Small-angle neutron scattering studies of natural aquatic colloids

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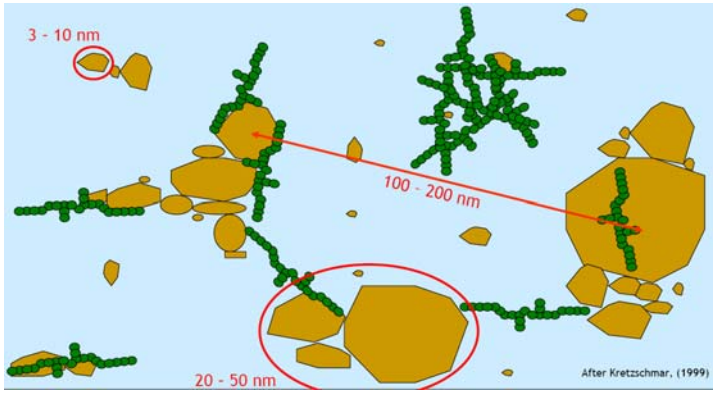
Key issues

- Aquatic colloids (naturally-occurring, sub-micron sized, heterogeneous mixtures of mineral particles and organic ligands) are increasingly attracting the attention of water quality scientists and environmental regulatory authorities because of their potential ecological impact.



Why SANS?

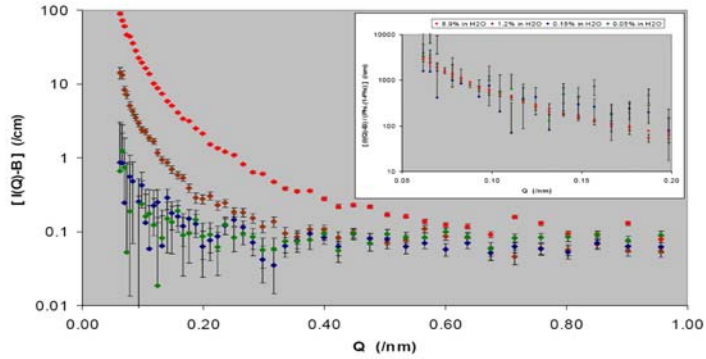
- A significant proportion of the normal aquatic mass transport involves particulates <200 nm in size. This, together with the natural turbidity of many aquatic dispersions, precludes use of light scattering. Microscopy and imaging both involve highly perturbing sample preparation techniques, and only count relatively small statistical sample sets.
- SANS (and SAXS) overcome these drawbacks – potentially permitting the study of a 'real world' aqueous sample – but SANS also offers the exciting possibility of using 'contrast matching' to selectively investigate organic (humic) and inorganic components of a natural aquatic colloid.

The Data

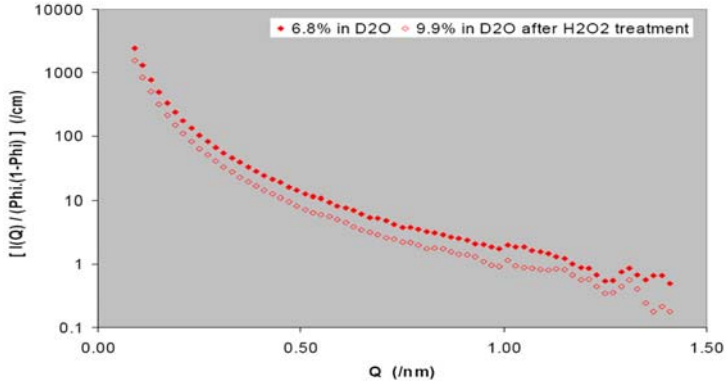
- A range of different natural aquatic colloids were collected by bottle immersion or vacuum-sampling:
- River Surface Bed Sediments - from different lowland freshwater catchments with different organic loadings
- River Water
- Overland Flow - from intensively managed fields; - during a storm event
- Agricultural Slurry (Liquid Manure)
- The sediments were characterised by XRD, XRF and gravimetric analyses
- Stretford Brook Bed Sediment: 49% illite, 31% 'expandable' illite/smectite, 6% kaolinite, 14% chlorite. Loss on ignition: 5.7%
- Priors Farm Sediment: 41% illite, 37% 'expandable' illite/smectite, 20% kaolinite, 2% chlorite. Loss on ignition: 18.8%
- SANS measurements were performed on the time-of-flight diffractometer LOQ at ISIS (see www.isis.rl.ac.uk for details). The samples were contained in quartz cuvettes that were slowly rotated about the axis of the neutron beam in order to offset the effects of sedimentation (arising from the high density of the mineral component). All measurements were made at room temperature (~20ºC).

The Results

- A first priority was to establish if SANS was feasible under conditions that were environmentally meaningful; e.g. in 'normal' water at realistic concentrations (~0.1-1 %w/w):



- When plotted as a log-log plot, the exponent n characterises the type of fractal structure that is present through the mass (Dm) and surface (Ds) fractal dimensions: n = 2.Dm – Ds. If n≤3 the scattering objects were mass fractals, and if n>3 they were surface fractals. Our aquatic colloids were fractals with rough surfaces; not discrete particles, platelets, or needle-like objects with well-defined interfaces.
- The Pit Slurry, which is entirely organic, appeared to behave more like a concentrated polymer solution or network. There is no evidence that these aquatic colloids have formed by Reaction-Limited (n~2.1-2.2) or Diffusion-Limited (n~1.7-1.8) Cluster Aggregation mechanisms.
- Quantitative analysis of the SANS data was performed by least-squares model-fitting analytic 'scattering functions' for 3 categories of object. Our aquatic colloids were mass fractals with evidence of density variations, not homogeneous spherical particles or aggregates. There appeared to be 3 characteristic length scales; ~3-10nm, ~20-50nm, and ~50-200nm
- Considerably smaller colloidal objects appear to be present in the Den Brook overland flow and stream runoff than is the case in the river sediments, perhaps because of preferential entrainment of finer particulates in the latter stages of overland flow generation.
- Peroxide digestion caused a small increase in the values of n and Dm (i.e. the colloidal objects are becoming less rough) and a decrease in the values of the fractal 'cut-off' length and 'effective radius-of-gyration' The longest characteristic length scales in our aquatic colloids appear to be associated with the organic component.



Summary

- Information such as that presented here has important implications for understanding the chemical and biological reactivity of aquatic colloids in the natural environment. For example, changes in the area or type of surface exposed may modify the rates of sorption and desorption of pollutants, and the compactness of the aggregates may influence the accessibility of nanopores to viruses, pollutants, and even oxygen.

Find out more…

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