ÉCOLE DOCTORALE
SCIENCES DE LA TERRE ET DE L'ENVIRONNEMENT
ET PHYSIQUE DE L'UNIVERS, PARIS

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Subject title:
In situ investigation of nanoparticles heteroaggregation processes in surface waters

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Host lab/ Team : **IPGP - Team ACE – UMR 7154**
Working group for Environmental and Soil chemistry, University of Kaiserslautern-Landau

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Presentation of the subject:

Context

Heteroaggregation is a crucial step in the fate of natural and anthropogenic nanoparticles (NPs) in environmental waters: heteroaggregation between NPs and suspended natural organic or mineral matter can significantly influence the transport and bioavailability of NPs. In order to obtain a realistic estimate of the attachment coefficient on natural surfaces, empirical data is usually obtained through laboratory experiments under highly controlled conditions in which the complexity and dynamics of the environmental medium are lost. The concentrations used are generally several orders of magnitude higher than predicted for natural waters due to limitations in detection methods. This project aims to develop and apply a method for the simultaneous quantification and characterization of heteroaggregates under natural conditions and at realistic concentrations. Our concept is based on the dialysis bag method which allows to expose in situ an NP-partner aggregation system in natural waters. This method has been successfully used to characterize the surface coating formed on NPs under natural conditions. Its applicability to a system containing two types of particles will be tested in this project. The single counting technique by ICP-TOF-MS will be used in order to i) count particles at realistic concentrations (ng/L) and ii) determine the elemental composition of each NP. Thus, it will allow us to quantify the amount of heteroaggregates formed under natural conditions and to calculate an attachment coefficient specific to each target heteroaggregate (natural particles, FeOx, clays and NPTiO_2). We will provide new information on the fate of nanoparticles in natural waters, which will help to understand geochemical cycles and the fate of emerging pollutants.

PhD thesis overview:

This PhD project aims to combine advanced methodologies to investigate heteroaggregation under environmental conditions and at realistic concentrations, particularly in situ in surface waters.

Hypotheses:

1. For electrostatically stabilized nanoparticles, the attachment efficiency between the nanoparticles (A) and their aggregation partner (B) in natural water α_{Hetero} varies significantly along a stream trajectory depending on water composition (pH, inorganic ions, TOC, organic matter composition). These variations cannot be predicted using classical DLVO-theory.
2. For nanoparticles with a point of zero charge near neutral pH and hydrophobic surfaces (e.g., TiO2-based nanoparticles from commercial products), α_{Hetero} remains high regardless of water composition and natural coating.
3. The formation of A-B dimers is the most significant type of aggregate under realistic conditions and environmentally relevant concentrations, regardless of water composition. Particle bridging (A-B-A) does not occur under environmental conditions due to the formation of a natural coating neutralizing positive charges on positively charged particles.
4. In calcareous waters, heteroaggregation of nanoparticles with natural particles is dominated by high levels of Ca^{2+}, masking electrostatic interactions and leading to diffusion-limited aggregation regardless of nanoparticle charge and coating.

Objectives:

1. Develop and optimize the dialysis bag method (DBM) for in situ heteroaggregation experiments, ensuring quality control and minimizing biases.
2. Develop sample and data processing methods using Time-Of-Flight ICPMS in single-particle mode (SP-ICP-TOF-MS) to quantify different types of heteroaggregates.
3. Apply the combined DBM-SP-ICP-TOF-MS method to determine α_{Hetero} for positively and negatively charged Au-nanoparticles with clay particles along two streams—one in a calcareous area and one with low Ca^{2+} concentration—affected by different spatially distributed sources.
4. Compare measured α_{Hetero} values to theoretical calculations to evaluate estimation methods and assess hypotheses 1 to 4.
5. Assess the composition of detected heteroaggregates and quantify the contribution of each aggregate type, focusing on the behavior of nanoparticles in calcareous versus non-calcareous waters to address the specific hypotheses.

Candidate profile:

Scientific training at Master 2 level or engineering degree in geosciences, environmental (geo)chemistry. Skills in analytical chemistry/geochemistry would be an advantage.

The candidate will join the university of Kaiserslautern-Landau (campus Landau) for 12 months then will finish the last two years in the ACE team at IPGP (Paris).