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Imaging of suspended macromolecules and colloids in glacial and alpine streams by atomic force microscopy

Numerous studies of suspended sediment within proglacial streams have been conducted (e.g. Richards and Moore, 2003; synthesis of data for 90 glacier basins by Gurnell and others, 1996); these have largely focused upon estimating suspended-sediment concentration/loads and variability in relation to discharge. In comparison, there has been limited research upon particle-size distributions of suspended sediment in glacial meltwaters (Fenn and Gomez, 1989), with reported particle-size data typically representing the dispersed particle fraction. Recently, Woodward and others (2002) identified aggregates and flocs in the $10–110\,\mu$m size range (fine silt to fine sand) for glacial meltwaters using scanning electron microscopy (SEM), after preparing the samples by sedimentation. Their results are significant as these composites more accurately characterize the "effective" particle-size that controls entrainment, transport and deposition processes. To our knowledge, no field or laboratory data have been published, and more specifically no imaging has been performed, for colloidal and macromolecular material from glacial or other alpine streams. Colloids and macromolecules are several orders of magnitude smaller $(1\,\text{nm}–1\,\mu$m) than other "suspended" particles studied to date within glacial meltwaters. In this short note, we use the technique of atomic force microscopy (AFM) to characterize colloidal material in stream-water samples from an alpine, glacierized (5%) catchment in the French Pyrenees.

Macromolecules and colloids are of major scientific interest and practical importance because they chemically bind trace pollutants (Lead and others, 1999), nutrients and pathogenic microorganisms, and so alter their fate and behaviour in the environment, including uptake and effects on biota (e.g. Carvalho and others, 1999). In addition, colloidal material may primarily determine aggregation and disaggregation processes by charge-based behaviour (Tipping and others, 1981) and/or bridging mechanisms (Buffle and others, 1998). To understand these processes, it is necessary to quantitatively assess the structure of these solid-phase materials and the relation of colloidal structure to environmental function. However, quantitative knowledge of structure is hindered by colloidal complexity, low concentration, and instability due to aggregation, microbial growth and other processes (Lead and others, 1997).

As a pilot study, water samples were collected toward the cessation of the 2002 melt season (2 September) from two streams within the lower valley of the Taillon–Gabiétous basin, French Pyrenees (study area described by Hannah and others, 2000). Stream-flow and water quality within the catchment are heavily influenced by the presence of two cirque glaciers: Taillon and Gabiétous (Smith and others, 2001). The basin geology is Marbore sandstone interspersed with limestone outcrops (upper valley) and limestone of the

Santonien and Conacien series (lower valley). Water samples were collected manually using 50 mL sterile polycarbonate flasks from: (1) stream A, the main Taillon glacial stream 1 km from the snout (discharge $Q = 0.4\,\text{m}^3\,\text{s}^{-1}$; suspended-sediment concentration (SSC) = 63 mg L^{-1}); and (2) stream B, the Tourettes stream ($\sim$50 m cross-valley from stream A) draining alpine hill slopes, groundwater (alluvial and karstic) springs and a limited snow- and ice-covered area ($Q = 0.6\,\text{m}^3\,\text{s}^{-1}$; SSC = 8 mg L^{-1}). Discharge and suspended-sediment concentrations on the sampling day (above) represent low-ambient, end-of-ablation-season values (cf. Smith and others, 2001). Sample flasks were maintained at stream temperature (6–9°C) by standing them within calm backwaters. Cleaved mica sheets were immersed in the sampled waters, left for 30 min, rinsed with pure water ($R = 18.2$ mΩcm) and dried under atmospheric conditions (following established protocols; e.g. Balnois and others, 1999; Muirhead and Lead, 2003). The mica sheets were stored at $\sim$4°C in the dark prior to analysis.

Colloids adsorb onto mica sheets based upon their ability to move (usually by diffusion), so smaller colloidal material is preferentially adsorbed. Although charge interactions play a role in surface adsorption of colloids onto the mica, other non-charge-based interactions also govern adsorption. For instance, negatively charged humic substances can adsorb onto negatively charged mica sheets; but they adsorb more readily at low pH when charges are reduced (Balnois and others, 1999).

The AFM measurements were performed using a Digital Instruments Dimension 3100 AFM in tapping and contact modes. In brief, the AFM tip scans across the mica surface, and interactive forces between the tip and surface result in topography-based deflections of the tip in the z axis (height above surface), which can be accurately recorded
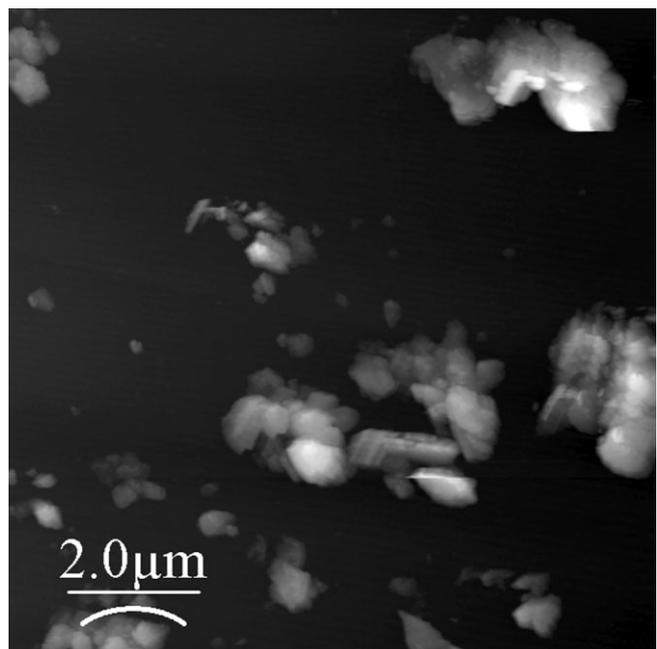
Fig. 1. Representative AFM image of colloidal material from stream A (glacial stream ~1 km from the snout).

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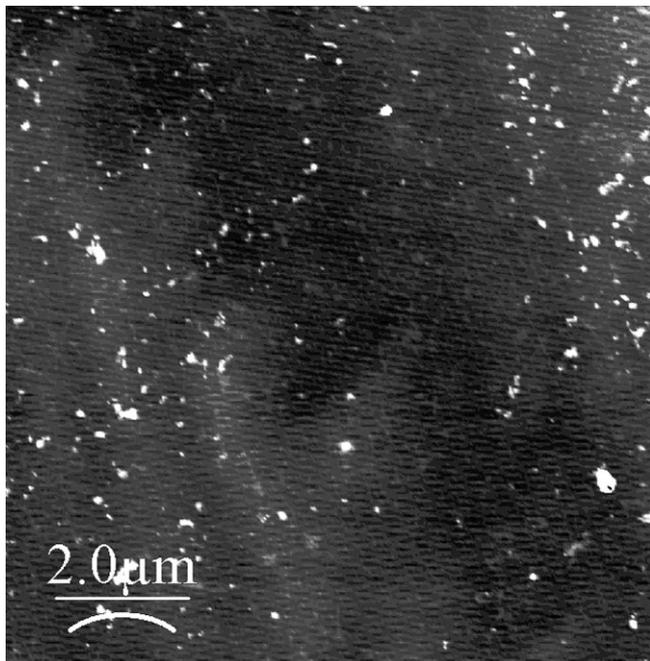
Fig. 2. Representative AFM image of colloidal material from stream B (alpine hill slope, spring-fed with limited melt-water contribution).

(Santschi and others, 1998). AFM is less perturbing to colloidal material than SEM, as measurements are performed under ambient conditions, maintaining colloids in a hydrated form. Heights from the mica sheet surface are used to estimate colloid diameter, since lateral dimensions overestimate colloid size (Balnois and others, 1999).

Typical AFM images are presented in Figures 1 (stream A) and 2 (stream B). Figure 1 shows a limited number of relatively large (mean height = 73 nm; range = 10–273 nm; $n = 20$) single particles or stacked plates, most likely of mineral origin. Based upon colloid morphology and knowledge of catchment geology, soils, hydro-geomorphology and hydro-chemistry, these are most probably carbonate or clay material derived from glacial erosion. In contrast to the main glacial stream, Figure 2 depicts a much greater number of smaller (mean height = 18 nm; range = 7–90 nm; $n = 20$) globular particles. Colloid morphology suggests that processes other than, or in addition to, glacial erosion (e.g. in situ microbial activity) influence these particles.

Other colloidal particles imaged (but not presented) for glacial stream A included microbes, primarily bacteria and flagellates. No such images were obtained for experimental mica sheets exposed only to pure water. Although microbes may be expected in these natural waters open to the atmosphere, we believe further study is necessary to ascertain whether microbes are truly present within glacial meltwaters or due to sample contamination.

A significant observation is the complete coating of the mica sheets by colloidal material after just 30 min exposure to the water samples from both streams. That is, the larger colloids (discussed above) do not rest directly on the mica sheet but upon a thin surface layer of colloidal material. Figure 3 provides quantitative evidence of this colloidal film, with much greater surface variability for the mica sheets exposed to glacial and alpine stream waters compared with an experimental mica-sheet blank (control). The absolute thickness of the colloidal layer cannot be determined from
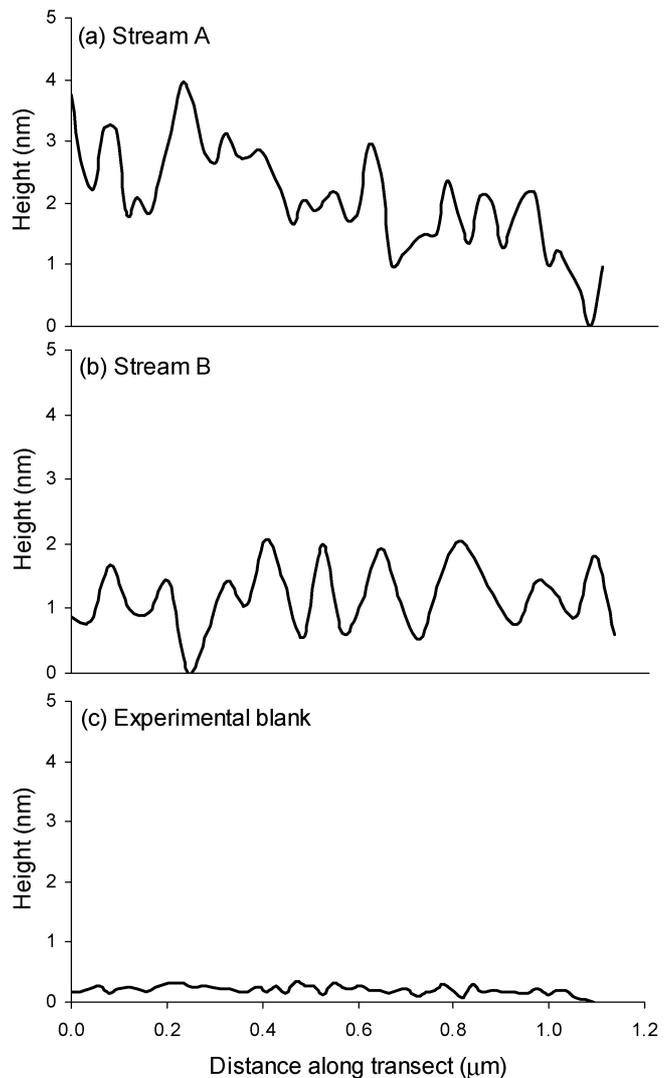
Fig. 3. Height variations along transects across separate mica sheets: (a) stream A (glacial stream ~1 km from the snout); (b) stream B (alpine hill slope, spring-fed with limited melt-water contribution); and (c) experimental blank (control).

these images as they can only illustrate relative surface elevations above the lowest point, which is not necessarily the underlying mica-sheet surface. Similar colloidal films have been observed for temperate river-water samples (Muirhead and Lead, 2003). For glacial and alpine stream samples, the surface colloidal coating is almost 100%, although coverage by discrete colloids is substantially lower. If this complete and rapid colloidal coverage is a widespread phenomenon in glacierized environments, it has important implications, as the surface layer is the primary location of colloid–solute interactions, and aggregation and disaggregation process.

We acknowledge that these AFM images of macromolecules and colloids from a glacial and an alpine stream are tentative and only indicative of a snapshot in time for a single glacierized basin. Further research is required to assess the wider significance of these initial results and to assess their spatial and temporal representativeness. Nonetheless, the use of AFM is a potentially very powerful approach to understanding the structure, functioning and behaviour of colloids and macromolecules in glacial and other alpine river systems. We invite comments on these preliminary findings.

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