mercury sulphide colloids (Lowry et al., 2004). Traces of iron, copper and zinc sulphide clusters were found in American rivers (Rozan et al., 2000). Thus, human activities can strongly modify the colloidal composition of natural waters when they are in contact with landfill fields, for instance. Natural colloids have been increasingly studied. Considering the recent development in analytical techniques (see chapter 3), a plenty of new natural particles will be surely discover in the future.

1.3 Engineered inorganic colloids

1.3.1 Most common inorganic nanomaterials and some of their applications

In the last decades, significant improvements in the synthesis, the characterization tools, and the understanding of physical properties on the nanoscale level have set the basis of an exponential growth of commercially available products containing nanomaterials (López-Serrano et al., 2014). Nano-engineering and nano-chemistry developed to a large extent during the last 15 years. As a proof of the dynamics of this research field, the most important journals in the field of nanosciences were created in the last 15 years; see for instance: Nano Letters (2001), Small (2005), Nature Nanotechnology (2006), Nano Today (2006), ACS Nano (2007) and Nano Research (2009). This is due to highly promising properties of nanomaterials. Beyond effects due to the high surface area of colloids, specific physical and chemical properties have been observed to appear at the nanoscale. Plasmon resonance observed through specific light absorbance of noble metals (Thanh, Maclean and Mahiddine, 2014), superparamagnetism of magnetite (Huber, 2005) and increased adsorption of molecules per unit of surface area on TiO_2 (Zhang et al., 1999) are classical examples of such properties restricted to the nanoscale.

Silver colloids represent 30% of the nanomaterials present in consumer products where they are usually used as antibacterial agent (Wijnhoven et al., 2009). For instance, "nano-silver" can be found in socks and washing machines (Benn and Westerhoff, 2008) or in medical products (López-Serrano et al., 2014). TiO_2 colloids have a high absorption band in the UV range and show interesting photocatalytic properties (Chen and Mao, 2007), which can be used in diverse fields such as in photovoltaic applications (Chen and Mao, 2007). TiO_2 colloids are also widely spread because of their low price and supposed minimal toxicity. They are used as whitening pigments (López-Serrano et al., 2014) in various paints and sunscreens (Labille et al., 2010), where they are sometimes doped with other metals (Chen and Mao, 2007) or implemented in composite structures (e.g. coated with alumina and polydimethylsiloxane in cosmetic application (Labille et al., 2010)). Magnetic colloids are less common but highly relevant for environmental applications. These particles are mainly made from iron oxides. As they are magnetic, they can be selectively extracted from a medium. Such particles are hence promising for water purification (Liu, Zhao and Jiang, 2008). For instance, removal of $Cr^{(VI)}$ by humic acids coated magnetic particles has been reported (Jiang et al., 2014). $Fe^{(0)}$ particles have been implemented for soil remediation (Zhang, 2003; Karn, Kuiken and Otto, 2009). Their high reactivity, surface area and mobility make them highly attractive for remediation of soil polluted with polychlorinated biphenyl compounds (McDowall, 2010; Wang and Zhang, 1997).

Probably less relevant for the environment, although attractive as model colloids due to their high chemical and colloidal stability, gold colloids are mostly used for biological and medicinal application (Sergeev, 2001), where they have been used as tracers (Lasne et al., 2006). Fluorescent quantum

dots (CdSe, CdS, CdZn, etc.) also find abounding applications for medical imaging or sensorics (López-Serrano et al., 2014). $Pd^{(0)}$ colloids are used as high efficiency catalysts for diverse reactions (Sergeev, 2001). CeO_2 is mostly used as nanomaterial in the automotive industry but also in diverse consumers products for his high oxygen storage, UV-absorbance and low redox potential of the $Ce^{(IV)}/Ce^{(III)}$ couple (Cornelis et al., 2011). $B^{(0)}$ colloids are used in rocket fuel (Liu et al., 2010).

These applications, far from being exhaustive, show the wide applicability of nanomaterials in chemistry, biology, physic, engineering sciences and environmental sciences. There is nowadays no doubt that, in the next decades, nanomaterials will become increasingly common in our all-day life and may even follow a similar development pattern than polymeric materials during the second half of the XXth century. In the latter case, it would be urgent to assess their risk for the health and the environment, before a comparable massive pollution becomes evident. Therefore, the understanding of their possible release into the environment is crucial.

1.3.2 Scenarios for release of nanomaterials in the environment

Numerous scenarios have been postulated for the release of colloidal pollutants in the environment. It is clear that the entrance of nanomaterials strongly depends on their initial composition and the manner they are implemented into a commercial product. Release through abrasion of paints and of construction materials is one of the most expected release pathway for TiO_2 colloids (Nowack et al., 2012). When nanomaterials accumulate in the urban water system, most of them will be adsorbed onto biosolids and can be amended on landfill and agricultural soils (Kiser et al., 2009). A portion of the colloids could also remain suspended in water and run out of waste water treatment plants (Benn and Westerhoff, 2008; Kaegi et al., 2011; Limbach et al., 2008; Kiser et al., 2009). Metallic and carbonaceous colloids are released in the atmosphere through waste incineration and reach other media after deposition or rainfall events (Nowack et al., 2012; Gottschalk et al., 2009). Washout of colloidal particles containing various heavy metals including Pb, As, Cr and Sn from waste leachates was observed (Hennebert et al., 2013). This demonstrates the possibility of the release of colloids by human activities in an accidental and unexpected manner. In addition, massive accidental pollution events during production or transport of engineered colloids will become increasingly probable in the future.

A difficulty of predicting the release of nanomaterial in the environment is that most engineered colloids may be strongly altered during their life-time and disposal time. For instance, silver colloids are sulphidized in waste water treatment plants and the particles that are released in the aquatic system are probably in the form of Ag_2S colloids (Kaegi et al., 2011). The hydrophobic coating of TiO_2 particles used in cosmetic products can be degraded during use, increasing the solubility of the particles (Labille et al., 2010). Partial or complete dissolution is expected for ZnO particles released in water due to the instability of this phase at neutral pH (Bian et al., 2011; Mohd Omar, Abdul Aziz and Stoll, 2014). Surprisingly, partial dissolution of TiO_2 particles in swimming pool has been reported (David Holbrook et al., 2013). Knowledge of the original materials produced by the industry is therefore insufficient for understanding their release and their fate. It is hence crucial to determine which transformations occur during the life-time of these materials and determine the actual characteristics of the particles released into the environment.

Modeling the fate of colloids is highly challenging because of the diverse parameters that have to be known for developing a reliable and realistic model. This is due to the uncertainty linked to the input parameters connected to the dynamic properties of colloids. For instance, attachment coefficients of colloids on different surfaces, bioassimilation and sedimentation rates are parameters requiring a

precise knowledge on the corresponding mechanisms. Since this precise knowledge is still not available for nanomaterials, such models are intrinsically imprecise. Nonetheless, they can be helpful to determine an order of magnitude for the concentration and the flux of colloids in different environmental media. Hoayang and Cohen proposed a multimedia distribution model for predicting the fate of diverse colloids in a given region (Liu and Cohen, 2014). The authors estimated the concentrations of engineered colloids remaining in a simulated open system (table 1.1). Considering the concentration, the most relevant materials are TiO_2, iron (metal or oxides), SiO_2, ZnO, CeO_2 and Al_2O_3. The concentration of silver is negligible in all media compared to the doses required to observed biological effects (Fabrega et al., 2011). All materials show similar tendency for the compartmental repartition expected silver and ZnO due to their ability to dissolve in environmental conditions. The highest concentrations were found in the sediment and in soil, while concentrations in water were in the ng L^{-1} range for most materials.

Table 1.1
Predicted order of magnitude for concentrations of various colloids in the end of one year. Simulation for the case of the region of Los Angeles. Colloids releases are to water and air only. Adapted from Hoayang and Cohen (Liu and Cohen, 2014).

Material	Soil (ng kg^{-1})	Atmosphere (pg m^3)	Water (ng L^{-1})	Sediment (µg kg^{-1})
TiO_2	100-1000	100-1000	100-1000	$1000-10^4$
SiO_2	100-1000	100-1000	100-1000	100-1000
Fe (metal and oxides)	100-1000	100-1000	100-1000	$1000-10^4$
ZnO	100-1000	100-1000	0.01-0.1	1-10
Al_2O_3	100-1000	100-1000	100-1000	$1000-10^4$
Nanoclays	10-100	10-100	1-10	100-1000
CeO_2	10-100	10-100	1-10	100-1000
Carbon nanotubes	10-100	10-100	0.1-1	10-100
Ag	1-10	1-10	$10^{-4}-10^{-3}$	0.01-0.1
Cu (metal and oxides)	1-10	1-10	0.01-0.1	1-10

At a first glance, these results suggest that most colloids will accumulate in the sediments and that this type of media would hence be the most relevant for studying their fate in the environment. However, the estimations of the transport rates by Hoayang and Cohen (table 1.2) suggest that the major part of the particles does not remain in the system but is transported out of the system in water or in the atmosphere (Liu and Cohen, 2014). In addition, it seems that there are few exchanges between air and other media and between soil and water. Therefore, the most important transport phenomena occur in water, in this model and the behavior of colloids in natural waters is decisive for their fate in the environment. Thus, this model suggests that it is crucial to understand the mechanisms determining the behavior of colloids in the aquatic system, especially the sedimentation and stabilization mechanisms.

Table 1.2
Predicted mass distribution and intermedia transport rate of TiO_2 colloids in the end of one year. Simulation for the case of the region of Los Angeles. The total release from the source is estimated to be 9266 kg/y. Adapted from Hoayang and Cohen (Liu and Cohen, 2014).

	Soil	Atmosphere	Water	Sediment
Source Release (% of total release)	0	9.30	90.70	0
Mass distribution (% of total amount)	2.53	0.03	1.30	96.15
Outflow (% of total release)	-	8.40	57.89	-
Major transport pathway	Wet deposition from the atmosphere	Re-suspension from the soil	-	Sedimentation

1.4 Fate in aquatic systems: relevant factors

Aquatic systems are composed of inorganic ions, organic (macro)molecules, natural colloids, microorganisms and natural surfaces (e.g. minerals, sediments, organisms). Each of these actors interacts directly or indirectly with engineered colloids when they are released into the aquatic systems. Figure 1.1 illustrates the complexity and the interconnectivity of the mechanisms determining the fate of engineered colloids in the aquatic systems. Aging processes such as adsorption of natural compounds, dissolution and agglomeration are mostly influenced by solution chemistry, although interactions with inorganic colloids and microorganisms are also important (Lowry et al., 2012; Christian et al., 2008; Batley, Kirby and McLaughlin, 2012). Transport processes are mostly influenced by the nature of the natural surfaces and the solution chemistry, whereas bioassimilation is influenced by all actors (Neal, 2008). Solution chemistry is clearly a central actor in all these processes, since it determines the physical and chemical properties of the engineered colloids. Nonetheless, all constituents of aquatic systems are highly interconnected as shown on the figure 1.1. Therefore, understanding such a complex system requires both accurate knowledge on the individual processes and a global interdisciplinary approach. Indeed, the screening of all influencing parameters on a systematical basis is under regular laboratory conditions unrealistic, since it implies the implementation of an excessively large number of experiments. Combination of experiments focused on the understanding of specific processes and pragmatic monitoring of contaminated realistic systems (e.g. mesocosms) is one of the best strategies for dealing with this complexity.

As each type of engineered colloid has specific properties due to the original material, the original capping agent and the prerelease aging process, their fate in aquatic systems should be investigated on an individual basis. Considering the high variety of engineered colloids patented in the last years (Leitch, Casman and Lowry, 2012) and the complexity of the various relevant processes occurring in the environment, it seems highly improbable that all these materials will be one day exhaustively investigated for their fate and impact on the environment. Therefore, an approach merging different types of colloids into groups showing similar properties in environmental media would be highly useful. Unfortunately, this is still not possible due to a lack of knowledge on the relevant processes. However, it is possible to propose hypothetic pathways based on the actual state of knowledge (Fabrega et al., 2011; Sharma, 2009; Lowry et al., 2012; von der Kammer et al., 2012). Depending on

the interaction pattern of the colloids released in aquatic systems, different plausible pathways can be described:

- Sedimentation out of the aquatic system to the sediment. This could be the case for colloids agglomerating to form heavier particles (homoagglomeration) or attaching to natural colloids (heteroagglomeration). Agglomeration may be reversible under some conditions (Baalousha, 2009; Mohd Omar, Abdul Aziz and Stoll, 2014; Loosli, Le Coustumer and Stoll, 2013).
- Immobilization due to attachment on natural surfaces/organisms. In this case, the affinity of colloids for natural surface is high and their mobility is highly reduced. Attachment may be reversible under some conditions (Franchi and O'Melia, 2003).
- Complete dissolution of the particle. It concerns thermodynamically unstable phases under environmental conditions (e.g. ZnO and to some extent silver). Particles do not exist as such and classical theories for the speciation of ions can be used.
- Remaining suspended in water. For highly stable particles which do not interact with environmental constituents or which are stabilized after interacting with them.
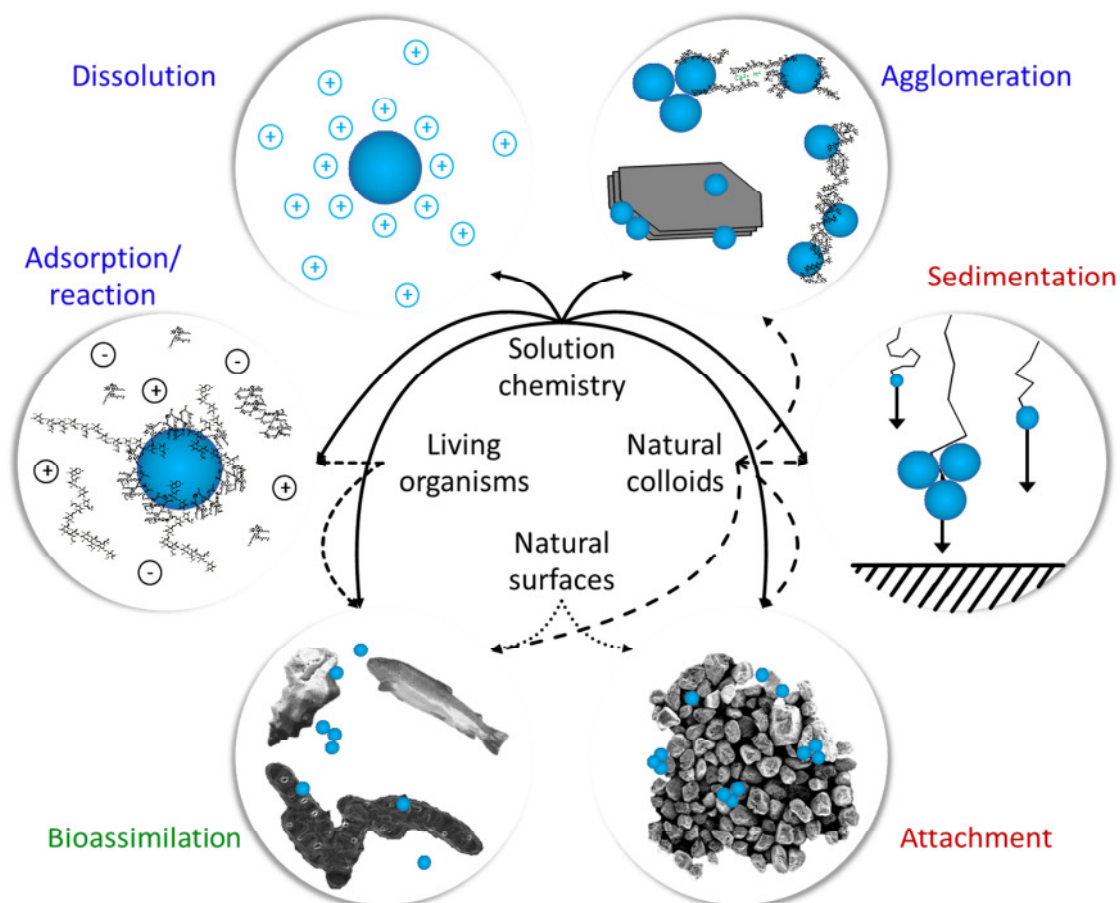
Figure 1.1: schematic description of the most relevant processes and actors determining the fate of engineered colloids in the environment. The processes written in blue participate to the colloids aging, while the processes written in red and green participate to the transport and toxicity of colloids, respectively. Arrows denote the influence of one type of actor on a process. Quantitative changes may be induced by changes in physical parameters such as temperature and shear forces (e.g. flow rate).

In order to determine which pathway will be followed by each group of merged engineered colloids, it is necessary to determine the main driving processes for these given types of particles. Based on precise knowledge of each individual process in the laboratory combined to investigations in more realistic media, the most relevant processes occurring in aquatic media could be identified.

Solution chemistry has a central role for determining the properties of colloids and, thus, the contribution of the different pathways to the global picture. For instance, the surface charge will determine the type and the amount of ions and dissolved organic matter (DOM) adsorbed onto the particles (see chapter 2) and the electrostatic forces between particles and other constituents (e.g. natural colloids and natural surfaces). Surface charge is itself influenced by the adsorption of DOM or inorganic ions and by the solution conditions (e.g. ionic strength and pH). Agglomeration is a well-known phenomenon in colloid chemistry which highly depends on the ionic strength, the ion valences and the nature of the particle coating (Hunter, 2001). Thus, inorganic ions usually strongly influence the agglomeration process (Hotze, Phenrat and Lowry, 2010; Petosa et al., 2010). DOM-colloids interactions and their consequences for the stability of colloids in environmental media are described in a review article as a part of this PhD-thesis (chapter 2). In this review the adsorption of DOM onto engineered or natural colloids is discussed. The formation of a DOM coating on the surface of the colloids deeply modifies their chemical and physical properties. The influence of DOM on agglomeration, attachment and dissolution of various colloids is also discussed in detail. Natural colloids and microorganisms can interact with engineered colloids by forming heteroagglomerates (Chowdhury, Walker and Mylon, 2013; Findlay, Thompson and Tipping, 1996; Wilkinson, Joz-Roland and Buffle, 1997). This is especially relevant as the concentration of natural colloids (mg L^{-1} range) is much higher than the expected concentration of engineered colloids (ng L^{-1} range).

Despite numerous laboratory studies (Batley, Kirby and McLaughlin, 2012; Aiken, Hsu-Kim and Ryan, 2011; Schaumann et al., 2014; Christian et al., 2008; Lowry et al., 2012; Levard et al., 2012), several isolated processes still remain a challenge to investigate. For instance, reversibility of agglomeration, hetero-agglomeration, dissolution and interactions of colloids with DOM and microorganisms are still not fully understood, especially for engineered colloids (Schaumann et al., 2014; Quik, van De Meent and Koelmans, 2014). However, these processes are highly important for identifying main pathways. In particular, nature and structure of DOM coating and its implication for agglomeration and attachment processes are still not known for several engineered colloids (e.g. silver, Ag_2S). In addition, the lack of an exhaustive review hindered a clear understanding of the numerous data available from the literature about DOM interactions with colloids. Furthermore, analytical techniques dedicated to the accurate determination of the size and shape of the targeted colloids in mixture containing different colloids are still not available on a routine basis.

2   Ph.D. project and structure of the dissertation

Understanding of the fate of engineered colloids in the environment requires a multidisciplinary approach relying on realistic large scale experiments and on laboratories studies of isolated processes. The project INTERNANO, financed by the German Research Foundation (Internano webpage, n.d.), has been dedicated to this task. The overall aim of INTERNANO is to obtain systematic understanding of the central mechanisms and environmental processes determining the fate and the impact of engineered nanoparticles towards microbial biofilms, aquatic invertebrates and transport mechanisms within the water-soil path. The objective is to understand how original material properties and environmental conditions determine the pathway of engineered

nanoparticles at the interfaces water-sediment water-soil. In the frame of this project, mesocosm and field experiments (bank filtration) have been planned for understanding colloids mobility and transfer from one media to the others in a pragmatic manner. In addition, diverse laboratory experiments carried out under standard conditions have been conducted for shedding light on the most relevant mechanisms occurring in environmental samples (agglomeration, dissolution, DOM-coating).

The present work was designed in the frame of the INTERNANO project and aimed at developing analytical tools for investigating the interactions of DOM with engineered colloids. The lack of a systematic review contributed to the difficulties in understanding the interactions of DOM with colloids in general. In order to fill this gap and to gain new knowledge out of a literature synthesis, a systematic literature review based on meta-analysis (around 260 articles) about DOM interactions with inorganic colloids was carried out (chapter 2). Such knowledge helped in the choice of analytical methods for addressing the remaining challenges.

From this review, it becomes clear that a better understanding of DOM interactions with inorganic colloids is needed; especially fractionation of DOM upon adsorption deserves further investigations. Improvements in the characterization methods for both colloids and DOM would be highly helpful for this task. Another conclusion of this review chapter was that new knowledge about the effect of DOM on the homo- or hetero-agglomeration requires dedicated analytical techniques. Information on the geometry of these agglomerates informs on the agglomeration mechanism (Adachi, 1995). Monitoring the morphology of hetero-agglomerates or flocs over the time requires measuring particle properties such as size, shape and elemental composition in environmental media on a routine basis. In addition, size measurements of colloids were also required for samples from mesocosm and field experiments carried out during the INTERNANO project.

A literature study of the potential of available analytical techniques for measuring these parameters in environmental samples (chapter 3, part 1) revealed that hydrodynamic chromatography (HDC) coupled to ICP-MS was one of the most promising techniques for this purpose. Simple implementation and method development combined to analytical versatility and robustness were convincing arguments for choosing HDC-ICP-MS as a central analytical technique in the exploration of DOM effect on agglomeration of silver colloids at low particle concentration. Furthermore, it was demonstrated that HDC-ICP-MS is suitable for the sizing of diverse colloids in samples with high organic loading (Tiede et al., 2010, 2009)

However, an exhaustive literature survey of the method development of HDC (chapter 3, part 2) showed that methodological aspects which are crucial for the measurement of colloids in complex media were not investigated for HDC-ICP-MS. In particular, it was unclear to which extent the method could be adapted to various samples with various requirements and if it could be used for the quantification of colloids. In order to be able to provide accurate results and to avoid or, at least, be aware of measurement artefacts, methodological developments of HDC-ICP-MS were undertaken (chapters 4-6).

In particular, the chapter 4 is dedicated to the validation of a quantification method for gold colloids and to the determination of the leeway of HDC-ICP-MS in terms of elution parameters. The adaptability of these parameters to the sample requirements is also discussed. This discussion was necessary for demonstrating the applicability to environmental samples, which is illustrated by two concrete environmentally relevant examples (silver colloids in reconstituted natural water; TiO_2 and ZnO colloids in sunscreen). Experiments with silver colloids and humic acids suggested that HDC is adapted for the sizing of colloids in media containing organic matter but could not be used for direct detection of DOM adsorbed on the colloid surface. The limits of HDC in term of particle properties

(composition and shape) are explored in the chapter 5, where the high versatility of HDC is demonstrated, despite strong limitations of the sizing of non-spherical particles. An experimental approach using HDC single particle ICP-MS (HDC-SP-ICP-MS) is proposed and tested for overcoming this difficulty and suggest a high potential of this coupling technique for the analysis of the shape of unknown particles. The ability of HDC-SP-ICP-MS for distinguishing colloids having different shapes is critically discussed in this chapter.

The potential of HDC-SP-ICP-MS for analyzing complex particles in environmental media was further explored. In the chapter 6, a new data-analysis method is proposed for analyzing the geometry of gold colloid agglomerates using this technique. This contribution was the result of a close collaboration with Mr. Denis Rakcheev, whose PhD project addresses the implementation of SP-ICP-MS for environmental samples. While Mr. Rakcheev developed the software for the data-analysis, the experimental design and the data analysis are due to the present author. The laboratory experiments were performed equally by these two authors.

In parallel to these methodological points, HDC was applied to diverse systems in the frame of several internal and external cooperation projects. Post-synthesis quality assessment and agglomeration kinetics experiments in Rhine River water and standard biological medium of silver colloids, prepared for common experiments in the frame of the project Internano, were carried out with Dr. George Metreveli (Metreveli, Philippe and Schaumann, 2014). Similar silver particles were measured after being aged in different soil solutions by Dr. Sondra Klitzke from the Technische Universität Berlin (non-published results). Magnetite colloids in presence and absence of humic acid were measured for M. Pavel Ondruch in the frame of the methods development of NMR-relaxometry (non-published results). Gold colloids functionalized with different polyethylene glycol based ligand with contrasting pK_a values were also measured in collaboration with Mr. Denis Rakcheev (non-published results). The formation of raspberry-like supramolecular assemblies of polyethylene oxide and polyacrylic acids was confirmed using HDC-UV, isothermal calorimetry, DLS and TEM (Chenal et al., 2014). The stabilizing effect of fulvic acids upon dissolution of uranyl phosphate colloids was demonstrated using HDC-ICP-MS in cooperation with Dr. Mohamed Azeroual (publication in preparation). Finally, the size of natural iron containing colloids formed under anoxic conditions in a lake was determined using HDC-ICP-MS in collaboration with Mrs. Jenny Bravidor from the Helmotz-Center for Environmental research in Magdeburg (Germany) (non-published results).

Based on this method development, the stability of silver colloids suspended in reconstituted natural water containing DOM and model inorganic colloids was studied (chapter 7). The discussion of the results and their implication for the environmental fate of silver colloids is combined with results and conclusions from a study carried out by Dr. George Metreveli (Metreveli, Philippe and Schaumann, 2014). Further attempts to explore these interactions on the molecular basis with HDC combined to UV and fluorescence detectors and with fluorescence spectroscopy are also reported. The conclusions of this chapter illustrate the complexity of the interactions between DOM and silver colloids and the difficulties to analyze both colloids and DOM in environmental media. Possible answers to these difficulties are proposed in the chapter 8, where further development and applications of advanced analytical techniques are proposed. In particular, the potential of HDC-SP-ICP-MS for determining the shape of complex particles and the application of ultra-high resolution mass spectrometry to the analysis of DOM fractionation upon adsorption onto engineered colloids are discussed.

References

Adachi, Y. (1995) "Dynamic aspects of coagulation and flocculation," *Advances in Colloids and Interface Science*. Elsevier, 56, pp. 1–31.

Aiken, G. R., Hsu-Kim, H. and Ryan, J. N. (2011) "Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids," *Environmental Science & Technology*. American Chemical Society, 45(8), pp. 3196–3201.

Allard, T., Menguy, N., Salomon, J., Calligaro, T., Weber, T., Calas, G. and Benedetti, M. (2004) "Revealing forms of iron in river-borne material from major tropical rivers of the Amazon Basin (Brazil) 1," *Geochimica et Cosmochimica Acta*. Elsevier, 68(14), pp. 3079–3094.

Auffan, M., Rose, J., Bottero, J. Y., Lowry, G. V., Jolivet, J. P. and Wiesner, M. R. (2009) "Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective," *Nature Nanotechnology*. Nature Publishing Group, 4(10), pp. 634–641.

Baalousha, M. (2009) "Aggregation and disaggregation of iron oxide nanoparticles: Influence of particle concentration, pH and natural organic matter," *Science of the Total Environment*. Elsevier, 407(6), pp. 2093–2101.

Batley, G. E., Kirby, J. K. and McLaughlin, M. J. (2012) "Fate and risks of nanomaterials in aquatic and terrestrial environments," *Accounts of Chemical Research*. ACS Publications, 46(3), pp. 854–862.

Bazylinski, D. A. and Frankel, R. B. (2004) "Magnetosome formation in prokaryotes," *Nature Reviews Microbiology*. Nature Publishing Group, 2(3), pp. 217–230.

Benn, T. M. and Westerhoff, P. (2008) "Nanoparticle silver released into water from commercially available sock fabrics," *Environmental Science & Technology*. ACS Publications, 42(11), pp. 4133–4139.

Bian, S. W., Mudunkotuwa, I. A., Rupasinghe, T. and Grassian, V. H. (2011) "Aggregation and dissolution of 4 nm ZnO nanoparticles in aqueous environments: influence of pH, ionic strength, size, and adsorption of humic acid," *Langmuir*. ACS Publications, 27(10), pp. 6059–6068.

Bonneville, S., Behrends, T., Cappellen, P. V., Hyacinthe, C. and Röling, W. F. M. (2006) "Reduction of Fe (III) colloids by Shewanella putrefaciens: A kinetic model," *Geochimica et Cosmochimica Acta*. Elsevier, 70(23), pp. 5842–5854.

Chen, X. and Mao, S. S. (2007) "Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications," *Chemical Reviews*. ACS Publications, 107(7), pp. 2891–2959.

Chenal, M., Rieger, J., Philippe, A. and Bouteiller, L. (2014) "High Yield Preparation of All-Organic Raspberry-like Particles by Heterocoagulation via Hydrogen Bonding Interaction," *Polymer*. Elsevier, 55, pp. 3516–3524.

Chowdhury, I., Walker, S. L. and Mylon, S. E. (2013) "Aggregate morphology of nano-TiO2: role of primary particle size, solution chemistry, and organic matter," *Environmental Science: Processes & Impacts*. Royal Society of Chemistry, 15(1), pp. 275–282.

Christian, P., von der Kammer, F., Baalousha, M. and Hofmann, T. (2008) "Nanoparticles: structure, properties, preparation and behaviour in environmental media," *Ecotoxicology*. Springer, 17(5), pp. 326–343.

Commission, E. (2011) "Commission recommendations on the definition of nanomaterial," *Official Journal of the European Union*.

Cornelis, G., Ryan, B., McLaughlin, M. J., Kirby, J. K., Beak, D. and Chittleborough, D. (2011) "Solubility and Batch Retention of CeO2 Nanoparticles in Soils," *Environmental Science & Technology*. ACS Publications.

David Holbrook, R., Motabar, D., Quiñones, O., Stanford, B., Vanderford, B. and Moss, D. (2013) "Titanium distribution in swimming pool water is dominated by dissolved species," *Environmental Pollution*. Elsevier, 181, pp. 68–74.

Definition of a nanomaterial (n.d.). http://ec.europa.eu/environment/chemicals/nanotech/faq/definition_en.htm (Accessed: 5, 2014).

Fabrega, J., Luoma, S. N., Tyler, C. R., Galloway, T. S. and Lead, J. R. (2011) "Silver nanoparticles: Behaviour and effects in the aquatic environment," *Environment International*. Elsevier, 37(2), pp. 517–531.

Findlay, A. D., Thompson, D. and Tipping, E. (1996) "The aggregation of silica and haematite particles dispersed in natural water samples," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Elsevier, 118(1), pp. 97–105.

Franchi, A. and O'Melia, C. R. (2003) "Effects of natural organic matter and solution chemistry on the deposition and reentrainment of colloids in porous media," *Environmental Science & Technology*. ACS Publications, 37(6), pp. 1122–1129.

Furukawa, Y., Watkins, J. L., Kim, J., Curry, K. J. and Bennett, R. H. (2009) "Aggregation of montmorillonite and organic matter in aqueous media containing artificial seawater," *Geochemical transactions*. Chemistry Central Ltd, 10(2), p. 11.

Gottschalk, F., Sonderer, T., Scholz, R. W. and Nowack, B. (2009) "Modeled environmental concentrations of engineered nanomaterials (TiO2, ZnO, Ag, CNT, fullerenes) for different regions," *Environmental Science & Technology*. ACS Publications, 43(24), pp. 9216–9222.

Hennebert, P., Avellan, A., Yan, J. and Aguerre-Chariol, O. (2013) "Experimental evidence of colloids and nanoparticles presence from 25 waste leachates," *Waste Management*. Elsevier, 33, pp. 1870–1881.

Hotze, E. M., Phenrat, T. and Lowry, G. V. (2010) "Nanoparticle aggregation: Challenges to understanding transport and reactivity in the environment," *Journal of Environmental Quality*. American Society of Agronomy, 39(6), pp. 1909–1924.

Huber, D. L. (2005) "Synthesis, properties, and applications of iron nanoparticles," *Small*. Wiley Online Library, 1(5), pp. 482–501.

Hunter, R. J. (2001) *Foundations of Colloid Science* . Second Edition, Oxford University (ed.). Oxford University Press.

Internano webpage (n.d.). http://www.uni-koblenz-landau.de/landau/fb7/umweltwissenschaften/forschung/internano (Accessed: 3, 2014).

Jiang, W., Cai, Q., Xu, W., Yang, M., Cai, Y., Dionysiou, D. D. and O'Shea, K. E. (2014) "Cr (VI) Adsorption and Reduction by Humic Acid Coated on Magnetite," *Environmental Science & Technology*. ACS Publications.

Kaegi, R., Voegelin, A., Sinnet, B., Zuleeg, S., Hagendorfer, H., Burkhardt, M. and Siegrist, H. (2011) "Behavior of metallic silver nanoparticles in a pilot wastewater treatment plant," *Environmental Science & Technology*. ACS Publications, 45(9), pp. 3902–3908.

Von der Kammer, F., Ferguson, P. L., Holden, P. A., Masion, A., Rogers, K. R., Klaine, S. J., Koelmans, A. A., Horne, N. and Unrine, J. M. (2012) "Analysis of engineered nanomaterials in complex matrices (environment and biota): general considerations and conceptual case studies," *Environmental Toxicology and Chemistry*. Wiley Online Library, 31(1), pp. 32–49.

Karn, B., Kuiken, T. and Otto, M. (2009) "Nanotechnology and in situ remediation: a review of the benefits and potential risks," *Environmental Health Perspectives*. National Institute of Environmental Health Science, 117(12), p. 1813.

Kiser, M., Westerhoff, P., Benn, T., Wang, Y., Perez-Rivera, J. and Hristovski, K. (2009) "Titanium nanomaterial removal and release from wastewater treatment plants," *Environmental Science & Technology*. ACS Publications, 43(17), pp. 6757–6763.

Labille, J., Feng, J., Botta, C., Borschneck, D., Sammut, M., Cabie, M., Auffan, M., Rose, J. and Bottero, J. Y. (2010) "Aging of TiO2 nanocomposites used in sunscreen. Dispersion and fate of the degradation products in aqueous environment," *Environmental Pollution*. Elsevier, 158(12), pp. 3482–3489.

Lasne, D., Blab, G. A., Berciaud, S., Heine, M., Groc, L., Choquet, D., Cognet, L. and Lounis, B. (2006) "Single nanoparticle photothermal tracking (SNaPT) of 5-nm gold beads in live cells," *Biophysical Journal*. Elsevier, 91(12), pp. 4598–4604.

Leitch, M. E., Casman, E. and Lowry, G. V. (2012) "Nanotechnology patenting trends through an environmental lens: analysis of materials and applications," *Journal of Nanoparticle Research*. Springer, 14(12), pp. 1–23.

Levard, C., Hotze, E. M., Lowry, G. V. and Brown, G. E. (2012) "Environmental Transformations of Silver Nanoparticles: Impact on Stability and Toxicity," *Environmental Science & Technology*. ACS Publications, 46, pp. 6900–6914.

Li, X., Lenhart, J. J. and Walker, H. W. (2010) "Dissolution-accompanied aggregation kinetics of silver nanoparticles," *Langmuir*. ACS Publications, 26(22), pp. 16690–16698.

Limbach, L. K., Bereiter, R., Müller, E., Krebs, R., Gälli, R. and Stark, W. J. (2008) "Removal of oxide nanoparticles in a model wastewater treatment plant: Influence of agglomeration and surfactants on clearing efficiency," *Environmental Science & Technology*. ACS Publications, 42(15), pp. 5828–5833.

Liu, H. H. and Cohen, Y. (2014) "Multimedia environmental distribution of engineered nanomaterials," *Environmental Science & Technology*. ACS Publications, 48(6), pp. 3281–3292.

Liu, J., Zhao, Z. and Jiang, G. (2008) "Coating Fe3O4 magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water," *Environmental Science & Technology*. ACS Publications, 42(18), pp. 6949–6954.

Liu, X., Wazne, M., Han, Y., Christodoulatos, C. and Jasinkiewicz, K. L. (2010) "Effects of natural organic matter on aggregation kinetics of boron nanoparticles in monovalent and divalent electrolytes," *Journal of Colloid and Interface Science*. Elsevier, 348(1), pp. 101–107.

Loosli, F., Le Coustumer, P. and Stoll, S. (2013) "TiO2 nanoparticles aggregation and disaggregation in presence of alginate and Suwannee River humic acids. pH and concentration effects on nanoparticle stability," *Water Research*. Elsevier, 47(16), pp. 6052–6063.

López-Serrano, A., Olivas, R. M., Landaluze, J. S. and Cámara, C. (2014) "Nanoparticles: a global vision. Characterization, separation, and quantification methods. Potential environmental and health impact," *Analytical Methods*. Royal Society of Chemistry, 6(1), pp. 38–56.

Lowry, G. V., Gregory, K. B., Apte, S. C. and Lead, J. R. (2012) "Transformations of Nanomaterials in the Environment," *Environmental Science & Technology*. ACS Publications, 46(13), pp. 6893–6899.

Lowry, G. V., Shaw, S., Kim, C. S., Rytuba, J. J. and Brown Jr, G. E. (2004) "Macroscopic and microscopic observations of particle-facilitated mercury transport from New Idria and Sulphur Bank mercury mine tailings," *Environmental Science & Technology*. ACS Publications, 38(19), pp. 5101–5111.

Lövestam, G., Rauscher, H., Roebben, G., Klüttgen, B. S., Gibson, N., Putaud, J.-P. and Stamm, H. (2010) "Considerations on a definition of nanomaterial for regulatory purposes," *Joint Research Centre (JRC) Reference Reports*.

Maynard, A. D. (2011) "Don't define nanomaterials," *Nature*. Nature Publishing Group, 475(7354), pp. 31–31.

McDowall, I. R. (2010) "Dioxin Remediation Technologies."

Metreveli, G., Philippe, A. and Schaumann, G. E. (2014) "Disaggregation of silver nanoparticle homoaggregates in a river water matrix," *Science of The Total Environment*, in press(doi:10.1016/j.scitotenv.2014.11.058).

Mohd Omar, F., Abdul Aziz, H. and Stoll, S. (2014) "Aggregation and disaggregation of ZnO nanoparticles: Influence of pH and adsorption of Suwannee River humic acid," *Science of the Total Environment*. Elsevier, 468, pp. 195–201.

Neal, A. L. (2008) "What can be inferred from bacterium-nanoparticle interactions about the potential consequences of environmental exposure to nanoparticles?," *Ecotoxicology*. Springer, 17(5), pp. 362–371.

Neal, A. L., Bank, T. L., Hochella, M. F. and Rosso, K. M. (2005) "Cell adhesion of Shewanella oneidensis to iron oxide minerals: Effect of different single crystal faces," *Geochem. Trans*, 6, pp. 77–84.

Nichols, G., Byard, S., Bloxham, M. J., Botterill, J., Dawson, N. J., Dennis, A., Diart, V., North, N. C. and Sherwood, J. D. (2002) "A review of the terms agglomerate and aggregate with a recommendation for nomenclature used in powder and particle characterization," *Journal of Pharmaceutical Sciences*. Wiley Online Library, 91(10), pp. 2103–2109.

Nowack, B., Ranville, J. F., Diamond, S., Gallego-Urrea, J. A., Metcalfe, C., Rose, J., Horne, N., Koelmans, A. A. and Klaine, S. J. (2012) "Potential scenarios for nanomaterial release and subsequent alteration in the environment," *Environmental Toxicology and Chemistry*. Wiley Online Library, 31(1), pp. 50–59.

Petosa, A. R., Jaisi, D. P., Quevedo, I. R., Elimelech, M. and Tufenkji, N. (2010) "Aggregation and deposition of engineered nanomaterials in aquatic environments: Role of physicochemical interactions," *Environmental Science & Technology*. ACS Publications, 44(17), pp. 6532–6549.

Quik, J. T., van De Meent, D. and Koelmans, A. A. (2014) "Simplifying modeling of nanoparticle aggregation-sedimentation behavior in environmental systems: A theoretical analysis," *Water research*. Elsevier, 62, pp. 193–201.

Rozan, T. F., Lassman, M. E., Ridge, D. P. and Luther, G. W. (2000) "Evidence for iron, copper and zinc complexation as multinuclear sulphide clusters in oxic rivers," *Nature*. Nature Publishing Group, 406(6798), pp. 879–882.

Schaumann, G. E., Philippe, A., Bundschuh, M., Metreveli, G. Klitzke, S., Rakcheev, D., Grüne, A., Kumahor, S. K., Kühn, M., Baumann, T., Lang, F., Manze, W., Schulz, R. and Vogel, H. (2014) "Understanding the fate and biological effects of Ag- and TiO2-nanoparticles in the environment: The quest for advanced analytics and interdisciplinary concepts," *Science of the Total Environment*, in press(doi:10.1016/j.scitotenv.2014.10.035).

Sergeev, G. B. (2001) "Nanochemistry of metals," *Russian Chemical Reviews*. Turpion Ltd, 70(10), pp. 809–825.

Sharma, V. K. (2009) "Aggregation and toxicity of titanium dioxide nanoparticles in aquatic environment—A Review," *Journal of Environmental Science and Health, Part A*. Taylor & Francis, 44(14), pp. 1485–1495.

Tebo, B. M., Bargar, J. R., Clement, B. G., Dick, G. J., Murray, K. J., Parker, D., Verity, R. and Webb, S. M. (2004) "Biogenic manganese oxides: properties and mechanisms of

formation," *Annual Review Earth Planetary Science*. Annual Reviews, 32, pp. 287–328.

Thanh, N. T. K., Maclean, N. and Mahiddine, S. (2014) "Mechanisms of Nucleation and Growth of Nanoparticles in Solution.," *Chemical Reviews*. doi: 10.1021/cr400544s.

Tiede, K., Boxall, A. B., Tiede, D., Tear, S. P., David, H. and Lewis, J. (2009) "A robust size-characterisation methodology for studying nanoparticle behaviour in 'real'environmental samples, using hydrodynamic chromatography coupled to ICP-MS," *Journal of Analytical Atomic Spectrometry*. Royal Society of Chemistry, 24(7), pp. 964–972.

Tiede, K., Boxall, A. B., Wang, X., Gore, D., Tiede, D., Baxter, M., David, H., Tear, S. P. and Lewis, J. (2010) "Application of hydrodynamic chromatography-ICP-MS to investigate the fate of silver nanoparticles in activated sludge," *Journal of Analytical Atomic Spectrometry*. Royal Society of Chemistry, 25(7), pp. 1149–1154.

Tipping, E. and Ohnstad, M. (1984) "Colloid stability of iron oxide particles from a freshwater lake," *Nature*. Nature Publishing Group, 308(15), pp. 266–268.

Wang, C. B. and Zhang, W. (1997) "Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs," *Environmental Science & Technology*. ACS Publications, 31(7), pp. 2154–2156.

Watson, J., Cressey, B., Roberts, A., Ellwood, D., Charnock, J. and Soper, A. (2000) "Structural and magnetic studies on heavy-metal-adsorbing iron sulphide nanoparticles produced by sulphate-reducing bacteria," *Journal of Magnetism and Magnetic Materials*. Elsevier, 214(1), pp. 13–30.

Wigginton, N. S., Haus, K. L. and Hochella Jr, M. F. (2007) "Aquatic environmental nanoparticles," *Journal of Environmental Monitoring*. Royal Society of Chemistry, 9(12), pp. 1306–1316.

Wijnhoven, S. W. P., Peijnenburg, W. J. G. M., Herberts, C. A., Hagens, W. I., Oomen, A. G., Heugens, E. H. W., Roszek, B., Bisschops, J., Gosens, I., Van De Meent, D. and others (2009) "Nano-silver-a review of available data and knowledge gaps in human and environmental risk assessment," *Nanotoxicology*. Informa UK Ltd UK, 3(2), pp. 109–138.

Wilkinson, K. J., Joz-Roland, A. and Buffle, J. (1997) "Different roles of pedogenic fulvic acids and aquagenic biopolymers on colloid aggregation and stability in freshwaters," *Limnology and Oceanography*. JSTOR, pp. 1714–1724.

Wilkinson, K. J. and Lead, J. R. (2007) *Environmental colloids and particles: behaviour, separation and characterisation*. John Wiley & Sons.

Zhang, H., Penn, R. L., Hamers, R. J. and Banfield, J. F. (1999) "Enhanced adsorption of molecules on surfaces of nanocrystalline particles," *The Journal of Physical Chemistry B*. ACS Publications, 103(22), pp. 4656–4662.

Zhang, W. (2003) "Nanoscale iron particles for environmental remediation: An overview," *Journal of Nanoparticle Research*. Springer, 5(3), pp. 323–332.

Chapter 2

Interactions of Dissolved Organic Matter with Inorganic Colloids and Nanoparticles: a Review

Allan Philippe and Gabriele E. Schaumann

Review article published in *Environmental Science & Technology*

Chapter 3

Evaluation of Current Techniques for Studying Colloids in Complex Media: Introduction to Nano-analytical Methods and Hydrodynamic Chromatography

Table of contents

1 The nano-analytical toolbox for environmental samples

1.1 Introduction

Studying how DOM influence the processes triggering the fate of engineered colloids, in particular homo/hetero-agglomeration and dissolution, requires monitoring the state of colloids in environmentally relevant media. The most important parameters characterizing the state of colloids are size, shape, mass, density, crystalline phase, charge, and elemental composition. Indeed, understanding agglomeration processes in the presence of DOM requires being able to distinguish between agglomerates formed by different mechanisms such as reaction limited agglomerates, diffusion limited agglomerates, flocs and hetero-agglomerates (chapter 2). Information on the mass, size, shape and elemental composition is essential for differentiating them. Furthermore, the adsorption mechanism of DOM onto the surface of colloids is partly determined by the surface chemistry (surface charge, exposed atomic planes, elemental composition).

Over the years, diverse techniques were developed for determining these parameters. In this section, the mostly used analytical methods will be briefly discussed in order to give an idea on the analytical "toolbox" currently available for colloids characterization (Tiede et al., 2008). In this work, only methods with a broad applicability will be addressed. Some techniques like UV-visible-, Raman-, IR-, EPR-, NMR-spectroscopy, HPLC, ESI-, MALDI-, TOF-mass spectrometry, can be applied to some specific samples (Tiede et al., 2008) but lack of versatility and will not be considered here. The focus will also be on the most used techniques for the characterization of colloids, especially sizing techniques. Therefore, this section does not comprehensively review nano-analytical techniques. Furthermore, the focus of this work is on aqueous samples. Methods dedicated to pedogenic or aerial particles are thus beyond the scope of this work.

One of the best strategies for characterizing colloids is to detect and analyze them individually. However, their small size makes their detection challenging. The use of microscopes with high magnification such as electron microscopy (EM) and atomic force microscopy (AFM) are the most efficient representatives of this category for dry samples (Burleson, Driessen and Penn, 2005). For liquid samples Coulter counter (CC) and, more recently, nanoparticle tracking analysis (NTA), laser induced breakdown detection (LIBD) and single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) were developed for detecting individual particles (Tiede et al., 2008; Hassellöv et al., 2008; Simonet and Valcárcel, 2009; Carr et al., 2009). These techniques can be designated as counting methods. The analytical output is the number concentration of particles and the number average of the measured property of the analyzed dispersion. Furthermore, only counting techniques can be used for determining particle concentration without calibration.

X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), energy dispersive X-ray spectroscopy (EDX) and other similar techniques can be used to determine the composition and crystal structure of the particle material (Burleson, Driessen and Penn, 2005). After appropriate separation and digestion steps, the composition of the colloids can be determined using classical elemental analysis such as inductively coupled plasma optical emission spectroscopy/mass spectrometry (ICP-OES/MS) (von der Kammer et al., 2012; Tiede et al., 2008). Detailed discussion about further advanced techniques for determining the elemental composition and the crystal structures of colloids can be found elsewhere (Burleson, Driessen and Penn, 2005).

In situ techniques for liquid samples became polpular with the advance of light scattering techniques (Finsy, 1994). Dynamic light scattering (DLS), multi-angle light scattering (MALS) and ζ-potential measurements rely on the analysis of signal from the whole sample and determinate overall average

values only. Data analysis is based on complex theories which imply several hypotheses on the sample (Finsy, 1994).

Separation techniques isolate the analyte based on one or several of its properties. Using appropriate calibration or theoretical models it is hence possible to quantify these properties. Most common separation techniques are asymmetrical flow-field flow fractionation (AF4), sedimentation field flow fractionation (Sed-FFF), size exclusion chromatography (SEC), analytical ultracentrifugation (AUC), hydrodynamic chromatography (HDC) and capillary electrophoresis (CE) (McHugh and Brenner, 1984; Fedotov et al., 2011; Lespes and Gigault, 2011). The analytical outputs depend on the separation mechanism and the detection system. Since most separation techniques can be coupled online with diverse detection techniques, diverse type of information on the sample can be collected in one measurement (Lespes and Gigault, 2011).

As each technique is based on different sizing principles and data evaluation, even techniques for measuring the same parameter can lead to different results. Therefore, it is useful to define the most important parameters measured by current methods (Hassellöv et al., 2008; Hunter, 2001; Striegel and Brewer, 2012):

- core diameter: diameter of the solid core of a particle. When multilayer particles are considered, the definition can be operationally based on the detection system. In such cases, the core corresponds to the extension of the most external layer which can be detected.
- effective diameter: geometric diameter of the particle (largest distance between two points belonging to the particle) independent of the composition of the particle.
- hydrodynamic diameter: diameter calculated from the diffusion coefficient by using the Stokes-Einstein equation.
- gyration diameter: the root mean square distance of the objects' parts from its center of gravity.

Figure 3.1 summarizes the different parameters and the corresponding techniques for measuring them. This scheme is not exhaustive but should give an idea on the difficulty of selecting analytical methods for the full characterization of colloidal suspensions. Indeed, it is highly improbable to find all these methods in a sole laboratory. Analysts have hence to find the most useful characterization methods for answering specific and well defined questions. In the case of DOM-colloids interactions, the major difficulties are linked to the media which should be realistic in terms of environmental conditions. Therefore, an ideal technique for such investigations should satisfy a set of criteria, which are described in the following section. Further sections present the most used techniques and finally compare them on the basis of these criteria.
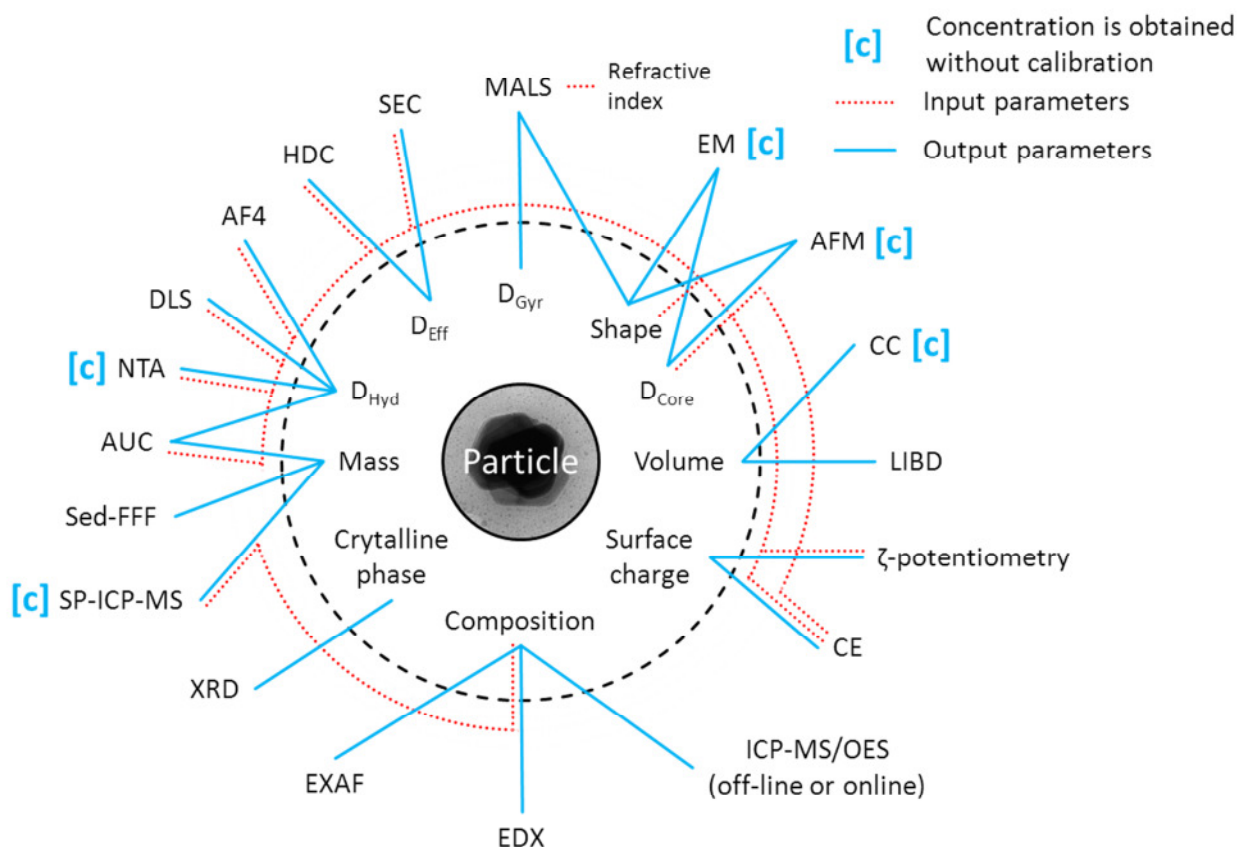
Figure 3.1: schematic summary of the analytical inputs and outputs of common analytical techniques for colloids characterization. Separation techniques are considered for themselves, without additional specific information from the detection system.

1.2 Requirements for environmental samples

1.2.1 Detection limit

Particle concentration is a crucial parameter for determining agglomeration processes, since it governs the ratio between homo- and hetero-agglomerates, for instance. As realistic concentrations of engineered colloids in the environment are most probably below 0.1 mg L^{-1} (Nowack et al., 2012), analytical techniques for sizing and quantifying them should remain accurate in the µg L^{-1} range. This is often a challenging task since, at these concentrations, the number of particles per liter become extremely small compared to molecular analytes for example. Thus, a realistic mass concentration for TiO$_2$ in surface water, as far as it can be predicted at present, could be 0.1 µg L^{-1} (Liu and Cohen, 2014) which correspond to 60 ng L^{-1} of Ti and 45 000 spherical particles with a diameter of 100 nm in one milliliter natural water (table 3.1). Although it is intuitively a large amount of particles it corresponds to less than 0.1 attomole of individual analytes (here a single particle as a whole) which is in the same order of magnitude than the limit of detection for the most advanced mass spectrometers (Watson and Sparkman, 2007). This underlines the difficulty encountered by measuring low concentrations of colloids and the strong limitation of using analytical tools dedicated to small molecules or proteins for characterizing them.

Table 3.1
Illustration of different types of concentrations for TiO_2 spherical particles.

Size (nm)	Concentration of TiO_2 in μg L^{-1}	Concentration in nb of part. L^{-1}	Concentration of particles in amol L^{-1}	Concentration of Ti in ng L^{-1}
5	0.1	3.6×10^{11}	600	60
20	0.1	5.6×10^{9}	9.4	60
50	0.1	3.6×10^{8}	0.6	60
100	0.1	4.5×10^{7}	0.07	60

Sample pre-concentration procedure involving, for instance, centrifugation, filtration, cloud-point extraction or separation using magnetic or electric field are helpful in some cases (Fabricius et al., 2013; Baalousha and Lead, 2012). However, these methods are rarely applicable on environmental samples because of the high natural colloidal background and preparation artefacts. Another strategy to overcome low analyte concentrations is to use a counting technique (see beneath) for detecting individual particles. In such cases, the detection limits can also refer to the minimal particle size detectable by the system.

1.2.2 Matrix effects and selectivity

Since environmental media contain high amount of diverse inorganic and organic compounds, an analytical technique should be widely independent on the presence of these components. For instance, surface water usually contains inorganic ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, HCO_3^-, etc.) which usually do not affect the sizing of particles, unless the respective sizing technique is highly sensitive to viscosity, density or refractive index. DOM can disturb the sizing of particles when large molecular agglomerates form in the presence of divalent cations (Caceci and Billon, 1990; Maurice and Namjesnik-Dejanovic, 1999; Tipping, 2002). For some techniques the effect of the matrix can be easily identified and corrected using calibrants measured in the same media as the analytes. However, the high variability of environmental samples makes this method often tedious. Separation techniques are generally robust upon matrix effects compared to other groups of methods because the colloidal analytes can be separated from their matrix and be detected and measured independently of ionic or molecular constituents.

Natural colloids represent one of the most difficult challenges for the detection and sizing of colloids in environmental matrices. Their concentrations can reach several mg L^{-1} in natural waters (Wigginton, Haus and Hochella Jr, 2007), which is much higher than the expected concentrations for engineered colloids. Distinguishing between natural and artificial colloids is a challenge for most techniques, especially if their size ranges overlay. At present, elemental or even isotope specific detection systems are the most practical tools for this challenge. This is one of the reasons of the recent development of separation methods coupled with ICP-MS detection systems.

1.2.3 Sample perturbation

Sample preparation is a critical step in the analytical procedure. For molecular analytes, an extraction procedure is often required prior to analysis. However, colloids can be sensitive to both chemical and physical processes. For instance, the drying step necessary for classical EM analysis can induce

agglomeration of the analytes and thus modifies the particle morphology to determine (Burleson, Driessen and Penn, 2005). This was a motivation for the development of environmental scanning electron microscopy, which can be used under lower vacuum and with an atmosphere saturated in water and thus limits, under some extend, drying artefacts (Tiede et al., 2008). In addition, non-perturbing sample preparations for electron microscopy using, for instance, ultracentrifugation or embedment in resins have been reported for natural samples (Perret et al., 1991). Sample perturbation for a given technique can hence be limited by developing appropriate preparation methods. However, such developments are usually tedious, time consuming and may lack of universality.

Separation techniques require usually less sample preparation and are therefore advantageous compared to techniques requiring sample drying. However, the effect of dilution in the carrier media and filtration, which are common preparation steps, should be investigated if they are required. Nonetheless, *in situ* methods remain the only fully non-perturbing analysis. As shown below (section 1.7) such methods are unfortunately often highly sensitive to matrix components, especially to natural colloids.

1.2.4   Cost/time efficiency

Most reviews on nano-analytic usually do not address cost or time efficiency issues. Although these criteria do not concern directly the scientific aspect of the research, this is often a crucial point for laboratory decision makers and for the planning of large scale experiments. For instance, the running of ten parallel mesocosm experiments can easily afford the measurement of hundreds of samples per week. It is obviously not realistic to consider a systematic characterization of these samples using EM or AFM. Furthermore, most laboratories cannot easily access expensive techniques such as transmission electron microscope or cyclotrons for X-ray spectroscopy analysis. A readily available, time efficient and affordable technique will often be preferred to more efficient but expensive devices.

Comparing accessible techniques, the measurement time is an important factor since colloids are often in metastable state and the risk of analytes alteration increases with time. For instance, typical measurement durations are between 20 and 45 minutes with AF4 (von der Kammer, Baborowski and Friese, 2005; Bolea et al., 2011; Giddings, 1993). Considering the necessity to replicate each measurement, the characterization of 100 suspensions requiring the same measurement conditions should take at least one week of full measurement. With HDC or SEC measurements could be done in 33 hours (McHugh and Brenner, 1984). A high sample throughput is only possible with fast and automatized techniques. However, the time required for the method development should always be considered, if required.

1.3   Microscopy techniques

Microscopy is often considered as the most effective way for analyzing colloidal suspensions. Indeed, analyzing and counting individual particles are possible by direct visualization. A distribution graph can thus be obtained directly from data extracted from pictures. It is often not possible to observe very light materials such as brushed polymers or small molecules and thus only the dense core of the

particles can be observed, unless an appropriate staining method is developed (Burleson, Driessen and Penn, 2005).

Since electromagnetic wavelengths in optical microscopes are on the same order of size than the particles to be measured, special microscopes have to be used for observing nanoparticles. X-ray microscopy can be applied for particles larger than 30 nm (Chen et al., 2011). X-ray microscopes operate like optical microscopes and can be used in situ on biological samples without preparation (Chen et al., 2011). Unfortunately, the required equipment (X-ray synchrotron) is rare and expensive and only few laboratories have access to such devices. This strongly limits the use of X-ray microscopy on a routine base.

Electron microscopes are much more common, although also relatively expensive. Transmission and scanning electron microscope are the most used electron optical systems for the characterization of colloids. For high resolution devices, even particles of a few nanometers can be detected. Since such systems have to operate under high vacuum for maintaining an acceptable resolution, samples have to be dried. The preparation of liquid samples is therefore a critical point. Drying can induce crystallization of salts, agglomeration of colloids or molecules and alteration of some structure such as gels (Burleson, Driessen and Penn, 2005). Efforts were done to develop sample preparation methods for environmental samples (Burleson, Driessen and Penn, 2005; Wilkinson et al., 1999; Perret et al., 1991) but these methods have to be adapted to the sample type and cannot avoid all drying artifacts mentioned above. SEM devices operating under low vacuum have been developed for the study of wet samples (Paul et al., 2005; Burleson, Driessen and Penn, 2005). Unfortunately, the resolution of these devices is much lower than traditional SEM. Nonetheless, such techniques are highly promising for the analysis of biological samples.

AFM can measure the interaction forces between a tip and the sample by rastering the tip over the sample surface or rastering the sample beneath the tip (Burleson, Driessen and Penn, 2005). Force measurements and topographic images with vertical and lateral resolutions in the sub-nanometer range can be obtained. AFM is useful for imaging the size, shape, and topography of colloids with or without solvent and, with modified AFM tips, measuring the forces of interaction between colloids as a function of solution chemistry (Burleson, Driessen and Penn, 2005). Thus, AFM was used for studying various natural colloids (Plaschke, Römer and Kim, 2002; Lead, Muirhead and Gibson, 2005; Baalousha and Lead, 2007). Analytes have to be adsorbed on a flat surface for imaging, which makes the sample preparation tedious for environmental samples (Baalousha and Lead, 2012).

Ultramicroscopy, also called nanotracking analysis (NTA), is a special mode of optical microscopy, where the suspension to be analyzed is illuminated by a laser. The light scattered by one particle can be seen by a classical optical microscope. Although the particle size cannot be determined directly, the diffusion coefficients of the colloids can be extracted by analyzing the movement of the particles using appropriate data evaluation software (Carr et al., 2009). The Stokes-Einstein equation is then used for converting diffusion coefficients into hydrodynamic diameters. Thus, results from NTA are in the form of a number weighted distribution hydrodynamic diameter. The method is formally *in situ* as it requires no sample preparation. In practice, samples often have to be diluted to reach an optimal particle concentration (Filipe, Hawe and Jiskoot, 2010). The size limit for the detection depends on the density of the particle material and is higher than for EM, for instance (Filipe, Hawe and Jiskoot, 2010). Since Stokes-Einstein equation is used, the shape of the particle has to be known in order to use the appropriate shape factor (Hunter, 2001).

1.4   Light scattering techniques

Light scattering techniques are popular techniques as they are in situ techniques and are easy to carry out with modern devices. While a sample is illuminated by a light source, the intensity of the scattered light is monitored at one angle and over time with DLS and at several angles simultaneously with MALS (Finsy, 1994). Some instruments can perform both types of analysis simultaneously. Visible light or X-rays can be used. Since overall intensity is monitored, parameters coming out are average values over the whole sample.

In DLS, the complex variations in intensity due to the Brownian motion of the particles are auto-correlated in order to extract a diffusion coefficient distribution by using complex algorithms (Finsy, 1994). As for NTA, the diffusion coefficient distribution can be translated into size distribution using Stokes-Einstein equation provided that particle shape is known. The resulting size distribution is intensity weighted. Since intensity is proportional to the sixth power of particle size, the size distribution is weighted by the fifth power of particle size (Finsy, 1994). The average size obtained by DLS is called the D_z-average hydrodynamic diameter ($D_{Z,Hyd}$) (Finsy, 1994):

$$D_{Z,Hyd} = \frac{\sum_i n_i d_i^6}{\sum_i n_i d_i^5} \tag{3.1}$$

where n_i denotes the number of particles with a diameter d_i. For polydisperse suspensions, this average can be much larger than the number average obtained with microscopy techniques, for instance. In other words, for highly polydisperse samples, the largest particles may be greatly overrepresented. Limit of detection for the concentration is usually in the mg L^{-1} range for most type of colloids, whereas the limit of detection for the particle size can reach several nanometers for the most performant devices. Since particle shape strongly influences the scattered intensity, the mean shape has to be known for interpreting DLS data (Lin et al., 1990).

When the intensity of the scattered light is measured at several angles, it is possible to determine the average diameter of gyration of a suspension, provided that the particle refractive index is known. Indication on the particle shape can also be obtained. For instance the fractal dimension of agglomerates can be directly determined using MALS (Bushell and Amal, 2000). Based on similar principles, small angle X-ray scattering and small angle neutron scattering can be used for particles in the range of some nanometers or for macromolecules (Gilbert, Lu and Kim, 2007; King and Jarvie, 2012).

1.5   Particle counting techniques

Particle counting techniques are highly interesting for characterizing colloidal suspensions since they combine the advantage of working directly with solution and the detection of individual particles. A number weighted size distribution is hence obtained directly from the data. Depending on the detection method, different parameters can be collected for each particle. Limit of detection is generally very low for concentrations since particles are individually detected. However, the limit of detection for size depends strongly on the detector and is usually higher than 10 nm. The risk of detecting several particles at once has also to be considered. Therefore, it is often necessary to dilute concentrated samples.

The oldest counting method is the Coulter counter. Suspended particles are forced to move through a narrow hole or tube by the mean of an electric field. If the size of one particle is on the same order of magnitude than the dimensions of the hole, the overall current will be sensitively affected by the path of this particle and a spike signal will be measured by monitoring the current intensity over the time. The spike intensity is related to the volume of the particle. The main drawback of this method is the high detection limit for the size (usually around 100 nm). However, future devices with improved materials and channels geometries may become available in the next years (Ito, Sun and Crooks, 2003; Zhe et al., 2007).

LIBD is a recent technique which is still under development (Hassellöv et al., 2008). The principle is based on the breakdown (formation of plasma) of small particles through focused pulsed laser illumination (Hassellöv et al., 2008). The small explosion induced by the path of small molecules through a laser beam with an appropriate intensity, can be detected using a CCD camera or a piezo-electric crystal. The intensity of the signal is related to the volume of the particles. Although LIBD is highly sensitive even for small particles (minimal size: 5 nm), the determination of the particle size requires calibrants with the same composition as the analytes. This is a major drawback for the analysis of samples with unknown or complex composition.

SP-ICP-MS is a promising method developed recently (Mitrano et al., 2011; Tuoriniemi, Cornelis and Hassellöv, 2012; Pace et al., 2012). SP-ICP-MS is based on the principle that at appropriate low concentrations, a suspension can be injected sufficiently slowly into a detector for detecting particle one by one. ICP-MS has been designed to detect and quantify with high sensitivity heavy elements in complex matrices. Liquid samples are pumped into a nebulizer which produces droplets of some micrometers. The droplet components are vaporized and ionized in argon plasma. Ions are guided into a quadrupole mass-spectrometer which determines the amount of ions having a defined mass over the time (figure 3.2).
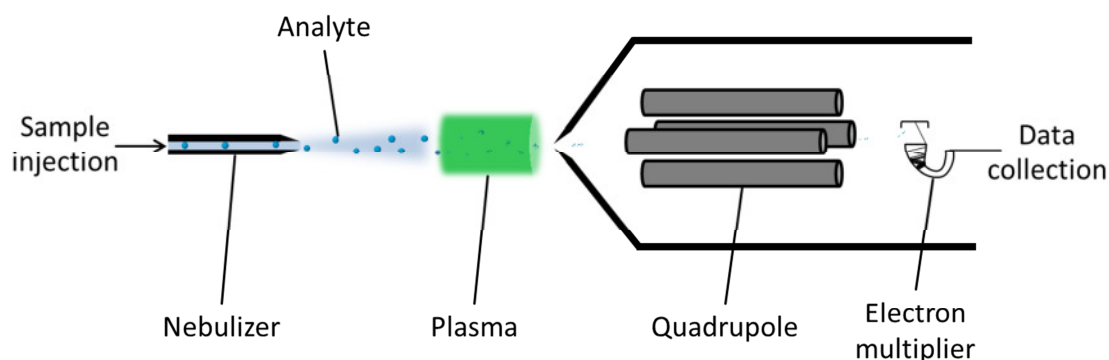
Figure 3.2: simplified principle of inductively coupled plasma mass spectrometry (ICP-MS).

This technique is highly sensitive for most heavy elements (limit of detection in the ng L^{-1} range for Ag, Au, Ce, Cs, Cd, Hg, etc.). With appropriate tuning parameters, this sensitivity is high enough for detecting an ions cloud produced by one single particle (figure 3.3). The intensity of the obtained spike signal is directly proportional to the amount of atoms of the detected element contained in one particle (Pace et al., 2012). If calibrants of the monitored element are available and provided that the composition of the analyte is known, an elemental mass can be calculated for each detected particle.
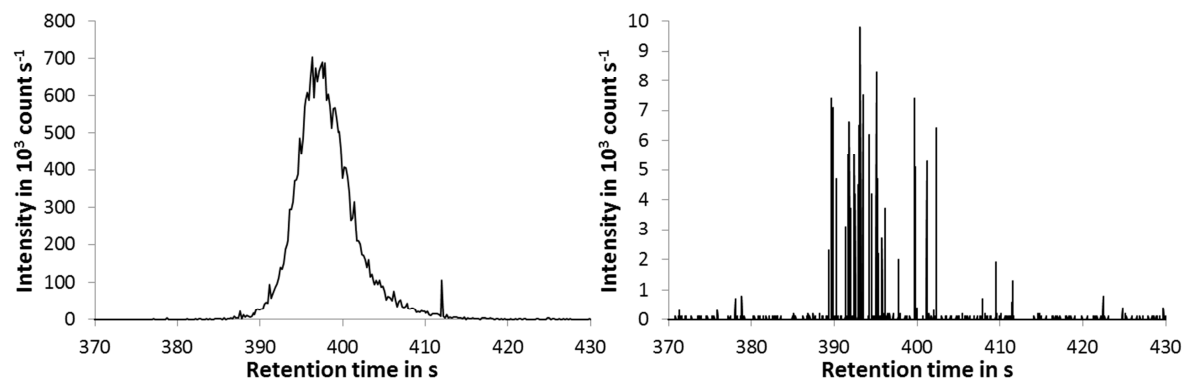
Figure 3.3: illustration of SP-ICP-MS detection principle. Left side: a pulse of 50 nm large gold particle dispersion was injected into the ICP-MS detector. Right side: the same dispersion was diluted 1:500 before injection. On the right graph signal spike represent single particle detection events.

1.6   Separation methods

For complex samples, separation of analytes from the medium is generally advantageous, especially if samples contain different types of colloids. Preparative centrifugation and filtration can be used for preparing sample (Fabricius et al., 2013; Tiede et al., 2008). However, these methods have to be validated by a size analysis. Combining separation and size analysis online is therefore highly interesting. The analytical output depends on both separation mechanism and detection system. Most separation mechanisms are based on the particle size, mass and surface charge. One major advantage of separation techniques is the possibility to combine different detectors online. Complementary detectors combination makes further discrimination between media components possible and may even be used to gain additional information on the analytes.

Analytical ultracentrifugation (AUC) is composed of a centrifuge equipped with a detector (usually turbidity or X-ray detectors) for monitoring the analyte sedimentation under a gravity field (Schuch and Wohleben, 2010; Wohlleben, 2012). With this technique, a mass distribution is obtained provided that the density of the analytes is known. Since this is generally not the case for environmental samples, an alternative method has to be used in such cases. For instance, the sample can be measured after dilution in pure water and in deuterated water in order to determine the absolute mass distribution of the suspension (Schuch and Wohleben, 2010). The shape of the particle influences also its sedimentation rate (Hunter, 2001). Therefore, the shape has to be known. One main disadvantage of AUC is that coupling with high performance detectors such as ICP-MS is technically not possible at present. As traditional detection systems used with AUC are often not selective and not appropriate for detecting trace amount of colloids, AUC is rarely used for environmental samples and is more dedicated to routine quality control (Wohlleben, 2012).

Sedimentation field flow fractionation is another method for determining the mass distribution of particles dispersion. The centrifugal force is applied on a flat tube where eluent is pumped at a defined flow velocity. The analytes are injected into this flow and are pushed by gravity to the external walls of the tube. Since the flow rate is reduced near to the wall, heavy particles will be slower than lighter particles by the combined effect of the gravity field and the flow profile (Giddings, 1993). This method can be coupled to diverse detectors including ICP-MS (Dubascoux et al., 2010), whereas it is limited to particles which sediment readily under fair centrifugal field; for most types of colloids, a minimal size of 50 nm is required (Fedotov et al., 2011).

Instead of gravity, an electric field can be used to separate particles by their overall electric charge (Lespes and Gigault, 2011; Jimenez et al., 2011). When a capillary is used as column for the migration, the technique is called capillary electrophoresis. Complex models can be used for determining the charge of particle from their migration time (Lespes and Gigault, 2011). There is thus no need of a calibration. CE has been coupled to detectors such as UV, laser induced fluorescence and ICP-MS for instance (Celiz et al., 2011; Lespes and Gigault, 2011). Unfortunately, charge determination with CE becomes highly challenging for environmental matrices and with natural colloids in general. Therefore, it can be carried out only with relatively simple suspensions.

Hydrodynamic chromatography can be used to separate particles by their size. Size separation occurs when particles flow in a pipe with a small intern diameter. In this case large particles cannot sample the whole parabolic flow velocity profile as they center of mass cannot approach near to the wall, whereas small particles can access to low velocity regions near the wall. Large particles will, therefore tend to elute earlier than small particles. Using an appropriate calibration method, it is possible to determine the effective diameter (geometric diameter for a sphere) of unknown samples. HDC is simple and robust but less efficient than other separation methods (McHugh and Brenner, 1984; Striegel and Brewer, 2012; Penlidis, Hamielec and MacGregor, 1983; Tiede et al., 2009). Particles with diameters in the size range 5-3000 nm can be separated using commercially available columns. Further details related to HDC about separation mechanism and coupling techniques can be found in section 2.

HDC can be carried out on packed monodisperse spheres columns. If the spheres used for the packing are porous with pores with size in the same range as the particles to analyze, size exclusion occurs and large particles elute faster than small particles, since the latter are retarded in some of the pores. Various SEC columns are commercially available. However they generally have relatively narrow separation ranges and are limited to the separation of particles smaller than 100 nm. While SEC is limited for particles, it is often the method of choice for studying natural or artificial macromolecules. Effective diameters can be calculated from HDC and SEC using size calibration.

Hydrodynamic diameter distribution can be determined with AF4. In AF4, the analytes are eluted through a flat channel. A crossflow stream, entering and exiting through permeable walls, drives components toward a membrane (Giddings, 1993). The pore size of the membrane determines the lower size limit for separation. Particles with high diffusion coefficients have access to a larger flow profile and hence elute faster than particles with lower diffusion coefficients. Particles from one nanometer to several micrometers can be separated. Diffusion coefficients can be determined from retention times using physical models (Giddings, 1993) or using size calibration curves (Gray et al., 2012). The Stokes-Einstein equation can be used to determine hydrodynamic diameters from diffusion coefficients (Giddings, 1993). AF4 has become very popular in environmental sciences due to its large size range, high resolution and mild elution conditions (Baalousha and Lead, 2007; Gimbert et al., 2007; Siripinyanond, Barnes and Amarasiriwardena, 2002).

Sed-FFF, AF4, SEC, HDC and CE can be combined with diverse detectors. Most used detectors are UV-visible, differential refractometry (DR) and fluorescence (FLD) detectors. Direct information on the size or the nature of the analytes cannot usually be obtained using these detectors and, therefore, the latter are used as unspecific detection systems for determining retention times. Detectors capable of determining particle properties in an online modus are highly interesting. Coupled to a separation system, multidimensional characterization can be carried out. For instance, coupling HDC, SEC or AF4 with DLS and MALS detectors was used to characterize the particle shape (Brewer and André M Striegel, 2011b; von der Kammer, Baborowski and Friese, 2005; Lespes and Gigault, 2011). The use of ICP-MS detectors becomes increasingly common in environmental sciences. ICP-MS is

isotope specific and has a detection limit in the range of ng L^{-1} for most elements (Lespes and Gigault, 2011). Thus, this technique is highly attractive for environmental samples and has been coupled to SEC (Jimenez et al., 2011), HDC (Tiede et al., 2009), AF4 (Dubascoux et al., 2010) and CE (Lespes and Gigault, 2011).

Furthermore, SP-ICP-MS has been used as a detector with HDC (Pergantis, Jones-Lepp and Heithmar, 2012). This coupling technique is especially interesting as it cumulates the advantages of a particle counter detector with the selectivity of ICP-MS detection. Combined to information obtained from the retention time particle size, mass and number concentration can be obtained in a single run (Pergantis, Jones-Lepp and Heithmar, 2012). Further developments of data analysis were performed throughout this work and further details can be found in chapter 6.

1.7   Comparison of sizing techniques

Comparing different sizing techniques is difficult, since the analytical outputs may intrinsically differ. The performance of an analytical device depends also on the analyte and the measurement context. Nonetheless, it is possible to compare the most common techniques used for the sizing of colloids based on several chosen criteria, which reflect the capability of a technique to measure environmentally relevant samples (figure 3.4a-b). No one of the most used techniques fulfills all requirements mentioned above. The choice of the analyst will thus depend on the type of analyte, the expected concentrations, the matrix components and the exact parameters to be determined.

In the case where sample preparation should be minimal and where natural colloids with the same size range than the analyte are present, SP-ICP-MS will be the method of choice provided that the analytes can be detected using this method. In another case where the limit of detection and the matrix are not an issue, DLS can be used with a fair confidence. For challenging samples with many requirements, a combination of complementary techniques (e.g. EM and SP-ICP-MS, DLS and SP-ICP-MS, AF4 and CC) will probably be the best solution. Some techniques such as NTA, HDC and SP-ICP-MS are relatively balanced and are useful for a broad range of sample types.

The present work aimed at further developing a method for the detection and sizing of colloids in samples containing natural waters (e.g. from the Rhine River and from mesocosm experiments) in order to be able to study their interaction with DOM under realistic conditions. Since we expected natural colloids to be present in our media, the matrix sensitivity was the most important parameter. In addition, the limit of detection should be lower than the average expected concentration of particles in natural waters (some µg L^{-1}) and cover the size range expected from single particles to potential agglomerates which remain suspended (around 5-1000 nm). The quantity and diversity of the measurements planned for the project made it important to reduce the measurement duration. From figures 3.4a-b, only separation techniques, EM and SP-ICP-MS are selective enough to avoid matrix effect (minimal matrix sensitivity). The conditions on the measurement duration make HDC and SEC the most competitive. However, SEC has a very narrow size range rendering this method unpractical for environmental samples.

Thus, HDC seemed to be the best compromise for a routine sizing method in this project. It should be noted that DLS, SP-ICP-MS, NTA and EM had to be used as complementary techniques for the full characterization of colloidal suspensions. It should be noted that AF4 would also have been a good compromise, although the measurement duration is high and method development long. HDC theory and implementation in environmental sciences will now be discussed in detail.
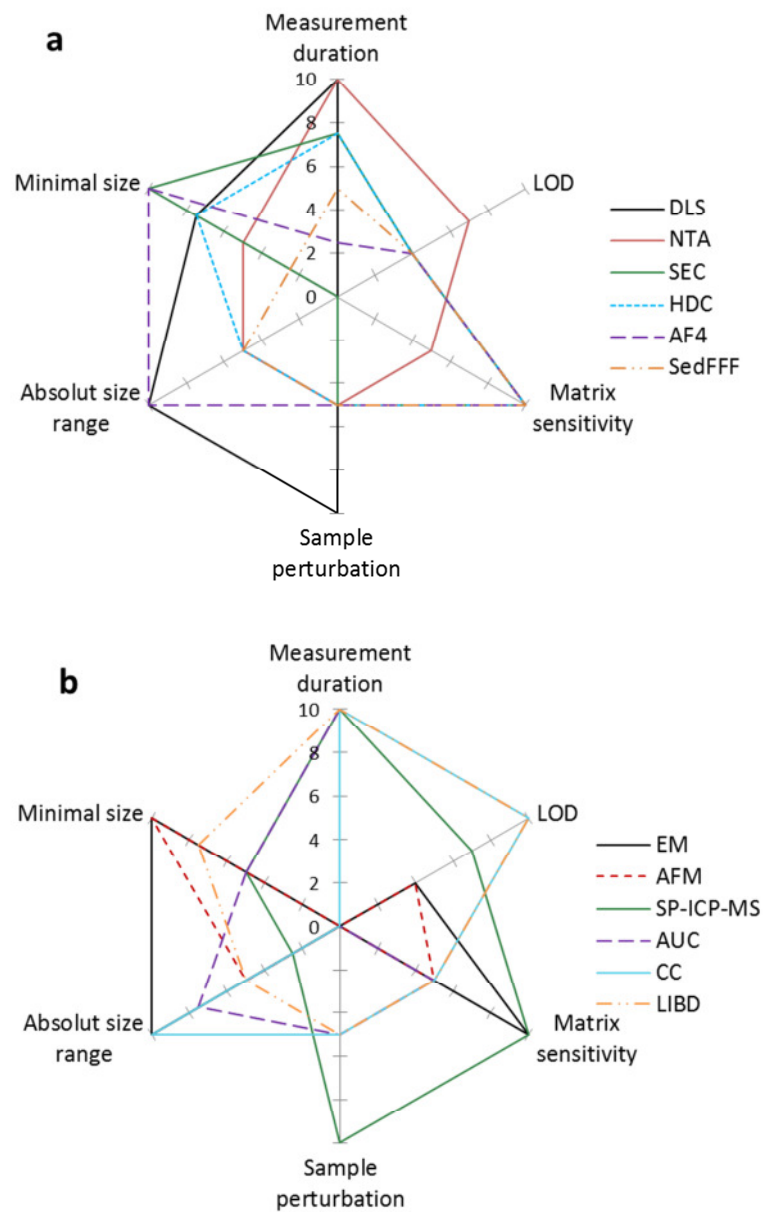
Figure 3.4a-b: Results of the evaluation of the fulfillment of the environmental samples requirements by most used sizing techniques. Details about the evaluation are provided in table 3.2.

Table 3.2
Qualitative criteria used for the evaluation of sizing techniques. The limit of detection (LOD) was calculated for silver particles for comparison purpose. Separation techniques are considered coupled with ICP-MS if this coupling was ever reported. Information about individual techniques was collected in dedicated review articles (Tiede et al., 2008; Lespes and Gigault, 2011; Hassellöv et al., 2008; Simonet and Valcárcel, 2009) and from personal experience.

Grade in normalized qualitative units	Measurement duration in min	LOD in ng L^{-1}	Matrix sensitivity	Sample perturbation	Size range broadness in nm	Minimal size nm
0	>60	100 000	Influenced by polsdispersity	Drying/ extraction	<100	100
2.5	45				300	50
4	45	100				
5	25		Influenced by other colloids of the same size	Dilution/ filtration	1 000	20-30
7		10				
7.5	8				3 000	5
8						
10	<8	0.1	No matrix influence	*In situ*/direct injection	>10 000	1

2 HDC-ICP-MS for environmental samples

2.1 Early history of HDC

H. Small reported the use of HDC as an analytical technique for the first time as he was working at the Dow Company (Small, 1974). He developed this technique for analyzing high molecular weight polymers, for which SEC could not be applied. Since he needed a sizing technique for quality control, it needed to be robust, fast and inexpensive. At that time, a wide range of elution conditions were tested for diverse polymers (Small, Saunders and Solc, 1976). Small's idea was based on a theory developed for explaining the elution of protein samples in narrow tubes (DiMarzio and Guttman, 1969, 1970). A more specific theory was proposed for HDC shortly after H. Small reported his invention (Stoisits, Poehlein and Vanderhoff, 1976). The effect of colloidal forces was described shortly afterwards in order to explain the dependence of elution time on ionic strength of the eluent (Prieve and Hoysan, 1978).

H. Small used packed column for his first experiments with HDC, probably because he had access through his company to highly monodisperse polymers beads which could be used for the column packing. However, it could be more straightforward to use capillaries as column considering the theoretical model of HDC. Indeed, capillaries were used with success and showed higher separation efficiency compared to packed beads HDC (Noel et al., 1978).

Difficulties arising from the limited colloidal stability of certain analytes prompted the first HDC specialists to add surfactants for stabilizing particles throughout elution (Nagy, Silebi and McHugh, 1981; Small, Saunders and Solc, 1976). Using eluents containing surfactant and low ionic strength, it was hence possible to stabilize most organic particles. However, the interpretation of the HDC

chromatogram in terms of particle size distribution remained a challenge. This was first made possible by using a computerized system and a UV-detector which could calculate the size distribution taking into account the effect of particle size on light adsorption (McGowan and Langhorst, 1982). More details about the early stage research in the field of HDC and SEC can be found in several reviews (McHugh and Brenner, 1984; Penlidis, Hamielec and MacGregor, 1983; Striegel and Brewer, 2012).

2.2   Theory of HDC

2.1.1   Separation mechanism

As denoted in the previous section, HDC can be performed using a capillary or a column packed with uniform microspheres. Interestingly, the model used for the capillary can be applied straightforwardly to the case of a packed column with excellent confidence with measurements (McHugh and Brenner, 1984). This simple model is described in figure 3.5. In a cylindrical tube a Poiseuille flow transports particles at different velocities. Because of steric exclusion, large particles can access only to the central region of the tube where the parabolic flow is the strongest and thus the average velocity the highest. Smaller particles can access to the region near to the wall; their average velocity is therefore lower. Thus, large particles will tend to elute faster than small particles and all particles will elute faster than or as fast as the eluent.
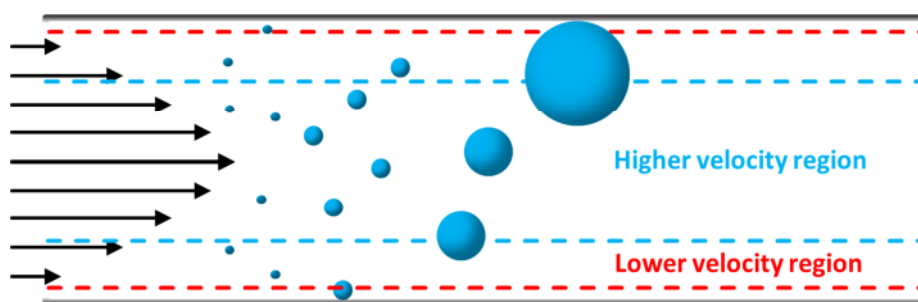
Figure 3.5: schematic description of the separation mechanism in HDC.

The model is based on the following hypotheses (Striegel and Brewer, 2012):
- the flow is laminar. There is hence an upper limit for the flow velocity and the pressure for a given chromatographic system.
- Particles efficiently sample the whole velocity profile. This is the case for colloidal particles as they have high diffusion coefficients, provided that the elution time is long enough.
- Effects of affinity or collision of the particles with themselves or the wall are negligible. This is correct when the particle concentration in the sample is small enough and when the electrostatic and chemical forces between the wall and the particles are weak.
- Particles are spherical or similar to spheres.
- The packed column can be approximated by parallel tubes with inner radius using the following formula:

$$r_0 = \frac{r_s}{3}\frac{\varepsilon}{1 - \varepsilon} \tag{3.2}$$

with r_s the average radius of the spheres used for the packing (usually from 1 to 50 μm) and ε the porosity of the column.

In order to quantify the theoretical retention factor in a system described in this model, the average flow linear velocity (m s^{-1}) of a fluid moving in the tube has to be calculated. Since the flow is laminar, the Poiseuille's formula can be used to derive (Stoisits, Poehlein and Vanderhoff, 1976):

$$v(r) = v_0 \left[1 - \left(\frac{r}{r_0}\right)^2\right]$$ (3.3)

where r denotes the radial coordinate of a particle in the hypothetic tube, r_0 is the inner radius of the tube, $v(r)$ the linear velocity at the coordinate r and v_0 is the maximal linear velocity given by:

$$v_0 = \frac{(\Delta P) r_0^2}{4\mu l}$$ (3.4)

with l the length of the column, ΔP the pressure drop into the column, and μ the dynamic viscosity of the eluent. The average velocity of the eluent and a particle with a diameter equal to a can thus be calculated by averaging the velocity over all possible positions inside the tube using the equations 3.5 and 3.6 respectively:

$$\bar{v} = \frac{\int_0^{r_0} v(r)\, r\, dr}{\int_0^{r_0} r\, dr} = \frac{v_0}{2}$$ (3.5)

$$\overline{v_p} = \frac{\int_0^{r_0-a} v(r)\, r\, dr}{\int_0^{r_0-a} r\, dr} = v_0 \left[1 - \frac{1}{2}(1 - \bar{a})^2\right]$$ (3.6)

with the reduced radius:

$$\bar{a} = \frac{a}{r_0}$$ (3.7)

The retention factor of an analyte (R$_F$) can be defined by the ratio of the average retention time of the particles (τ_p) measured and the average retention time of a marker usually corresponding to the retention time calculated from the average fluid velocity (τ_0). The use of a retention factor makes possible to evacuate all parameters related to the elution conditions as shown in the following formula:

$$R_F = \frac{\tau_p}{\tau_0} = \frac{v_0}{v_p} = (1 + 2\bar{a} - \bar{a}^2)^{-1}$$ (3.8)

This simple model successfully described the elution of spherical particles in HDC in most cases encountered in the literature and with diverse types of particles (Stoisits, Poehlein and Vanderhoff, 1976; Chun, Park and Kim, 1990; Tijssen, Bos and Van Kreveld, 1986; McHugh and Brenner, 1984). However, some more advanced models have been proposed for describing additional second order effects occurring during the elution. The asymmetry of the flow profile at the scale of a particle induces a rotation of this particle which can influence its trajectory (figure 3.6a). This effect depends

partly on the hardness of the particle material. For instance a hard sphere would be more influenced by rotation than a permeable sphere (Tijssen, Bos and Van Kreveld, 1986). Mathematically this effect can be taken into consideration by using a constant multiplying the quadratic term in the formula 3.9 (Tijssen, Bos and Van Kreveld, 1986):

$$R_F = (1 + 2\bar{a} - C\bar{a}^2)^{-1} \tag{3.9}$$

where $C = 4.89$ for hard spheres and $C = 4.03$ for permeable spheres (Tijssen, Bos and Van Kreveld, 1986). In practice, this second order effect is most often neglected.

When particles are larger than 1 µm, the so called "pinch effect" may become non-negligible (Noel et al., 1978) (figure 3.6b). This effect is formally due to the loss of kinetic energy of the liquid when a particle moves to the center of the tube. This effect can be taken into consideration by correcting the formula 3.3 as the influence of the particle on the flow profile cannot be neglected anymore (McHugh and Brenner, 1984).

$$v_p(r) = v_o \left[1 - \left(\frac{r}{r_0} \right)^2 - \gamma \bar{a}^2 \right] \tag{3.10}$$

γ is a complex function of r, r_0 and a. The average particle velocity can be calculated only numerically (McHugh and Brenner, 1984). Since this effect has a minimal impact on the retention factor of particle smaller than 1 µm (McHugh and Brenner, 1984), it will be further ignored.
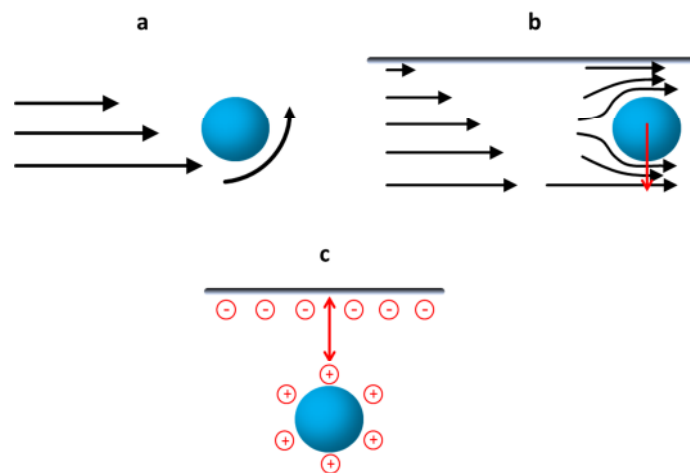
Figure 3.6: schematic description of second order effects occurring during the elution in HDC. a: Rotation induced by the flow profile. b: Pinch effect. c: Electrostatic interactions between particles and wall.

Coulomb and Van der Waals forces can occur between particle and wall (figure 3.6c). They can be considered by inserting the overall interaction potential of a particle with the wall in the equations 3.5 and 3.6:

$$\bar{v} = \frac{\int_0^{r_0} v(r) e^{\left(-\frac{\varphi}{kT} \right)} r \, dr}{\int_0^{r_0} e^{\left(-\frac{\varphi}{kT} \right)} r \, dr} \tag{3.11}$$

$$\overline{v_p} = \frac{\int_0^{r_0-a} v(\mathrm{r}) \, e^{\left(-\frac{\varphi}{kT}\right)} r \, dr}{\int_0^{r_0-a} e^{\left(-\frac{\varphi}{kT}\right)} \mathrm{r} \, dr}$$ (3.12)

where φ is the interaction potential depending on r and calculated using, for instance, the DLVO theory (Prieve and Hoysan, 1978), k is the Boltzmann constant and T the temperature. These equations are generally not relevant for routine measurements since the effect of electrostatic interactions on the retention factor are minimal at low ionic strength and in the presence of surfactants. At high ionic strength, the electrostatic potential between the wall and the particles is dominated by Van der Waals forces and can influence the elution (Prieve and Hoysan, 1978). In such cases, the separation mechanism is complex and depends on particle size, surface charge and material (Hamaker constant). This mode is denoted "potential barrier chromatography" (McHugh and Brenner, 1984; Prieve and Hoysan, 1978; Silebi and McHugh, 1978) and can be considered as the equivalent of affinity chromatography for colloids.

More advanced theories for predicting retention factors in HDC were developed recently: the probability for a spherical particle of a given diameter to be found at a given distance from the center of the tube was calculated using a derivation of the dynamic density functional theory (Almenar and Rauscher, 2011). Another model has been proposed for the prediction of an HDC-chromatogram with the help of fractal theory (Guillaume, Robert and Guinchard, 2001). The effect of particle flexibility and shape (rigid rods and ellipsoidal shape) were partially described using simulation and advanced hydrodynamic theories (Chun, Park and Kim, 1990; Staben, Zinchenko and Davis, 2003). However, these theories did not find any practical application until now.

2.1.2   Dispersion and selectivity

The problem of determining the contribution of the Brownian dispersion to the peak broadness is crucial for the interpretation of a HDC-chromatogram obtained with a UV-detector or a refractometer. However, a theoretical approach for considering this problem was developed relatively late in HDC history (Stegeman, Kraak and Poppe, 1993). In packed bed HDC the plate height has been described (Striegel and Brewer, 2012):

$$\mathrm{H} = \frac{BD_m}{\langle v \rangle} + \frac{d}{\left(\frac{D_m}{\langle v \rangle d} + \frac{1}{1.4}\right)}$$ (3.13)

where B is a constant having a value of 1.2-1.4, D_m is the molecular diffusion coefficient, $\langle v \rangle$ is the linear eluent velocity and $d = 2a$ the diameter of the particles. The first term in the equation describes the longitudinal diffusion and the second term depicts the effect of convective mixing (Venema et al., 1997). In HDC of colloids, the longitudinal diffusion term is typically negligible compared with the convective mixing term because of the small diffusion coefficient of these analytes (Striegel and Brewer, 2012).

For polydisperse samples, the broadness of the size distribution contributes mostly to the peak broadness (Venema et al., 1997). This contribution can be estimated with the following formula:

$$\mathrm{H}_{pol} = lS^2(\mathrm{PI} - 1)$$ (3.14)

with l the column length, PI the polydispersity index (ratio of the mass weighted over the number weighted average molecular mass) and S the size-based selectivity defined as the intrinsic capability of a technique to separate analytes according to their size. This parameter can be calculated by using the formula 3.15 (Lespes and Gigault, 2011):

$$S = \left| \frac{d(\log \tau_p)}{d(\log d)} \right|$$

(3.15)

where τ_p is determined experimentally using standard suspensions with known d. Unfortunately the definition of polydispersity index used above is restricted to polymers. However, the size-base selectivity can be used directly for comparing separation performances for particles of undefined material.

This parameter is also useful for comparing performances of different size separation techniques. Selectivity values for the main separation techniques used for particle characterization are shown in the table 3.3. As it can be seen, HDC has lower size selectivity than other techniques. However, this low performance is compensated by its high flexibility, simplicity and robustness towards sample matrix (Tiede et al., 2009).

Table 3.3
Size selectivity range for the main separation techniques used for particle characterization. Adapted from Lespes and Gigault (Lespes and Gigault, 2011).

Technique	Size range (nm)	Optimal selectivity	Usual selectivity
Size exclusion chromatography	0.1-100	0.2	0.05-0.15
Hydrodynamic chromatography	5 to few 1000	0.1	0.02-0.1
Capillary hydrodynamic chromatography	10 to few 1000	0.2	0.05-0.15
Flow-FFF	1 to 50 000	1	0.5-1
Sedimentation-FFF	50 to 50 000	3	0.5-2.5
Thermal-FFF	30 to 10 000	0.5-1.5	0.6-1
Electrical-FFF	10 to 2500	1	0.4-1
Capillary electrophoresis	0.1 to 2000	0.4	0.4

2.3 Further advances and derived techniques

HDC was implemented mostly in polymer science and biology. Examples of latex analyzed with HDC are plentiful and can be found in the first articles dealing with HDC. In the field of biology, HDC was successfully applied, for instance, to the analysis of liposomes (Brewer and André M Striegel, 2011a; Helsper et al., 2012; Yegin and Lamprecht, 2006) and DNA (Liu et al., 2013). Consequently, relatively few publications address the implementation of HDC for inorganic colloids although the technique can be applied to, theoretically, any type of colloids. SiO_2 colloids were measured by HDC (Stegeman et al., 1990; Takeuchi, Aspanut and Lim, 2009). Tiede *et al*. demonstrated the wide applicability of HDC by measuring Fe_2O_3, TiO_2, Al_2O_3, silver, and gold particles (Tiede et al., 2009).

Recent efforts in improving the capability and performance of HDC indicate that this technique will be more and more applied in diverse fields. The resolution in packed beads HDC can be improved by

decreasing the polydispersity of the packing material (Thompson, Lieberman and Jorgenson, 2009). However, few possibilities to improve the resolution remained for packed beads HDC. Since commercial HDC columns became available and standardized, efforts to create columns with higher performances decreased.

The conformation of some soft polymers can change depending on the flow velocity in packed beads HDC (Li, Liu and GENG, 2009). Such polymers take an extended conformation and have to "slalom" between the beads of the packing. This mode called "slalom chromatography" can be used for determining coil-stretch transition of some polymers (Liu, Radke and Pasch, 2005) and is therefore an interesting extension of HDC.

Early and recent efforts were addressed to the further development of capillary HDC, which was applied, for instance, to polymers (de Jaeger, Trappers and Lardon, 1986; DosRamos and Silebi, 1990; Korolev et al., 2012), paints components and pollen (Brough, Hillman and Perry, 1981). At present, capillaries with inner diameter smaller than 1 µm are commercially available, making the separation of small particles possible using capillary HDC. For instance, large DNA molecules could be separated with a high resolution using capillary HDC (Liu et al., 2013). Certainly, this technique will find further applications in the future.

When a wide capillary (typically between 0.1 and 1 mm) is used, the hydrodynamic separation as described above is weak. However there is a measurable effect of the flow on the shape of the elution peak. Using adequate calibration procedure the average size of colloids can be estimated by considering the shape of the elution peak provided that the polydispersity of the distribution is low enough (Fischer and Giersig, 1994). This special mode of capillary HDC is called "wide bore capillary HDC" and has the advantage to be low cost and easy to implement. This technique was used coupled with ICP-MS for monitoring adsorption of lanthanides onto lecithin vesicles (Umehara et al., 2012).

As for many other separation techniques, an on-chip version was developed for HDC with resolution power comparable to packed bead HDC (Blom et al., 2003). Advantages of an on-chip version are low eluent and sample consumption and speed of analysis (70 s). Remaining challenges are the automation of the sample injection and coupling with detection techniques such as ICP-MS.

Although interesting improvements of the separation technique were carried out, the most important recent developments of HDC concerned detection systems. To avoid confusion between the different variants of HDC, the abbreviation HDC will denote packed beads HDC in the rest of this text unless otherwise stated.

2.4   Detection systems

At the beginning of HDC development, the most used detectors were dedicated to the detection of polymers. Therefore, the most common detectors used with HDC are still UV-visible, optical density detectors and differential refractometer (DR) (Penlidis, Hamielec and MacGregor, 1983; Striegel and Brewer, 2012). The particle sizes and distributions were derived through the application of calibration curves constructed with standards that were not always similar to the analytes themselves. Consequently the accuracy of this approach is suspect, and the information obtained fairly limited.

The advantage of using complementary detection systems online with HDC was demonstrated by Striegel and Brewer for HDC (Brewer and Striegel, 2010, 2009). They combined online DR, MALS, DLS and differential viscosimetry (VISC) for a full characterization of polymers (Brewer and Striegel, 2010,

2009). The distribution of the following parameters can be obtained through combinations of these detectors:

- MALS-DR: molar mass and radius of gyration.
- DLS-DR: hydrodynamic radius.
- MALS-VISC-DR: viscometric radius and shape/compactness through a dimensionless parameter.
- MALS-DLS: shape/compactness through a dimensionless parameter.

This combination of detectors was helpful to characterize the shape of ellipsoidal and string-of-pearls like silica particles (Brewer and André M Striegel, 2011b; Brewer and André M Striegel, 2011). Unfortunately, these detectors are helpless for particle concentrations in the $\mu g\ L^{-1}$ range as their detection limits is usually in the $mg\ L^{-1}$ range. In addition, these techniques are fairly limited for analyzing mixtures of particles with different elemental composition as typically found in environmental samples.

First coupling of HDC with ICP-MS has been reported for packed beads HDC (Tiede et al., 2009, 2010). High sensitivity and elemental selectivity make the ICP-MS detector especially useful for samples with complex matrix as discussed previously (section 3.2). Detection limits are element dependent and are in the $\mu g\ L^{-1}$ range for most common elements (e.g. Ti, Fe, Al) and in the $ng\ L^{-1}$ for rare elements (e.g. Au, Ag, Ce) (Tiede et al., 2009, 2010). ICP-MS signal has been shown to be correlated with the quantity of ions produced as the particles pass through the plasma. This quantity is supposed to be independent of size since particles smaller than 500 nm are completely atomized in the plasma (Dubascoux et al., 2010). For this reason, it can be assumed that the number of counts registered by the detector is proportional to the number of atoms passing through the detector and thereafter to the mass of the particles. Thus, an HDC chromatogram can be interpreted as the elemental mass-weighted distribution of the injected sample through the use of appropriate calibrants. This is a major advantage of mass spectrometer detectors compared to classical detectors, for which a complex analysis of the signal is required and imply hypotheses on the nature of the analytes. In a more anecdotal manner, HDC was coupled with MALDI-TOF-MS for characterizing liposomes in beverage matrices at very low concentrations (Helsper et al., 2012).

A laser counting method was developed for capillary HDC (Zarrin and Dovichi, 1985). This technique has the advantage to be versatile and to provide number concentration. SP-ICP-MS used as a detector with HDC combined the advantages of a counting method and elemental specificity (Pergantis, Jones-Lepp and Heithmar, 2012). As explained above, the mass of unknown particles can be determined on a single particle basis using SP-ICP-MS. When combined to HDC, mass and effective diameter of each detected particle can be determined by using SP-ICP-MS, provided that appropriate calibrants are available (figure 3.7).
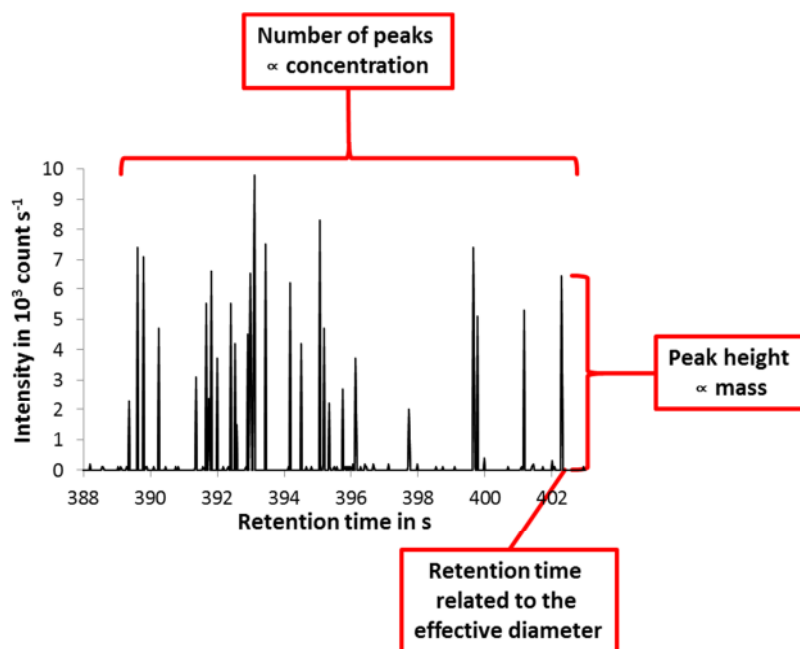
Figure 3.7: Illustration of chromatogram interpretation for HDC-SP-ICP-MS.

2.5 Application to environmental samples

Considering the maximal detection limit required for analyzing natural samples, ICP-MS is clearly the detector of choice for environmental samples. Indeed, most elements can be quantified within concentration ranges expected for engineered colloids in the environment (Lespes and Gigault, 2011). In addition, ICP-MS is isotope specific what can be used in some cases for distinguishing between natural and artificial colloids if their respective isotopic ratios differ.

Previous works have demonstrated the robustness of HDC-ICP-MS for sizing colloids in complex matrices (Tiede et al., 2010, 2009). Since HDC separation mechanism is simple and based on particle size only, the implementation and method development are highly simplified. Furthermore, no matrix effects have been reported until now. The sample preparation is minimal. If particle concentration exceeds the maximum value tolerated by the detectors, sample has to be diluted. In practice, samples containing particles larger than the limit of size resolution of the column have to be filtered. Measurement duration is typically less than ten minutes and a high sample throughput can be achieved using an automatic sampling system. Thus, requirements of robustness and quickness are met by HDC. With three measurement replicates for each sample around 200 samples can be measured in one week in an optimal case. These performances make HDC-ICP-MS highly competitive compared to AF4 or microscopy and are the reasons why this technique was chosen for further developments in this PhD-project.

However, the analytical "robustness" of HDC-ICP-MS was not quantified and the method was still not tested for the quantification of colloids in environmental media. If the applicability of the method has been proven (Tiede et al., 2010, 2009), it was still unknown how accurate the sizing with HDC could be under environmental conditions (presence of DOM, natural colloids, etc.). Furthermore, the application of HDC-ICP-MS to sample having different shapes was not reported, although such particles are expected from anthropogenic or natural sources (Gallego-Urrea et al., 2014; Pillai and Kamat, 2004). In addition, studying agglomeration processes influenced or not by DOM usually

implies determining the size of particles having complex shapes. Complex adsorption layers on colloid surface with different chemical properties are expected to occur in environmental media (chapter 2). Therefore, the effect of different coatings with different chemical properties on the accuracy of HDC should be also investigated.

3   Contribution of this work

Considering the above-mentioned knowledge gaps, the objectives of this PhD work concerning HDC was to explore and validate the potential of HDC-ICP-MS for the monitoring of colloids properties (size, concentration, composition, shape) in environmental samples. In particular, a better description of the interactions of colloids with DOM in complex media was expected with this technique. This thematic was developed around the following three axes:

- method development and validation of HDC-ICP-MS (chapter 4),
- exploration of the limitations of the method (chapter 5)
- and extension of the capability of HDC using HDC-SP-ICP-MS (chapter 6).

In particular, the following questions are discussed in details:

- which operating parameters can be adapted to the sample specificity, which ones are crucial for the accuracy of the sizing? These questions are answered in the chapter 4, where the effects of flowrate and eluent composition are reported and in the chapter 5, where the effect of the temperature is reported.
- Can HDC-ICP-MS be used for quantification in environmental matrices (high ionic and organic background and presence of natural colloids)? The quantification of gold particles and ions in a simulated fresh water sample was validated in the chapter 4.
- How universal is an HDC method for the sizing of diverse particles? The effects of particle composition, coating and shape are discussed in detail in the chapter 5.
- How can HDC-ICP-MS helps in understanding relevant environmental processes for engineered colloids? The stability of silver colloids in simulated environmental media was investigated using HDC-ICP-MS (chapter 4). HDC-SP-ICP-MS was used for investigating the morphology of gold colloids agglomerates (chapter 6) giving indications on the agglomeration mechanism.

Furthermore, a concrete application of HDC-ICP-MS for the study of interactions between silver colloids and various DOM is described in the chapter 7. Further outlooks for the development of HDC-ICP-MS and HDC-SP-ICP-MS and their applications in environmental sciences are discussed in the chapter 8.

References

Almenar, L. and Rauscher, M. (2011) "Dynamics of colloids in confined geometries," *Journal of Physics: Condensed Matter*. IOP Publishing, 23, p. 184115.

Baalousha, M. and Lead, J. (2007) "Characterization of natural aquatic colloids (< 5 nm) by flow-field flow fractionation and atomic force microscopy," *Environmental Science & Technology*. ACS Publications, 41(4), pp. 1111–1117.

Baalousha, M. and Lead, J. (2012) "Rationalizing nanomaterial sizes measured by atomic force microscopy, flow field-flow fractionation, and dynamic light scattering: sample preparation, polydispersity, and particle structure," *Environmental Science & Technology*. ACS Publications, 46(11), pp. 6134–6142.

Blom, M. T., Chmela, E., Oosterbroek, R. E., Tijssen, R. and Van Den Berg, A. (2003) "On-chip hydrodynamic chromatography separation and detection of nanoparticles and biomolecules," *Analytical Chemistry*. ACS Publications, 75(24), pp. 6761–6768.

Bolea, E., Jiménez-Lamana, J., Laborda, F. and Castillo, J. (2011) "Size characterization and quantification of silver nanoparticles by asymmetric flow field-flow fractionation coupled with inductively coupled plasma mass spectrometry," *Analytical and Bioanalytical Chemistry*. Springer, 401(9), pp. 2723–2732.

Brewer, A. K. and Striegel, A. M. (2011a) "Characterizing a spheroidal nanocage drug delivery vesicle using multi-detector hydrodynamic chromatography," *Analytical and Bioanalytical Chemistry*. Springer, 399(4), pp. 1507–1514.

Brewer, A. K. and Striegel, A. M. (2011) "Characterizing string-of-pearls colloidal silica by multidetector hydrodynamic chromatography and comparison to multidetector size-exclusion chromatography, off-line multiangle static light scattering, and transmission electron microscopy," *Analytical Chemistry*. ACS Publications, 83(8), pp. 3068–3075.

Brewer, A. K. and Striegel, A. M. (2011b) "Characterizing the size, shape, and compactness of a polydisperse prolate ellipsoidal particle via quadruple-detector hydrodynamic chromatography," *Analyst*. Royal Society of Chemistry, 136(3), pp. 515–519.

Brewer, A. K. and Striegel, A. M. (2010) "Hydrodynamic chromatography of latex blends," *Journal of Separation Science*. Wiley Online Library, 33(22), pp. 3555–3563.

Brewer, A. K. and Striegel, A. M. (2009) "Particle size characterization by quadruple-detector hydrodynamic chromatography," *Analytical and Bioanalytical Chemistry*. Springer, 393(1), pp. 295–302.

Brough, A., Hillman, D. and Perry, R. (1981) "Capillary hydrodynamic chromatography-an investigation into operational characteristics," *Journal of Chromatography A*. Elsevier, 208(2), pp. 175–182.

Burleson, D. J., Driessen, M. D. and Penn, R. L. (2005) "On the characterization of environmental nanoparticles," *Journal of Environmental Science and Health, Part A*. Taylor \& Francis, 39(10), pp. 2707–2753.

Bushell, G. and Amal, R. (2000) "Measurement of fractal aggregates of polydisperse particles using small-angle light scattering," *Journal of Colloid and Interface Science*. Elsevier, 221(2), pp. 186–194.

Caceci, M. S. and Billon, A. (1990) "Evidence for large organic scatterers (50-200 nm diameter) in humic acid samples," *Organic Geochemistry*. Elsevier, 15(3), pp. 335–350.

Carr, R., Hole, P., Malloy, A., Nelson, P., Wright, M. and Smith, J. (2009) "Applications of nanoparticle tracking analysis in nanoparticle research-a mini-review," *European Journal of Parenteral & Pharmaceutical Sciences*, 14(2), pp. 45–50.

Celiz, M. D., Colón, L. A., Watson, D. F. and Aga, D. S. (2011) "Study on the effects of humic and fulvic acids on quantum dot nanoparticles using capillary electrophoresis with laser-induced fluorescence detection," *Environmental Science & Technology*. ACS Publications, 45(7), pp. 2917–2924.

Chen, H.-H., Chien, C.-C., Petibois, C., Wang, C.-L., Chu, Y. S., Lai, S.-F., Hua, T.-E., Chen, Y.-Y., Cai, X., Kempson, I. M. and others (2011) "Quantitative analysis of nanoparticle internalization in mammalian cells by high resolution X-ray microscopy," *Journal of Nanobiotechnology*. BioMed Central Ltd, 9(1), p. 14.

Chun, M. S., Park, O. O. and Kim, J. K. (1990) "Flow and dynamic behavior of dilute polymer solutions in hydrodynamic chromatography," *Korean Journal of Chemical Engineering*. Springer, 7(2), pp. 126–137.

DiMarzio, E. and Guttman, C. (1969) "Separation by flow," *Journal of Polymer Science Part B: Polymer Letters*. Wiley Online Library, 7(4), pp. 267–272.

DiMarzio, E. and Guttman, C. (1970) "Separation by flow," *Macromolecules*. ACS Publications, 3(2), pp. 131–146.

DosRamos, J. G. and Silebi, C. A. (1990) "The determination of particle size distribution of submicrometer particles by capillary hydrodynamic fractionation (CHDF)," *Journal of Colloid and Interface Science*. Elsevier, 135(1), pp. 165–177.

Dubascoux, S., Le Hecho, I., Hassellöv, M., Von Der Kammer, F., Gautier, M. P. and Lespes, G. (2010) "Field-flow fractionation and inductively coupled plasma mass spectrometer coupling: History, development and applications," *Journal of Analytical Atomic Spectrometry*. Royal Society of Chemistry, 25(5), pp. 613–623.

Fabricius, A.-L., Duester, L., Meermann, B. and Ternes, T. A. (2013) "ICP-MS-based characterization of inorganic nanoparticles—sample preparation and off-line fractionation strategies," *Analytical and Bioanalytical Chemistry*. Springer, pp. 1–13.

Fedotov, P. S., Vanifatova, N. G., Shkinev, V. M. and Spivakov, B. Y. (2011) "Fractionation and characterization of nano-and microparticles in liquid media," *Analytical and Bioanalytical Chemistry*. Springer, 400, pp. 1787–1804.

Filipe, V., Hawe, A. and Jiskoot, W. (2010) "Critical evaluation of Nanoparticle Tracking Analysis (NTA) by NanoSight for the measurement of nanoparticles and protein aggregates,"

Pharmaceutical Research. Springer, 27(5), pp. 796–810.

Finsy, R. (1994) "Particle sizing by quasi-elastic light scattering," *Advances in Colloids and Interface Science*. Elsevier, 52, pp. 79–143.

Fischer, C.-H. and Giersig, M. (1994) "Analysis of colloids: VII. Wide-bore hydrodynamic chromatography, a simple method for the determination of particle size in the nanometer size regime," *Journal of Chromatography A*. Elsevier, 688(1), pp. 97–105.

Gallego-Urrea, J. A., Hammes, J., Cornelis, G. and Hassellöv, M. (2014) "Multimethod 3D characterization of natural plate-like nanoparticles: shape effects on equivalent size measurements," *Journal of Nanoparticle Research*. Springer, 16(5), pp. 1–17.

Giddings, J. C. (1993) "Field-flow fractionation: analysis of macromolecular, colloidal, and particulate materials," *Science*. American Association for the Advancement of Science, 260(5113), pp. 1456–1465.

Gilbert, B., Lu, G. and Kim, C. S. (2007) "Stable cluster formation in aqueous suspensions of iron oxyhydroxide nanoparticles," *Journal of Colloid and Interface Science*. Elsevier, 313(1), pp. 152–159.

Gimbert, L. J., Hamon, R. E., Casey, P. S. and Worsfold, P. J. (2007) "Partitioning and stability of engineered ZnO nanoparticles in soil suspensions using flow field-flow fractionation," *Environmental Chemistry*. CSIRO, 4(1), pp. 8–10.

Gray, E. P., Bruton, T. A., Higgins, C. P., Halden, R. U., Westerhoff, P. and Ranville, J. F. (2012) "Analysis of gold nanoparticle mixtures: a comparison of hydrodynamic chromatography (HDC) and asymmetrical flow field-flow fractionation (AF4) coupled to ICP-MS," *Journal of Analytical Atomic Spectrometry*. Royal Society of Chemistry, 27(9), pp. 1532–1539.

Guillaume, Y. C., Robert, J. F. and Guinchard, C. (2001) "A mathematical model for hydrodynamic and size exclusion chromatography of polymers on porous particles," *Analytical Chemistry*. ACS Publications, 73(13), pp. 3059–3064.

Hassellöv, M., Readman, J. W., Ranville, J. F. and Tiede, K. (2008) "Nanoparticle analysis and characterization methodologies in environmental risk assessment of engineered nanoparticles," *Ecotoxicology*. Springer, 17(5), pp. 344–361.

Helsper, J. P., Peters, R. J., Brouwer, L. and Weigel, S. (2012) "Characterisation and quantification of liposome-type nanoparticles in a beverage matrix using hydrodynamic chromatography and MALDI-TOF mass spectrometry," *Analytical and Bioanalytical Chemistry*. Springer, pp. 1–9.

Hunter, R. J. (2001) *Foundations of Colloid Science* . Second Edition, Oxford University (ed.). Oxford University Press.

Ito, T., Sun, L. and Crooks, R. M. (2003) "Simultaneous determination of the size and surface charge of individual nanoparticles using a carbon nanotube-based Coulter counter," *Analytical Chemistry*. ACS Publications, 75(10), pp. 2399–2406.

De Jaeger, N. C., Trappers, J. L. and Lardon, P. (1986) "An investigation into capillary hydrodynamic chromatography," *Particle & Particle Systems Characterization*. Wiley Online Library, 3(4), pp. 187–191.

Jimenez, M., Gomez, M., Bolea, E., Laborda, F. and Castillo, J. (2011) "An approach to the natural and engineered nanoparticles analysis in the environment by inductively coupled plasma mass spectrometry," *International Journal of Mass Spectrometry*. Elsevier, 307(1), pp. 99–104.

Von der Kammer, F., Baborowski, M. and Friese, K. (2005) "Field-flow fractionation coupled to multi-angle laser light scattering detectors: Applicability and analytical benefits for the analysis of environmental colloids," *Analytica chimica acta*. Elsevier, 552(1), pp. 166–174.

Von der Kammer, F., Ferguson, P. L., Holden, P. A., Masion, A., Rogers, K. R., Klaine, S. J., Koelmans, A. A., Horne, N. and Unrine, J. M. (2012) "Analysis of engineered nanomaterials in complex matrices (environment and biota): general considerations and conceptual case studies," *Environmental Toxicology and Chemistry*. Wiley Online Library, 31(1), pp. 32–49.

King, S. M. and Jarvie, H. P. (2012) "Exploring how organic matter controls structural transformations in natural aquatic nanocolloidal dispersions," *Environmental Science & Technology*. ACS Publications, 46(13), pp. 6959–6967.

Korolev, A., Viktorova, E., Orekhov, V. and Kurganov, A. (2012) "Unusually high efficiency of the separation of polymers by hydrodynamic chromatography on hollow capillary columns," *Russian Journal of Physical Chemistry A, Focus on Chemistry*. Springer, 86(7), pp. 1161–1164.

Lead, J., Muirhead, D. and Gibson, C. (2005) "Characterization of freshwater natural aquatic colloids by atomic force microscopy (AFM)," *Environmental Science & Technology*. ACS Publications, 39(18), pp. 6930–6936.

Lespes, G. and Gigault, J. (2011) "Hyphenated analytical techniques for multidimensional characterisation of submicron particles: A review," *Analytica Chimica Acta*. Elsevier, 692(1), pp. 26–41.

Li, J. J., Liu, P. and GENG, X. D. (2009) "Two dynamic chromatographies and their application," *Chinese Journal of Analytical Chemistry*. Elsevier, 37(7), pp. 1082–1087.

Lin, M., Lindsay, H., Weitz, D., Klein, R., Ball, R. and Meakin, P. (1990) "Universal diffusion-limited colloid aggregation," *Journal of Physics: Condensed Matter*. IOP Publishing, 2(13), pp. 3093–3113.

Liu, H. H. and Cohen, Y. (2014) "Multimedia environmental distribution of engineered nanomaterials," *Environmental Science & Technology*. ACS Publications, 48(6), pp. 3281–3292.

Liu, L., Veerappan, V., Pu, Q., Cheng, C., Wang, X., Lu, L., Allen, R. D. and Guo, G. (2013) "High-Resolution Hydrodynamic Chromatographic Separation of Large DNA Using Narrow, Bare Open Capillaries: A Rapid and Economical Alternative Technology to Pulsed-Field Gel Electrophoresis?," *Analytical Chemistry*. ACS Publications, 86(1), pp. 729–736.

Liu, Y., Radke, W. and Pasch, H. (2005) "Coil-stretch transition of high molar mass polymers in packed-column hydrodynamic chromatography," *Macromolecules*. ACS Publications, 38(17), pp. 7476–7484.

Maurice, P. and Namjesnik-Dejanovic, K. (1999) "Aggregate structures of sorbed humic substances observed in aqueous solution," *Environmental Science & Technology*. ACS Publications, 33(9), pp. 1538–1541.

McGowan, G. R. and Langhorst, M. A. (1982) "Development and application of an integrated, high-speed, computerized hydrodynamic chromatograph," *Journal of Colloid and Interface Science*. Elsevier, 89(1), pp. 94–106.

McHugh, A. J. and Brenner, H. (1984) "Particle size measurement using chromatography," *Critical Reviews in Analytical Chemistry*. Taylor & Francis, 15(1), pp. 63–117.

Mitrano, D. M., Lesher, E. K., Bednar, A., Monserud, J., Higgins, C. P. and Ranville, J. F. (2011) "Detecting nanoparticulate silver using single-particle inductively coupled plasma-mass spectrometry," *Environmental Toxicology and Chemistry*. Wiley Online Library, 31(1), pp. 115–121.

Nagy, D., Silebi, C. and McHugh, A. (1981) "Hydrodynamic chromatography—an evaluation of several features," *Journal of Colloid and Interface Science*. Elsevier, 79(1), pp. 264–267.

Noel, R. J., Gooding, K. M., Regnier, F. E., Orr, C. and Mullins, M. (1978) "Capillary hydrodynamic chromatography," *Journal of Chromatography A*. Elsevier, 166(2), pp. 373–382.

Nowack, B., Ranville, J. F., Diamond, S., Gallego-Urrea, J. A., Metcalfe, C., Rose, J., Horne, N., Koelmans, A. A. and Klaine, S. J. (2012) "Potential scenarios for nanomaterial release and subsequent alteration in the environment," *Environmental Toxicology and Chemistry*. Wiley Online Library, 31(1), pp. 50–59.

Pace, H. E., Rogers, N. J., Jarolimek, C., Coleman, V. A., Gray, E. P., Higgins, C. P. and Ranville, J. F. (2012) "Single Particle Inductively Coupled Plasma-Mass Spectrometry: A Performance Evaluation and Method Comparison in the Determination of Nanoparticle Size," *Environmental Science & Technology*. ACS Publications, 46(22), pp. 12272–12280.

Paul, S., Jamie, R., Harrison, R. M., Jones, I. P. and Stoll, S. (2005) "Characterization of humic substances by environmental scanning electron microscopy," *Environmental Science & Technology*. ACS Publications, 39(7), pp. 1962–1966.

Penlidis, A., Hamielec, A. and MacGregor, J. (1983) "Hydrodynamic and Size Exclusion Chromatography of Particle Suspensions-An Update," *Journal of Liquid Chromatography*. Taylor & Francis, 6(S2), pp. 179–217.

Pergantis, S. A., Jones-Lepp, T. L. and Heithmar, E. M. (2012) "Hydrodynamic chromatography online with single particle-inductively coupled plasma mass spectrometry for ultratrace detection of metal-containing nanoparticles," *Analytical Chemistry*. ACS Publications, 84(15), pp. 6454–6462.

Perret, D., Leppard, G. G., Müller, M., Belzile, N., De Vitre, R. and Buffle, J. (1991) "Electron microscopy of aquatic colloids: non-perturbing preparation of specimens in the field," *Water Research*. Elsevier, 25(11), pp. 1333–1343.

Pillai, Z. S. and Kamat, P. V. (2004) "What factors control the size and shape of silver nanoparticles in the citrate ion reduction method?," *The Journal of Physical Chemistry B*. ACS Publications, 108(3), pp. 945–951.

Plaschke, M., Römer, J. and Kim, J. (2002) "Characterization of Gorleben groundwater colloids by atomic force microscopy," *Environmental Science & Technology*. ACS Publications, 36(21), pp. 4483–4488.

Prieve, D. C. and Hoysan, P. M. (1978) "Role of colloidal forces in hydrodynamic chromatography," *Journal of Colloid and Interface Science*. Elsevier, 64(2), pp. 201–213.

Schuch, H. and Wohleben, W. (2010) "Measurement of Particle Size Distribution of Polymer Latexes," in Luis M. Gugliotta and Jorge R. Veda (ed.).

Silebi, C. A. and McHugh, A. J. (1978) "An analysis of flow separation in hydrodynamic chromatography of polymer latexes," *AIChE Journal*. Wiley Online Library, 24(2), pp. 204–212.

Simonet, B. M. and Valcárcel, M. (2009) "Monitoring nanoparticles in the environment," *Analytical and Bioanalytical Chemistry*. Springer, 393(1), pp. 17–21.

Siripinyanond, A., Barnes, R. M. and Amarasiriwardena, D. (2002) "Flow field-flow fractionation-inductively coupled plasma mass spectrometry for sediment bound trace metal characterization," *Journal of Analytical Atomic Spectrometry*. Royal Society of Chemistry, 17(9), pp. 1055–1064.

Small, H. (1974) "Hydrodynamic chromatography a technique for size analysis of colloidal particles," *Journal of Colloid and Interface Science*. Elsevier, 48(1), pp. 147–161.

Small, H., Saunders, F. L. and Solc, J. (1976) "Hydrodynamic chromatography a new approach to particle size analysis," *Advances in Colloids and Interface Science*, 6, pp. 237–266.

Staben, M. E., Zinchenko, A. Z. and Davis, R. H. (2003) "Motion of a particle between two parallel plane walls in low-Reynolds-number Poiseuille flow," *physics of fluids*, 15, pp. 1711–1733.

Stegeman, G., Kraak, J. C. and Poppe, H. (1993) "Dispersion in packed-column hydrodynamic chromatography," *Journal of Chromatography A*. Elsevier, 634(2), pp. 149–159.

Stegeman, G., Oostervink, R., Kraak, J., Poppe, H. and Unger, K. (1990) "Hydrodynamic chromatography of macromolecules on small spherical non-porous silica particles," *Journal of Chromatography A*. Elsevier, 506, pp. 547–561.

Stoisits, R. F., Poehlein, G. W. and Vanderhoff, J. W. (1976) "Mathematical modeling of hydrodynamic chromatography," *Journal of Colloid and Interface Science*. Elsevier, 57(2),

pp. 337–344.

Striegel, A. M. and Brewer, A. K. (2012) "Hydrodynamic Chromatography," *Annual Review of Analytical Chemistry*. Annual Reviews, 5, pp. 15–34.

Takeuchi, T., Aspanut, Z. and Lim, W. L. (2009) "Hydrodynamic Chromatography of Silica Colloids on Small Spherical Nonporous Silica Particles," *Analytical Sciences*. J-STAGE, 25(2), pp. 301–306.

Thompson, J. W., Lieberman, R. A. and Jorgenson, J. W. (2009) "Hydrodynamic chromatography for the size classification of micron and sub-micron sized packing materials," *Journal of Chromatography A*. Elsevier, 1216(45), pp. 7732–7738.

Tiede, K., Boxall, A. B., Tiede, D., Tear, S. P., David, H. and Lewis, J. (2009) "A robust size-characterisation methodology for studying nanoparticle behaviour in 'real' environmental samples, using hydrodynamic chromatography coupled to ICP-MS," *Journal of Analytical Atomic Spectrometry*. Royal Society of Chemistry, 24(7), pp. 964–972.

Tiede, K., Boxall, A. B., Wang, X., Gore, D., Tiede, D., Baxter, M., David, H., Tear, S. P. and Lewis, J. (2010) "Application of hydrodynamic chromatography-ICP-MS to investigate the fate of silver nanoparticles in activated sludge," *Journal of Analytical Atomic Spectrometry*. Royal Society of Chemistry, 25(7), pp. 1149–1154.

Tiede, K., Boxall, A., Tear, S., Lewis, J., David, H. and Hassellov, M. (2008) "Detection and characterization of engineered nanoparticles in food and the environment-a review," *Food Additives and Contaminants*, 25(07), pp. 795–821.

Tijssen, R., Bos, J. and Van Kreveld, M. E. (1986) "Hydrodynamic chromatography of macromolecules in open microcapillary tubes," *Analytical Chemistry*. ACS Publications, 58(14), pp. 3036–3044.

Tipping, E. (2002) *Cation binding by humic substances*. Cambridge University Press.

Tuoriniemi, J., Cornelis, G. and Hassellöv, M. (2012) "Size discrimination and detection capabilities of single-particle ICPMS for environmental analysis of silver nanoparticles," *Analytical Chemistry*. ACS Publications, 84(9), pp. 3965–3972.

Umehara, R., Miyahara, H., Okino, A., Harada, M. and Okada, T. (2012) "Wide-bore capillary hydrodynamic chromatography with ICP-MS detection for evaluation of lanthanide uptake by molecular aggregates.," *Analytical Sciences: the International Journal of the Japan Society for Analytical Chemistry*, 28(4), p. 359.

Venema, E., de Leeuw, P., Kraak, J., Poppe, H. and Tijssen, R. (1997) "Polymer characterization using on-line coupling of thermal field flow fractionation and hydrodynamic chromatography," *Journal of Chromatography A*. Elsevier, 765(2), pp. 135–144.

Watson, J. T. and Sparkman, O. D. (2007) *Introduction to mass spectrometry: instrumentation, applications, and strategies for data interpretation*. John Wiley & Sons.

Wigginton, N. S., Haus, K. L. and Hochella Jr, M. F. (2007) "Aquatic environmental nanoparticles," *Journal of Environmental Monitoring*. Royal Society of Chemistry, 9(12), pp.

1306–1316.

Wilkinson, K. J., Balnois, E., Leppard, G. G. and Buffle, J. (1999) "Characteristic features of the major components of freshwater colloidal organic matter revealed by transmission electron and atomic force microscopy," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Elsevier, 155(2-3), pp. 287–310.

Wohlleben, W. (2012) "Validity range of centrifuges for the regulation of nanomaterials: from classification to as-tested coronas," *Journal of Nanoparticle Research*. Springer, 14(12), pp. 1–18.

Yegin, B. A. and Lamprecht, A. (2006) "Lipid nanocapsule size analysis by hydrodynamic chromatography and photon correlation spectroscopy," *International Journal of Pharmaceutics*. Elsevier, 320(1), pp. 165–170.

Zarrin, F. and Dovichi, N. J. (1985) "Particle counting by laser light scatter for capillary hydrodynamic chromatography," *Analytical Chemistry*. ACS Publications, 57(9), pp. 1826–1829.

Zhe, J., Jagtiani, A., Dutta, P., Hu, J. and Carletta, J. (2007) "A micromachined high throughput Coulter counter for bioparticle detection and counting," *Journal of Micromechanics and Microengineering*. IOP Publishing, 17(2), p. 304.

Chapter 4

Evaluation of Hydrodynamic Chromatography Coupled with UV-Visible, Fluorescence and Inductively Coupled Plasma Mass Spectrometry Detectors for Sizing and Quantifying Colloids in Environmental Media

Allan Philippe and Gabriele E. Schaumann (2014)
Research article published in *PLoS ONE*

Chapter 5

Evaluation of hydrodynamic chromatography coupled with inductively coupled plasma mass spectrometry detector for analysis of colloids in environmental media – Effects of colloids composition, coating and shape

Allan Philippe, Marie Gangloff, Denis Rakcheev and
Gabriele E. Schaumann (2014)

http://pubs.rsc.org/en/content/articlelanding/2014/ay/c4ay01567c/unauth#!divAbstract

Chapter 6

Hydrodynamic Chromatography Coupled with Single Particle-Inductively Coupled Plasma Mass Spectrometry for Investigating Nanoparticles Agglomerates

Denis Rakcheev, Allan Philippe and Gabriele E. Schaumann (2013)
Research article published in *Analytical Chemistry*

Chapter 7

Interactions of Dissolved Organic Matter with Silver Colloids

Preliminary Study

Table of contents

1 Introduction

In order to further test HDC-ICP-MS for exploring DOM-colloids interactions, the method was applied to the study of the effects of DOM on the stability of silver colloids. Silver colloids are one of the most used engineered colloids and could represent a risk for the environment in the future (Levard et al., 2012; Fabrega et al., 2011). Studying their fate in environmental media is crucial for evaluating this risk. Furthermore, few are known about DOM interactions with silver colloids (chapter 2). As shown in the chapter 2, the mode of adsorption depends strongly on the initial capping agent and it is still unclear which DOM molecules are involved in the adsorption process.

Agglomeration of silver colloids was already observed under environmental conditions (Li, Lenhart and Walker, 2010; Badawy et al., 2010; Huynh and Chen, 2011; Stebounova, Guio and Grassian, 2011; Furman, Usenko and Lau, 2013), although at relatively high particle concentrations (mg L^{-1}). In addition, heteroagglomeration of silver colloids with natural colloids and the effect of polysaccharides or proteins on colloidal stability have not yet been addressed. In the frame of the INTERNANO project and in order to implement HDC-ICP-MS to samples near to natural ones, a set of preliminary studies was carried out for determining the effect of DOM on the stability of silver colloids at low concentrations (µg L^{-1} range) in reconstituted surface waters. These experiments aimed at constructing a methodological basis for future more systematical investigations.

As HDC-ICP-MS could not be used to detect DOM adsorbed onto colloids, probably due to the amount of adsorbed molecules which was lower than the limit of detection of our fluorescence detector (chapter 4), other techniques had to be explored to investigate adsorption mechanisms. Fluorescence spectroscopy was useful to investigate interactions between fulvic and humic acids and silver, iron and iron oxide colloids (Dong and Lo, 2012; Manoharan, Ravindran and Anjali, 2014; Manciulea, Baker and Lead, 2009). Indeed, fluorescence spectroscopy can be used to gain information on the interactions between a fluorophore (in the mentioned references, a part of the humic substances) and other molecules or particles by monitoring fluorescence quenching or enhancement in their presence (Schmidt, 2000).

Fluorescence quenching is a process which decreases the intensity of the fluorescence emission (Schmidt, 2000). Quenching may occur as either static or dynamic. Dynamic quenching is a process where the fluorophore and the quencher come into contact during the lifetime of the excited state, while static quenching is a process where non-fluorescent complexes of the ground state fluorophore are formed. For monodisperse systems, fluorescence quenching data follow the Stern–Volmer equation (Manciulea, Baker and Lead, 2009):

$$\frac{I_F}{I_Q} = 1 + K[Q] \tag{6.1}$$

where I_F and I_Q are the fluorescence intensity in the absence and the presence of quencher respectively, K a constant characterizing the quenching mechanism and $[Q]$ the concentration of quencher. In ideal systems (far away from ours), dynamic quenching can be identified when increase in temperature induces an increase in K, while a decrease in K is characteristic for static quenching. A linear form of the right part of the equation 6.1 indicate a simple quenching mechanism, non-linearity indicates a combination of static and dynamic quenching. Molecular polydispersity, as for humic acids, can also induce a complex non-linear combination of quenching mechanisms.

Quenching of humic acid fluorescence was observed for iron oxide (Manciulea, Baker and Lead, 2009), $Fe^{(0)}$ colloids (Dong and Lo, 2012) and β-D-glucose-coated gold colloids (Pallem, Stretz and Wells, 2009), while fluorescence enhancement was noticed with citrate coated gold colloids (Pallem, Stretz and Wells, 2009) and silver colloids (Manoharan, Ravindran and Anjali, 2014). However, the interpretation of these results is matter of discussion as humic substances are composed of thousands of different molecules involved in intermolecular interactions (Nebbioso and Piccolo, 2013; Piccolo, 2001). Indeed, adsorption of humic substances onto colloids may disrupt intermolecular structures containing fluorophores and hence modify their spectroscopic properties without involving interaction of these fluorophores with the surface. Therefore, fluorescence enhancement and quenching may not result only from the interaction of fluorophores with the surface. Since the actual understanding of the intermolecular structure of humic substances does not allow resolving those complex interactions, other complementary methods should be used for confirming results obtained with fluorescence spectroscopy. Nonetheless, fluorescence quenching is a practical indicator for DOM adsorption and can be easily measured in situ.

In this chapter, further investigation of silver colloid interaction with DOM using HDC-UV-FLD-ICP-MS and UV-fluorescence spectroscopy are discussed in the light of results from a study of silver colloid agglomeration in the presence and the absence of Suwannee River humic acids (SRHA) obtained in cooperation with Dr. George Metreveli (Metreveli, Philippe and Schaumann, 2014). Using HDC-ICP-MS made possible to study particle stability at low concentrations (µg L^{-1} range), while fluorescence experiments gives hints about the nature of DOM coating on silver colloids, despite strong limitations.

2   Material and methods

Miscellaneous materials

All Chemicals obtained from the suppliers were used without further purification. Milli-Q water (MQW, resistivity = 18 MΩ cm) was used for all dilutions and sample preparations. Moderately soft water (MSW) was produced according to a standard procedure from the American Environmental Protection Agency (United States Environmental Protection Agency, n.d.) and contained: $NaHCO_3$ (p.a., Merck), $CaSO_4·2H_2O$ (p.a., Merck), $MgSO_4·7H_2O$ (p.a., Roth), and KCl (p.a., Merck) at the following concentrations: 96, 60, 122, 86, and 4 mg L^{-1}, respectively. Standard Suwannee River humic acids (SRHA) were provided by the International Humic Substances Society. Bovine serum albumin (BSA, Sigma-Aldrich, ≥99%) was used as model protein. Polygalacturonic acid (25-50 kDa, Alfa Aesar) was used for modeling natural polysaccharides. The components used for the HDC eluent and the tuning of the ICP-MS detector are described in the chapter 4. pH adjustments was carried on with HNO_3 (sub-boiled) and NaOH (Merk, Titrisol) when required.

Reference colloids

The standard citrate-stabilized gold particles (Aldrich, Germany) used in the chapters 4 and 5 were used as size calibrants for the HDC-ICP-MS measurements. The silver particles stabilized with citric acid and bare silica particles purchased from Nanocomposix (respectively 20 nm and 200 nm in size, further characteristics can be found in chapter 5) were used for the HDC-ICP-MS experiments. Silver colloids synthesized in house by Dr. George Metreveli using citrate reduction method were used for

the fluorescence spectroscopy experiments. The following method was followed for the synthesis: 1.290 g (5 mmol) trisodium citrate (Sigma-Aldrich) and 169.9 mg (1 mmol) silver nitrate (≥ 99.9%, p.a., Roth) were dissolved in 950 mL and 50 mL deionised water respectively. The pH value of the trisodium citrate solution was adjusted to 11 using 1 mol L^{-1} NaOH solution (Roth) and the solution was let for refluxing under magnetic stirring. The solution of silver nitrate was added dropwise within 5 min to the boiling solution of trisodium citrate. The mixture was further refluxed and stirred for 20 min and cooled to room temperature. Deionised water was added to obtain a final volume of 1 L. Final solutions have a final pH value of 8.9. The synthesised dispersions were stored in the dark at 4°C. Characterization of similar dispersions with TEM, HDC-ICP-MS and DLS can be found elsewhere (Metreveli, Philippe and Schaumann, 2014).

For fluorescence experiments, the silver dispersion was purified by centrifugation for decreasing the concentration of residual citrate. 5 mL of the dispersion were centrifuged at 30 000 rpm for 30 min. The four upper milliliters were then removed and the settled particles were redispersed in MQW. This procedure was repeated three times. Unfortunately, adhesion onto the wall of the tube resulted in important loss of particles (43-70%, determined by ICP-OES).

HDC-ICP-MS

An HDC-column type 2 (Agilent) was used for measuring the size of the incubated dispersions. Equipment and elution conditions are described in the chapter 4. The wavelength of the UV-detector was optimized for detecting SiO$_2$ particles under these elution conditions (λ_{abs} = 300 nm), while the fluorescence detector was used to detect humic acid (λ_{ext} = 430 nm, λ_{em} = 500 nm) when it was present in the sample. Time marking was carried on by monitoring the ^{138}Ba background as explained in the chapter 3. The dwell time for silver was 60 ms.

Fluorescence spectroscopy

Fluorescence measurements were carried on with a Perkin Elmer LS 55 fluorescence spectrometer. Emission spectra were performed from 270 to 600 nm with a 2 nm step and an excitation wavelength of 230 nm. Photomultiplier tube voltage was set to 750 V with emission and excitation slit set to 1.25 mm (5 nm with a grating dispersion of 4 nm mm^{-1}). Emission spectra were corrected for removing the first and second filter-inner effects using the following formula (Gu and Kenny, 2008):

$$\frac{F_{ideal}}{F_{obs}} = \frac{2.3 a_{ex} \Delta x 10^{a_{ex} x_1}}{1 - 10^{-a_{ex} \Delta x}} \frac{2.3 a_{em} \Delta y 10^{a_{em} y_1}}{1 - 10^{-a_{em} \Delta y}} \tag{II.1}$$

where F_{ideal} and F_{obs} are the emission intensity after and before correction, respectively, a_{ex} and a_{em} are the absorbance of the mixture at the excitation and emission wavelengths, respectively, and Δx, Δy, x_1 and y_1 denote parameters related to the beam and device geometry and were chosen, as a first approximation, to be as following: $\Delta x = \Delta y = 0.125$ cm and $x_1 = y_1 = 0.4375$ cm. More accurate corrections of the inner filter effects based on programmable algorithms have been reported (Gu and Kenny, 2008; Kubista et al., 1994; Ohno, 2002). However, our correction was fully satisfying for the range of absorbance of our samples (< 0.5). Samples were measured in dedicated quartz cuvettes (1 cm path length).

Respective DOM and silver particles stock solutions were diluted to the wanted concentrations in MSW in 15 mL polypropylene tubes. pH was adjusted with HNO$_3$ or NaOH, if required. The mixture

was slowly stirred (orbital shaker) for at least one hour before fluorescence quenching experiments were carried out.

Incubation experiments

In a glass beaker, SiO_2 particles (final concentration: 10 mg L^{-1}) were added to a solution of SRHA, BSA or alginate (5 mg L^{-1}) diluted in MSW and with a pH adjusted to the desired value. The dispersion was magnetically stirred for 15 min. Silver colloids (final concentration: 5 µg L^{-1}) were added and the dispersion stirred for one more hour. After this incubation time, the solution was directly poured into a HPLC-vial and analyzed with HDC-ICP-MS.

3   Results and discussion

3.1   Stability of silver colloids in reconstituted natural water

In order to obtain a first idea of the stability of silver colloids in a simulated natural medium at realistic concentrations, incubation experiments were performed. Silver colloids were added to reconstituted natural water containing DOM and SiO_2 colloids. SiO_2 colloids served as representatives of negatively charged natural colloids and were therefore at much higher concentrations than the silver particles (10 mg L^{-1} and 5 µg L^{-1}, respectively). This concentration ratio is representative of the expected realistic ratios which suggest that heteroagglomeration may be the predominant process in natural waters (Quik et al., 2012; Quik, van De Meent and Koelmans, 2014). It has to be noted that these concentrations are much more realistic than in the previously reported studies on silver colloids stability in simulated environmental media (Li, Lenhart and Walker, 2010; Badawy et al., 2010; Huynh and Chen, 2011; Stebounova, Guio and Grassian, 2011; Furman, Usenko and Lau, 2013). Three types of DOM were tested in order to investigate the relevance of the nature of DOM on the agglomeration behavior of silver colloids. We chose Suwannee River humic acids (SRHA), alginate and bovine serum albumin (BSA) to represent the three main types of DOM. Indeed, these compounds have been used to model natural humic substances, polysaccharides and proteins, respectively (Erhayem and Sohn, 2014; Huangfu et al., 2013). We carried out experiments at different pH values for investigating the effect of this parameter in the range of natural pH values.

Monitoring the average size of the colloidal silver suspension prior and after incubation is a straightforward method for monitoring their stability in a given medium. An increase in the average size of particles indicates agglomeration or covering with a thick organic layer. A decrease in size indicates particle dissolution. The presence of a high concentration of SiO_2 colloids compared to silver colloids excludes the use of DLS and NTA for sizing silver colloids. However, all components could be resolved and the silver colloids accurately measured using HDC-UV-FLD-ICP-MS, a combination of detectors described in the chapter 4, as shown in the figure 7.1.

Since the excitation and emission wavelengths were optimized for selectively detecting fluorescent humic acids molecules, only SRHA was detected using FLD detector. The signal intensity was near the detection limit as only a small portion of the SRHA molecules fluoresce at those particular wavelengths. The retention time of SRHA corresponds to molecules smaller than 20 nm, thus no SRHA was detected in the colloidal range. However, this does not clearly indicate a lack of SRHA adsorption onto colloids, as the detection limit of the FLD was probably too high for detecting the small amount of adsorbed SRHA. In addition, fluorescence quenching could also occur when SRHA

adsorbed onto the surface of colloids and the possibility that non-fluorescing molecules adsorb preferentially onto colloids cannot be ruled out. Nonetheless, the clear identification of the major part of fluorescent SRHA can be carried out using FLD.
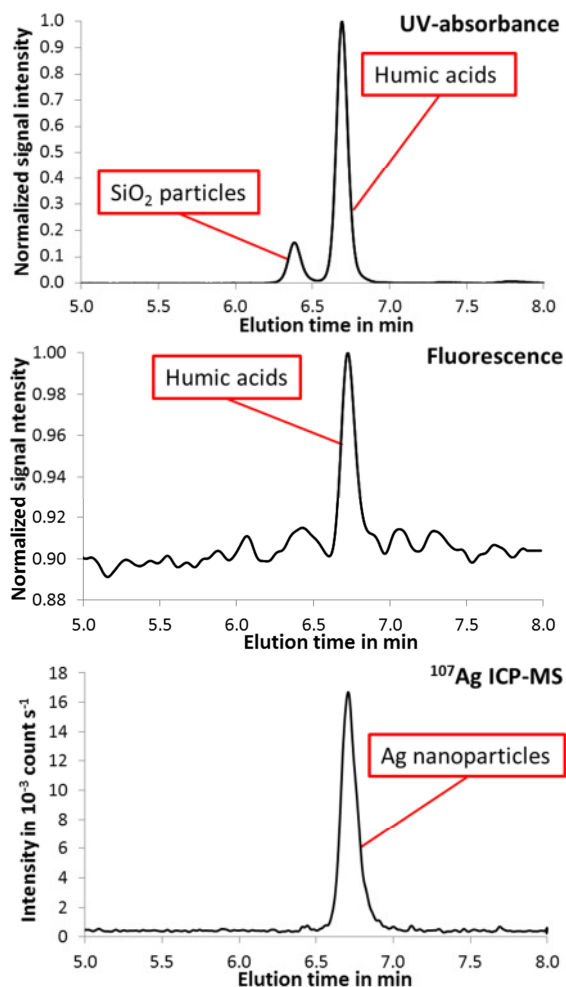
Figure 7.1: example of HDC-UV-FLD-ICP-MS chromatograms of silver colloids incubated in a simulated natural water (moderately hard synthetic water) containing humic acids and SiO₂. Absorbance wavelength was 300 nm. Excitation and emission wavelengths were 430 nm and 500 nm respectively. The three main components of the dispersion are perfectly resolved on this example.

For all systems studied the DOM present and the SiO_2 colloids could be detected with the UV-visible detector. As SiO_2 colloids were resolved from the ionic background by HDC and the peak of SRHA could be clearly identified in the range of small molecules, they could be successfully identified using the UV-detector (UVD) at an absorption wavelength of 300 nm (figure 7.1). Silver particles were detected only with the ICP-MS detector, as the used concentrations were well below the detection limits of our UVD and FLD. Thus, the three major components of the natural medium could be detected and the average size of the two types of particles could be determined independently. This confirms the applicability of HDC-UV-FLD-ICP-MS to samples containing high amounts of inorganic ions, DOM and background inorganic colloids compared to the concentration of the targeted engineered colloids.

The size of the silver particles was determined from their retention factor using the same calibration procedure as explained in the chapters 4 and 5. The results of the size measurements after incubation in the simulated natural medium at different pH values and with different DOM are

summarized in the figure 7.2. The initial size of the silver colloids was 27.4 ± 3.1 nm. After incubation, the size of the silver particles remained in the range of 25-35 nm for all solution conditions indicating that the particles remained stable. Differences in size were in the range of the confidence intervals at 95 %. Since the size of the silver particles remained constant over the incubation time (27.6 ± 3.3 nm) in the absence of DOM, it is highly probable that agglomeration was negligible in this time frame. Similarly the size of SiO_2 particles remained stable over the incubation time with an average final size corresponding to their initial size.

Since SiO_2 particles are negatively charged over a wide range of pH (Rezwan et al., 2005), they were probably strongly electrostatically stabilized and remained therefore stable even in pure water. DOM adsorbed onto the surface of particles could also be an additional stabilizing factor as shown in chapter 2. As remarked above, silver colloids are highly diluted and homoagglomeration is hence statistically not favored compared to heteroagglomeration with SiO_2 particles. Furthermore, both SiO_2 and Ag particles are strongly negatively charged and hence electrostatically stabilized. Therefore homo- and heteroagglomeration were not expected to be determining factors for the behavior of silver colloids during the incubation time. Our observations that the average particle size remains constant after the incubation time confirm this assumption. Since particle size remain constant, it is highly probable that dissolution of the silver colloids did not occur under these conditions.
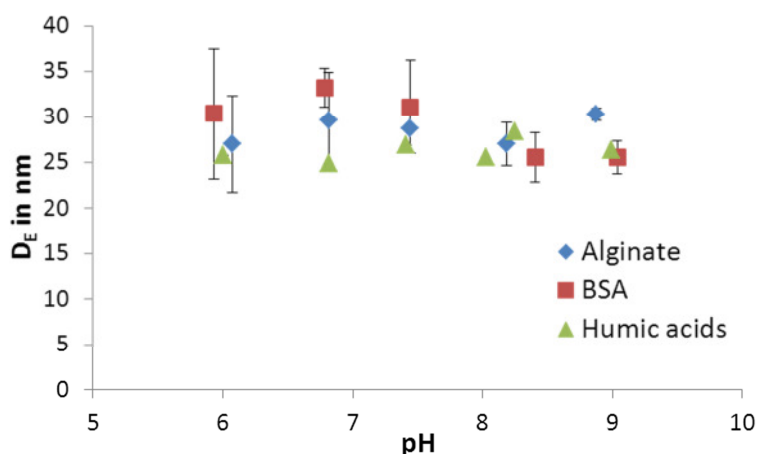
Figure 7.2: Effective diameter (D_E) measured using HDC-ICP-MS of Ag$^{(0)}$ colloids (nominal diameter: 20 nm, concentration: 5 µg L^{-1}) incubated for one hour in reconstituted moderately hard natural water spiked with 10 mg L^{-1} of SiO_2 particles and 5 mg L^{-1} of organic matter (alginate, humic acids or BSA) and adjusted at different pH. Error bars represent the confidence intervals at 95% measured with three measurement replicates.

Silver colloids were stable at all pH values tested indicating that the influence of pH is irrelevant under these conditions. As the effect of pH changes in a natural range on the surface charge of both SiO_2 and silver particles is expected to be minimal (Rezwan et al., 2005; Badawy et al., 2010), changes in pH are not expected to strongly influence the agglomeration processes in our case as confirmed by these results. Furthermore, inside the confidence intervals (95%), no difference between humic acids, BSA, and alginate was observed. This indicates that DOM does not strongly destabilize the silver particles in those ranges of particle concentrations and pH.

These findings demonstrate that silver colloids may, under some conditions, remain stable in the environment, at least in cases when heteroagglomeration is unfavorable. In our case, this is probably mostly due to their low concentration and to the strong negative surface charges of both silver and

SiO_2 particles. However, further experiments should be performed at a longer time scale to investigate the stability of silver particles on the long term.

3.2 Fluorescence study of silver colloids and humic acid

These preliminary experiments aimed at exploring the capability of fluorescence spectroscopy for studying qualitatively and quantitatively fluorescent humic acids adsorption onto colloids. At first, a simple correction method was tested for removing filter effects occurring in the range of humic acids concentrations that we used. This appeared to be crucial, as demonstrated by the important gap (almost 100% intensity difference) between corrected and uncorrected humic acids calibration curve obtained at optimal excitation and emission wavelengths (figure 7.3). Filter effects occur when exciting and/or emitting light is absorbed by the sample. As this effect increases with the concentration of the absorbent, the intensity of filter effects increases with the concentration (figure 7.3). This problem is well-known and several corrections techniques have been proposed (Gu and Kenny, 2008; Kubista et al., 1994; Ohno, 2002; Tucker, Amszi and Acree, 1992). In our case a simple correction method detailed in the experimental section was fully satisfying and a linear dependence of the fluorescence intensity on the fluorophores concentration was obtained for the concentrations between 0.1 and 15 mg L^{-1}.
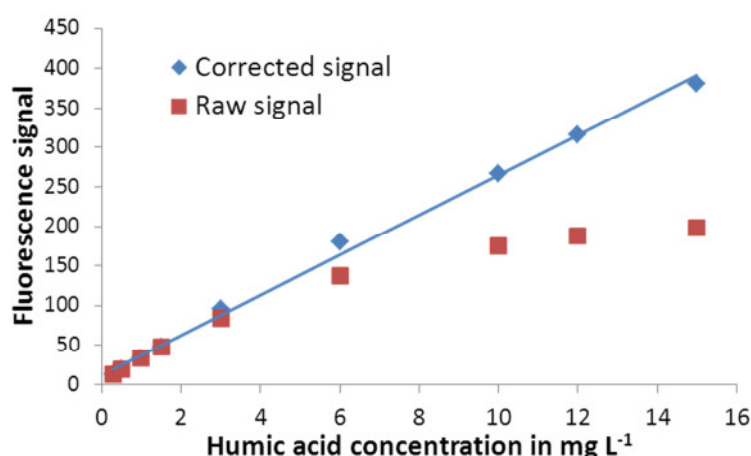
Figure 7.3: Fluorescence calibration curves for humic acid measured at an excitation and emission wavelengths of 230 nm and 440 nm respectively. Curve obtained before and after correction of the inner and outer filter effects are shown. The correlation coefficient of the regression line is 0.9968.

Our first approach was to study the effect of silver colloids on SRHA fluorescence. However, mixing particles and humic acids never resulted in significant and reproducible changes neither in the pattern nor in the intensity (corrected or not) of the fluorescence. Experiments were performed with silver colloids concentrations in the range of 0.5-5 mg L^{-1}. Higher concentrations were problematic since the fluorescence of silver colloids became significant compare to the fluorescence of the humic acids and varies non-trivially with the concentration. The lack of fluorescence inhibition/enhancement can be rationalized in several ways:

- Fluorophores do not adsorb onto particles.
- Fluorophores adsorb onto the surface without any effect on the fluorescence or with compensating effects (enhancement for some fluorophores and inhibition for others).

- The sorption of fluorophores is compensated by the thermodynamically driven structural reorganization of humic acids in the solution, which could induce a release of previously inhibited fluorophores.

As our (lack of) observations stand variations in particle concentration and pH, the second and third explanations seem highly improbable. Therefore, we suggest that fluorophores barely adsorb onto our citrate coated silver particles. This hypothesis deeply compromises further investigation of DOM sorption by citrate stabilized silver colloids using fluorescence spectroscopy.

3.3 Influence of humic acids on the agglomeration mechanism of silver colloids

The previous results concerning silver colloids stability and fluorescence quenching of SRHA could suggest that the adsorption of SRHA on citrate stabilized silver colloids is limited and that SRHA does not affect the agglomeration processes. From this point of view, it is interesting to discuss published results obtained in collaboration with Dr. George Metreveli (Metreveli, Philippe and Schaumann, 2014). These results were obtained in the frame of a study addressing the homoagglomeration and disagglomeration of silver colloids in Rhine River water. All experimental details are described in the corresponding reference (Metreveli, Philippe and Schaumann, 2014). The experimental determination of attachment efficiencies in reconstituted natural water (Rhine River) in the presence and in the absence of SRHA indicated a clear effect of SRHA on the colloidal stability of silver colloids (Metreveli, Philippe and Schaumann, 2014). This complex effect could be only explained by the adsorption of SRHA on silver colloids, as observed for other colloidal systems (chapter 2). The adsorption of SRHA increases the density of negative charges on the particle surface and, therefore, increases the repulsive electrostatic potential between two particles. This effect was reflected by the reduction of the attachment efficiency of more than 50% in the presence of SRHA, at Ca^{2+} concentrations smaller than 2 mmol L^{-1} (Metreveli, Philippe and Schaumann, 2014). Moreover, additional contribution of steric forces was strongly suggested by the constant attachment efficiency obtained for Ca^{2+} concentrations between 2-3 mmol L^{-1}, whereas cation bridging flocculation, indicated by attachment efficiencies larger than one, was observed at higher concentrations. These results and their interpretation indirectly demonstrate that SRHA interact with citrate stabilized silver colloids. Therefore, the supposed lack of adsorption of the fluorescent SRHA molecules on silver colloids cannot be generalized and non-fluorescent molecules could be the main contributors to the adsorbed layer.

The concentrations of the most relevant cations for the agglomeration process in Rhine River were: 0.53 mmol L^{-1}, 0.53 mmol L^{-1} and 1.5 mmol L^{-1} for Na^+, Mg^{2+} and Ca^{2+}, respectively. The natural concentration of Ca^{2+} was near to the critical coagulation concentration (CCC). On the other hand, the concentrations of the most relevant cations in MSW were: 1.14 mmol L^{-1}, 0.49 mmol L^{-1} and 0.35 mmol L^{-1} for Na^+, Mg^{2+} and Ca^{2+}, respectively. As the Schulze-Hardy rule predicts, divalent cations had the major influence on the agglomeration of colloids in water (Verrall, Warwick and Fairhurst, 1999; Petosa et al., 2010). This was also observed for silver particles in reconstituted Rhine River water. Since the concentration of Ca^{2+} in MSW was lower than the CCC measured in the simulated Rhine water with similar silver colloids (citrate stabilized), it is highly probable that the concentration of divalent cations in MSW was not sufficient for destabilizing these colloids. Furthermore, the cation concentration was far below the minimal concentration at which molecular bridging could be clearly

observed ($[Ca^{2+}]$ = 4 mmol L^{-1}). Bridging flocculation was thus unlikely to occur in the incubation experiments reported in the section 3.1. In addition, the aggregation rate decreased linearly with the initial particle concentration in simulated Rhine water (Metreveli, Philippe and Schaumann, 2014). Since the initial particle concentration was 5 µg L^{-1} in our incubation experiments in MSW, it is expected that the time frame of these experiments (one hour) was too short for observing homoagglomeration under these conditions. Therefore, the results obtained at low particle concentrations and in MSW are consistent with the results obtained in reconstituted Rhine water.

4 Conclusion

The findings presented in this chapter indicate that, pH and DOM may not be decisive parameters for the colloidal stability of silver colloids at low particle and ion concentrations. The findings for the two systems presented here (MSW containing DOM and reconstituted Rhine water) cannot be generalized and cannot be rigorously compared, as the compositions of the media and the particles used slightly differed. Nonetheless, the results obtained for these two systems are consistent and suggest that citrate stabilized silver colloids can be stable for at least one hour under natural conditions.

The presence of natural colloids may not change this situation if their surface charge is similar compared to citrate stabilized silver particles, as observed in MSW with SiO_2 colloids. However, other natural colloids should be tested to further explore this hypothesis. Heteroagglomeration with aluminosilicates and iron oxides, which can be positively charged at natural pH values (Kretzschmar, Sticher and Hesterberg, 1997; Gu et al., 1995), will be tested in the second phase of the project INTERNANO. HDC-ICP-MS will certainly play a central role in these investigations, as its usefulness for selectively detecting and sizing colloids at low concentrations in complex media is demonstrated.

The clear effect of DOM on colloidal stability indirectly confirms that DOM adsorb on citrate stabilized silver colloids. However, the fractionation process of DOM upon adsorption onto silver colloids still needs to be investigated. Unfortunately, neither HDC-ICP-MS nor DLS provide information on the adsorption mechanism itself. The application of fluorescence spectroscopy to the monitoring of humic acids adsorption still requires further methodological developments. If no interaction has been observed for the system tested (purified citrate stabilized silver colloids in MSW), the adsorption of non-fluorescent molecules cannot be excluded with this method. Therefore, the study of DOM fractionation requires a different analytical approach with a higher molecular resolution such as sorption isotherms combined with electrospray ionization ultra-high resolution mass spectrometry (Galindo and Del Nero, 2014). This aspect will be further discussed in the next chapter.

References

Badawy, A. M. E., Luxton, T. P., Silva, R. G., Scheckel, K. G., Suidan, M. T. and Tolaymat, T. M. (2010) "Impact of environmental conditions (pH, ionic strength, and electrolyte type) on the surface charge and aggregation of silver nanoparticles suspensions," *Environmental Science & Technology*. ACS Publications, 44(4), pp. 1260–1266.

Dong, H. and Lo, I. (2012) "Influence of humic acid on the colloidal stability of surface-modified nano zero-valent iron," *Water Research*. Elsevier, 47, pp. 419–427.

Erhayem, M. and Sohn, M. (2014) "Stability studies for titanium dioxide nanoparticles upon adsorption of Suwannee River humic and fulvic acids and natural organic matter," *Science of the Total Environment*. Elsevier, 468, pp. 249–257.

Fabrega, J., Luoma, S. N., Tyler, C. R., Galloway, T. S. and Lead, J. R. (2011) "Silver nanoparticles: Behaviour and effects in the aquatic environment," *Environment International*. Elsevier, 37(2), pp. 517–531.

Furman, O., Usenko, S. and Lau, B. L. (2013) "Relative importance of the humic and fulvic fractions of natural organic matter in the aggregation and deposition of silver nanoparticles," *Environmental Science & Technology*. ACS Publications, 47(3), pp. 1349–1356.

Galindo, C. and Del Nero, M. (2014) "Molecular level description of the sorptive fractionation of a fulvic acid on Aluminum oxide by use of ESI-FTMS," *Environmental Science & Technology*. ACS Publications.

Gu, B., Schmitt, J., Chen, Z., Liang, L. and McCarthy, J. F. (1995) "Adsorption and desorption of different organic matter fractions on iron oxide," *Geochimica et Cosmochimica Acta*. Elsevier, 59(2), pp. 219–229.

Gu, Q. and Kenny, J. E. (2008) "Improvement of inner filter effect correction based on determination of effective geometric parameters using a conventional fluorimeter," *Analytical Chemistry*. ACS Publications, 81(1), pp. 420–426.

Huangfu, X., Jiang, J., Ma, J., Liu, Y. and Yang, J. (2013) "Aggregation Kinetics of Manganese Dioxide Colloids in Aqueous Solution: Influence of Humic Substances and Biomacromolecules," *Environmental Science & Technology*. ACS Publications, 47(18), pp. 10285–10292.

Huynh, K. A. and Chen, K. L. (2011) "Aggregation kinetics of citrate and polyvinylpyrrolidone coated silver nanoparticles in monovalent and divalent electrolyte solutions," *Environmental Science & Technology*. ACS Publications, 45(13), pp. 5564–5571.

Kretzschmar, R., Sticher, H. and Hesterberg, D. (1997) "Effects of adsorbed humic acid on surface charge and flocculation of kaolinite," *Soil Science Society of America Journal*. Soil Science Society of America, 61(1), pp. 101–108.

Kubista, M., Sjöback, R., Eriksson, S. and Albinsson, B. (1994) "Experimental correction for the inner-filter effect in fluorescence spectra," *Analyst*. The Royal Society of Chemistry, 119(3), pp. 417–419.

Levard, C., Hotze, E. M., Lowry, G. V. and Brown, G. E. (2012) "Environmental Transformations of Silver Nanoparticles: Impact on Stability and Toxicity," *Environmental Science & Technology*. ACS

Publications, 46, pp. 6900–6914.

Li, X., Lenhart, J. J. and Walker, H. W. (2010) "Dissolution-accompanied aggregation kinetics of silver nanoparticles," *Langmuir*. ACS Publications, 26(22), pp. 16690–16698.

Manciulea, A., Baker, A. and Lead, J. R. (2009) "A fluorescence quenching study of the interaction of Suwannee River fulvic acid with iron oxide nanoparticles," *Chemosphere*. Elsevier, 76(8), pp. 1023–1027.

Manoharan, V., Ravindran, A. and Anjali, C. (2014) "Mechanistic Insights into Interaction of Humic Acid with Silver Nanoparticles," *Cell biochemistry and Biophysics*. Springer, 68(1), pp. 127–131.

Metreveli, G., Philippe, A. and Schaumann, G. E. (2014) "Disaggregation of silver nanoparticle homoaggregates in a river water matrix," *Science of The Total Environment*. Elsevier.

Nebbioso, A. and Piccolo, A. (2013) "Molecular characterization of dissolved organic matter (DOM): a critical review," *Analytical and Bioanalytical Chemistry*. Springer, 405(1), pp. 109–124.

Ohno, T. (2002) "Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter," *Environmental Science & Technology*. ACS Publications, 36(4), pp. 742–746.

Pallem, V. L., Stretz, H. A. and Wells, M. J. (2009) "Evaluating aggregation of gold nanoparticles and humic substances using fluorescence spectroscopy," *Environmental Science & Technology*. ACS Publications, 43(19), pp. 7531–7535.

Petosa, A. R., Jaisi, D. P., Quevedo, I. R., Elimelech, M. and Tufenkji, N. (2010) "Aggregation and deposition of engineered nanomaterials in aquatic environments: Role of physicochemical interactions," *Environmental Science & Technology*. ACS Publications, 44(17), pp. 6532–6549.

Piccolo, A. (2001) "The supramolecular structure of humic substances," *Soil Science*, 166(11), p. 810.

Quik, J. T., van De Meent, D. and Koelmans, A. A. (2014) "Simplifying modeling of nanoparticle aggregation-sedimentation behavior in environmental systems: A theoretical analysis," *Water research*. Elsevier, 62, pp. 193–201.

Quik, J. T. K., Stuart, M. C., Wouterse, M., Peijnenburg, W., Hendriks, A. J. and van de Meent, D. (2012) "Natural colloids are the dominant factor in the sedimentation of nanoparticles," *Environmental Toxicology and Chemistry*. Wiley Online Library, 31, pp. 1019–1022.

Rezwan, K., Studart, A., Vörös, J. and Gauckler, L. (2005) "Change of zeta-potential of biocompatible colloidal oxide particles upon adsorption of bovine serum albumin and lysozyme," *The Journal of Physical Chemistry B*. ACS Publications, 109(30), pp. 14469–14474.

Schmidt, W. (2000) *Optische Spektroskopie, Eine Einführung, 2. Auflage*, Wiley-VCH (ed.).

Stebounova, L. V., Guio, E. and Grassian, V. H. (2011) "Silver nanoparticles in simulated biological media: a study of aggregation, sedimentation, and dissolution," *Journal of Nanoparticle Research*. Springer, 13, pp. 1–12.

Tucker, S. A., Amszi, V. L. and Acree, W. E. (1992) "Primary and secondary inner filtering. Effect of K2Cr2O7 on fluorescence emission intensities of quinine sulfate," *Journal of Chemical Education*. ACS

Publications, 69(1), p. A8.

United States Environmental Protection Agency (n.d.). http://water.epa.gov/scitech/methods/cwa/wet/upload/2007_07_10_methods_wet_disk2_atx7-10.pdf (Accessed: 8, 2014).

Verrall, K. E., Warwick, P. and Fairhurst, A. J. (1999) "Application of the Schulze-Hardy rule to haematite and haematite/humate colloid stability," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Elsevier, 150(1-3), pp. 261–273.

Chapter 8

Conclusions and Outlook

Table of contents

1   Conclusions about investigations of DOM interactions with engineered colloids

The methodological development of HDC-ICP-MS demonstrates the efficiency of this method for exploring interactions between colloids and DOM. Indeed, DOM adsorbs onto colloids and thus modifies their stability by influencing agglomeration and dissolution processes and, probably, by reacting with their surface. These processes can be straightforwardly monitored using HDC-ICP-MS, as demonstrated by the present work since size, composition, concentration and (in some cases) shape can be determined accurately and selectively at low concentrations. As versatility and limitations were systematically investigated, it is now possible to apply this method with high confidence to complex samples such as natural ones. Heteroagglomeration can be monitored by taking advantage of the possibility to simultaneously monitor several elements with the ICP-MS detector. Further insights into agglomeration mechanisms as influenced by DOM could be gained if differentiation between agglomerates formed by homoagglomeration and bridging flocculation would be possible. For this question, further developments of HDC-SP-ICP-MS could be helpful, as discussed in the next section.

However, investigating DOM fractionation upon colloids remains challenging and mainly unaddressed for engineered colloids, although it is a crucial aspect. This is due to the necessity to fully characterize DOM. This characterization remains challenging due to the high complexity of their molecular structures. In fact, complex mixtures such as humic substances cannot be investigated in detail without the use of dedicated powerful analytical techniques. Our attempts to identify which fractions of humic acids adsorb onto silver colloids using fluorescence spectroscopy shows how difficult it is to draw clear conclusions from overall measurements. It is clear that fluorescence spectroscopy cannot be used alone to address DOM fractionation.

Since around ten years, ultra-high resolution mass spectrometry (UHR-MS) appeared as a technical solution for identifying thousands of molecules contained in DOM (Sleighter and Hatcher, 2007; Koch et al., 2005; Nebbioso and Piccolo, 2013). These techniques provide mass-charge ratios sufficiently precise for assigning an exact molecular formula to most of the detected molecules. Thousands of molecules can thus be partly identified in one measurement. This made possible to study the evolution of the DOM composition during various processes at a molecular resolution. Moreover, advances in the analysis of these molecular formulas have made possible to connect specific molecular properties such as aliphaticity, aromaticity and acidity to specific processes (Galindo and Del Nero, 2014; Riedel, Biester and Dittmar, 2012). For instance, Batch sorption experiments were recently performed for investigating fractionation of DOM upon adsorption onto aluminum oxide and cations complexation in synthetic and natural waters respectively (Galindo and Del Nero, 2014; Riedel, Biester and Dittmar, 2012). Such approaches are highly promising for the identification of the molecules adsorbing on engineered colloids in natural waters. They could be combined to sorption isotherms experiments at different pH and ionic compositions in order to identify the most relevant parameters for the DOM fractionation and, hence, to be able to postulate sorption mechanisms and structures of the coating.

Further insight into the structure of the DOM coating, especially the nature of the DOM-surface bond, could be gained using Fourier's transform-IR and surface enhanced Raman spectroscopy in aqueous media using methods already established (Del Nero et al., 2010; Sánchez-Cortés et al., 1998). Combined to a precise picture of the type of molecules adsorbed on the surface of colloids, this information could be used for a systematic description of the DOM coating. The consequences of this coating on the colloidal, chemical and biological properties of engineered colloids would be, hence, better understood and better predictable.

Another crucial aspect of the interactions of DOM with colloids is the influence of DOM on the agglomeration process. If studies addressing the (de)stabilizing effects of DOM are abundant, the consequences for the final structure of agglomerates under environmental conditions are still unknown. In fact, systematical studies of the structure of agglomerate (reaction limited, diffusion limited, flocs, stability upon shear forces, etc.) in dependence of the concentration and the type of DOM still lack. Furthermore, monitoring agglomerates morphology over time would make possible to resolve different agglomeration mechanisms occurring at the same time. This remains difficult due to the lack of dedicated analytical methods for monitoring the size of colloids in complex media. In addition, the determination of the morphology of agglomerates remains a challenge, even at high concentrations (mg L^{-1}). The combination of DLS and MALS can be used for exploring the morphology of flocs and fractal agglomerates (Bushell and Amal, 2000; Amal, Raper and Waite, 1990; Biggs et al., 2000), although such experiments remain far from being routinely applicable and require a complex, case by case data analysis. On the contrary, electron microscopy and/or AFM provide direct information on the morphology of complex agglomerates (Perret et al., 1991; Wilkinson, Stoll and Buffle, 1995; Wilkinson et al., 1999), provided that the sample preparation is non-perturbing and that the image analysis is rigorous. Unfortunately, microscopy methods cannot be used for a large number of samples because of the long time required for producing and analyzing pictures.

Monitoring of colloid size and hence their agglomeration in environmental media is possible using HDC-ICP-MS. The morphology of agglomerates can also be studied by determining parameters such as fractal dimension or density using HDC-SP-ICP-MS, provided that their shape does not differ strongly from a sphere. Further studies addressing the effect of DOM on agglomeration mechanism of colloids will hence be performed with this technique in the future. In particular, HDC-ICP-MS should be adapted for monitoring heteroagglomeration.

Since the study of DOM interaction with engineered nanoparticle strengthened the need of advanced nano-analytical techniques, a significant part of this work was oriented to the development of analytical methods for environmental samples. This revealed new potential of HDC-ICP-MS and stimulated further advances in its development, as discussed below.

2 Outlook for the development of analytical techniques

HDC as a separation technique is analytically robust because of its simple separation mechanism. Therefore, parameters which are usually crucial for affinity chromatography or size exclusion chromatography such as flow-rate, temperature and eluent chemical composition are not determining in HDC. However, ions and surfactants concentrations are known to be important factors for the analyte recovery, which are usually high for stable particles (Prieve and Hoysan, 1978). These facts are of practical interest since it makes the implementation of HDC for new samples or new coupling techniques fairly straightforward. In fact, the above mentioned parameters are almost fully adaptable to the sample and/or coupling requirement.

The model considering that particles are eluted through a cylindrical tube adequately describes the elution behavior and seems to be universal. The most important consequence of this universality is the almost complete insensitivity of the size measurement towards particle composition and coating. Therefore, it is possible to use universal calibrants. This is crucial for the analysis of unknown samples, especially environmental ones. The diversity of the concrete implementations of HDC in this PhD-thesis and in the collaboration works illustrates the robustness of HDC and the usefulness of using a multi-detector approach in analytical chemistry. Although the price of this robustness is a poor resolution,

HDC remains highly competitive compared to other separation techniques, especially AF4 and SEC due to its potential high sample throughput, high recoveries and straightforward method development, if any is required.

If HDC-ICP-MS was hence successfully validated for environmental samples, methodological questions concerning the sizing and the quantification of some specific samples still remain. Although the results of the chapter 4 indicate that soft agglomerates remain stable throughout the elution, weaker structures like flocs may be fragmented during the elution due to the high pressure and the shear forces and the estimation of their sizes could be biased. In order to avoid this bias, comparison of measurements done at different flow rates and temperatures (and consequently different pressures and viscosities) can help in quantifying the effect of shear forces on such structures. In such cases, it may be even possible to quantify the physical properties of the measured particles if an adequate model is developed.

Simultaneous characterization of ions and particles was validated for gold only, although it is a very useful feature for systems where particulate and solute can coexist (e.g. Ag$^{(0)}$, ZnO, CuO colloids). For that, one have to face possible lost through adsorption on the walls of the packing. Such problems could be solved by adapting the eluent to maintain such ions in the liquid phase using specific hydrophilic ligands or optimized pH conditions. Method optimization for silver ions is ongoing in our laboratory.

A major difficulty remains for the sizing of non-spherical particles, especially if the shape is also unknown. Since the elution factor also depends on both particle size and shape, the approach of using spherical calibrants for determining the size is not correct anymore. This difficulty can be partially solved by implementing SP-ICP-MS, since it has the potential to resolve particles with similar retention factors but different masses, however, most real samples will probably remain challenging. The potential of this method can be extended by improving the size resolution of HDC. Using longer columns or even capillaries instead of packed beads columns can help reducing the high additional dispersion of the retention factor due to the low size resolution. It should be noted that the characterization of low concentrated non-spherical particles is still highly challenging for all existing separation techniques. Advances in this field would be hence useful for a broad scientific community.

Combination of HDC with further analytical techniques such as AF4 would be highly interesting for identifying the shape of unknown particles. Indeed, the ratio of hydrodynamic diameter and effective diameter obtained using AF4 and HDC, respectively, could be used for empirically describing particle shape, while the elemental composition can be obtained from the ICP-MS detector. Development of physical models for the elution behavior of non-spherical particles in AF4 or HDC would be highly useful for investigating such results quantitatively.

The possibility of carrying out off-line measurements with HDC has also to be commented. The characterization of samples fractionated with HDC is possible using electron microscopy, AFM or NTA for instance (Proulx and Wilkinson, 2014). Indeed, these techniques can be applied to highly diluted samples. The additional dilution of the analytes due to the fractionation process does hence not represent a critical issue. Since the most part of matrix components are removed throughout fractionation, the accuracy of such off-line characterization methods can be significantly increased. In fact, the analysis of low concentrated colloids suspensions is often highly simplified by the removal of the matrix components. If natural colloids differ strongly from the engineered colloids by the size, it is even possible to fractionate the later and thus obtained a suspension which can be analyzed by matrix sensitive techniques such as NTA. Highly promising is the off-line coupling of HDC with NTA. An on-line coupling is theoretically possible if the effect of the continuous flow in HDC can be considered during the track analysis by the NTA software. A feasibility study should hence be performed.

HDC-SP-ICP-MS has further applications in colloids and environmental sciences. For each particle, two parameters can be measured: D_C, which can be directly recalculated into mass if the composition is known and D_E determined using HDC. Since the latter will be biased if the shape is non-spherical, the retention factors should be corrected using a physical model. Theoretical approaches using simulation of the translational and rotational movement of cylindrical or ellipsoidal nanoparticles in a Poiseuille flow near to a wall were developed and could be implemented to HDC (Ali, 2012). However, this approach implies that the analytes are not a mixture of particles with different shapes. Another more empirical approach would be to compare data from unknown samples with data from standard suspensions having diverse shapes and sizes and to identify various groups of particles represented by different cloud shapes on the $D_C(D_E)$ graph. A third independent parameter can hence be gained using HDC-SP-ICP-MS if the suspension is polydisperse, which is almost always the case for environmental samples.

This would help discriminating between different objects of different shapes such as cylinders, plates, cubes and spheres (**figure 8.1a, b and d**) and could even theoretically be used for distinguishing salts, oxides or sulfides from metallic particles (**figure 8.1.c**). The discrimination should be much more efficient for large particles (several hundreds of nm). This approach could have some application in the industry, where quality control is essential and should address both size and shape. In environmental sciences, one could also use HDC-SP-ICP-MS for identifying unknown natural colloids. A database of $D_C(D_E)$ graphs could be built for comparison purpose. This technique would offer major possibilities for the fast determination of elemental composition, concentration and structure of natural colloids in a single technique provided that the technique is further developed and optimized.

The commercialization of more performant devices in the future will help detecting smaller particles. Increase in time resolution and sensitivity will make systematical multi-elemental analysis possible on a single particle basis. The analysis of the $D_C(D_E)$ graphs for identifying the shape of unknown particles will be more accurate if the particle composition can be determined, as less hypotheses will be required. If appropriate multi-elemental calibration is carried out, it would be even possible to obtained three dimensional graphs with two different elemental masses and the effective diameter. Such graphs would be extremely useful for the characterization of large number of heteroagglomerates, which is, until now, highly challenging, even with electron microscopy. However, heteroagglomerates can already be partially characterized (estimated size, elemental composition) using HDC-ICP-MS since multi-elemental analysis is straightforward in this case. Monitoring of gold, silver, silver sulfide and TiO_2 nanoparticles heteroagglomeration with natural colloids using HDC(-SP)-ICP-MS is planned in the frame of the prolongation of the project INTERNANO.

These perspectives demonstrate that the full potential of HDC-ICP-MS is still underexploited in environmental sciences. Although HDC has been neglected in the last decades for more advanced separation techniques (SEC, FFF), the case of HDC illustrates perfectly that simple systems are not always the most explored and can be, despite of it, highly promising.
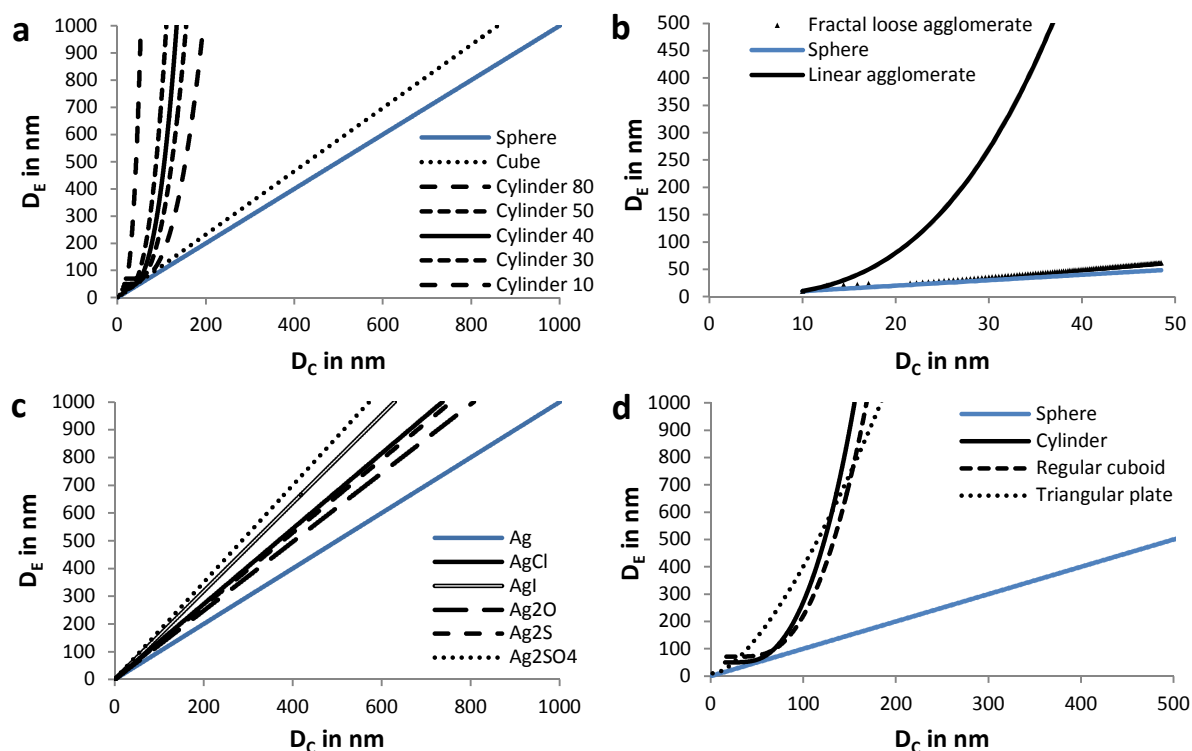
Figure 8.1: theoretical effective diameter (D_E) over the elemental core diameter (D_C), which is defined as the diameter of a fictitious sphere composed of the pure respective element. Calculations are based on geometric considerations. a: $D_E(D_C)$ curve for particles with different shapes and aspect ratio. The curve of cylinder was calculated with different widths (denoted in nm by the number after the word cylinder). b: $D_E(D_C)$ curve for 10 nm agglomerated particles and spherical particles. The linear model for agglomerates corresponds to the case of perfectly linear agglomerate (fractal dimension = 1). The fractal model described in the chapter 6 was used to estimate de curve for loose fractal agglomerates containing more than 9 particles. The points corresponding to 1 to 5 particles per agglomerates were calculated using Euclidian geometry. c: $D_E(D_C)$ curve for particles containing silver with different chemical composition d: $D_E(D_C)$ curve for particles with different shapes usually obtained during the synthesis of metallic particles.

As one single technique will probably never be sufficient for the complete characterization of colloids in the environment, HDC should be combined with other complementary analytical methods as microscopy and ζ-potential, for instance. It should also be integrated into a more complete strategy for characterizing colloids in natural media. Indeed, extraction of analytes from their original matrices and sample preparation prior to analysis are crucial issues, which remain mostly unaddressed (Baalousha and Lead, 2012; Fabricius et al., 2013). The development of sampling strategies dedicated to the systematical characterization of colloids in surface waters or other media will make the systematical monitoring of natural and artificial colloids in the environment possible in a near future. The high amount of accurate data produced could be used for improving the accuracy of the actual multimedia models for predicting the fate of colloids. The accuracy of the risk assessment of artificial colloids released from commercial product to the environment would thus be considerably improved. On the other hand, systematical monitoring of natural colloids could also improve the understanding of the element cycle and the fate of various pollutants in diverse ecosystems and thus increase our ability to predict the dispersion of pollutants and global mechanisms such as climatic changes.

References

Ali, A. (2012) *Theoretical and Numerical Calculations for the Dynamics of Colloidal Suspensions of Molecular Particles in flowing solution inside Mesopores*.

Amal, R., Raper, J. A. and Waite, T. D. (1990) "Fractal structure of hematite aggregates," *Journal of Colloid and Interface Science*. Elsevier, 140(1), pp. 158–168.

Baalousha, M. and Lead, J. (2012) "Rationalizing nanomaterial sizes measured by atomic force microscopy, flow field-flow fractionation, and dynamic light scattering: sample preparation, polydispersity, and particle structure," *Environmental Science & Technology*. ACS Publications, 46(11), pp. 6134–6142.

Biggs, S., Habgood, M., Jameson, G. J. and Yan, Y. (2000) "Aggregate structures formed via a bridging flocculation mechanism," *Chemical Engineering Journal*. Elsevier, 80(1), pp. 13–22.

Bushell, G. and Amal, R. (2000) "Measurement of fractal aggregates of polydisperse particles using small-angle light scattering," *Journal of Colloid and Interface Science*. Elsevier, 221(2), pp. 186–194.

Fabricius, A.-L., Duester, L., Meermann, B. and Ternes, T. A. (2013) "ICP-MS-based characterization of inorganic nanoparticles—sample preparation and off-line fractionation strategies," *Analytical and Bioanalytical Chemistry*. Springer, pp. 1–13.

Galindo, C. and Del Nero, M. (2014) "Molecular level description of the sorptive fractionation of a fulvic acid on Aluminum oxide by use of ESI-FTMS," *Environmental Science & Technology*. ACS Publications.

Koch, B. P., Witt, M., Engbrodt, R., Dittmar, T. and Kattner, G. (2005) "Molecular formulae of marine and terrigenous dissolved organic matter detected by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry," *Geochimica et Cosmochimica Acta*. Elsevier, 69(13), pp. 3299–3308.

Nebbioso, A. and Piccolo, A. (2013) "Molecular characterization of dissolved organic matter (DOM): a critical review," *Analytical and Bioanalytical Chemistry*. Springer, 405(1), pp. 109–124.

Del Nero, M., Galindo, C., Barillon, R., Halter, E. and Madé, B. (2010) "Surface reactivity of alpha-Al2O3 and mechanisms of phosphate sorption: In situ ATR-FTIR spectroscopy and zeta potential studies," *Journal of Colloid and Interface Science*. Elsevier, 342(2), pp. 437–444.

Perret, D., Leppard, G. G., Müller, M., Belzile, N., De Vitre, R. and Buffle, J. (1991) "Electron microscopy of aquatic colloids: non-perturbing preparation of specimens in the field," *Water Research*. Elsevier, 25(11), pp. 1333–1343.

Prieve, D. C. and Hoysan, P. M. (1978) "Role of colloidal forces in hydrodynamic chromatography," *Journal of Colloid and Interface Science*. Elsevier, 64(2), pp. 201–213.

Proulx, K. and Wilkinson, K. (2014) "Separation, detection and characterization of engineered nanoparticles in natural waters using hydrodynamic chromatography and multi-method detection (light scattering, analytical ultracentrifugation and single particle ICP-MS)," *Environmental Chemistry*. CSIRO.

Riedel, T., Biester, H. and Dittmar, T. (2012) "Molecular fractionation of dissolved organic matter with metal salts," *Environmental Science & Technology*. ACS Publications, 46(8), pp. 4419–4426.

Sánchez-Cortés, S., Francioso, O., Ciavatta, C., Garcia-Ramos, J. and Gessa, C. (1998) "pH-dependent adsorption of fractionated peat humic substances on different silver colloids studied by surface-enhanced Raman spectroscopy," *Journal of Colloid and Interface Science*. Elsevier, 198(2), pp. 308–318.

Sleighter, R. L. and Hatcher, P. G. (2007) "The application of electrospray ionization coupled to ultrahigh resolution mass spectrometry for the molecular characterization of natural organic matter," *Journal of Mass Spectrometry*. Wiley Online Library, 42(5), pp. 559–574.

Wilkinson, K. J., Balnois, E., Leppard, G. G. and Buffle, J. (1999) "Characteristic features of the major components of freshwater colloidal organic matter revealed by transmission electron and atomic force microscopy," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Elsevier, 155(2-3), pp. 287–310.

Wilkinson, K., Stoll, S. and Buffle, J. (1995) "Characterization of NOM-colloid aggregates in surface waters: Coupling transmission electron microscopy staining techniques and mathematical modelling," *Fresenius' Journal of Analytical Chemistry*. Springer, 351(1), pp. 54–61.

Annex 1

Supporting Information of the Chapter 2

Interactions of dissolved organic matter with inorganic colloids: a review

(supporting information)

ALLAN PHILIPPE[+], GABRIELE E. SCHAUMANN[+]*

[+]Institute for Environmental Sciences, Department of Environmental and Soil Chemistry,

University Koblenz-Landau, Fortstraße 7, D-76829, Landau, Germany

CONTENT.

Table S1

Table S1. Results of the literature screening sorted by colloid principal element (alphabetical order) and chronological order.

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
1998	$Ag^{(0)}$	15 nm	spherical	humic acids, fulvic acids	Investigation of sorption mechanism, characterization of DOM-coating	1
2009	$Ag^{(0)}$	15 nm	n. d.	humic acids, fulvic acids	Qualitative analysis of nanoparticles in specific matrixes	2
2010	$Ag^{(0)}$	2 nm	spheroid	humic acids, fulvic acids	Monitoring of nanoparticle dissolution	3
2011	$Ag^{(0)}$	30 - 50 nm	spherical	polysaccharide (alginate)	Monitoring of nanoparticle dissolution, quantification of stability or persistence of nanoparticles	4
2011	$Ag^{(0)}$	20 nm	spherical	total DOM	Quantification of stability or persistence of nanoparticles	5
2011	$Ag^{(0)}$	4 nm, 9 nm, 10 nm	n. d.	total DOM	Quantification of stability or persistence of nanoparticles	6
2011	$Ag^{(0)}$	71 nm	spherical	humic acids	Aggregation/coagulation kinetics	7
2011	$Ag^{(0)}$	29 nm	n. d.	humic acids, fulvic acids	Quantification of stability or persistence of nanoparticles	8
2011	$Ag^{(0)}$ (-citrate)	40 nm	spherical	humic acids	Sedimentation, monitoring of nanoparticle dissolution, mass transfer or deposition of nanoparticles	9
2011	$Ag^{(0)}$ (-PVP)	50 nm	cube-like	humic acids	Sedimentation, monitoring of nanoparticle dissolution, mass transfer or deposition of nanoparticles	9
2012	$Ag^{(0)}$	39 nm	spherical	humic acids	Adsorption isotherms of DOM on nanoparticles, monitoring of nanoparticle dissolution, quantification of stability or persistence of nanoparticles	10
2012	$Ag^{(0)}$ (-citrate)	19 nm	spherical	amino acid (cysteine)	Aggregation/coagulation kinetics, monitoring of nanoparticle dissolution, surface charge determination	11
2012	$Ag^{(0)}$ (-PVP)	8 nm	spherical	amino acid (cysteine)	Aggregation/coagulation kinetics, monitoring of nanoparticle dissolution, surface charge determination	11
2012	$Ag^{(0)}$	44 - 120 nm	irregular	biomass (sewage sludge)	Analysis of aggregate morphology, qualitative analysis of nanoparticles in specific matrixes, quantification of nanoparticles in specific matrixes	12
2012	$Ag^{(0)}$ (-gum Arabic)	12 nm	n. d.	plant exudates, polysaccharide (gum Arabic)	Analysis of aggregate morphology, monitoring of nanoparticle dissolution	13
2012	$Ag^{(0)}$ (-PVP)	49 nm	n. d.	plant exudates, polymer (PVP)	Analysis of aggregate morphology, monitoring of nanoparticle dissolution	13
2012	$Ag^{(0)}$	30 - 50 nm	n. d.	humic acids, biofilm (*Pseudomonas fluorescence*)	Monitoring of nanoparticle dissolution	14
2012	$Ag^{(0)}$	10 - 30 nm	spheroidal	humic acids, biofilm (*Pseudomonas fluorescence*)	Monitoring of nanoparticle dissolution	14
2012	$Ag^{(0)}$	10 - 30 nm	irregular	synthetic humic acids	Reaction kinetics and mechanism between DOM and particle	15
2013	$Ag^{(0)}$	17 nm	spherical	fulvic acids	Aggregation/coagulation kinetics, surface charge determination	16
2013	$Ag^{(0)}$	n. d.	n. d.	humic acids, fulvic acids	Characterization of DOM coating, investigation of sorption mechanism	17
2013	$Ag^{(0)}$	50 nm	spherical	humic acids, fulvic acids	Aggregation/coagulation kinetics, mass transfer or deposition of nanoparticles	18

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
2013	$Ag^{(0)}$	56 nm	spherical	total DOM, amino acid (cysteine)	Monitoring of nanoparticle dissolution, quantification of stability or persistence of nanoparticles	19
1981	Al_2O_3	30 nm	spherical	total DOM	Adsorption isotherms of DOM on nanoparticles	20
1982	Al_2O_3	30 nm	spherical	total DOM	Adsorption isotherm of DOM on nanoparticles, characterization of DOM-coating, investigation of sorption mechanism, surface charge determination	21
1994	Al_2O_3	26 nm	spherical	humic acids, fulvic acids	Adsorption isotherms of DOM on nanoparticles	22
1994	Al_2O_3	15 nm	spherical	total DOM, humic acids, fulvic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, monitoring of desorption	23
1996	Al_2O_3	1330 nm	spherical	humic acids, fulvic acids	Aggregation/coagulation kinetics, adsorption isotherms of DOM on nanoparticles, surface charge determination	24
1998	Al_2O_3	1540 nm	n. d.	humic acids	Quantification of stability or persistence of nanoparticles, surface charge determination	25
1999	Al_2O_3	<150 nm	n. d.	humic acids, salicylic acid, gallic acid	Sedimentation, adsorption isotherms of DOM on nanoparticles, surface charge determination	26
2004	Al_2O_3	<189 nm	spherical	protein (bovine serum albumin)	Investigation of sorption mechanism, surface charge determination, characterization of DOM-coating	27
2005	Al_2O_3	116 nm	spherical	proteins (bovine serum albumin, lysozyme)	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, surface charge determination	28
2007	Al_2O_3	300 nm	spherical	total DOM, humic acids, fulvic acids	Rheology, surface charge determination	29
2007	Al_2O_3	300 nm	spherical	total DOM, humic acids, fulvic acids	Rheology, modeling of adsorption	30
2008	Al_2O_3	60 nm	spherical	humic acids	Aggregation/coagulation kinetics, surface charge determination, analysis of aggregate morphology	31
2009	Al_2O_3	40 - 50 nm	n. d.	humic acids	Aggregation/coagulation kinetics, characterization of DOM-coating, surface charge determination	32
2009	Al_2O_3	60 nm, 150 nm	n. d.	humic acids	Characterization of DOM-coating, adsorption isotherms of DOM on nanoparticles, surface charge determination	33
1977	$Al(OH)_3$ (gibbsite)	n. d.	n. d.	humic acids, fulvic acids	Adsorption isotherms of DOM on nanoparticles, investigation of sorption mechanism, characterization of DOM-coating	34
2006	$Al(OH)_3$ (gibbsite)	n. d.	n. d.	humic acids, polysaccharide	Adsorption isotherms of DOM on nanoparticles, monitoring of desorption, competition of DOM with other ions or molecules for the adsorption onto nanoparticles, ions/molecules sorption	35
1983	aluminosilicate (kaolinite, illite, montmorillonite)	>100 nm	n. d.	total DOM	Sedimentation	36

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
1983	aluminosilicate (chlorite, illite, montmorillonite)	>100 nm	n. d.	total DOM	Sedimentation	36
2009	aluminosilicate (betonite)	6000 - 9000 nm	n. d.	humic acids, fulvic acids	Disaggregation kinetics	37
1994	aluminosilicate (chlorite)	125000 - 500000 nm	plates	total DOM, humic acids, fulvic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, monitoring of desorption	23
1993	aluminosilicate (illite)	100 - 1000 nm	Irregular	total DOM	Aggregation/coagulation kinetics, surface charge determination	38
1993	aluminosilicate (illite)	100 - 1000 nm	irregular	total DOM	Aggregation/coagulation kinetics, surface charge determination	39
1995	aluminosilicate (illite)	100 - 1000 nm	irregular	total DOM	Aggregation/coagulation kinetics, surface charge determination	40
1977	aluminosilicate (imogolite)	n. d.	n. d.	fulvic acids	Adsorption isotherms of DOM on nanoparticles, investigation of sorption mechanism, characterization of DOM-coating	34
1982	aluminosilicate (kaolinite)	n. d.	n. d.	total DOM	Adsorption isotherms of DOM on nanoparticles, investigation of sorption mechanism, characterization of DOM-coating	21
1986	aluminosilicate (kaolinite)	3700 nm	n. d.	humic acids	Aggregation/coagulation kinetics, quantification of stability or persistence of nanoparticles, adsorption isotherms of DOM on nanoparticles	41
1994	aluminosilicate (kaolinite)	100 - 4000 nm	plates	total DOM, humic acids, fulvic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, monitoring of desorption	23
1997	aluminosilicate (kaolinite)	<1000 nm	plates	humic acids	Quantification of stability or persistence of nanoparticles, adsorption isotherms of DOM on nanoparticles, surface charge determination	42
1998	aluminosilicate (kaolinite)	<1000 nm	n. d.	humic acids	Aggregation/coagulation kinetics, surface charge determination	43
1999	aluminosilicate (kaolinite)	n. d.	plates	total DOM	Adsorption isotherms of DOM on colloid, characterization of DOM-coating	44
1999	aluminosilicate (kaolinite)	2000 nm	n. d.	humic acids, salicylic acid, gallic acid	Sedimentation, adsorption isotherms of DOM on nanoparticles, surface charge determination	26
2000	aluminosilicate (kaolinite)	500 nm	plates	total DOM	Adsorption isotherms of DOM on colloid, characterization of DOM-coating	45
2002	aluminosilicate (kaolinite)	n. d.	plates	humic acids	Transport experiments, surface charge determination	46
2003	aluminosilicate (kaolinite)	n. d.	n. d.	humic acids, fulvic acids	Adsorption kinetics, adsorption isotherms of DOM on nanoparticles, investigation of sorption mechanism	47
2004	aluminosilicate (kaolinite)	<2000 nm	n. d.	humic acids	Adsorption isotherms of DOM on nanoparticles, surface charge determination, rheology	48
2005	aluminosilicate (kaolinite)	n. d.	plates	humic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, characterization of DOM-coating	49
2012	aluminosilicate (kaolinite)	<2000 nm	plates	humic acids, fulvic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, characterization of DOM-coating	50
2004	aluminosilicate (laponite)	30 nm	plates	biofilm (bacteria: *Pseudomonas aeruginosa*)	Transport experiments	51

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
2007	aluminosilicate (laponite)	30 nm	plates	biofilm (*Pseudomonas aeruginosa*)	Transport experiments	52
1994	aluminosilicate (montmorillonite)	<1000 nm	plates	total DOM, humic acids, fulvic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, monitoring of desorption	23
1997	aluminosilicate (montmorillonite)	10-2000 nm	n. d.	fulvic acids, polysaccharides	Analysis of aggregate morphology, qualitative analysis of nanoparticles in specific matrixes, quantification of nanoparticles in specific matrixes	53
1999	aluminosilicate (montmorillonite)	<1000 nm	n. d.	humic acids, salicylic acid, gallic acid	Sedimentation, adsorption isotherms of DOM on nanoparticles, surface charge determination	26
2000	aluminosilicate (montmorillonite)	1000 nm	plates	total DOM	Adsorption isotherms of DOM on nanoparticles, characterization of DOM-coating	45
2001	aluminosilicate (montmorillonite)	n. d.	n. d.	compost leachate	Adsorption isotherms of DOM on colloid, characterization of DOM-coating, monitoring of reaction between DOM and colloid	54
2004	aluminosilicate (montmorillonite)	<1000 nm	n. d.	humic acids	Adsorption isotherms of DOM on nanoparticles, surface charge determination, rheology	48
2005	aluminosilicate (montmorillonite)	n. d.	plates	humic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, characterization of DOM-coating	49
2005	aluminosilicate (montmorillonite)	1000 nm	n. d.	polysaccharides	Aggregation/coagulation kinetics, disaggregation kinetics, rheology	55
2007	aluminosilicate (montmorillonite)	n. d.	n. d.	humic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles	56
2007	aluminosilicate (montmorillonite)	n. d.	n. d.	humic acids	Rheology, surface charge determination	56
2009	aluminosilicate (montmorillonite)	<1000 nm	plates	humic acids, polysaccharide (chitin)	Aggregation/coagulation kinetics, surface charge determination	57
2012	aluminosilicate (montmorillonite)	n. d.	plates	humic acids	Aggregation/coagulation kinetics, surface charge determination, modeling of aggregation	58
2013	aluminosilicate (montmorillonite)	n. d.	plates	humic acids	Aggregation/coagulation kinetics, surface charge determination	59
1995	aluminosilicate (saprolite)	>100 nm	n. d.	total DOM, humic acids	Transport experiments, behavior during filtration processes	60
2012	aluminosilicate (smectite)	<2000 nm	plates	humic acids, fulvic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, characterization of DOM-coating	50
1994	aluminosilicate (vermiculite)	125 µm - 4000 µm	plates	total DOM, humic acids, fulvic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, monitoring of desorption	23
2012	aluminosilicate (vermiculite)	<2000 nm	plates	humic acids, fulvic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, characterization of DOM-coating	50
2008	Au$^{(0)}$ (-citrate)	16 nm	spherical	humic acids	Stability or persistence of nanoparticles, analysis of aggregate morphology	61

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
2008	$Au^{(0)}$ (-acrylate)	20 nm	spherical	humic acids	Quantification of stability or persistence of nanoparticles, analysis of aggregate morphology	61
2009	$Au^{(0)}$	5 - 6 nm	n. d.	humic acids	Characterization of DOM-coating	62
2010	$Au^{(0)}$	5 -12 nm	spherical	humic acids	Aggregation/coagulation kinetics, analysis of aggregate morphology, surface charge determination	63
2012	$Au^{(0)}$	7 nm	spherical	fulvic acids	Qualitative analysis of nanoparticles in specific matrixes	64
2012	$Au^{(0)}$	12 nm	spherical	total DOM, humic acids, fulvic acids	Aggregation/coagulation kinetics, characterization of DOM-coating, measure of the hydrodynamic layer thickness	65
2013	$Au^{(0)}$	43 nm, 68 nm	spherical	total DOM	Aggregation/coagulation kinetics, characterization of DOM-coating, surface charge determination	66
2013	$Au^{(0)}$	14 nm	spherical	total DOM	Quantification of stability or persistence of nanoparticles	67
2010	$B^{(0)}$	25 nm, 40 nm	irregular	humic acids, polysaccharide (alginate)	Aggregation/coagulation kinetics, analysis of aggregate morphology, surface charge determination	68
2011	$Ca_{10}(PO_4)_5(OH)_2$ (hydroxylapatite)	20 * 100 nm	rod	humic acids	Transport experiments	69
2012	$Ca_{10}(PO_4)_5(OH)_2$ (hydroxylapatite)	20 * 100 nm	rod	humic acids	Transport experiments	70
2012	$Ca_{10}(PO_4)_5(OH)_2$ (hydroxylapatite)	20 * 100 nm	rod	humic acids	Transport experiments	71
2009	CdSe (quantum dots)	3 nm	n. d.	total DOM, humic acids, fulvic acids	Analysis of aggregate morphology, determination of hydrophobicity	72
2010	CdSe (quantum dots)	3 nm, 4 nm, 11 nm	spheroid	humic acids, fulvic acids	Determination of hydrophobicity	73
2011	CdSe/ZnS (quantum dots)	10 nm	n. d.	biofilm (*Pseudomonas aeruginosa*)	Transport experiments	74
2012	CdSe (quantum dots)	<10 nm	n. d.	alga exudates (phytoplankton)	Stability or persistence of nanoparticles, monitoring of dissolution	75
2013	CdSe and CdTe	10 - 50 nm	spherical	lipid and total DOM	Deposition experiments, surface charge determination	76
2010	CeO_2	67 * 8 nm	rod	total DOM	Aggregation/coagulation kinetics, sedimentation, surface charge determination, qualitative analysis of nanoparticles in specific matrixes	77
2010	CeO_2	20 nm	n. d.	total DOM	Quantification of stability or persistence of nanoparticles, sedimentation, surface charge determination	78
2011	CeO_2	14 nm	n. d.	total DOM	Quantification of stability or persistence of nanoparticles, quantification of nanoparticles in specific matrixes	79
2012	CeO_2	5 nm	spherical	humic acids, fulvic acids, polysaccharides (cellulose, alginate), citric acid	Transport experiments	80
2013	CeO_2	17 - 100 nm	irregular	fulvic acids, gum Arabic	Analysis of nanoparticles in specific matrixes	81

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
2012	$Cu^{(0)}$	10 nm	irregular	citric acid, oxalic acid	Monitoring of nanoparticle dissolution, characterization of DOM-coating, surface charge determination	82
2012	$Cu^{(0)}$	10 - 50 nm	spheroid	Fulvic and humic acids	Transport experiments	83
2012	CuO	24 nm	irregular	citric acid, oxalic acid	Monitoring of nanoparticle dissolution, characterization of DOM-coating, surface charge determination	82
1979	CuS	40 nm	spherical	humic acids, proteins, amino acids (tyrosine, glutamate), sucrose	Aggregation/coagulation kinetics	84
2007	$Fe^{(0)}$	10 - 90 nm	spheroid	humic acids	Adsorption kinetics, ions/molecules sorption, adsorption isotherms of DOM on nanoparticles, competition of DOM with other ions or molecules for the adsorption onto nanoparticles, surface charge determination	85
2008	$Fe^{(0)}$	10 - 80 nm	irregular	carboxymethylcellulose, polyaspartate	Aggregation/coagulation kinetics, sedimentation, adsorption isotherms of DOM on nanoparticles, hydrodynamic layer thickness, modeling of aggregation/coagulation	86
2008	$Fe^{(0)}$	<200 nm	irregular	polysaccharides (guar gum, alginate, potato starch)	Aggregation/coagulation kinetics, sedimentation, surface charge determination	87
2009	$Fe^{(0)}$	n. d.	irregular	total DOM	Transport experiments, sedimentation, adsorption isotherms of DOM on nanoparticles	88
2010	$Fe^{(0)}$	n. d.	n. d.	humic acids, polyaspartate, polystyrenesulfonate	Adhesion of nanoparticles on bacteria	89
2012	$Fe^{(0)}$	4 nm, 7 nm, 9 nm	irregular	humic acids	Sedimentation, investigation of sorption mechanism, characterization of DOM-coating	90
2013	$Fe^{(0)}$	<100 nm	irregular	rhamnolipids, soy protein	Aggregation/coagulation kinetics, surface charge determination, transport experiment	91
2013	$Fe^{(0)}$	<10 nm	irregular	humic acids	Sedimentation, surface charge determination, analysis of aggregate morphology	92
1981	Fe_2O_3 (hematite)	20 nm	spherical	humic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, surface charge determination	93
1984	Fe_2O_3 (hematite)	n. d.	n. d.	humic acids, tannic acid, polymer (polyvinylpyridine)	Behavior during filtration processes	94
1990	Fe_2O_3 (hematite)	<100 nm	spherical	humic acids, fulvic acids, fatty acids (propionic acid, caprylic acid, capric acid, lauric acid), polyaspartic acid	Aggregation/coagulation kinetics, adsorption isotherms of DOM on nanoparticles	95
1992	Fe_2O_3 (hematite)	70 nm	spherical	fulvic acids	Aggregation/coagulation kinetics, analysis of aggregate morphology, adsorption isotherms of DOM on nanoparticles	96
1993	Fe_2O_3 (hematite)	170 nm	spherical	humic acids, fulvic acids	Transport experiments, adsorption isotherms of DOM on nanoparticles, surface charge determination	97

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
1993	Fe$_2$O$_3$ (hematite)	70 - 360 nm	plates	fulvic acids	Quantification of stability or persistence of nanoparticles	98
1993	Fe$_2$O$_3$ (hematite)	60 nm	spherical	total DOM, polyaspartic acid, polyacrylic acid	Aggregation/coagulation kinetics, characterization of DOM-coating, modeling of adsorption	99
1994	Fe$_2$O$_3$ (hematite)	150 - 300 nm	spherical	total DOM	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, characterization of DOM-coating	100
1994	Fe$_2$O$_3$ (hematite)	125 - 500 μm	spherical	total DOM, humic acids, fulvic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, monitoring of desorption	23
1995	Fe$_2$O$_3$ (hematite)	170 nm	spherical	humic acids, fulvic acids	Transport experiments, characterization of DOM-coating	101
1995	Fe$_2$O$_3$ (hematite)	200 nm	spherical	total DOM	Adsorption kinetics, monitoring of desorption, investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles	102
1995	Fe$_2$O$_3$ (hematite)	50 - 500 nm	n. d.	total DOM, humic acids	Transport experiments, behavior during filtration processes	60
1995	Fe$_2$O$_3$ (hematite)	49 nm	spherical	polymer (polyacrylic acid)	Aggregation/coagulation kinetics, analysis of aggregate morphology	103
1996	Fe$_2$O$_3$ (hematite)	200 nm	n. d.	total DOM, polymer (polyacrylic acid), phthalic acid, salicylic acid	Adsorption isotherms of DOM on nanoparticles, ions/molecules sorption, competition of DOM with other ions or molecules for the sorption sites	104
1997	Fe$_2$O$_3$ (hematite)	122 nm	spheroid	humic acids	Transport experiments	105
1998	Fe$_2$O$_3$ (hematite)	50 nm	parallelograms	humic acids	Investigation of sorption mechanism, ions/molecules sorption, adsorption isotherms of DOM on nanoparticles, measure of the hydrodynamic layer thickness, modeling of adsorption	106
1998	Fe$_2$O$_3$ (hematite)	86 nm, 212 nm, 402 nm, 570 nm	spherical	humic acids	Investigation of sorption mechanism, ions/molecules sorption, adsorption isotherms of DOM on nanoparticles, measure of the hydrodynamic layer thickness, modeling of adsorption	106
1998	Fe$_2$O$_3$ (hematite)	50 nm	parallelograms	humic acids, fulvic acids	Adsorption kinetics, investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, modeling of adsorption	107
1999	Fe$_2$O$_3$ (hematite)	99 nm	n. d.	humic acids, polysaccharide (polygalacturonic acid)	Investigation of sorption mechanism, adsorption isotherms of DOM on colloid, hydrodynamic layer thickness, adsorption modeling	108
1999	Fe$_2$O$_3$ (hematite)	180 nm	spherical	humic acids	Aggregation/coagulation kinetics, adsorption isotherms of DOM on nanoparticles	109
2003	Fe$_2$O$_3$ (hematite)	42 nm	spherical	polysaccharide (schizophyllan)	Aggregation/coagulation kinetics, analysis of aggregate morphology, modeling of aggregation/coagulation	110
2003	Fe$_2$O$_3$ (hematite)	n. d.	n. d.	humic acids, fulvic acids	Adsorption kinetics, adsorption isotherms of DOM on nanoparticles, investigation of sorption mechanism, characterization of DOM-coating	47
2003	Fe$_2$O$_3$ (hematite)	103 nm	spherical	humic acids	Rheology, adsorption isotherms of DOM on nanoparticles, determination of surface free energy	111

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
2004	Fe_2O_3 (hematite)	84 nm	spherical	humic acids	Aggregation/coagulation kinetics, analysis of aggregate morphology, surface charge determination, analysis of nanoparticles in specific matrixes	112
2004	Fe_2O_3 (hematite)	50 nm	n. d.	humic acids	Adsorption isotherms of DOM on nanoparticles, surface charge determination, rheology	48
2006	Fe_2O_3 (hematite)	75 nm	spherical	polysaccharide (alginate)	Aggregation/coagulation kinetics, analysis of aggregate morphology	113
2007	Fe_2O_3 (hematite)	75 nm	spherical	polysaccharide (alginate)	Aggregation/coagulation kinetics, analysis of aggregate morphology, adhesion forces between DOM and nanoparticles (AFM)	114
2008	Fe_2O_3 (hematite)	6 - 7 nm	spherical	humic acids	Characterization of DOM-coating, surface charge determination, analysis of aggregate morphology, Analysis of nanoparticles in specific matrixes	115
2009	Fe_2O_3 (hematite)	20 nm, 100 nm	spherical	humic acids	Quantification of stability or persistence of nanoparticles, surface charge determination, disaggregation kinetics, analysis of aggregate morphology	116
2009	Fe_2O_3 (hematite)	7 nm	spherical	fulvic acids	Characterization of DOM-coating, Stability of nanoparticles	117
2009	Fe_2O_3 (hematite)	around 20 nm	spherical	fulvic acids	Modeling of adsorption and aggregation	118
2009	Fe_2O_3 (hematite)	200 nm	n. d.	total DOM	Aggregation/coagulation kinetics, adsorption isotherms of DOM on colloid	119
2010	Fe_2O_3 (hematite)	50 nm	spherical	dicarboxylic acids	Aggregation/coagulation kinetics	120
2010	Fe_2O_3 (hematite)	40nm	n. d.	polysaccharide (carboxymethylcellulose), polyaspartate, polystyrenesulfonate	Transport experiments	121
2013	Fe_2O_3 (hematite)	53 nm	spherical	fulvic acids	Aggregation/coagulation kinetics, quantification of stability or persistence of nanoparticles, surface charge determination	122
2011	magnetic Fe_2O_3	10 nm	spherical	humic acids	Aggregation/coagulation kinetics, characterization of DOM-coating	123
2003	Fe_3O_4 (magnetite)	n. d.	n. d.	humic acids	Characterization of DOM-coating, adsorption isotherms of DOM on colloid	124
2004	Fe_3O_4 (magnetite)	10 nm	n. d.	humic acids	Adsorption isotherms of DOM on nanoparticles, surface charge determination, rheology	48
2006	Fe_3O_4 (magnetite)	<10 nm	n. d.	humic acids	Aggregation/coagulation kinetics, analysis of aggregate morphology, adsorption isotherms of DOM on nanoparticles	125
2008	Fe_3O_4 (magnetite)	10 nm	spheroid	humic acids	Ion/molecule sorption	126
2010	Fe_3O_4 (magnetite)	58 nm	spherical	humic acids	Aggregation/coagulation kinetics, surface charge determination	127

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
2013	Fe$_3$O$_4$ (magnetite)	<10 nm	n. d.	humic acids	Aggregation/coagulation kinetics, adsorption isotherms of DOM on colloid	128
1981	amorphous Fe(OH)$_3$ gel	6 nm	spherical	humic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, surface charge determination	93
2013	amorphous Fe(OH)$_3$ gel	<200 nm	n. d.	humic acids	Characterization of DOM-coating, ions/molecules sorption	129
1977	FeO(OH) (goethite)	n. d.	n. d.	humic acids, fulvic acids	Adsorption isotherms of DOM on nanoparticles, investigation of sorption mechanism, characterization of DOM-coating	34
1981	FeO(OH) (goethite)	500 * 50 nm	rod	humic acids	Investigation of sorption mechanism, adsorption isotherms of DOM on colloid, surface charge determination	93
1981	FeO(OH) (goethite)	n. d.	n. d.	humic acids	Adsorption isotherms of DOM on colloid, investigation of sorption mechanism	93
1982	FeO(OH) (goethite)	500 * 50 nm	rod	humic acids, fulvic acids	Surface charge determination	130
1990	FeO(OH) (goethite)	n. d.	n. d.	total DOM, humic acids, fulvic acids	Surface charge determination	131
1997	FeO(OH) (goethite)	n. d.	n. d.	fulvic acids	Adsorption isotherms of DOM on colloid, monitoring of desorption, characterization of DOM-coating	132
1999	FeO(OH) (goethite)	n. d.	rod	total DOM	Adsorption isotherms of DOM on colloid, characterization of DOM-coating	44
2000	FeO(OH) (goethite)	n. d.	n. d.	fulvic acids	Adsorption isotherms of DOM on colloid, investigation of sorption mechanism, modeling of adsorption	133
2001	FeO(OH) (goethite)	1500 * 150 * 40 nm	rod	total DOM, fulvic acids	Adsorption kinetics, adsorption isotherms of DOM on colloid	134
2001	FeO(OH) (goethite)	n. d.	n. d.	compost leachate	Adsorption isotherms of DOM on colloid, characterization of DOM-coating, monitoring of reaction between DOM and colloid	54
2003	FeO(OH) (goethite)	n. d.	n. d.	fulvic acids	Adsorption isotherms of DOM on colloid, modeling of adsorption	135
2008	FeO(OH) (goethite)	n. d.	spherical	humic acids, fulvic acids	Competition of DOM with other ions or molecules for the adsorption onto nanoparticles, investigation of sorption mechanism, modeling of adsorption	136
2011	HfO$_2$	6 nm	ellipsoid	humic acids	Characterization of DOM-coating, determination of hydrophobicity	137
2011	Hf$_x$Zr$_{1-x}$O$_2$	<10 nm	ellipsoid, spherical	humic acids	Characterization of DOM-coating, determination of hydrophobicity	137
1999	HgS	10 - 50 nm	n. d.	total DOM, humic acids, fulvic acids	Quantification of stability or persistence of nanoparticles, reaction kinetics	138
2009	HgS	5 nm	n. d.	humic acids, fulvic acids, amino acid (serine, cysteine), glycolate	Aggregation/coagulation kinetics, determination of hydrophobicity	139
2010	HgS	70 nm	irregular	amino acids (cysteine, serine)	Aggregation/coagulation kinetics, adsorption isotherms of DOM on colloid	140
2010	HgS	1 - 2 nm	spherical	humic acids, fulvic acids	Monitoring of nanoparticle dissolution, reaction mechanism	141

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
1972	latex	>100 nm	n. d.	natural particulate matter (bacteria, small algae, detritus)	Surface charge determination	142
1989	latex	490 nm	spherical	polysaccharide (polygalacturonic acid)	Disaggregation kinetics, Aggregation/coagulation kinetics, characterization of DOM-coating, surface charge determination, adsorption isotherms of DOM on nanoparticles, measure of the hydrodynamic layer thickness	143
1993	latex	156 nm	spherical	humic acids, fulvic acids	Transport experiments, adsorption isotherms of DOM on colloid, surface charge determination	97
1994	latex	885 nm	spherical	polyvinylpyridine	Disaggregation kinetics, analysis of aggregate morphology	144
2001	latex (-sulfate)	110 nm	spherical	humic acids, polysaccharides	Disaggregation kinetics, adsorption isotherms of DOM on colloid, analysis of aggregate morphology, measure of the hydrodynamic layer thickness	145
2001	latex (-amidine)	120 nm	spherical	humic acids, polysaccharides	Disaggregation kinetics, adsorption isotherms of DOM on colloid, analysis of aggregate morphology, measure of the hydrodynamic layer thickness	145
2002	latex	310 nm	n. d.	humic acids	Transport experiments	146
2003	latex	98 nm	spherical	humic acids	Transport experiments, adsorption isotherms of DOM on nanoparticles	147
2008	latex	50 nm, 110 nm, 1500 nm	n. d.	humic acids	Transport experiments	148
2011	latex	2600 nm	spherical	humic acids, fulvic acids	Transport experiments, surface charge determination, measure of the hydrodynamic layer thickness	149
2011	latex (-carboxyl)	20 nm	n. d.	biofilm (*Pseudomonas aeruginosa*)	Transport experiments	74
2011	latex (-sulfate)	1000 nm	n. d.	biofilm (*Pseudomonas aeruginosa*)	Transport experiments	74
1983	Mn_3O_4	n. d.	spherical	humic acids	Adsorption isotherms of DOM on nanoparticles, surface charge determination	150
2001	MnO_2	n. d.	n. d.	compost leachate	Adsorption isotherms of DOM on colloid, characterization of DOM-coating, monitoring of reaction between DOM and colloid	54
2013	MnO_2	24 - 105 nm	irregular	humic acids, fulvic acids, polysaccharide (alginate), protein (bovine serum albumin)	Aggregation/coagulation kinetics, analysis of aggregate morphology	151
1983	MnOOH	100 nm	plates	humic acids	Adsorption isotherms of DOM on colloid, surface charge determination	150
2009	NiO	750 nm	n. d.	total DOM	Aggregation/coagulation kinetics, adsorption isotherms of DOM on colloid	119
2011	Si	51 nm, 94 nm, 138 nm	spheroid	humic acids	Aggregation/coagulation kinetics, analysis of aggregate morphology	153
1972	SiO_2	>100 nm	n. d.	natural particulate matter (bacteria, small algae, detritus)	Surface charge determination	142

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
1982	SiO_2	n. d.	n. d.	total DOM	Adsorption isotherm of DOM on nanoparticles, characterization of DOM-coating, investigation of sorption mechanism, surface charge determination	21
1986	SiO_2	4000 nm	n. d.	humic acids	Aggregation/coagulation kinetics, quantification of stability or persistence of nanoparticles, adsorption isotherms of DOM on nanoparticles	41
1993	SiO_2	140 - 190 nm	spherical	fulvic acids	Stability or persistence of nanoparticles	98
2004	SiO_2	5000 nm	spherical	fulvic acids	Adhesion forces between DOM and colloid (AFM), measure of the hydrodynamic layer thickness	154
2005	SiO_2	92 nm	spherical	proteins (bovine serum albumin, chicken hen egg white lysozyme)	Investigation of sorption mechanism, adsorption isotherms of DOM on colloid, surface charge determination	28
2009	SiO_2	30 nm	spherical	humic acids	Characterization of DOM-coating, adsorption isotherms of DOM on colloid, surface charge determination	33
2009	SiO_2	740 nm	n. d.	total DOM	Aggregation/coagulation kinetics, adsorption isotherms of DOM on colloid	119
2011	SiO_2	150 nm	n. d.	humic acids, fulvic acids, polyaccharide (alginate)	Aggregation/coagulation kinetics	155
2013	SiO_2	≤ 5000 nm	n. d.	humic acids	Surface charge determination	156
2013	SiO_2	20 - 30 nm	n. d.	humic acids	Characterization of DOM-coating, ions/molecules sorption	129
1982	TiO_2	n. d.	n. d.	total DOM	Adsorption isotherm of DOM, characterization of DOM-coating, investigation of sorption mechanism, surface charge determination	21
1999	TiO_2	6 nm, 16 nm	spheroid	fatty acids (acetic acid, valeric acid, adipic acid), oxalic acid	Adsorption isotherms of DOM on nanoparticles, modeling of adsorption	157
2005	TiO_2	271 nm	spherical	proteins (bovine serum albumin, chicken hen egg white lysozyme)	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, surface charge determination	28
2008	TiO_2	5 nm, 32 nm	n. d.	fatty acid (adipic acid), oxal acid	Aggregation/coagulation kinetics, adsorption isotherms of DOM on nanoparticles	158
2009	TiO_2	3 nm	spheroid	fulvic acids	Surface charge determination	159
2009	TiO_2	10 nm	n. d.	polysaccharide (cellulose)	Transport experiments	160
2009	TiO_2	50 nm	n. d.	humic acids	Characterization of DOM-coating, adsorption isotherms of DOM on nanoparticles, surface charge determination	33
2009	TiO_2	530 nm	n. d.	total DOM	Aggregation/coagulation kinetics, adsorption isotherms of DOM on nanoparticles	119
2010	TiO_2	27 nm	spheroid	total DOM	Aggregation/coagulation kinetics, sedimentation, surface charge determination, analysis of nanoparticles in specific matrixes	77

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
2010	TiO_2	30 nm	n. d.	polysaccharide (carboxymethylcellulose), polyaspartate, polystyrenesulfonate	Transport experiments	121
2011	TiO_2	30 nm	spherical	fulvic acids	Sedimentation, surface charge determination	161
2011	TiO_2	20 nm	spherical	total DOM, dissolved organic matter	Sedimentation	162
2011	TiO_2	27 nm	spheroid	humic acids	Aggregation/coagulation kinetics, surface charge determination, mass transfer or deposition of nanoparticles	163
2012	TiO_2	10 * 40 nm	rod	humic acids	Transport experiments, Aggregation/coagulation kinetics, adsorption isotherms of DOM on nanoparticles, surface charge determination, measure of the hydrodynamic layer thickness	164
2013	TiO_2	20 – 30 nm	spherical	total DOM	Surface charge determination, sedimentation, disaggregation kinetics	165
2013	$H_xNa_{2-x}Ti_3O_7$	8 * >100 nm	rod	total DOM	Surface charge determination, sedimentation, disaggregation kinetics	165
2013	TiO_2- $H_xNa_{2-x}Ti_3O_7$	8 * >100 nm	rod	total DOM	Surface charge determination, sedimentation, disaggregation kinetics	165
2012	TiO_2	18 nm	n. d.	humic acids, bacteria (*E. coli*)	Mass transfer or deposition of nanoparticles, surface charge determination, characterization of DOM-coating, transport experiments	166
2012	TiO_2	30 nm	irregular	bacteria (*Pseudomonas aeruginosa*), polysaccharide (alginate)	Reaction kinetics, adhesion of nanoparticles on bacteria	167
2012	TiO_2	6 - 74 nm	irregular	humic acids	Sedimentation, quantification of stability or persistence of nanoparticles	168
2012	TiO_2	44 - 120 nm	irregular	biomass (sewage sludge)	Analysis of aggregate morphology, qualitative analysis of nanoparticles in specific matrixes, quantification of nanoparticles in specific matrixes	12
2013	TiO_2	6 nm, 13 nm, 23 nm	n. d.	humic acids	Aggregation/coagulation kinetics, analysis of aggregate morphology, surface charge determination	169
2013	TiO_2	52 nm	n. d.	humic acids, polysaccharide (alginate)	Adsorption kinetics, quantification of stability or persistence of nanoparticles, surface charge determination	170
2013	TiO_2	100 - 365 nm	n. d.	humic acids	Quantification of stability or persistence of nanoparticles, surface charge determination	171
2009	ZnO	20 nm	n. d.	humic acids	Characterization of DOM-coating, adsorption isotherms of DOM on nanoparticles, surface charge determination	33
2009	ZnO	320 nm	n. d.	total DOM	Aggregation/coagulation kinetics, adsorption isotherms of DOM on nanoparticles	119
2010	ZnO	20 nm	n. d.	humic acids	Mass transfer or deposition of nanoparticles	172
2010	ZnO	24 nm	spheroid	total DOM	Aggregation/coagulation kinetics, sedimentation, surface charge determination, qualitative analysis of nanoparticles in specific matrixes	77
2011	ZnO	4 nm	spherical	humic acids	Monitoring of nanoparticle dissolution, analysis of aggregate morphology, characterization of DOM-coating, surface charge determination	173

Table S1. Continued

Year	Colloid type (-capping agent)	Particle size	Shape	Organic matter used	Type of experiment	Ref
2012	ZnO	330 - 380 nm	n. d.	humic acids, polaysaccharide (alginate)	Transport experiments	174
2013	ZnO	<100 nm	n. d.	humic acids	Characterization of DOM-coating, ions/molecules sorption	129
2008	ZnS	>100 nm	n. d.	humic acids, amino acids (cysteine, serine), glutathione, glycolate, oxalate	Aggregation/coagulation kinetics	175
2010	ZnS	65 nm	irregular	amino acids (cysteine, serine)	Aggregation/coagulation kinetics, adsorption isotherms of DOM on nanoparticles	140
2011	ZnS	<10 nm	irregular	humic acids, fulvic acids	Aggregation/coagulation kinetics, characterization of coating, surface charge determination	176
2005	ZrO_2	73 nm	spherical	proteins (bovine serum albumin, chicken hen egg white lysozyme)	Investigation of sorption mechanism, adsorption isotherms of DOM on nanoparticles, surface charge determination	28
2011	ZrO_2	3 nm	spherical	humic acids	Characterization of DOM-coating, determination of hydrophobicity	137

References

(1)   Sánchez-Cortés, S.; Francioso, O.; Ciavatta, C.; Garcia-Ramos, J.; Gessa, C. pH-dependent Adsorption of Fractionated Peat Humic Substances on Different Silver Colloids Studied by Surface-enhanced Raman Spectroscopy. *Journal of Colloid and Interface Science* **1998**, *198*, 308–318.

(2)   Cumberland, S. A.; Lead, J. R. Particle Size Distributions of Silver Nanoparticles at Environmentally Relevant Conditions. *Journal of Chromatography A* **2009**, *1216*, 9099–9105.

(3)   Liu, J.; Hurt, R. H. Ion Release Kinetics and Particle Persistence in Aqueous Nano-silver Colloids. *Environmental Science & Technology* **2010**, *44*, 2169–2175.

(4)   Chappell, M. A.; Miller, L. F.; George, A. J.; Pettway, B. A.; Price, C. L.; Porter, B. E.; Bednar, A. J.; Seiter, J. M.; Kennedy, A. J.; Steevens, J. A. Simultaneous Dispersion-dissolution Behavior of Concentrated Silver Nanoparticle Suspensions in the Presence of Model Organic Solutes. *Chemosphere* **2011**, *84*, 1108–1116.

(5)   Chinnapongse, S. L.; MacCuspie, R. I.; Hackley, V. A. Persistence of Singly Dispersed Silver Nanoparticles in Natural Freshwaters, Synthetic Seawater, and Simulated Estuarine Waters. *Science of the Total Environment* **2011**, *409*, 2443–2450.

(6)   Delay, M.; Dolt, T.; Woellhaf, A.; Sembritzki, R.; Frimmel, F. H. Interactions and Stability of Silver Nanoparticles in the Aqueous Phase: Influence of Natural Organic Matter (NOM) and Ionic Strength. *Journal of Chromatography A* **2011**, *1218*, 4206–4212.

(7)   Huynh, K. A.; Chen, K. L. Aggregation Kinetics of Citrate and Polyvinylpyrrolidone Coated Silver Nanoparticles in Monovalent and Divalent Electrolyte Solutions. *Environmental Science & Technology* **2011**, *45*, 5564–5571.

(8)   Piccapietra, F.; Sigg, L.; Behra, R. Colloidal Stability of Carbonate-coated Silver Nanoparticles in Synthetic and Natural Freshwater. *Environmental Science & Technology* **2011**, *46*, 818–825.

(9)   Thio, B. J. R.; Montes, M.; Mahmoud, M. A. E.; Lee, D. W.; Zhou, D.; Keller, A. A. Mobility of Capped Silver Nanoparticles Under Environmentally Relevant Conditions. *Environmental Science & Technology* **2011**, *46*, 6985–6991.

(10)   Gao, J.; Powers, K.; Wang, Y.; Zhou, H.; Roberts, S. M.; Moudgil, B. M.; Koopman, B.; Barber, D. S. Influence of Suwannee River Humic Acid on Particle Properties and Toxicity of Silver Nanoparticles. *Chemosphere* **2012**, *89*, 96–101.

(11)   Gondikas, A. P.; Morris, A.; Reinsch, B. C.; Marinakos, S. M.; Lowry, G. V.; Hsu-Kim, H. Cysteine-induced Modifications of Zero-valent Silver Nanomaterials: Implications for Particle Surface Chemistry, Aggregation, Dissolution, and Silver Speciation. *Environmental Science and Technology-Columbus* **2012**, *46*, 7037.

(12)   Kim, B.; Murayama, M.; Colman, B. P.; Hochella, M. F. Characterization and Environmental Implications of Nano-and Larger TiO2 Particles in Sewage Sludge, and Soils Amended with Sewage Sludge. *Journal of Environmental Monitoring* **2012**, *14*, 1128–1136.

(13)   Unrine, J. M.; Colman, B. P.; Bone, A. J.; Gondikas, A. P.; Matson, C. W. Biotic and Abiotic Interactions in Aquatic Microcosms Determine Fate and Toxicity of Ag Nanoparticles. Part 1. Aggregation and Dissolution. *Environmental Science & Technology* **2012**, *46*, 6915–6924.

(14)   Wirth, S. M.; Lowry, G. V.; Tilton, R. D. Natural Organic Matter Alters Biofilm Tolerance to Silver Nanoparticles and Dissolved Silver. *Environmental Science & Technology* **2012**, *46*, 12687–12696.

(15)   Litvin, V. A.; Galagan, R. L.; Minaev, B. F. Kinetic and Mechanism Formation of Silver Nanoparticles Coated by Synthetic Humic Substances. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2012**, *414*, 234–243.

(16)   Baalousha, M.; Nur, Y.; Römer, I.; Tejamaya, M.; Lead, J. Effect of Monovalent and Divalent Cations, Anions and Fulvic Acid on Aggregation of Citrate-coated Silver Nanoparticles. *Science of the Total Environment* **2013**, *454*, 119–131.

(17)   Lau, B. L.; Hockaday, W. C.; Ikuma, K.; Furman, O.; Decho, A. W. A Preliminary Assessment of the Interactions Between the Capping Agents of Silver Nanoparticles and Environmental Organics. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2013**, *435*, 22–27.

(18)   Furman, O.; Usenko, S.; Lau, B. L. Relative Importance of the Humic and Fulvic Fractions of Natural Organic Matter in the Aggregation and Deposition of Silver Nanoparticles. *Environmental Science & Technology* **2013**, *47*, 1349–1356.

(19)   Pokhrel, L. R.; Dubey, B.; Scheuerman, P. R. Impacts of Select Organic Ligands on the Colloidal Stability, Dissolution Dynamics, and Toxicity of Silver Nanoparticles. *Environmental Science & Technology* **2013**, *47*, 12877–12885.

(20)   Davis, J. A.; Gloor, R. Adsorption of Dissolved Organics in Lake Water by Aluminum Oxide. Effect of Molecular Weight. *Environmental Science & Technology* **1981**, *15*, 1223–1229.

(21)   Davis, J. A. Adsorption of Natural Dissolved Organic Matter at the Oxide/water Interface. *Geochimica et Cosmochimica Acta* **1982**, *46*, 2381–2393.

(22)   Schlautman, M. A.; Morgan, J. J. Adsorption of Aquatic Humic Substances on Colloidal-size Aluminum Oxide Particles: Influence of Solution Chemistry. *Geochimica et Cosmochimica Acta* **1994**, *58*, 4293–4303.

(23)   Zhou, J. L.; Rowland, S.; Fauzi, R.; Mantoura, C.; Braven, J. The Formation of Humic Coatings on Mineral Particles Under Simulated Estuarine Conditions—a Mechanistic Study. *Water Research* **1994**, *28*, 571–579.

(24)   Chandrakanth, M. S.; Amy, G. L. Effects of Ozone on the Colloidal Stability and Aggregation of Particles Coated with Natural Organic Matter. *Environmental Science & Technology* **1996**, *30*, 431–443.

(25)   Elfariss, F.; Nabzar, L.; Ringenbach, E.; Pefferkorn, E. Polyelectrolytic Nature of Humic Substances-aluminum Ion Complexes Interfacial Characteristics and Effects on Colloid Stability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1998**, *131*, 281–294.

(26)   Tombácz, E.; Filipcsei, G.; Szekeres, M.; Gingl, Z. Particle Aggregation in Complex Aquatic Systems. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1999**, *151*, 233–244.

(27)   Rezwan, K.; Meier, L. P.; Rezwan, M.; Vörös, J.; Textor, M.; Gauckler, L. J. Bovine Serum Albumin Adsorption onto Colloidal Al2O3 Particles: A New Model Based on Zeta Potential and UV-vis Measurements. *Langmuir* **2004**, *20*, 10055–10061.

(28)   Rezwan, K.; Studart, A.; Vörös, J.; Gauckler, L. Change of Zeta-potential of Biocompatible Colloidal Oxide Particles Upon Adsorption of Bovine Serum Albumin and Lysozyme. *The Journal of Physical Chemistry B* **2005**, *109*, 14469–14474.

(29)   Harbour, P. J.; Dixon, D. R.; Scales, P. J. The Role of Natural Organic Matter in Suspension Stability: 1. Electrokinetic-rheology Relationships. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2007**, *295*, 38–48.

(30)   Harbour, P. J.; Dixon, D. R.; Scales, P. J. The Role of Natural Organic Matter in Suspension Stability: 2. Modelling of Particle-particle Interaction. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2007**, *295*, 67–74.

(31)   Ghosh, S.; Mashayekhi, H.; Pan, B.; Bhowmik, P.; Xing, B. Colloidal Behavior of Aluminum Oxide Nanoparticles as Affected by pH and Natural Organic Matter. *Langmuir* **2008**, *24*, 12385–12391.

(32)   Ghosh, S.; Mashayekhi, H.; Bhowmik, P.; Xing, B. Colloidal Stability of Al2O3 Nanoparticles as Affected by Coating of Structurally Different Humic Acids. *Langmuir* **2009**, *26*, 873–879.

(33)   Yang, K.; Lin, D.; Xing, B. Interactions of Humic Acid with Nanosized Inorganic Oxides. *Langmuir* **2009**, *25*, 3571–3576.

(34)   Parfitt, R.; Fraser, A.; Farmer, V. Adsorption on Hydrous Oxides. III. Fulvic Acid and Humic Acid on Goethite, Gibbsite and Imogolite. *Journal of Soil Science* **1977**, *28*, 289–296.

(35)   Guan, X.-H.; Shang, C.; Chen, G.-H. Competitive Adsorption of Organic Matter with Phosphate on Aluminum Hydroxide. *Journal of Colloid and Interface Science* **2006**, *296*, 51–58.

(36)   Gibbs, R. J. Effect of Natural Organic Coatings on the Coagulation of Particles. *Environmental Science & Technology* **1983**, *17*, 237–240.

(37)   Bilanovic, D. D.; Kroeger, T. J.; Spigarelli, S. A. Behaviour of Humic-bentonite Aggregates in Diluted Suspensions. *Water SA* **2007**, *33*.

(38)   Heil, D.; Sposito, G. Organic Matter Role in Illitic Soil Colloids Flocculation: I. Counter Ions and pH. *Soil Science Society of America Journal* **1993**, *57*, 1241–1246.

(39)   Heil, D.; Sposito, G. Organic Matter Role in Illitic Soil Colloids Flocculation: II. Surface Charge. *Soil Science Society of America Journal* **1993**, *57*, 1246–1253.

(40)   Sposito, G.; Heil, D. Organic Matter Role in Illitic Soil Colloids Flocculation: III. Scanning Force Microscopy. *Soil Science Society of America Journal* **1995**, *59*, 266–269.

(41)   Jekel, M. R. The Stabilization of Dispersed Mineral Particles by Adsorption of Humic Substances. *Water Research* **1986**, *20*, 1543–1554.

(42)   Kretzschmar, R.; Sticher, H.; Hesterberg, D. Effects of Adsorbed Humic Acid on Surface Charge and Flocculation of Kaolinite. *Soil Science Society of America Journal* **1997**, *61*, 101–108.

(43)   Kretzschmar, R.; Holthoff, H.; Sticher, H. Influence of pH and Humic Acid on Coagulation Kinetics of Kaolinite: A Dynamic Light Scattering Study. *Journal of Colloid and Interface Science* **1998**, *202*, 95–103.

(44)   Meier, M.; Namjesnik-Dejanovic, K.; Maurice, P. A.; Chin, Y.-P.; Aiken, G. R. Fractionation of Aquatic Natural Organic Matter Upon Sorption to Goethite and Kaolinite. *Chemical Geology* **1999**, *157*, 275–284.

(45)   Specht, C.; Kumke, M.; Frimmel, F. Characterization of NOM Adsorption to Clay Minerals by Size Exclusion Chromatography. *Water Research* **2000**, *34*, 4063–4069.

(46)   Akbour, R. A.; Douch, J.; Hamdani, M.; Schmitz, P. Transport of Kaolinite Colloids Through Quartz Sand: Influence of Humic Acid, Ca2+, and Trace Metals. *Journal of Colloid and Interface Science* **2002**, *253*, 1–8.

(47)   Hur, J.; Schlautman, M. A. Molecular Weight Fractionation of Humic Substances by Adsorption onto Minerals. *Journal of Colloid and Interface Science* **2003**, *264*, 313–321.

(48)   Tombácz, E.; Libor, Z.; Illes, E.; Majzik, A.; Klumpp, E. The Role of Reactive Surface Sites and Complexation by Humic Acids in the Interaction of Clay Mineral and Iron Oxide Particles. *Organic Geochemistry* **2004**, *35*, 257–267.

(49)   Feng, X.; Simpson, A. J.; Simpson, M. J. Chemical and Mineralogical Controls on Humic Acid Sorption to Clay Mineral Surfaces. *Organic Geochemistry* **2005**, *36*, 1553–1566.

(50)   Zhang, L.; Luo, L.; Zhang, S. Integrated Investigations on the Adsorption Mechanisms of Fulvic and Humic Acids on Three Clay Minerals. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2012**, *406*, 84–90.

(51)   Leon-Morales, C. F.; Leis, A. P.; Strathmann, M.; Flemming, H. C. Interactions Between Laponite and Microbial Biofilms in Porous Media: Implications for Colloid Transport and Biofilm Stability. *Water Research* **2004**, *38*, 3614–3626.

(52)   Leon Morales, C. F.; Strathmann, M.; Flemming, H. C. Influence of Biofilms on the Movement of Colloids in Porous Media. Implications for Colloid Facilitated Transport in Subsurface Environments. *Water Research* **2007**, *41*, 2059–2068.

(53)   Wilkinson, K. J.; Joz-Roland, A.; Buffle, J. Different Roles of Pedogenic Fulvic Acids and Aquagenic Biopolymers on Colloid Aggregation and Stability in Freshwaters. *Limnology and Oceanography* **1997**, 1714–1724.

(54)   Chorover, J.; Amistadi, M. K. Reaction of Forest Floor Organic Matter at Goethite, Birnessite and Smectite Surfaces. *Geochimica et Cosmochimica Acta* **2001**, *65*, 95–109.

(55)   Labille, J.; Thomas, F.; Milas, M.; Vanhaverbeke, C. Flocculation of Colloidal Clay by Bacterial Polysaccharides: Effect of Macromolecule Charge and Structure. *Journal of Colloid and Interface Science* **2005**, *284*, 149–156.

(56)   Majzik, A.; Tombácz, E. Interaction Between Humic Acid and Montmorillonite in the Presence of Calcium Ions II. Colloidal Interactions: Charge State, Dispersing And/or Aggregation of Particles in Suspension. *Organic Geochemistry* **2007**, *38*, 1330–1340.

(57)   Furukawa, Y.; Watkins, J. L.; Kim, J.; Curry, K. J.; Bennett, R. H. Aggregation of Montmorillonite and Organic Matter in Aqueous Media Containing Artificial Seawater. *Geochemical transactions* **2009**, *10*, 11.

(58)   Furukawa, Y.; Watkins, J. L. Effect of Organic Matter on the Flocculation of Colloidal Montmorillonite: a Modeling Approach. *Journal of Coastal Research* **2012**, *28*, 726–737.

(59)   Borgnino, L. Experimental Determination of the Colloidal Stability of Fe (III)-montmorillonite: Effects of Organic Matter, Ionic Strength and pH Conditions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2013**, *423*, 178–187.

(60)   Kretzschmar, R.; Robarge, W. P.; Amoozegar, A. Influence of Natural Organic Matter on Colloid Transport Through Saprolite. *Water Resources Research* **1995**, *31*, 435–445.

(61)   Diegoli, S.; Manciulea, A. L.; Begum, S.; Jones, I. P.; Lead, J. R.; Preece, J. A. Interaction Between Manufactured Gold Nanoparticles and Naturally Occurring Organic Macromolecules. *Science of the Total Environment* **2008**, *402*, 51–61.

(62)   Pallem, V. L.; Stretz, H. A.; Wells, M. J. Evaluating Aggregation of Gold Nanoparticles and Humic Substances Using Fluorescence Spectroscopy. *Environmental Science & Technology* **2009**, *43*, 7531–7535.

(63)   Stankus, D. P.; Lohse, S. E.; Hutchison, J. E.; Nason, J. A. Interactions Between Natural Organic Matter and Gold Nanoparticles Stabilized with Different Organic Capping Agents†. *Environmental Science & Technology* **2011**.

(64)   Hitchman, A.; Sambrook Smith, G. H.; Ju-Nam, Y.; Sterling, M.; Lead, J. R. The Effect of Environmentally Relevant Conditions on PVP Stabilised Gold Nanoparticles. *Chemosphere* **2013**, *90*, 410–416.

(65)   Nason, J. A.; McDowell, S. A.; Callahan, T. W. Effects of Natural Organic Matter Type and Concentration on the Aggregation of Citrate-stabilized Gold Nanoparticles. *Journal Environmental Monitoring* **2012**, *14*, 1885–1892.

(66)   Liu, J.; Legros, S.; von der Kammer, F.; Hofmann, T. Natural Organic Matter Concentration and Hydrochemistry Influence Aggregation Kinetics of Functionalized Engineered Nanoparticles. *Environmental Science & Technology* **2013**, *47*, 4113–4120.

(67)   Louie, S. M.; Tilton, R. D.; Lowry, G. V. Effects of Molecular Weight Distribution and Chemical Properties of Natural Organic Matter on Gold Nanoparticle Aggregation. *Environmental Science & Technology* **2013**, *47*, 4245–4254.

(68)   Liu, X.; Wazne, M.; Han, Y.; Christodoulatos, C.; Jasinkiewicz, K. L. Effects of Natural Organic Matter on Aggregation Kinetics of Boron Nanoparticles in Monovalent and Divalent Electrolytes. *Journal of Colloid and Interface Science* **2010**, *348*, 101–107.

(69)   Wang, D.; Chu, L.; Paradelo, M.; Peijnenburg, W. J.; Wang, Y.; Zhou, D. Transport Behavior of Humic Acid-modified Nano-hydroxyapatite in Saturated Packed Column: Effects of Cu, Ionic Strength, and Ionic Composition. *Journal of Colloid and Interface Science* **2011**, *360*, 398–407.

(70)   Wang, D.; Bradford, S. A.; Harvey, R. W.; Hao, X.; Zhou, D. Transport of ARS-labeled Hydroxyapatite Nanoparticles in Saturated Granular Media Is Influenced by Surface Charge Variability Even in the Presence of Humic Acid. *Journal of Hazardous Materials* **2012**, *229*, 170–176.

(71)   Wang, D.; Bradford, S. A.; Harvey, R. W.; Gao, B.; Cang, L.; Zhou, D. Humic Acid Facilitates the Transport of ARS-labeled Hydroxyapatite Nanoparticles in Iron Oxyhydroxide-coated Sand. *Environmental Science & Technology* **2012**, *46*, 2738–2745.

(72)   Navarro, D. A. G.; Watson, D. F.; Aga, D. S.; Banerjee, S. Natural Organic Matter-mediated Phase Transfer of Quantum Dots in the Aquatic Environment. *Environmental Science & Technology* **2009**, *43*, 677–682.

(73)   Navarro, D. A.; Banerjee, S.; Aga, D. S.; Watson, D. F. Partitioning of Hydrophobic CdSe Quantum Dots into Aqueous Dispersions of Humic Substances: Influence of Capping-group Functionality on the Phase-transfer Mechanism. *Journal of Colloid and Interface Science* **2010**, *348*, 119–128.

(74)   Tripathi, S.; Champagne, D.; Tufenkji, N. Transport Behavior of Selected Nanoparticles with Different Surface Coatings in Granular Porous Media Coated with Pseudomonas

Aeruginosa Biofilm. *Environmental Science & Technology* **2011**, *46*, 6942–6949.

(75)   Zhang, S.; Jiang, Y.; Chen, C.-S.; Spurgin, J.; Schwehr, K. A.; Quigg, A.; Chin, W.-C.; Santschi, P. H. Aggregation, Dissolution, and Stability of Quantum Dots in Marine Environments: Importance of Extracellular Polymeric Substances. *Environmental Science & Technology* **2012**, *46*, 8764–8772.

(76)   Quevedo, I. R.; Olsson, A. L.; Tufenkji, N. Deposition Kinetics of Quantum Dots and Polystyrene Latex Nanoparticles onto Alumina: Role of Water Chemistry and Particle Coating. *Environmental Science & Technology* **2013**, *47*, 2212–2220.

(77)   Keller, A. A.; Wang, H.; Zhou, D.; Lenihan, H. S.; Cherr, G.; Cardinale, B. J.; Miller, R.; Ji, Z. Stability and Aggregation of Metal Oxide Nanoparticles in Natural Aqueous Matrices. *Environmental Science & Technology* **2010**, *44*, 1962–1967.

(78)   Quik, J. T. K.; Lynch, I.; Hoecke, K. V.; Miermans, C. J. H.; Schamphelaere, K. A. C. D.; Janssen, C. R.; Dawson, K. A.; Stuart, M. A. C.; Meent, D. V. D. Effect of Natural Organic Matter on Cerium Dioxide Nanoparticles Settling in Model Fresh Water. *Chemosphere* **2010**, *81*, 711–715.

(79)   Van Hoecke, K.; De Schamphelaere, K. A.; Van der Meeren, P.; Smagghe, G.; Janssen, C. R. Aggregation and Ecotoxicity of CeO2 Nanoparticles in Synthetic and Natural Waters with Variable pH, Organic Matter Concentration and Ionic Strength. *Environmental Pollution* **2011**, *159*, 970–976.

(80)   Liu, X.; Chen, G.; Su, C. Influence of Collector Surface Composition and Water Chemistry on the Deposition of Cerium Dioxide Nanoparticles: QCM-D and Column Experiment Approaches. *Environmental Science & Technology* **2012**, *46*, 6681–6688.

(81)   Schwabe, F.; Schulin, R.; Limbach, L. K.; Stark, W.; Bürge, D.; Nowack, B. Influence of Two Types of Organic Matter on Interaction of CeO2 Nanoparticles with Plants in Hydroponic Culture. *Chemosphere* **2013**, *91*, 512–520.

(82)   Mudunkotuwa, I. A.; Pettibone, J. M.; Grassian, V. H. Environmental Implications of Nanoparticle Aging in the Processing and Fate of Copper-based Nanomaterials. *Environmental Science & Technology* **2012**, *46*, 7001–7010.

(83)   Jones, E. H.; Su, C. Fate and Transport of Elemental Copper (Cu0) Nanoparticles Through Saturated Porous Media in the Presence of Organic Materials. *Water Research* **2012**, *46*, 2445–2456.

(84)   Horzempa, L. M.; Helz, G. R. Controls on the Stability of Sulfide Sols: Colloidal Covellite as an Example. *Geochimica et Cosmochimica Acta* **1979**, *43*, 1645–1650.

(85)   Giasuddin, A. B.; Kanel, S. R.; Choi, H. Adsorption of Humic Acid onto Nanoscale Zerovalent Iron and Its Effect on Arsenic Removal. *Environmental Science & Technology* **2007**, *41*, 2022–2027.

(86)   Phenrat, T.; Saleh, N.; Sirk, K.; Kim, H. J.; Tilton, R. D.; Lowry, G. V. Stabilization of Aqueous Nanoscale Zerovalent Iron Dispersions by Anionic Polyelectrolytes: Adsorbed

Anionic Polyelectrolyte Layer Properties and Their Effect on Aggregation and Sedimentation. *Journal of Nanoparticle Research* **2008**, *10*, 795–814.

(87)   Tiraferri, A.; Chen, K. L.; Sethi, R.; Elimelech, M. Reduced Aggregation and Sedimentation of Zero-valent Iron Nanoparticles in the Presence of Guar Gum. *Journal of Colloid and Interface Science* **2008**, *324*, 71–79.

(88)   Johnson, R. L.; Johnson, G. O. B.; Nurmi, J. T.; Tratnyek, P. G. Natural Organic Matter Enhanced Mobility of Nano Zerovalent Iron. *Environmental Science & Technology* **2009**, *43*, 5455–5460.

(89)   Li, Z.; Greden, K.; Alvarez, P. J. J.; Gregory, K. B.; Lowry, G. V. Adsorbed Polymer and NOM Limits Adhesion and Toxicity of Nano Scale Zerovalent Iron to E. Coli. *Environmental Science & Technology* **2010**, *44*, 3462–3467.

(90)   Dong, H.; Lo, I. Influence of Humic Acid on the Colloidal Stability of Surface-modified Nano Zero-valent Iron. *Water Research* **2012**, *47*, 419–427.

(91)   Basnet, M.; Ghoshal, S.; Tufenkji, N. Rhamnolipid Biosurfactant and Soy Protein Act as Effective Stabilizers in the Aggregation and Transport of Palladium-Doped Zerovalent Iron Nanoparticles in Saturated Porous Media. *Environmental Science & Technology* **2013**, *47*, 13355–13364.

(92)   Dong, H.; Lo, I. Influence of Calcium Ions on the Colloidal Stability of Surface-modified Nano Zero-valent Iron in the Absence or Presence of Humic Acid. *Water Research* **2013**, *47*, 2489–2496.

(93)   Tipping, E. Adsorption by Goethite (alpha-FeOOH) of Humic Substances from Three Different Lakes. *Chemical Geology* **1981**, *33*, 81–89.

(94)   Cameron, A.; Liss, P. The Stabilization of "dissolved" Iron in Freshwaters. *Water Research* **1984**, *18*, 179–185.

(95)   Liang, L.; Morgan, J. J. Chemical Aspects of Iron Oxide Coagulation in Water: Laboratory Studies and Implications for Natural Systems. *Aquatic Sciences-Research Across Boundaries* **1990**, *52*, 32–55.

(96)   Amal, R.; Raper, J.; Waite, T. Effect of Fulvic Acid Adsorption on the Aggregation Kinetics and Structure of Hematite Particles. *Journal of Colloid and Interface Science* **1992**, *151*, 244–257.

(97)   Amirbahman, A.; Olson, T. M. Transport of Humic Matter-coated Hematite in Packed Beds. *Environmental Science & Technology* **1993**, *27*, 2807–2813.

(98)   Ledin, A.; Karlsson, S.; Allard, B. Effects of pH, Ionic Strength and a Fulvic Acid on Size Distribution and Surface Charge of Colloidal Quartz and Hematite. *Applied Geochemistry* **1993**, *8*, 409–414.

(99)   Tiller, C. L.; O'Melia, C. R. Natural Organic Matter and Colloidal Stability: Models and Measurements. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*

1993, *73*, 89–102.

(100)   Gu, B.; Schmitt, J.; Chen, Z.; Liang, L.; McCarthy, J. F. Adsorption and Desorption of Natural Organic Matter on Iron Oxide: Mechanisms and Models. *Environmental Science & Technology* **1994**, *28*, 38–46.

(101)   Amirbahman, A.; Olson, T. M. Deposition Kinetics of Humic Matter-coated Hematite in Porous Media in the Presence of Ca2+. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1995**, *99*, 1–10.

(102)   Gu, B.; Schmitt, J.; Chen, Z.; Liang, L.; McCarthy, J. F. Adsorption and Desorption of Different Organic Matter Fractions on Iron Oxide. *Geochimica et Cosmochimica Acta* **1995**, *59*, 219–229.

(103)   Zhang, J.; Buffle, J. Kinetics of Hematite Aggregation by Polyacrylic Acid: Importance of Charge Neutralization. *Journal of Colloid and Interface Science* **1995**, *174*, 500–509.

(104)   Gu, B.; Mehlhorn, T. L.; Liang, L.; McCarthy, J. F. Competitive Adsorption, Displacement, and Transport of Organic Matter on Iron Oxide: I. Competitive Adsorption. *Geochimica et Cosmochimica Acta* **1996**, *60*, 1943–1950.

(105)   Kretzschmar, R.; Sticher, H. Transport of Humic-coated Iron Oxide Colloids in a Sandy Soil: Influence of Ca2+ and Trace Metals. *Environmental Science & Technology* **1997**, *31*, 3497–3504.

(106)   Vermeer, A.; Van Riemsdijk, W.; Koopal, L. Adsorption of Humic Acid to Mineral Particles. 1. Specific and Electrostatic Interactions. *Langmuir* **1998**, *14*, 2810–2819.

(107)   Vermeer, A.; Koopal, L. Adsorption of Humic Acids to Mineral Particles. 2. Polydispersity Effects with Polyelectrolyte Adsorption. *Langmuir* **1998**, *14*, 4210–4216.

(108)   Au, K. K.; Penisson, A. C.; Yang, S.; O'Melia, C. R. Natural Organic Matter at Oxide/water Interfaces: Complexation and Conformation. *Geochimica et Cosmochimica Acta* **1999**, *63*, 2903–2917.

(109)   Verrall, K. E.; Warwick, P.; Fairhurst, A. J. Application of the Schulze-Hardy Rule to Haematite and Haematite/humate Colloid Stability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1999**, *150*, 261–273.

(110)   Ferretti, R.; Stoll, S.; Zhang, J.; Buffle, J. Flocculation of Hematite Particles by a Comparatively Large Rigid Polysaccharide: Schizophyllan. *Journal of Colloid and Interface Science* **2003**, *266*, 328–338.

(111)   Ramos-Tejada, M.; Ontiveros, A.; Viota, J.; Durán, J. Interfacial and Rheological Properties of Humic Acid/hematite Suspensions. *Journal of Colloid and Interface Science* **2003**, *268*, 85–95.

(112)   Mylon, S. E.; Chen, K. L.; Elimelech, M. Influence of Natural Organic Matter and Ionic Composition on the Kinetics and Structure of Hematite Colloid Aggregation:

Implications to Iron Depletion in Estuaries. *Langmuir* **2004**, *20*, 9000–9006.

(113) Chen, K. L.; Mylon, S. E.; Elimelech, M. Aggregation Kinetics of Alginate-coated Hematite Nanoparticles in Monovalent and Divalent Electrolytes. *Environmental Science & Technology* **2006**, *40*, 1516–1523.

(114) Chen, K. L.; Mylon, S. E.; Elimelech, M. Enhanced Aggregation of Alginate-coated Iron Oxide (hematite) Nanoparticles in the Presence of Calcium, Strontium, and Barium Cations. *Langmuir* **2007**, *23*, 5920–5928.

(115) Baalousha, M.; Manciulea, A.; Cumberland, S.; Kendall, K.; Lead, J. R. Aggregation and Surface Properties of Iron Oxide Nanoparticles: Influence of pH and Natural Organic Matter. *Environmental Toxicology and Chemistry* **2008**, *27*, 1875–1882.

(116) Baalousha, M. Aggregation and Disaggregation of Iron Oxide Nanoparticles: Influence of Particle Concentration, pH and Natural Organic Matter. *Science of the Total Environment* **2009**, *407*, 2093–2101.

(117) Manciulea, A.; Baker, A.; Lead, J. R. A Fluorescence Quenching Study of the Interaction of Suwannee River Fulvic Acid with Iron Oxide Nanoparticles. *Chemosphere* **2009**, *76*, 1023–1027.

(118) Seijo, M.; Ulrich, S.; Filella, M.; Buffle, J.; Stoll, S. Modeling the Adsorption and Coagulation of Fulvic Acids on Colloids by Brownian Dynamics Simulations. *Environmental Science & Technology* **2009**, *43*, 7265–7269.

(119) Zhang, Y.; Chen, Y.; Westerhoff, P.; Crittenden, J. Impact of Natural Organic Matter and Divalent Cations on the Stability of Aqueous Nanoparticles. *Water Research* **2009**, *43*, 4249–4257.

(120) Lenhart, J. J.; Heyler, R.; Walton, E. M.; Mylon, S. E. The Influence of Dicarboxylic Acid Structure on the Stability of Colloidal Hematite. *Journal of Colloid and Interface Science* **2010**, *345*, 556–560.

(121) Phenrat, T.; Song, J. E.; Cisneros, C. M.; Schoenfelder, D. P.; Tilton, R. D.; Lowry, G. V. Estimating Attachment of Nano-and Submicrometer-particles Coated with Organic Macromolecules in Porous Media: Development of an Empirical Model. *Environmental Science & Technology* **2010**, *44*, 4531–4538.

(122) Palomino, D.; Stoll, S. Fulvic Acids Concentration and pH Influence on the Stability of Hematite Nanoparticles in Aquatic Systems. *Journal of Nanoparticle Research* **2013**, *15*, 1–8.

(123) Ghosh, S.; Jiang, W.; McClements, J. D.; Xing, B. Colloidal Stability of Magnetic Iron Oxide Nanoparticles: Influence of Natural Organic Matter and Synthetic Polyelectrolytes. *Langmuir* **2011**, *27*, 8036–8043.

(124) Illés, E.; Tombácz, E. The Role of Variable Surface Charge and Surface Complexation in the Adsorption of Humic Acid on Magnetite. *Colloids and Surfaces A:*

Physicochemical and Engineering Aspects **2003**, *230*, 99–109.

(125) Illés, E.; Tombácz, E. The Effect of Humic Acid Adsorption on pH-dependent Surface Charging and Aggregation of Magnetite Nanoparticles. *Journal of Colloid and Interface Science* **2006**, *295*, 115–123.

(126) Liu, J.; Zhao, Z.; Jiang, G. Coating Fe3O4 Magnetic Nanoparticles with Humic Acid for High Efficient Removal of Heavy Metals in Water. *Environmental Science & Technology* **2008**, *42*, 6949–6954.

(127) Hu, J.-D.; Zevi, Y.; Kou, X.-M.; Xiao, J.; Wang, X.-J.; Jin, Y. Effect of Dissolved Organic Matter on the Stability of Magnetite Nanoparticles Under Different pH and Ionic Strength Conditions. *Science of the Total Environment* **2010**, *408*, 3477–3489.

(128) Tombácz, E.; Tóth, I.; Nesztor, D.; Illés, E.; Hajdú, A.; Szekeres, M.; Vékás, L. Adsorption of Organic Acids on Magnetite Nanoparticles, pH-dependent Colloidal Stability and Salt Tolerance. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2013**, *435*, 91–96.

(129) Yang, Y.; Saiers, J. E.; Barnett, M. O. Impact of Interactions Between Natural Organic Matter and Metal Oxides on the Desorption Kinetics of Uranium from Heterogeneous Colloidal Suspensions. *Environmental Science & Technology* **2013**, *47*, 2661–2669.

(130) Tipping, E.; Cooke, D. The Effects of Adsorbed Humic Substances on the Surface Charge of Goethite ([alpha]-FeOOH) in Freshwaters. *Geochimica et Cosmochimica Acta* **1982**, *46*, 75–80.

(131) Beckett, R.; Le, N. P. The Role or Organic Matter and Ionic Composition in Determining the Surface Charge of Suspended Particles in Natural Waters. *Colloids and Surfaces* **1990**, *44*, 35–49.

(132) Wang, L.; Chin, Y.-P.; Traina, S. J. Adsorption of (poly) Maleic Acid and an Aquatic Fulvic Acid by Geothite. *Geochimica et Cosmochimica Acta* **1997**, *61*, 5313–5324.

(133) Filius, J. D.; Lumsdon, D. G.; Meeussen, J. C.; Hiemstra, T.; Van Riemsdijk, W. H. Adsorption of Fulvic Acid on Goethite. *Geochimica et Cosmochimica Acta* **2000**, *64*, 51–60.

(134) Zhou, Q.; Maurice, P. A.; Cabaniss, S. E. Size Fractionation Upon Adsorption of Fulvic Acid on Goethite: Equilibrium and Kinetic Studies. *Geochimica et Cosmochimica Acta* **2001**, *65*, 803–812.

(135) Filius, J. D.; Meeussen, J. C.; Lumsdon, D. G.; Hiemstra, T.; van Riemsdijk, W. H. Modeling the Binding of Fulvic Acid by Goethite: The Speciation of Adsorbed FA Molecules. *Geochimica et Cosmochimica Acta* **2003**, *67*, 1463–1474.

(136) Weng, L.; Van Riemsdijk, W. H.; Hiemstra, T. Humic Nanoparticles at the Oxide-Water Interface: Interactions with Phosphate Ion Adsorption. *Environmental Science & Technology* **2008**, *42*, 8747–8752.

(137) Navarro, D. A.; Depner, S. W.; Watson, D. F.; Aga, D. S.; Banerjee, S. Partitioning Behavior and Stabilization of Hydrophobically Coated HfO2, ZrO2 and HfxZr1- xO2 Nanoparticles with Natural Organic Matter Reveal Differences Dependent on Crystal Structure. *Journal of Hazardous Materials* **2011**, *196*, 302–310.

(138) Ravichandran, M.; Aiken, G. R.; Ryan, J. N.; Reddy, M. M. Inhibition of Precipitation and Aggregation of Metacinnabar (mercuric Sulfide) by Dissolved Organic Matter Isolated from the Florida Everglades. *Environmental Science & Technology* **1999**, *33*, 1418–1423.

(139) Deonarine, A.; Hsu-Kim, H. Precipitation of Mercuric Sulfide Nanoparticles in NOM-containing Water: Implications for the Natural Environment. *Environmental Science & Technology* **2009**, *43*, 2368–2373.

(140) Gondikas, A. P.; Jang, E. K.; Hsu-Kim, H. Influence of Amino Acids Cysteine and Serine on Aggregation Kinetics of Zinc and Mercury Sulfide Colloids. *Journal of Colloid and Interface Science* **2010**, *347*, 167–171.

(141) Slowey, A. J. Rate of Formation and Dissolution of Mercury Sulfide Nanoparticles: The Dual Role of Natural Organic Matter. *Geochimica et Cosmochimica Acta* **2010**, *74*, 4693–4708.

(142) Neihof, R. A.; Loeb, G. I. The Surface Charge of Particulate Matter in Seawater. *Limnology and Oceanography* **1972**, 7–16.

(143) Yokoyama, A.; Srinivasan, K.; Fogler, H. Stabilization Mechanism by Acidic Polysaccharides. Effects of Electrostatic Interactions on Stability and Peptization. *Langmuir* **1989**, *5*, 534–538.

(144) Ouali, L.; Pefferkorn, E. Fragmentation of Colloidal Aggregates Induced by Polymer Adsorption. *Journal of Colloid and Interface Science* **1994**, *168*, 315–322.

(145) Walker, H. W.; Bob, M. M. Stability of Particle Flocs Upon Addition of Natural Organic Matter Under Quiescent Conditions. *Water Research* **2001**, *35*, 875–882.

(146) Davis, C.; Eschenazi, E.; Papadopoulos, K. Combined Effects of Ca 2+ and Humic Acid on Colloid Transport Through Porous Media. *Colloid & Polymer Science* **2002**, *280*, 52–58.

(147) Franchi, A.; O'Melia, C. R. Effects of Natural Organic Matter and Solution Chemistry on the Deposition and Reentrainment of Colloids in Porous Media. *Environmental Science & Technology* **2003**, *37*, 1122–1129.

(148) Pelley, A. J.; Tufenkji, N. Effect of Particle Size and Natural Organic Matter on the Migration of Nano-and Microscale Latex Particles in Saturated Porous Media. *Journal of Colloid and Interface Science* **2008**, *321*, 74–83.

(149) Morales, V. L.; Zhang, W.; Gao, B.; Lion, L. W.; Bisogni Jr, J. J.; McDonough, B. A.; Steenhuis, T. S. Impact of Dissolved Organic Matter on Colloid Transport in the Vadose Zone: Deterministic Approximation of Transport Deposition Coefficients from

Polymeric Coating Characteristics. *Water Research* **2011**, *45*, 1691–1701.

(150) Tipping, E.; Heaton, M. The Adsorption of Aquatic Humic Substances by Two Oxides of Manganese. *Geochimica et Cosmochimica Acta* **1983**, *47*, 1393–1397.

(151) Huangfu, X.; Jiang, J.; Ma, J.; Liu, Y.; Yang, J. Aggregation Kinetics of Manganese Dioxide Colloids in Aqueous Solution: Influence of Humic Substances and Biomacromolecules. *Environmental Science & Technology* **2013**, *47*, 10285–10292.

(152) Koukal, B.; Rossé, P.; Reinhardt, A.; Ferrari, B.; Wilkinson, K. J.; Loizeau, J. L.; Dominik, J. Effect of Pseudokirchneriella subcapitata(Chlorophyceae) Exudates on Metal Toxicity and Colloid Aggregation. *Water Research* **2007**, *41*, 63–70.

(153) Liu, X.; Wazne, M.; Chou, T.; Xiao, R.; Xu, S. Influence of Ca2+ and Suwannee River Humic Acid on Aggregation of Silicon Nanoparticles in Aqueous Media. *Water Research* **2011**, *45*, 105–112.

(154) Assemi, S.; Hartley, P. G.; Scales, P. J.; Beckett, R. Investigation of Adsorbed Humic Substances Using Atomic Force Microscopy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2004**, *248*, 17–23.

(155) Abe, T.; Kobayashi, S.; Kobayashi, M. Aggregation of Colloidal Silica Particles in the Presence of Fulvic Acid, Humic Acid, or Alginate: Effects of Ionic Composition. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2011**, *379*, 21–26.

(156) Schneider, O. D.; Weinrich, L. A.; Giraldo, E.; LeChevallier, M. W. Impacts of Salt Type and Concentration on Coagulation of Humic Acid and Silica. *Journal of Water Supply: Research and Technology* **2013**, *62*, 339–349.

(157) Zhang, H.; Penn, R. L.; Hamers, R. J.; Banfield, J. F. Enhanced Adsorption of Molecules on Surfaces of Nanocrystalline Particles. *The Journal of Physical Chemistry B* **1999**, *103*, 4656–4662.

(158) Pettibone, J. M.; Cwiertny, D. M.; Scherer, M.; Grassian, V. H. Adsorption of Organic Acids on TiO2 Nanoparticles: Effects of pH, Nanoparticle Size, and Nanoparticle Aggregation. *Langmuir* **2008**, *24*, 6659–6667.

(159) Domingos, R. F.; Tufenkji, N.; Wilkinson, K. J. Aggregation of Titanium Dioxide Nanoparticles: Role of a Fulvic Acid. *Environmental Science & Technology* **2009**, *43*, 1282–1286.

(160) Joo, S. H.; Al-Abed, S. R.; Luxton, T. Influence of Carboxymethyl Cellulose for the Transport of Titanium Dioxide Nanoparticles in Clean Silica and Mineral-coated Sands. *Environmental Science & Technology* **2009**, *43*, 4954–4959.

(161) Li, S.; Sun, W. A Comparative Study on Aggregation/sedimentation of TiO2 Nanoparticles in Mono-and Binary Systems of Fulvic Acids and Fe (III). *Journal of Hazardous Materials* **2011**, *197*, 70–79.

(162)   Ottofuelling, S.; Von Der Kammer, F.; Hofmann, T. Commercial Titanium Dioxide Nanoparticles in Both Natural and Synthetic Water: Comprehensive Multidimensional Testing and Prediction of Aggregation Behavior. *Environmental Science & Technology* **2011**, *45*, 10045–10052.

(163)   Thio, B. J. R.; Zhou, D.; Keller, A. A. Influence of Natural Organic Matter on the Aggregation and Deposition of Titanium Dioxide Nanoparticles. *Journal of Hazardous Materials* **2011**, *189*, 556–563.

(164)   Chen, G.; Liu, X.; Su, C. Distinct Effects of Humic Acid on Transport and Retention of TiO2 Rutile Nanoparticles in Saturated Sand Columns (supporting Information). *Environmental Science & Technology* **2012**, *46*, 7142–7150.

(165)   Liu, W.; Sun, W.; Borthwick, A. G. L.; Ni, J. Comparison on Aggregation and Sedimentation of Titanium Dioxide, Titanate Nanotubes and Titanate nanotubes-TiO2: Influence of pH, Ionic Strength and Natural Organic Matter. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2013**, *434*, 319–328.

(166)   Chowdhury, I.; Cwiertny, D. M.; Walker, S. L. Combined Factors Influencing the Aggregation and Deposition of nano-TiO2 in the Presence of Humic Acid and Bacteria. *Environmental Science & Technology* **2012**, *46*, 6968–6976.

(167)   Hessler, C. M.; Wu, M. Y.; Xue, Z.; Choi, H.; Seo, Y. The Influence of Capsular Extracellular Polymeric Substances on the Interaction Between TiO2 Nanoparticles and Planktonic Bacteria. *Water Research* **2012**.

(168)   Horst, A. M.; Ji, Z.; Holden, P. A. Nanoparticle Dispersion in Environmentally Relevant Culture Media: a TiO 2 Case Study and Considerations for a General Approach. *Journal of Nanoparticle Research* **2012**, *14*, 1–14.

(169)   Chowdhury, I.; Walker, S. L.; Mylon, S. E. Aggregate Morphology of nano-TiO2: Role of Primary Particle Size, Solution Chemistry, and Organic Matter. *Environmental Science: Processes & Impacts* **2013**, *15*, 275–282.

(170)   Loosli, F.; Le Coustumer, P.; Stoll, S. TiO2 Nanoparticles Aggregation and Disaggregation in Presence of Alginate and Suwannee River Humic Acids. pH and Concentration Effects on Nanoparticle Stability. *Water Research* **2013**, *47*, 6052–6063.

(171)   Yang, X.; Cui, F. Stability of Nano-sized Titanium Dioxide in an Aqueous Environment: Effects of pH, Dissolved Organic Matter and Divalent Cations. *Water Science & Technology* **2013**, *68*, 276–282.

(172)   Jiang, X.; Tong, M.; Li, H.; Yang, K. Deposition Kinetics of Zinc Oxide Nanoparticles on Natural Organic Matter Coated Silica Surfaces. *Journal of Colloid and Interface Science* **2010**, *350*, 427–434.

(173)   Bian, S. W.; Mudunkotuwa, I. A.; Rupasinghe, T.; Grassian, V. H. Aggregation and Dissolution of 4 Nm ZnO Nanoparticles in Aqueous Environments: Influence of pH, Ionic Strength, Size, and Adsorption of Humic Acid. *Langmuir* **2011**, *27*, 6059–6068.

(174)   Jiang, X.; Tong, M.; Kim, H. Influence of Natural Organic Matter on the Transport and Deposition of Zinc Oxide Nanoparticles in Saturated Porous Media. *Journal of Colloid and Interface Science* **2012**, *386*, 34–43.

(175)   Lau, B. L.; Hsu-Kim, H. Precipitation and Growth of Zinc Sulfide Nanoparticles in the Presence of Thiol-containing Natural Organic Ligands. *Environmental Science & Technology* **2008**, *42*, 7236–7241.

(176)   Deonarine, A.; Lau, B. L. T.; Aiken, G. R.; Ryan, J. N.; Hsu-Kim, H. Effects of Humic Substances on Precipitation and Aggregation of Zinc Sulfide Nanoparticles. *Environmental Science and Technology-Columbus* **2011**, *45*, 3217.

Annex 2

Supporting Information of the Chapter 5

Evaluation of hydrodynamic chromatography coupled with inductively coupled plasma mass spectrometry detector for analysis of colloids in environmental media – Effects of colloids properties (supporting information)

A. Philippe[+], M. Gangloff[+], D. Rakcheev[+], G. E. Schaumann[+]*

[+]Institute for Environmental Sciences, Department of Environmental and Soil Chemistry, University Koblenz-Landau, Landau, Germany

*Email address: schaumann@uni-landau.de

Content

Figure S1

Figure S2

Figure S1: Representative SEM picture obtained using a back scattering electron detector of the silver pentagonal prisms (nominal length of 165 nm).
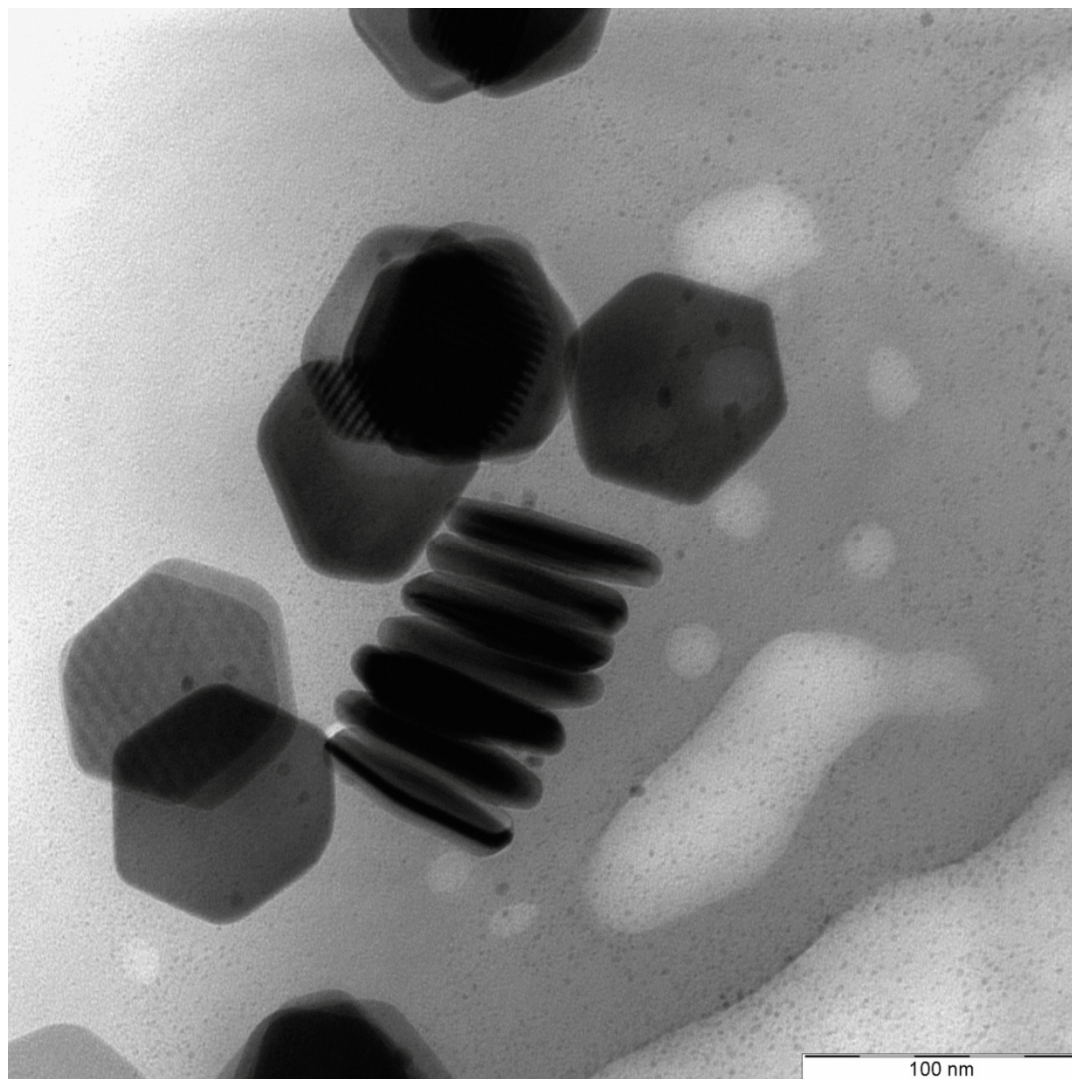
Figure S2: Representative TEM picture of silver hexagonal prisms (nominal length of 80 nm).

Annex 3

Supporting Information of the Chapter 6

HYDRODYNAMIC CHROMATOGRAPHY COUPLED WITH SINGLE PARTICLE-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR INVESTIGATING NANOPARTICLES AGGLOMERATES

Denis Rakcheev[§,‡], Allan Philippe[§,‡], Gabriele E. Schaumann[§,]*

[§] Institute for Environmental Sciences, Department of Environmental and Soil Chemistry, University Koblenz-Landau, Landau, Germany. [‡] These Authors contributed equally to this work. Correspondence should be addressed to schaumann@uni-landau.de

ABSTRACT

This supplementary information contains the characterization of the gold nanoparticle standards in this study, the experimental setup for the HPLC, ICP-MS, and DLS equipment, the description of the program used for the data analysis. In addition, the results of the calibration curves for the mass and the effective diameter, the comparison table of the initial size of the calibrants, and the DLS measurement of the agglomeration procedure of the 10 nm gold nanoparticles are presented.

TABLE OF CONTENT	Page

MATERIALS AND METHODS

Characterization of the NIST gold nanoparticles.

These particles were certified reference material. The report of investigation given by the supplier reported the following results:

Table S-1: Reference value mean size and expanded uncertainty average particle size (diameter), in nm (information provided by the supplier)

Technique	Analyte form	Particle size (nm)
Atomic force microscopy	Dry, deposited on substrate	8.5 ± 0.3
Scanning electron microscopy	Dry, deposited on substrate	9.9 ± 0.1
Transmission electron microscopy	Dry, deposited on substrate	8.9 ± 0.1
Differential mobility analysis	Dry, aerosol	11.3 ± 0.1
Dynamic light scattering	Liquid suspension	13.5 ± 0.1
Small-angle X-ray scattering	Liquid suspension	9.1 ± 1.8

TEM micrographs were provided and shown that the particles were spherical.

Size measurement of the gold calibrants. The core and hydrodynamic diameters of the gold particles from 50 nm to 250 nm were examined using respectively SEM and NTA. These two methods were chosen because the results are directly expressed as a number average with individual values for each measured particles that was then converted into volume weighted distribution reflecting the signal obtained from the ICP-MS. Nanoparticle-tracking analyses were performed with a LM20 (Nanosight) analyser following a common procedure. Confidence intervals at 95% were calculated from at least three measurements. A Quanta250 (FEI) scanning electron microscope equipped with an X-ray diffraction system (Quantax; Bruker) was used for the microscopic characterization of the colloid standards. 1 µL of the dispersion was deposed on an aluminium support covered by a carbon tape and dried in the air

for 15 min. Samples were then directly analysed under high vacuum using the Everhart Thornley detector for particles larger than 100 nm or the backscattered electron detector for particles smaller than 100 nm. The elemental composition of the particles was verified by X-ray analysis. For each sample the diameter of 150-200 particles were measured manually. Comparison of SEM and NTA results is represented in the **figure S-1**.
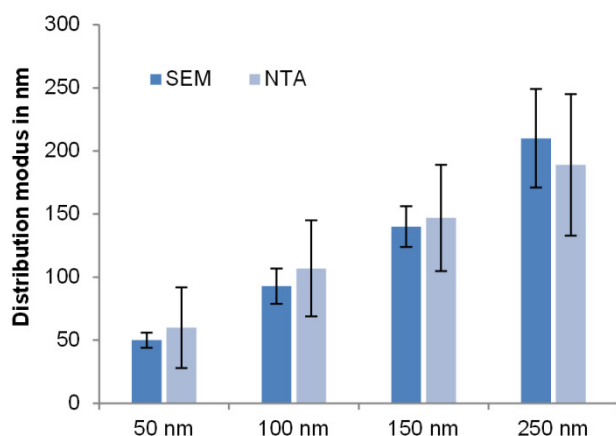

Figure S-1: Comparison of SEM and NTA results for the gold calibrants used in this study. Core diameters measured using SEM and hydrodynamic diameters measured using NTA. The modus shown are from the non-weighted distribution. The values given on the horizontal axis are indicative nominal values provided by the supplier without further information. The bars represent the standard deviation of the respective number average distribution. The confidence interval at 95% for the NTA values (over four measurements) were 4%, 10%, 8% and 13% for the particles with nominal diameters: 50, 100, 150 and 250 nm respectively.

HPLC-system. Size separation was achieved at room temperature using PL-PSDA type 1 and type 2 hydrodynamic chromatography columns (Agilent, Germany, separation range 5–300 nm and 20-1200 nm, respectively) connected to an Agilent 1200 HPLC system (Agilent, Germany). The eluent was prepared using MQW, 0.536 g L^{-1} (2 mM) $Na_2PO_4 \cdot 7H_2O$ (Aldrich purity > 99 %), 0.5 %w/w (60 mM) formaldehyde solution (Alfa Aesar, 37 % w/w H_2O, 7-8 % MeOH), 0.5 g L^{-1} (1.8 mM) sodium dodecyl sulphate (Alfa Aesar), 1 g L^{-1} (3.2 mM) Brij L23 (Alfa Aesar) and 1 g L^{-1} (3.2 mM) Triton X-100 (Alfa Aesar). pH was adjusted to 7.5-8 with HNO_3 (sub-boiled) and NaOH (Merk, titrisol). Injection volume was 10 µl. Flow rate

program was adapted to optimise separation efficiency and to maximise the time during which the particle reaching the detector. It was thus possible to increase the number of particles analysed for one injection while maintaining a concentration low enough for single particle analysis. Around 6000 particles were injected per sample during calibration. The flow rate program was as follows: 0-5 min: 2.1 mL min^{-1}; 5-5.5 min: linear decreased to 0.5 mL min^{-1}; from 5.5 min to the end: 0.5 mL min^{-1}.

ICP-MS system. The ICP-MS detector is a quadrupole-ICP-MS XSeries 2 (Thermo Fisher) equipped with a platinum-sample-cone and a PTFE spray chamber thermostated by a Peltier-cooler. The parameters were optimised prior to each run using a tuning solution containing HDC-eluent and standards of gold nanoparticles. Typical values for these parameters are listed in **table S-2**.

Table S-2: ICP-MS parameters used in this study

Extraction	L1	L2	QP Focus	D1	D2	Octopole Bias	L3
-125 V	-1.29 kV	-88.6 V	4.3 V	-47.1 V	-144 V	-5 V	-194.6 V
Forward power	**Horizontal**	**Vertical**	**DA**	**Cool**	**Aux. gas flux**	**Nebuliser gas flow**	**Hexapole bias**
1.4 kW	40 mm	448 mm	-18 V	13.4 °C	0.82 L min^{-1}	0.78 L min^{-1}	-3 V
Sampling depth	**Nebuliser Temperature**	**Dwell time**					
40 mm	3 °C	5 ms					

Due to short dwell time (5 ms) the amount of collecting data exceeds the limits of PlasmaLab$^{®}$ Software that leads their losses. In order to overcome this, data collection starts only 8 min after injection and contains data of the last four minutes of the region where the particles elute. This allowed reducing the amount of collected data points and made possible reading and saving the data.

Description of the VBA macro for data analysis. The processing of the data includes four automated steps using an algorithm developed in Visual Basic (Microsoft Excel VBA) to process the large amount of data (~60000 data points). In step one, the background signal (around 5000 cps for the experiments reported here) monitored in the absence of the sample, is removed. In step two, the average retention time and the average spike signal intensities are calculated. Aberrant D_C and retention time values (isolated values much higher or lower than the average) are removed in step three by applying the Grubbs' test. The test parameters are as follows: two-sided test, significance level $\alpha = 99\%$, Student's coefficient $t_\infty = 2.560$, degree of freedom $N > 120$. Outliers are due to unavoidable remnants from suspensions injected prior to the experiments. To estimate an order of magnitude, we counted random spike signals occurring during an HDC run when no sample was injected. Generally, we observed around 20 of these particles per run, which we consider negligible compared to the 1000 to 3000 spikes observed from the sample. Step four consists of repetitions of steps two and three until there are no outliers remaining. The obtained results are used for further calculations of aggregate density and fractal dimension as described below.

DLS system. A Delsa Nano C particle analyser from Beckmann-Coulter (laser wavelength: 658 nm, scattering angle: 165°, temperature: 20 °C) was used for the light scattering measurements. Z-average hydrodynamic diameter was calculated using the CONTIN method. Measure position was 6.15 mm above the bottom of the vials. Cuvettes polystyrene was used. The intensity attenuation was optimized every 300 repetitions (one repetition took around 2s).
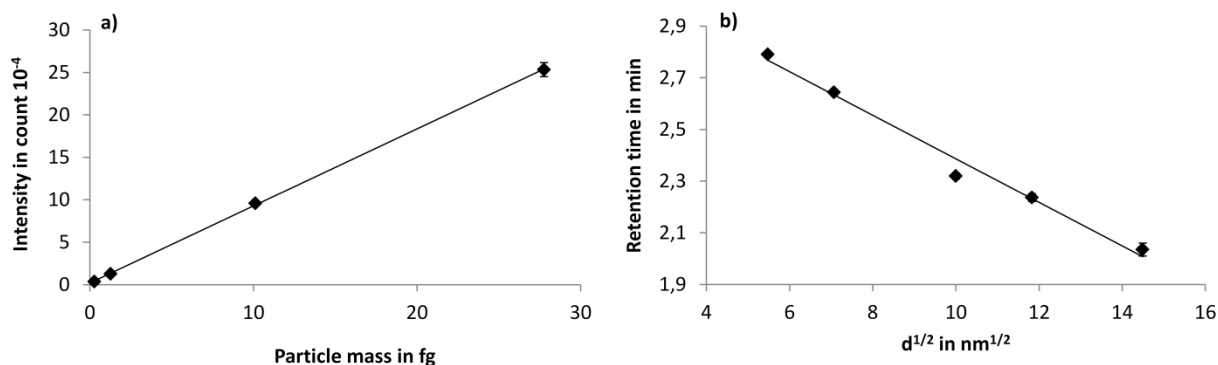
RESULTS

Figure S-2: Calibration curves obtained for gold colloids standards (30 nm, 50 nm, 100 nm and 150 nm) using HDC-sp-ICP-MS. a: spike intensity function of the particle mass (calculated assuming spherical geometry). b: retention time function of the square root of the particle diameter (measured by SEM). Each dot represents the average of 10 replicates and the bars represent the confidence interval at 95%.

Table S-2: Comparison of core diameters obtained from SEM and sp-ICP-MS (spike height) analysis. The distribution modus and standard deviation and the relative difference between the standard deviations obtained from both methods are given.

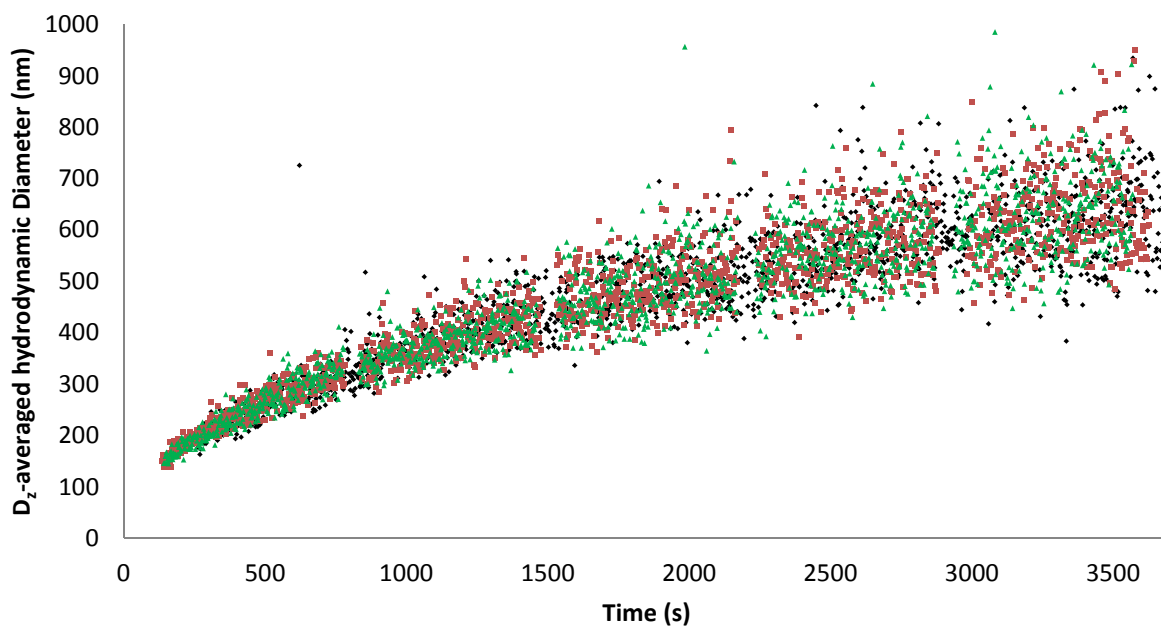| Nominal size in nm		50	100	150
Modus in nm	SEM	50	92	141
	sp-ICP-MS	50	104	147
SD in nm	SEM	6.2	13.9	16.1
	sp-ICP-MS	8.5	18.6	27.6
Diff SD in %		15.4	14.5	26.4

Figure S-3: D_z-averaged hydrodynamic diameter measured with dynamic light scattering over the time for the 10 nm gold nanoparticles suspension (3.58 mg L^{-1}) destabilized using $CaCl_2$ (5 mM) following the same protocol used for the experiments with the HDC-sp-ICP-MS. Three replicates were analyzed and are represented by three different colors.