Experimental report

23/09/2021

Proposal:	**9-12-597**	**Council:**	10/2019
Title:	Dissolved organic matter in soil: Interactions with mineral surfaces		
Research area:	Chemistry		

This proposal is a new proposal

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Samples:	Fe2O3 FeOOH Soil organic matter

Instrument	Requested days	Allocated days	From	To
D11	3	0		
D33	3	0		
D22	3	2	24/09/2020	26/09/2020

Abstract:

Dissolved organic matter (DOM) is ubiquitous in terrestrial and aquatic ecosystems where it serves several important functions. It plays a central role in the landscape carbon balance, connects the terrestrial and aquatic environments, and acts as a vector for both nutrients and contaminants. DOM is made of molecularly dispersed compounds and suspended objects with a size below 0.2 micrometer. The interaction between DOM and minerals leads to the formation of DOM-mineral colloids. Recently, these colloidal associations have been proposed to stabilize organic matter against microbial decomposition. Yet, very little is known about the colloidal properties of the DOM-mineral associations. The aim of this proposal is to investigate DOM-mineral interactions by adding known amounts of goethite (FeOOH) or hematite (Fe2O3) to DOM and observe their effect on DOM aggregation and adsorption. We will explore contrast variation to highlight the scattering from DOM and mineral individually. The results will allow us to characterize DOM and its interactions with relevant mineral particles.

Introduction

Dissolved organic matter (DOM) is ubiquitous in terrestrial and aquatic ecosystems, where it serves several important functions. It plays a central role in the landscape carbon balance, connects the terrestrial and aquatic environments, and acts as a vector for both nutrients and contaminants. DOM consists of molecularly dissolved compounds and suspended objects with a size below 200 nm, including components such as carbohydrates, aliphatic compounds, and small acids. The fate of DOM, i.e. whether it is sequestered or mineralized, will affect the CO_2 balance of the atmosphere and thus ultimately the climate.

The formation of mineral-associated organic matter (MAOM) has been proposed to stabilise DOM against microbial decomposition [1, 2]. These kinds of interactions may also stabilise iron from precipitation in aquatic environments, increasing the export of iron into the sea, where it historically has been a limiting factor of primary production [3]. With these experiments, we aimed to investigate the aggregation and adsorption behaviour of DOM in the presence of mineral particles, to better understand the interactions between organic material and iron minerals, and how those may affect microbial degradation kinetics.

Contrast matching SANS was utilised to visualise the behaviour of DOM and mineral particles individually. The match point of DOM was investigated in a previous study at ILL (exp 9-10-1590) and determined to a solvent composition of 30% D_2O. Only one mineral, hematite (α-Fe_2O_3), out of the proposed two was investigated due to the limited beam time. Hematite has a theoretical scattering length density higher than that of D_2O, so 100% D_2O was used as the solvent to minimise its scattering intensity as much as possible. From previous experiments, we know that DOM has a negative ζ-potential, while hematite has a positive ζ-potential, and dynamic light scattering (DLS) has shown that aggregation takes place when the two components are mixed.

Experiment

DOM was extracted at room temperature in 30% and 100% D_2O from a boreal forest soil. Hematite particles were synthesised using forced hydrolysis and solvent exchanged to solutions of 30% or 100% D_2O, respectively. All solutions had a final pH of 5.5.

Due to the ongoing pandemic, the samples were mailed in to the ILL and the measurements performed by the local contacts without any members of the experimental team on site.

The single components, as well as mixtures with increasing concentration of mineral or DOM (stated as the concentration of total organic carbon (TOC)) were measured at 25°C in quartz cuvettes (type 404-QS, Hellma) using a tumbling rack to avoid sedimentation. A path length of 2 mm was used for samples in 100% D_2O and 1 mm for samples in 30% D_2O. The SANS measurements were performed using three instrument configurations with sample to detector distances 2 m and 8 m (with a neutron wavelength of 4.6 Å), and 17.6 m (with a neutron wavelength of 11.5 Å) resulting in a q-range of 0.001-0.6 $Å^{-1}$.

The SANS data was corrected for dark current, empty cell scattering, transmission, and dead-time losses, then brought to absolute scale and azimuthally averaged. The data showed a flat region at high q-values which was used for solvent and incoherent background subtraction.

Results

SANS results for DOM in 100% D_2O, mixed with increasing concentrations of hematite in 100% D_2O, are shown in Figure 1A. The DOM scattering pattern is in good agreement with SAXS data previously obtained. No change was observed in the scattering pattern of DOM with addition of hematite particles, indicating that it does not change structure or re-organises in other ways. This also show that the hematite was matched well enough to not contribute to the scattering signal. The data is believed to reflect fractal clusters and was fitted in SasView using the Beaucage model [4, 5], giving a radius of gyration (R_g) of 67 nm and a Porod exponent of 2.7.

The scattering from hematite in 30% D_2O, mixed with increasing concentrations of DOM in 30% D_2O, is shown in Figure 1B. Based on evidence from cryo-TEM (see Figure 2A and B), the scattering pattern from hematite alone was fitted using the fractal model in SasView, describing fractal-like aggregates of spherical building blocks [6, 7]. Note that the primary hematite particles are not spherical but rather diamond shaped with an average side length of 22 nm. With a polydispersity of 0.4 (based on TEM images), the fit gave a radius of the building blocks of 7 nm, a fractal dimension of 2.4 and a correlation length of 40 nm. A Guinier regime was visible in this data set, but with the addition of DOM, the intensity at low q increased. This indicates that the hematite particles aggregated into larger clusters, something that was confirmed by cryo-TEM (see Figure 2C and D). The scattering data of aggregated hematite could also be described using the fractal model, by increasing the correlation length. However, since the new Guinier regime was outside the accessible q-range, a correct value of the correlation length could not be determined. It can only be stated that it should be $>>1/q_{min}$, which in this case means larger than 100 nm.

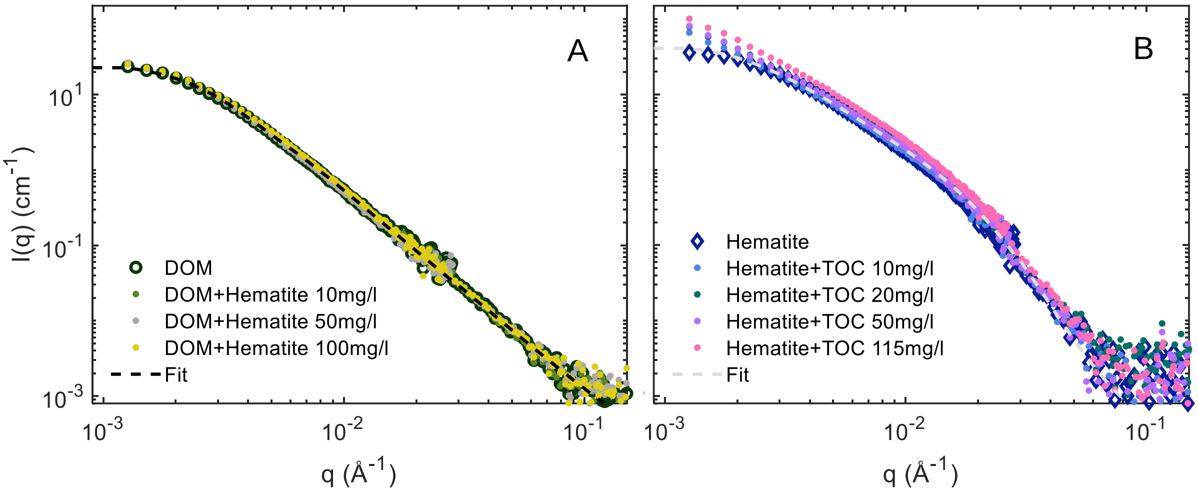

Figure 1. A) SANS data of pure DOM in a solvent of 100% D_2O (circles) mixed with three different concentrations of hematite (dots). The TOC concentration of the DOM is 123 mg/l in all samples. The dashed line corresponds to the best fit using the Beaucage model. B) SANS data of pure hematite in a solvent of 30% D_2O (diamonds) mixed with four different concentrations of DOM, stated by the TOC concentration (dots). The hematite concentration of all samples is 528 mg/l. The dashed line shows a fit using the fractal model.

The data from this experiment tells us that DOM strongly promotes aggregation of hematite nano particles. When DOM-hematite aggregates are formed, it is the hematite particles which adsorbs onto DOM colloids, which themselves do not change shape. Possibly, a fraction of molecularly dissolved DOM, not visible in SANS or cryo-TEM, is involved in the aggregation, explaining why no change was observed for the colloidal fraction. A manuscript is in preparation (as of September 2021) where these SANS results are combined and compared with results from SAXS, DLS and cryo-TEM.

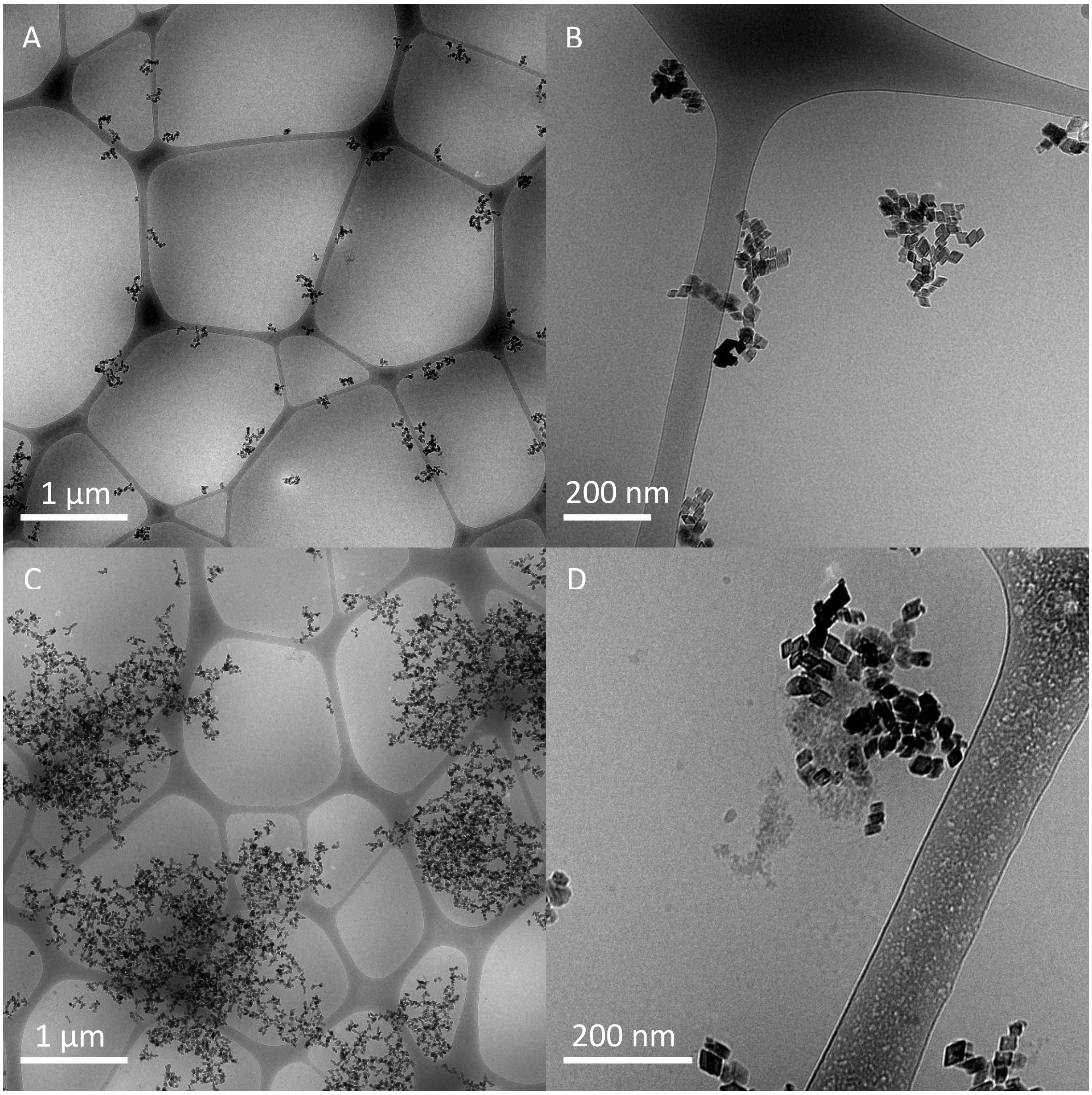

Figure 2. Cryo-TEM images of A-B) pure hematite at a concentration of 50 mg/l and C-D) hematite at a concentration of 528 mg/l mixed with DOM at a TOC of 10 mg/l.

References

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