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Holistic Strategy to Study Nanoparticles and Metallic Trace Elements in Surface Waters

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Abstract: - Emergent Contaminants (ECs) including nanoparticles (NPs) are preoccupation cause for concern for the scientific community, industrials, territorial communities and the general public. High production volume, potential release from consumer product, environmental exposure, we need to measure the environmental concentrations of NPs and their behavior in natural waters. This is too complicated given the complexity of natural particles and the similarity of Engineering NanoParticles (ENPs) with Natural NanoParticles (NNPs) called here NPs. Thus, we need new methods/protocols dedicated to NPs as ECs which cover the sampling strategy, the analysis and the data valorization using new approaches, theory, paradigms!

Our objective is to propose a global approach addressing the above mentioned concerns conveying: sampling, analysis and concept(s) dedicated to Metallic Trace Elements (MTEs) and Nanoparticles (NPs).

- **Sampling:** A crucial point due to the representativeness of the samples regarding a water mass (notion of flux) whose matrix integrates organic matter, chemical elements (from the major to the trace) ligands, biological compounds and contaminants such as MTEs and NPs?

- **Analysis:** Once a representative sample is obtained, how to analyze with minimum artefacts (fractionation, metastable complexes over time, endogenous reaction between the different components, etc.)? What are the basic parameters necessary for understanding the fate of TMEs and NPs in the water column?

- **Concept(s):** it should be holistic which means able to describe the main scenario allowing for consideration of the parameters controlling the fate and behavior of MTE and NPs.

Holistic approach consists of sampling devices adapted to the target elements, user-friendly, easy to analyze using a dedicated analytical platform that fits the concept of physical chemical speciation.

Key-Words: - Nanoparticle, Metallic Trace Elements, Surface Water, In-situ sensors, Analytical, Colloids, Dissolved, Labile, Concept, Holistic, Aggregation, Disaggregation.

1 Introduction

Nanoparticles (NPs) and Emerging Contaminants (ECs) are a real preoccupation both for scientific, industry, environmental agencies, political authorities as well as the public society. A debate about the advantages and disadvantages of NPs started some years ago. Our purpose is not to discuss of this but evaluate NPs and ECs trends, when they are disseminated in the biosphere. Just some facts concerning the NPs: the global nanotechnology market has doubled between 2011 (\$20.1 billion) to 2016 (\$39.2 billion) [1]. Global consumption of nanocomposites was estimated at 118768 tons for a value of over \$800 million in 2010. By 2016, the market reached around 308,000 tons for a value of \$1.6 billion [2]. Recent data about fine particles (size < 1 μm) in the atmosphere reveal high impact on the human health. With 7 million premature deaths, including almost 600 000 for Europe in 2012, the global cost for WHO Europe is estimated for the year 2010 at \$1575 trillion [3]. According to the UN, 23 m³/s of wastewater is discharged directly into the environment. In developing countries, 90% of wastewater is released into the natural environment without any treatment. According to the WHO, 3.4 million people die each year from aquatic pollution. With 3.1% of deaths in the world is explained by poor water quality in terms of sanitation and hygiene, it should be related to the 2.6 billion people without sanitary facilities. If the main source of water contamination is due to biological form (fecal peril), the exposure to "emerging" contaminants, become a societal problem. Indeed, in the case of Metallic Trace Elements (MTE), it is a diffuse long-term pollution with bio-accumulative effects throughout the trophic chain. The presence of NPs in waste stream is a fact which increases each year [4]. Despite abundant literature on NPs, their effects on cells and DNA remains largely undervalued. Producers communicate little about the impact of their products on the living and our feedback is still scarce. Some authors suggest significant effects on health and the environment [5]. The main difficulties related to the study of MTE and NPs in surface waters are threefold: their sampling and detection, their qualitative and quantitative characterization and the interpretation of the data according to which concept(s)? Our objective is to propose a holistic approach covering sampling, analysis and concept(s).

Sampling: A crucial point due to the representativeness of the samples with respect to water mass (notion of flux) whose matrix integrates organic matter, chemical elements (from the major to the trace) ligands, biological compounds and contaminants such as MTEs and NPs?

Analysis: Once a sample is obtained, how to analyze with minimum perturbation (fractionation, metastable complexes over time, endogenous reaction between the different components, etc.)? What set of parameters are necessary for understanding the fate of MTEs and NPs in the water column?

Concept(s): or approaches should be holistic, which means being able to describe the main scenario allowing consideration of the main or principal parameters controlling the fate and behavior of MTE and NPs. Holistic approach is not related only to a discipline but it is a global way integrating and updating methods, concepts and tools to investigate novel materials, compounds in all the human and natural compartments.

In this paper we will describe sampling strategies, methods and tools dedicated to MTEs and NPs analysis. It consists of sampling devices adapted to the specific target elements, user-friendly and easy to analyze using a dedicated analytical platform that is fit to the physico-chemical speciation approach. By using such conceptual approach, we are able to measure important characteristics controlling of the MTE and NPs concentrations, properties, behavior, transformation, and potential impact in the environment [7]. By considering continental waters as a complex and dynamic matrix including a mixture of particles, colloids and dissolved species, aggregation/ disaggregation and NPs surface coating must be apprehended to explain the evolution of MTE and NPs into this system [8]. Their compartments identified it should be possible to determine a soft, green and efficient treatment of contaminated waters

2 Materials and Methods

2.1 Sampling strategy

Transport and fate of metallic trace elements (MTE) and nanoparticles (NPs) require sophisticated tools and approaches. Meanwhile the

concepts have to be defined especially for surface water quality assessment. Classic approaches are based on total fraction and filtrated ones ($< 0.45 \mu\text{m}$). A bias is often observed by considering the filtrated fraction equivalent to dissolved one. In fact it recovers a part of particle, colloidal, nanoparticulate and dissolved fractions. To precise which fraction carries traces metals or nanoparticles, it is crucial to use another protocol. Few studies are based on ultra-filtration (bypassed at $0.01 \mu\text{m}$) allowing true dissolved fraction separation; and so what about the other fractions able to trap contaminants? Another problem encountered by hydro-geochemist is the transfer from a fraction to another one. This phenomenon is called colloidal pumping [8] occurring in all surface waters when physical and/or chemical parameters change such as NOM concentration, pH, Ionic strength [9] or by the influence of biological activities induced by bacteria and micro-organisms [10, 11]. In such case, it is fundamental to work onto samples well identified in term of fractions. First strategy is based on separative techniques: passive (filtration, centrifugation) or dynamic (field flow field fractionation or 4F) to perform analysis on "perfectly" identified fractions. One limitation by operating with separative techniques resides into the possibility (or not) to identify the relationships between traces elements, nanoparticles and colloids and particles.

On the over hand, whole-sample analysis is difficult due to the extrema heterogeneity and complexity of environmental samples, in term of size, chemical composition, etc. The role and impact of NOM in determining the fate and transport of emergent pollutants [12], trace metals [13, 14] and nanoparticles is highly important [15]. If metals or nanoparticles concentrations in total fraction can be done more or less in a user-friendly manner, to getting the information of on the labile or dissolved fraction is more complex. Sample preparation protocols differ and can induce some bias. Generally, to access to the labile trace metal fraction, it is recommended to add some drops of acid (HCl, HNO₃, mix HCl-HNO₃). Some authors [16] recommend digestion activation under microwave, sonic agitation etc. All of them are empirical and nor necessary fully validated to do what they are claimed to do. For example, to get MTEs, NPs into the total fractions of water exhibiting NOM high concentration, it is recommended to destroy organic part of the NOM by addition of hydroxide peroxide (H₂O₂) followed by acid addition and microwave

digestion. In such case what really do we measure? Are we sure to determine to extract the real true dissolved fraction, called dissolved or labile? What is the signification of MTEs and NPs obtained on the total fraction: how to discriminate neogenic from anthropic origin? In fact, it becomes hard to know exactly, on many studies, what has been done.

Thus, studies without errors estimation should be rejected. On other hand we have to inform in detail the protocol used and to present data with internal errors based on standard deviation (sd), percentage ($\pm x \%$), confidence interval, etc. As soon as the same protocol has been used, it is not so much important (depending of the purpose of course) to get "exact" values but to inform about the values plus error to be able to determine or precise the trends of the trace metals, nanoparticles concentration evolution into water matrix.

The rules and protocols can become complex, time overload, expensive, and in developing countries quite impossible to apply high quality level analysis due to lack in some basic infrastructures, or qualified technicians/staffs. Recently, some progresses have been made on dedicated in-situ sample based on nanogel encapsulated with a geometry minimizing artefact during their deployment [6]. Nevertheless, some strategic alternatives can be considered. Based on our experiences, we introduce point of view from analytical platform up to the concept. First to avoid or to minimize sampling transport and conservation, we recommend to use in-situ passive sensors (Table 1) to get data about labile fraction associated with grab samples (minimum of 4 times 250 ml). Of course we recommend using the suggested protocol which should allow getting reliable high value data (Fig.1). Actually there are many different kinds of "In-situ passive" samplers or probes (electrochemical, biological and diffusive ones) available. To avoid extensive discussion about the different solutions, our study is based on our own experience on diffusive gradient in thin-films. Recent technological development is to move from film or 2D geometry to bulk ones (3D). They allow better performance by minimizing some inherent default of 2D ones. Main advantages and limitations of different sampling solutions integrating the Diffusive Milli-Gel (DMG) are listed above (table1). Figure 1 provides a conceptual schematic of the options and strategies allowing reliable data collections. Scientists involved in water analysis have to keep in mind that water media is a complex matrix

Type (target)	Appearance	Advantages	Disadvantages
Grad sample (any contaminants)	Recipients adapted to the contaminants	Traditional Rapid Total/Colloid/Labil Detection	\$\$\$ (technician,) Transport/Conservation Punctual If NOM : complex
DGTs (main trace metals, Hg, P ₂ O ₅ , NH ₄)	2D	Feedback Fluxes 3F (friendly, flexible & few \$	Time of deployment Detection limit Breakable 2D Selective Extraction procedure
POCIS (polar compounds)	2D	Feedback Fluxes 2F ± \$\$	
LDP (hydrophobic compounds)	2D	Feedback Fluxes 2F ± \$\$	
DMG (any contaminants)	3D	Fluxes 3F No extraction Adapted/dedicated \$	New Not commercial Lab scale production Few feedback

Table 1: Recommended protocols for estimating concentrations of Labile and Total fraction in waters

containing organic, inorganic, biological particles. These compounds have size from the nm up to several μm. While in chemistry, classification is based on concentrations named major, minor and trace elements. Their physical states are classified as follow: (truly) dissolved (when size < 1 nm), colloids (1nm<colloids<1μm) and absorbed or

associated to particles (>1μm). Generally, colloids are mainly attributed to Natural Organic Matter (NOM) which differs of Dissolved Organic Matter (DOM). Colloids are flexible objects which vary in term of sizes and their electrical properties in relation with the physical and chemical context.

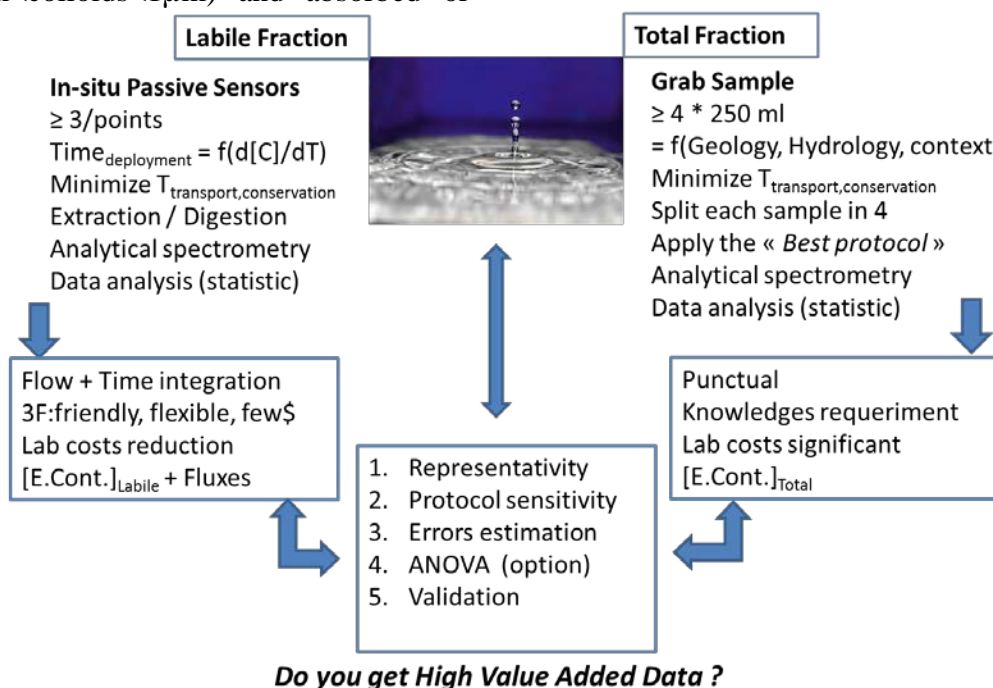


Figure 1: Conceptual approach to estimate labile and/or total fraction of water samples

Thus, to study one or more components becomes tricky and needs several methods to provide a reliable and precise picture of natural water components.

2.2 Analytics

Once a representative sample is obtained, how to analyze with minimum artefacts/perturbations (fractionation, metastable complexes over time, endogenous reaction between the different components, etc.)? What are the basic parameters necessary for understanding the fate of TMEs and NPs in the water column? Unique technique with low sensitivity, high sensibility and able to discriminate data in function of the size, shape distributions should be an ideal. Thus what parameters are essential? From this basic question, what analytical strategy can be considered? In a first step, field parameters have to be measured. Actually there is a real pertinent commercial offer allowing user-friendly parameter measurement. Objective is not to present all the precaution and recommendations requested to obtain a value representative of a parameter but to illustrate the importance of the parameter listed (Table 2). They represent a state dimension of a very complex media called water. For example, if you consider the Ionic Strength (IS), which represent the ionic balance of water, its value can act of many causes and issues as represented in figure 2 [17]. Such parameter can provide information on charge screening effects, specific adsorption processes, if a detailed

analysis of the ionic water composition is performed for example by using ionic chromatography. Ionic strength is also a key parameter, when NPs stability and critical coagulation-aggregation conditions have to be estimated [18]. An important part of experiments are carried out with unstable NPs agglomerating prior to or throughout the experiments. NPs characterization can be made using dynamic light scattering (DLS), laser diffraction, electrophoretic measurements and nanoparticle tracking analysis (NTA). NTA is relatively new technique in the field of nanoparticle visualization and sizing and provides using an original approach count, concentration and diffusion coefficient distributions. Since size distribution using NTA is calculated on a particle-by-particle basis the technique partially overcomes some of the inherent problems and bias associated with the analysis of polydisperse samples. NPs stability and acid-base properties as a function of pH can be investigated by combining DLS and zeta (ζ) potential determination (from electrophoretic mobility measurements). To be able to discriminate NPs, MTEs and other components of a water matrix, spectroscopic methods are also very useful although not always

Parameter	Unit	Remark
Temperature	°C	Useful for modeling
Conductivity	S/m	Often considered related to IS
Turbidity	NTU	Can informed about TDS
Dissolved O ₂	% [O ₂]	Important in term of water quality
Biochemical Demand in Oxygen (DBO ₅)	mg/L [O ₂]	MO # (2 DBO ₅ + DCO) / 3
Chemical Demand in Oxygen (DCO)	mg/L [O ₂]	Informed on biota
Dissolved CO ₂	mg/L [CO ₂]	For water quality evaluation, origin and water rock interactions
Hardness	mg/L de CaCO ₃ +MgCO ₃	
Alcalinity	mg/LCaCO ₃)	
Total dissolved solids (TDS)	mg/L	Point onto colloidal fractions also
Ionic Strength (IS)	mol/L	See figure 2 from EPA
Oxydation Reduction Potential (ORP)	mV	Electron activity measurement

Table 2: some of key parameters useful to estimate the water quality

sufficient. The structure (crystalline, amorphous, in-between), the texture (size, shape, distribution), elementary composition are requested. To identify these parameters, Imaging techniques are of great interest and complementary with spectroscopic ones. Imaging tools can work from macroscopic to nanoscopic scale. To our point of view (S)TEM/X-EDS is particularly well adapted.

Associated with image analysis it is possible to quantify the parameters targeted such as size, shape, structure, composition. Figure 3 provides a view of the data obtained by the techniques integrated into our analytical platform. It associate spectroscopic techniques and images ones. The Flow Field-Fractionation (4F) dynamically separate the different components and associated

with UV, FLD and/or MALLS determine key parameters such size, shape. By coupling it with ICPMS the chemistry at the ppt level can be obtained as a function of the size of the compounds. By collecting the fraction issued from the 4F, it is possible by (S)TEM/X-EDS to confirm the exact size distribution, structure (physical state) and elemental composition but at

the ppm level. In parallel Zetametry coupled with DLS provide size distributions, agglomeration and the Zeta potential (surface charge state). It gives information in term of agglomeration and disaggregation mechanisms and behavior predictions.

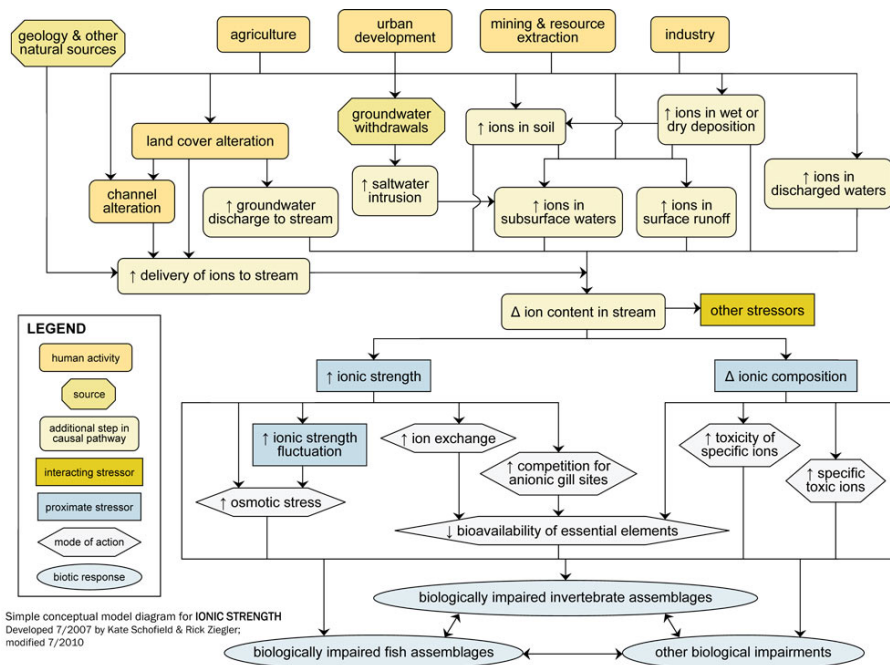


Figure 2: Ionic Strength: Simple Conceptual Diagram (from Ziegler & Schofield)

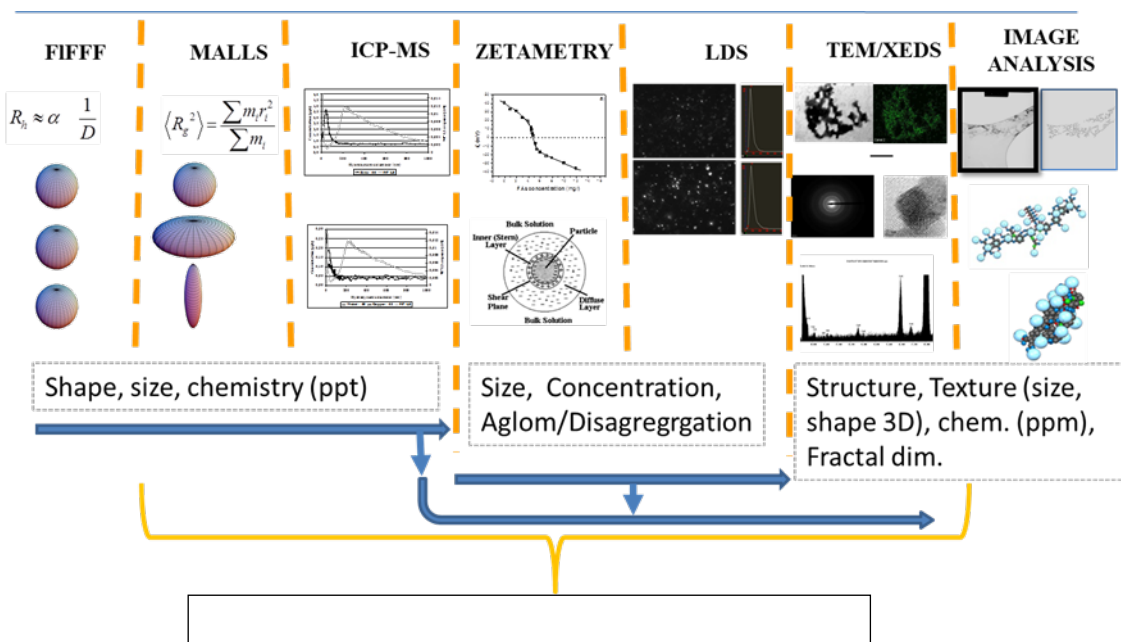


Figure 3: Analytical platform allowing the determination of the properties of MTE and NPs and to estimate their trends in term of aggregation/dissolution mechanisms

2.3 Concepts

Once reliable qualitative and quantitative data are obtained, the next step consists of integrating them with theories, and basic concepts/principles. In chemistry, the concept of the speciation emerged

some years ago. It is based on the Pearson acid base concept (Hard Soft Acids and Bases (HSBA) theory) [19] and application in environmental chemistry [20]. On the same way, physical speciation approach is based on topochemistry

reaction [21]. Recently, this theory has been applied to describe the evolution of natural organic colloids (humic acids) with metallic trace elements (MTEs) in natural surface water [7]. To integrate all the components of natural water matrix, many objects and compounds have to be considered to describe perfectly the water and the relationship between the different fractions. Figures 5 & 6 give an idea of the complexity of a

heterogeneous system like natural waters impacted by anthropic contaminants as NPs & MTEs. They illustrate the possible mechanisms between each compartments and compounds. Note that biological compartment is not taken into account except for the biopolymers as they correspond to natural macromolecules (algae, bacteria & cell debris, etc.).

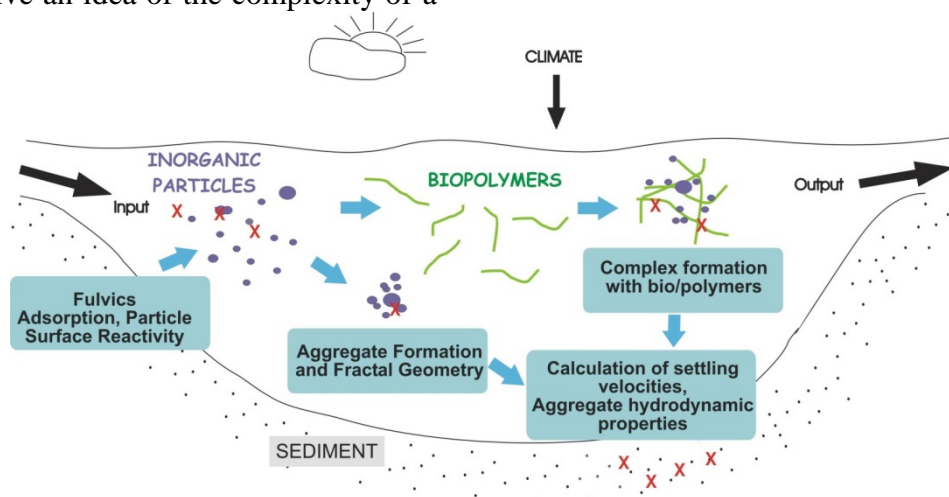


Figure 5: Conceptual schema of the interactions between inorganic particles, bio-organic polymers and contaminants in surface waters (From Stoll S.)

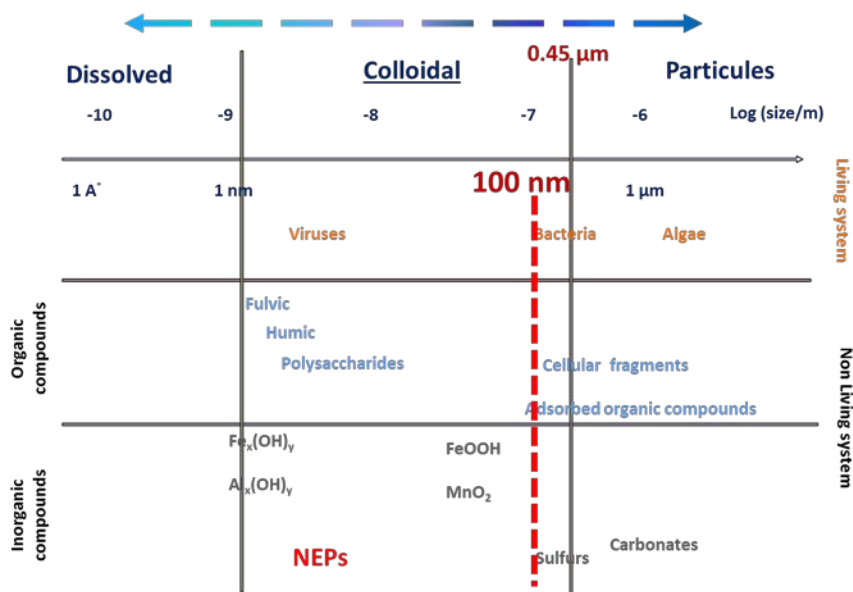


Figure 6: Schema of a natural water matrix exhibiting the different components which can be presents. The red dash line marks the limit of nanoparticles & nanomaterials (from Baalousha M.).

3 Results and Discussion

Relationships between NPs, MTEs and NOM are of great importance to understand their behaviour and trends into natural waters. NOM is normally present in aquatic systems at the mg/L level and it is now clearly established that the presence of NOM will largely modify NPs surfaces and such surface modifications will have a significant impact on their fate, transport, reactivity, uptake

by organisms, and toxicity properties. The available information on the interaction processes between NPs and NOM suggests complex chemical reactions and adsorption processes at the NPs surfaces which at the end result in NPs agglomeration, stabilization, disagglomeration or NP dissolution. On the other hand, the understanding of agglomeration or

disagglomeration, which is also an important issue, requires knowledge of the influence of a large number of parameters including; i) NOM concentration, molecular weight distribution, molecular composition and properties, conformation, hydrophobicity, charge density; ii) NPs size distribution and concentration, crystalline phase, geometry, surface charge and chemistry, and iii) solution properties such as pH,

temperature, ionic strength and composition (including the colloidal fraction). So far, analytical tools are required to study in a systematic way the interactions between NOM and NPs, adsorption and coating mechanisms (involving electrostatic interactions, hydrophobic forces, H-bonding, cation bridging, ligand exchange, etc), then the resulting NPs stability and properties, such as

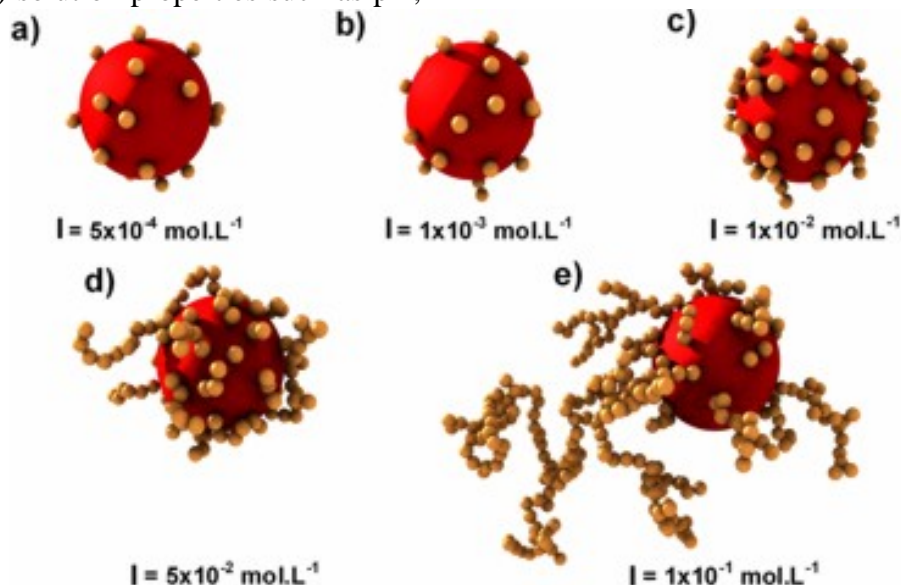


Figure 7: Fulvic Acid- hematite structures obtained at different ionic strengths as indicated. The hematite particle is the central particle and fulvic acids are the small ones. At low ionic strength, only a monolayer of FA is observed at the hematite surface. By increasing the ionic strength, not only the number of adsorbed Fulvic Acid, but also the thickness of adsorbed FA increases.

ageing, properties and impact of surface coating. It should be noted that combining quantitative results from different studies is also very difficult, owing to the fact that each nanoparticle type and aquatic system is unique. To illustrate some mechanisms, simulation can be a powerful solution to give evidence of complex and heterogeneous pathways (Fig.7). Another study on the MTE trends in Adour River (France) put into evidence the metals distribution of MTEs (Cr)

species between Humic Acid (HA). A simulation based on steric approach put in evidence the importance of the HA conformation regarding its capacity to fix Cr atoms during hetero-aggregation mechanisms (Fig.8). The physical speciation integrates the mechanisms of aggregation-dissociation of particles, ions with larger compounds regarding the zeta potential distribution, IS, pH, concentrations parameters used in the example presented below.

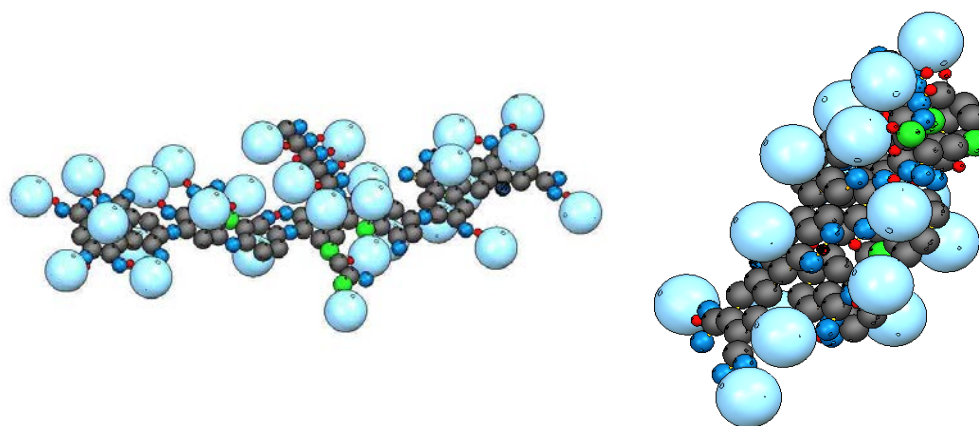


Figure 8: Hetero- aggregation simulation between Humic Acid (HA) molecule (black-green-blue-red atoms) and Cr (light blue) atoms in high steric conformation (left) and the same in low steric conformation (right) . The Cr ratio varies from 29 Cr atoms in planar HA (left) versus 18 on the condensed HA (right). (From El Kahid K. & Le Coustumer) P)

4 Conclusion

In term of analytical strategy used for natural waters impacted by NPs and/or MTEs it can become very complex to provide information for each elements present: their texture and structure, concentration, mobility, capacity to evolve under agglomeration-disaggregation mechanisms, etc. An ideal hyphenated platform has been developed from 2006 and adapted to different samples collected which allows facing and describing complex heterogeneous media. Some case studies have been explored such as the Loire River [7], Garonne River [10], Adour River [22], Pasig River [23, 24] and Lake of Geneva [25]. The rivers cases can be discussed in the results part as part of clarifying the holistic approach. Based from our studies the use of the DGTs is efficient in application to the Pasig River, situated in a developing country. The fate and the occurrence of the trace metals were coherent to its hydro and physico-chemical background. With the differing conditions of the dynamic natural tropical aqueous system, trace metals responded accordingly in terms of its concentration. Projections of the water resource managements were able to follow and proposed. Next steps will consist in developing solutions adapted to the problem of micro-nanoplastics dispersed into surface waters. In our point of view, holistic approach is able to face the paradigm of global vision in predicting the behavior and trends of nanocompounds in natural waters combining different scale from macroscopic to nanoscopic.

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