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Assessment of cross-flow filtration for the size fractionation of freshwater colloids and particles

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Abstract

This research has evaluated the ability of cross-flow filtration (CFF) to perform correct size fractionation of natural aquatic colloids (materials from 1 nm to 1 μm in size) and particles (>1 μm) using scanning electron microscopy (SEM) combined with atomic force microscopy (AFM). SEM provided very clear images at high lateral resolution (ca. 2–5 nm), whereas AFM offered extremely low resolution limits (sub-nanometer) and was consequently most useful for studying very small material. Both SEM and AFM were consistent in demonstrating the presence of colloids smaller than 50 nm in all fractions including the retentates (i.e. the fractions retained by the CFF membrane), showing that CFF fractionation is not fully quantitative and not based on size alone. This finding suggests that previous studies that investigated trace element partitioning between dissolved, colloidal and particulate fractions using CFF may need to be re-visited as the importance of particles and large colloids may have been over-estimated. The observation that ultra-fine colloidal material strongly interacted with and completely coated a mica substrate to form a thin film has important potential implications for our understanding of the behaviour of trace elements in aquatic systems. The results suggest that clean, 'pure' surfaces are unlikely to exist in the natural environment. As surface binding of trace elements is of great importance, the nature of this sorbed layer may dominate trace element partitioning, rather than the nature of the bulk particle.

Keywords: Cross-flow filtration; Aquatic colloids and particles; Fractionation; Scanning electron microscopy; Atomic force microscopy

1. Introduction

The chemical speciation, biological availability and residence time of trace metals in natural waters are primarily influenced by their interaction with and by the stability of colloids and particles. As a result, considerable effort has focused on investigating such interactions with natural aquatic systems [1,2]. Natural aquatic colloids and particles have been defined as materials with sizes ranging between 1 nm and 1 μm [3], and greater than 1 μm, respectively. Colloids are ubiquitous in natural aquatic systems and are composed of phases, such as inorganic oxides (e.g. of aluminium, iron, manganese and silicon), organic humic and fulvic substances and polysaccharides, carbonates, clays and microbes including viruses and bacteria. They are present in relatively low mass concentrations but at much higher number concentrations. The individual components are generally intimately associated with each other to form complex mixtures [4]. However, their heterogeneous character, their easily denatured structure, their instability, their small size and low concentration are the main causes of the difficulty in sampling, separating and characterising them. Reliable, unbiased and minimally perturbing methods for their handling are therefore primary requirements if accurate information is to be obtained.

In recent years, a number of fractionation methods have been developed and used on natural systems (split-thin flow fractionation (SPLITT) [5], field-flow fractionation (FFF) [6,7] and cross-flow filtration (CFF)) [8–10]. In particular, CFF has become the most important and most widely used

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technique for isolating colloids in natural systems and for indicating the importance of colloids in metal binding [11–14]. CFF allows the processing of large quantities of water and clogging of the membrane is thought to be reduced compared to standard filtration [15]. To our knowledge, this contention has not been fully supported by firm data. In addition, there are still few controlled laboratory studies on the implementation of rigorous experimental protocols and operational procedures during CFF fractionation [16], although recent studies recommended the use of high concentration factors (CFs; defined as the ratio of the feed flow rate to the retentate flow rate) to minimise the entrainment of colloids smaller than the molecular weight cut-off of the membranes into the retentate fraction [10]. These authors also recommended the use of a series of CFs to test the ultra-filtration behaviour of the elements of interest, and to extract correct permeate values, which should, in principle, remain constant if they can freely pass through the ultra-filtration membrane, independently of the CF value chosen [10]. However, the use of high CFs may also produce further changes in colloid structure and is also not fully supported in the literature [17]. Ultimately, our understanding of the CFF process and the correct interpretation of size fractionation data requires complete knowledge of the fractionation and redistribution behaviour of chemical species (e.g. organic and inorganic colloids, major ions, trace metals, nutrients) [16]. To this effect, several studies have focussed on optimising CFF usage, essentially by measuring chemical parameters such as dissolved organic carbon [14,18,19], isotopic ^{13}C and ^{14}C and elemental C and N composition of colloidal organic matter [19], optical absorbance and humic and protein fluorescence [14,18,20], organic nitrogen and phosphorus and C/N elemental ratios [21], colloidal aluminium and iron [22], but few studies have tested the potential uncertainties in CFF separation using physical techniques [23]. This is surprising since CFF is primarily a means of performing size fractionation studies, implicitly using the nominal pore size as the de facto size of the colloids and particles in the retentate or permeate. A recent study provided evidence that CFF separation was not consistent with the nominal pore sizes of the membranes and that CFF may not be fully quantitative [23]. Further work is therefore required to better understand the limitations of CFF in separating colloids and particles in well defined size fractions.

This study has therefore examined the ability of CFF to perform adequate fractionation of freshwater colloids and particles. Atomic force microscopy (AFM) was used in combination with scanning electron microscopy (SEM) to investigate size distribution and conformation before and after size fractionation.

2. Experimental

2.1. Sampling of river water and size fractionation

Surface water samples (25–50 l) were collected in translucent high density polyethylene drums (Fisher UK Ltd.) from the River Cole (UK Ordnance Survey Reference SP 201895). The River Cole is a pre-dominantly, but not entirely, urban river in the West Midlands (UK) [24] and is classified under the chemically based General Quality Assessment (GQA) scheme used by the UK regulator Environment Agency as a Grade C river (i.e. of 'fairly good' quality, with a dissolved oxygen content greater than 60% saturation and a biochemical oxygen demand (BOD) of less than 6 mg l^{-1}). Sampling was performed at about 2 m from the bank and just below the water surface. Care was taken not to disturb and sample sedimented particles lying at the bottom of the river. At the time of sampling, the water temperature was 21 °C and the pH was 7.7. All containers used for sampling were cleaned in 10% nitric acid ('AnalaR', Merck UK Ltd.) solution for 24 h, and thoroughly rinsed with ultra-pure water (Barnstead EASYpure RO system; $R = 18.2$ mΩ cm^{-1}) prior to their use. A final rinse was performed with the river water and the washings were discarded.

Colloidal and particulate separation of the river water was performed using a commercial Millipore Pellicon 2 benchtop cross-flow filtration device (Millipore UK Ltd.) within 3 h following sampling. Analysis of all fractions using SEM and AFM was performed within 3 days of sampling as colloidal and particulate matter in freshwater has previously been shown to be fairly stable over a 2–3-day period [25,26]. A three-step fractionation protocol was adopted. The bulk water from the river was first fractionated using a 0.45 μm Durapore^{TM} polyvinylidene fluoride cassette filter with a surface area of 0.5 m^2, which generated a permeate (i.e. the fraction passing through the CFF membrane) and a retentate (i.e. the fraction retained by the membrane), hereafter abbreviated P_1 and R_1, respectively. P_1 was further fractionated through a 0.1 μm Durapore^{TM} polyvinylidene fluoride cassette filter with a surface area of 0.5 m^2. The two final fractions were called P_2 and R_2. The corresponding operationally defined size classes were >0.45, 0.1–0.45 and <0.1 μm. The three-step protocol was performed at a concentration factor of about 5. Immediately after each fractionation, the membranes were thoroughly cleaned until their permeability was consistent with manufacturer's instructions. When not in use, the CFF membranes were stored at 4 °C in 0.5% sodium azide. Prior to CFF fractionation, the membranes were preconditioned with 10 l of the corresponding samples, which was then discarded to prevent sample contamination during fractionation.

Upon completion of each CFF separation step, the colloidal and particulate fractions were refrigerated at 4 °C and stored in the dark in polyethylene bottles (pre-cleaned as above). The potential of the combined use of two microscopic techniques, namely SEM and AFM, to be used to examine the ability of CFF to perform adequate size separation of river water was tested. The results were discussed in the light of the suitability of CFF for the investigation of trace element partitioning in natural waters.

2.2. Scanning electron microscopy imaging

High vacuum SEM experiments were carried out on a JEOL 1200EX SEM microscope operating at an acceleration voltage of 40 kV to obtain information on morphologies and size distribution of vacuum-dried colloidal and particulate matter. The preparation of samples for SEM observations involved spreading droplets of CFF-produced samples onto clean electron microscopy support stubs, allowing them to air dry and coating them with platinum in an Emscope SC 500 sputter coater. The size distribution of deposited materials was determined by measuring the lateral dimensions of around 250 single particles.

2.3. Atomic force microscopy imaging

Specimens for AFM analysis were prepared following an established adsorption technique [4,27]. Briefly, substrates, which consisted of freshly cleaved muscovite mica wafers with dimensions 1 cm × 1 cm × 0.1 cm, were first thoroughly rinsed at room temperature with ultra-pure water ($R = 18.2\ \mathrm{m\Omega\ cm^{-1}}$). The substrates were then immersed vertically in a sample for 30 min. Upon removal from the solutions, the mica sheets were gently rinsed by immersion in ultra-pure water in order to remove any non-adsorbed material from the surface. They were then allowed to dry under ambient conditions in enclosed Petri dishes to prevent airborne contamination. The surface of the substrate was scanned and an image of adsorbed materials was recorded using tapping mode AFM (Dimension 3100, Digital Instruments). Tapping mode was used to ensure the minimum disturbance of weakly adsorbed colloids, as lateral and vertical forces are minimised. The sample was imaged at 20 °C, at atmospheric pressure and at 60% relative humidity. The AFM analysis was performed over an area of typically 1–10 μm. Height measurements above the mica surface were taken as indicative of colloid diameters, since the lateral measurements are often over-estimated owing to the geometry of the probe [4]. About 250 colloids were used to estimate colloidal size distribution for each sample. For every sample studied, cross-sections were recorded and roughness analysis of the surface was performed by calculating the root mean square roughness using the AFM software.

3. Results and discussion

3.1. Scanning electron microscopy imaging of the River Cole and the CFF-generated fractions

SEM is a powerful microscopy technique that offers a high lateral resolution (ca. 1 nm). As a result, it has often been used to visualise environmental aquatic colloids and particles [28]. However, the technique involves examination of the samples in high vacuum conditions and may lead to artefacts due to the potential redistribution of particulate components during the preparation of the samples. Evidence of its use in assessing the experimental cut-off of CFF membranes has been reported recently [23], where the vacuum drying reduced average particle size by ca. 50%. In this study, the ability of CFF to perform adequate size fractionation of colloids and particles from a river water was assessed by SEM.

Images of clean electron microscopy stubs were recorded (results not shown) in order to correctly interpret the SEM images of samples, and showed an unsmoothed surface with distinct stripes up to 1 μm wide and with no discernible particles. Figs. 1 and 2 illustrate representative high vacuum SEM micrographs of the River Cole and the CFF-generated fractions at CF of ca. 5. Several distinct particle morphologies were identified. The most dominant material in all fractions were irregularly shaped colloids and particles, although other morphologies were also observed, including fibrillar material and small branched aggregates (Fig. 1b and c), presumably debris of biological cells and their exudates (Figs. 1d and 2g). Larger aggregates, composed of a number of small discrete particles, were also seen (e.g. Figs. 1b and 2(a and b)). The average dimensions of the irregularly shaped structures ranged from a few tens of nanometers to a few micrometers. SEM provided very clear images of dried and coated samples for the River Cole and the retentate R_1 (Figs. 1(a and b) and 2(a and b)), whereas the images of the other fractions showed fewer discrete colloids and particles, presumably due to surface coverage by a film composed of small organic macromolecules that had flattened following drying. Colloidal films have already been reported by means of AFM for temperate river-water samples [27], lake water [23] and glacial and alpine streams [29]. The surface of the stub did not appear to have been evenly covered by the film. Indeed, Fig. 1c–e exhibited a patchiness with contrast changes over very short distances. The patchiness may have reflected a non-uniform topography induced by the irregular sorption of colloids and a surface film or perhaps was due to vacuum drying. The presence of the patchiness could not be unambiguously explained here but it may have been due to the presence of troughs, which could have scatter electrons away from the detector, or to localised coverage by less electron-dense particles such as natural organic matter.

Qualitative analysis of the SEM images suggested that CFF fractionation had not been consistent with nominal pore sizes of the membranes. For instance, high magnification SEM micrographs showed the presence of a large number of fine colloids (<200 nm) in all fractions including the retentates (Fig. 2b and f). This observation was consistent with a previous study that applied CFF for the fractionation of lake water [23]. This observed limitation of CFF fractionation is likely to be due to the complexity of suspended material in aquatic environments. Indeed, environmental particles are physically and chemically heterogeneous, with varying composition, structures, sizes, densities, functionalities and molecular masses. As a consequence, such particles will have distinctly different degrees of affinity with the membrane. Organic molecules such as humic substances are known ex-

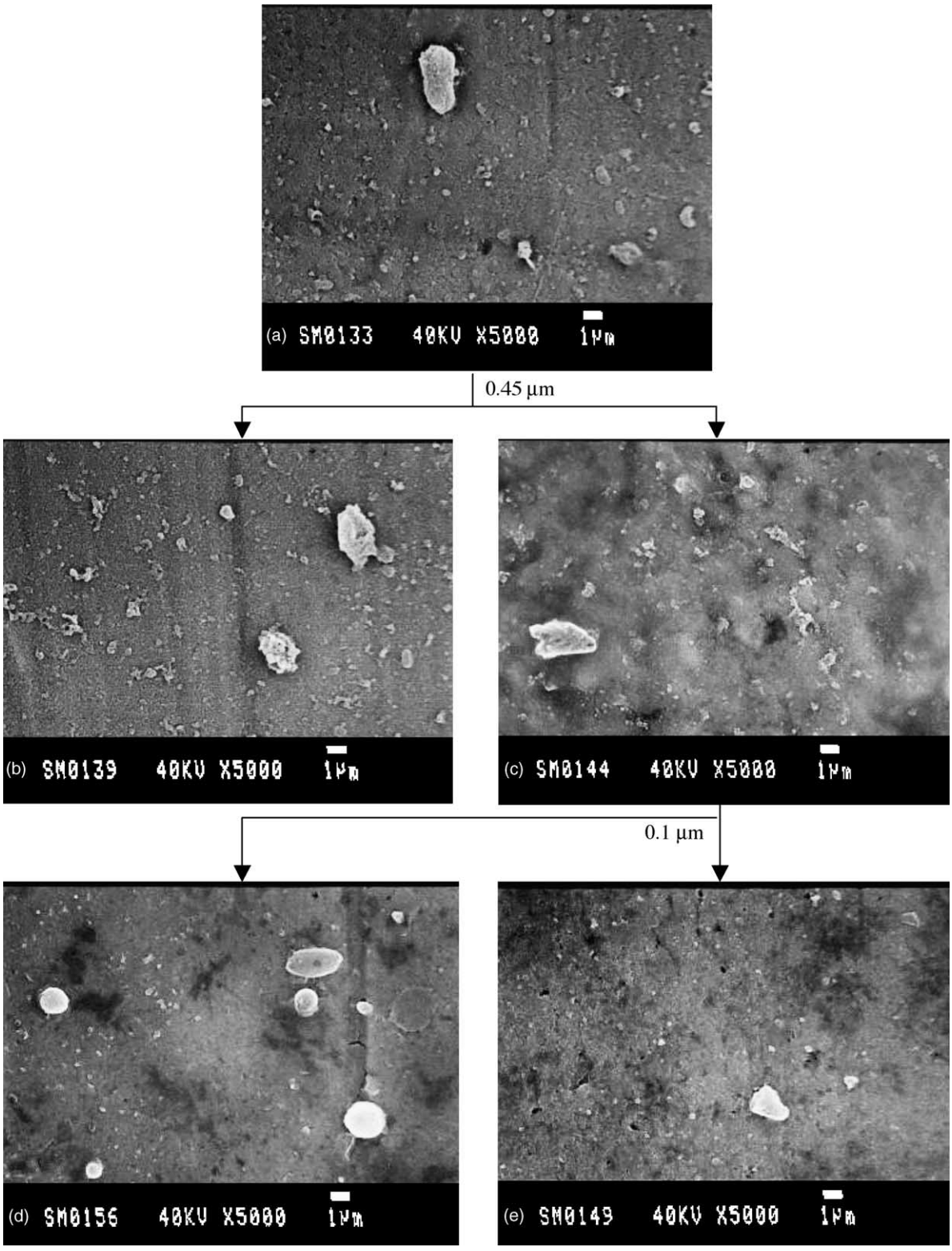

Fig. 1. SEM micrographs of natural aquatic colloids and particles from: (a) River Cole, (b) retentate R_1, (c) permeate P_1, (d) retentate R_2 and (e) permeate P_2 (CFF fractionation at CF of ca. 5.0; acceleration voltage of 40 kV; magnification of ×5000).

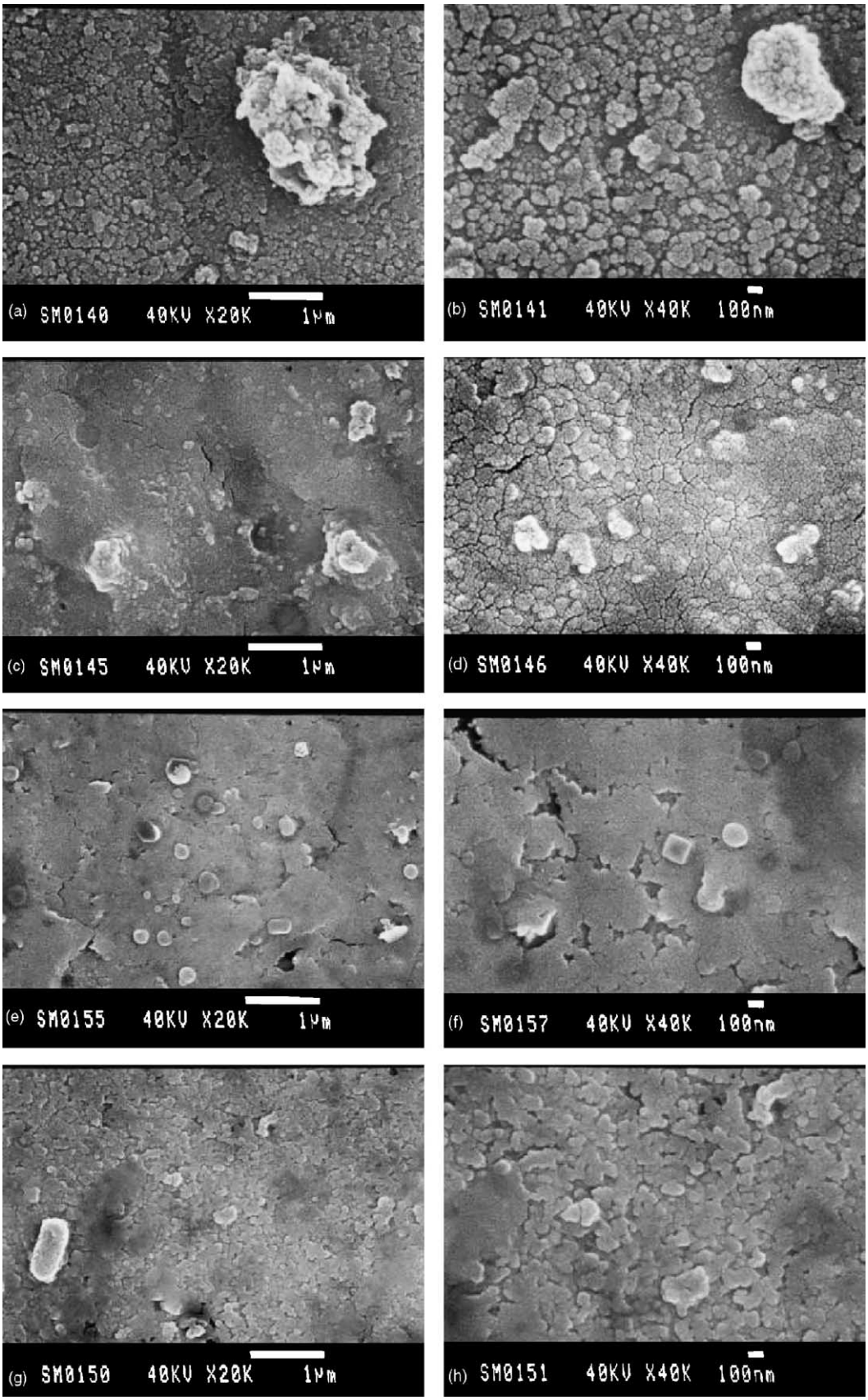

Fig. 2. High magnification SEM micrographs of natural aquatic colloids and particles from (a and b) retentate R_1, (c and d) permeate P_1, (e and f) retentate R_2 and (g and h) permeate P_2 (CFF fractionation at CF of ca. 5.0; acceleration voltage of 40 kV; magnification of $\times$40,000).

amples of particles that are characterised by high adsorption properties. Therefore, these complex polydisperse mixtures may promote gel layer formation at the surface of the CFF membranes, with their subsequent clogging and enhanced fouling which deteriorates their performance [30]. In addition, a previous study [31] documented that the surface of fibrillar material in natural waters may be covered by small colloids, suggesting the presence of structured aggregates in the water. The fact that such loose aggregates in the water itself could be retained by the CFF membrane, along with

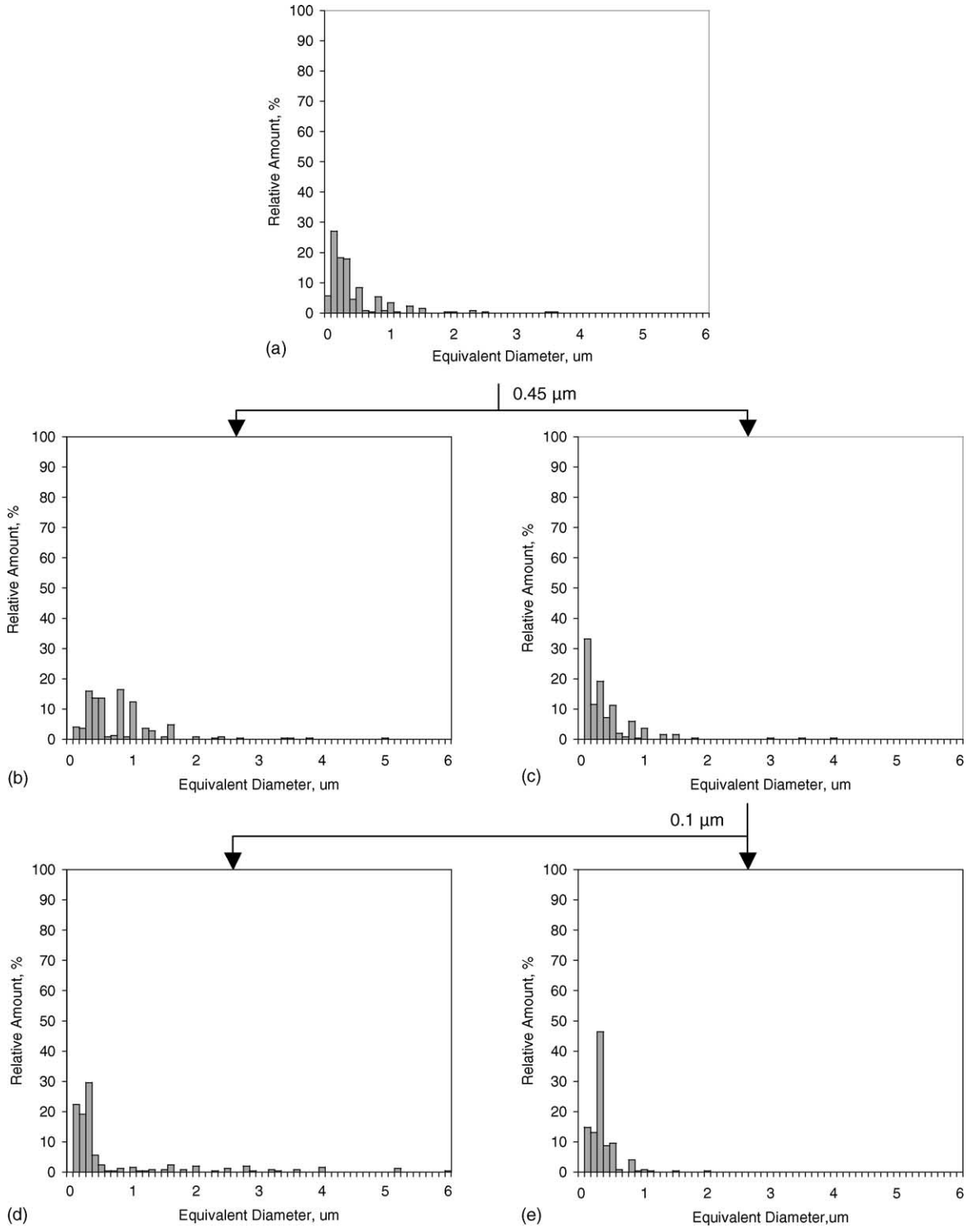

Fig. 3. Size distribution histograms from SEM analysis (CFF fractionation at CF of ca. 5.0; number of particles measured: 250).

the adsorbed colloids, may also explain the occurrence of colloids smaller than the nominal pore size in the retentate. The SEM images also showed the presence of colloids and particles larger than the cut-offs in some of the fractions (Figs. 1(c–e) and 2(a and b)). Some of them were easily identified as aggregates composed of smaller discrete particles (Fig. 2d, f and h) that could have formed either during the fractionation process or during drying of the samples prior to SEM observation. In particular, Fig. 2f exhibits a large number of discrete particles that had agglomerated on the surface of the stub, making their individual observation problematic. A recent paper [32] has demonstrated how drying processes may alter the conformation of humic substances through aggregation in the relative humidity range 25–100%. The applicability of SEM for the fully quantitative observation of natural aquatic colloids and particles and for the assessment of CFF fractionation was therefore questionable, although some qualitative indications were obtained. Along with the above aggregates, what appeared to be discrete particles larger than the cut-offs were also observed (e.g. Fig. 1d). The presence in the permeate of particles larger than the nominal pore size is surprising. However, Dai et al. [17] made indirect observations, which he attributed to the permeation of high molecular weight molecules. These authors recommended the use of low CFs to minimise this artefact. These observations can also be rationalised both by the non-size fractionation produced by the depth filter in the sub-micrometer range [33] and by conformation changes during and after fractionation, induced by changes in the solution chemistry (e.g. possible increased concentration at and just above the membrane surface). The results confirmed the operational nature of the fractions produced by CFF [23], something, which in practice, is frequently ignored by CFF users. Further work is clearly required in this area in order to fully optimise CFF operating conditions and ensure it is suitable for use as a size fractionation method in natural waters.

The qualitative observations made above were supported by the size distributions of deposited material that had been quantified based on the SEM images (Fig. 3). Analysis of the river fraction revealed that the lower size range (<0.45 μm) was dominant (ca. 72%) by number, although a small percentage of material of several micrometers were also present (Fig. 3a). The populations of particles estimated using SEM were different between the retentates and the corresponding permeates, suggesting that fractionation occurred to some extent. However, as mentioned earlier, colloids smaller than the membrane cut-offs were found in the retentate, confirming that CFF fractionation was not quantitative and not based on size only [23]. The presence of these small colloids in the retentate may have been caused by the retention of low molecular weight molecules by the membrane [19]. In addition, aggregates, that were composed of discrete particles, and larger than the cut-offs, were also identified, suggesting that the use of SEM for the observation of aquatic colloids and particles was not satisfactory.

3.2. Atomic force microscopy imaging of the River Cole and the CFF-generated fractions

AFM is a technique of immense value for visualising and analysing very fine colloids (<100 nm), and has recently been used to image humic substances [34–36], freeze-dried marine water samples [31] and colloids from river waters [27]. In the present study, AFM has been used to examine CFF-generated colloidal fractions. No discernible colloids or particles were identified on mica sheets that had been exposed to ultra-pure water (results not shown). Fig. 4a and b exhibited typical AFM micrographs of the River Cole and the permeate P_1, respectively. Only very fine colloids were adsorbed onto the mica sheets. In the present study, adsorbed colloids were essentially irregularly shaped (Fig. 4). Smaller amount of fibrillar material was also identified. The particle size dis-

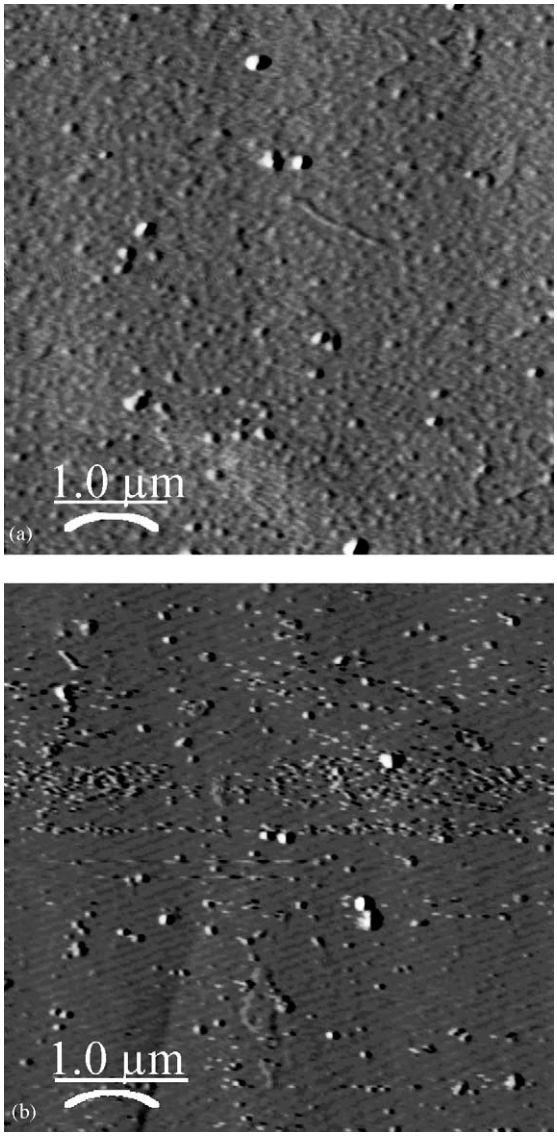

Fig. 4. AFM micrographs of natural colloidal material from (a) River Cole and (b) permeate P_1 adsorbed on mica.

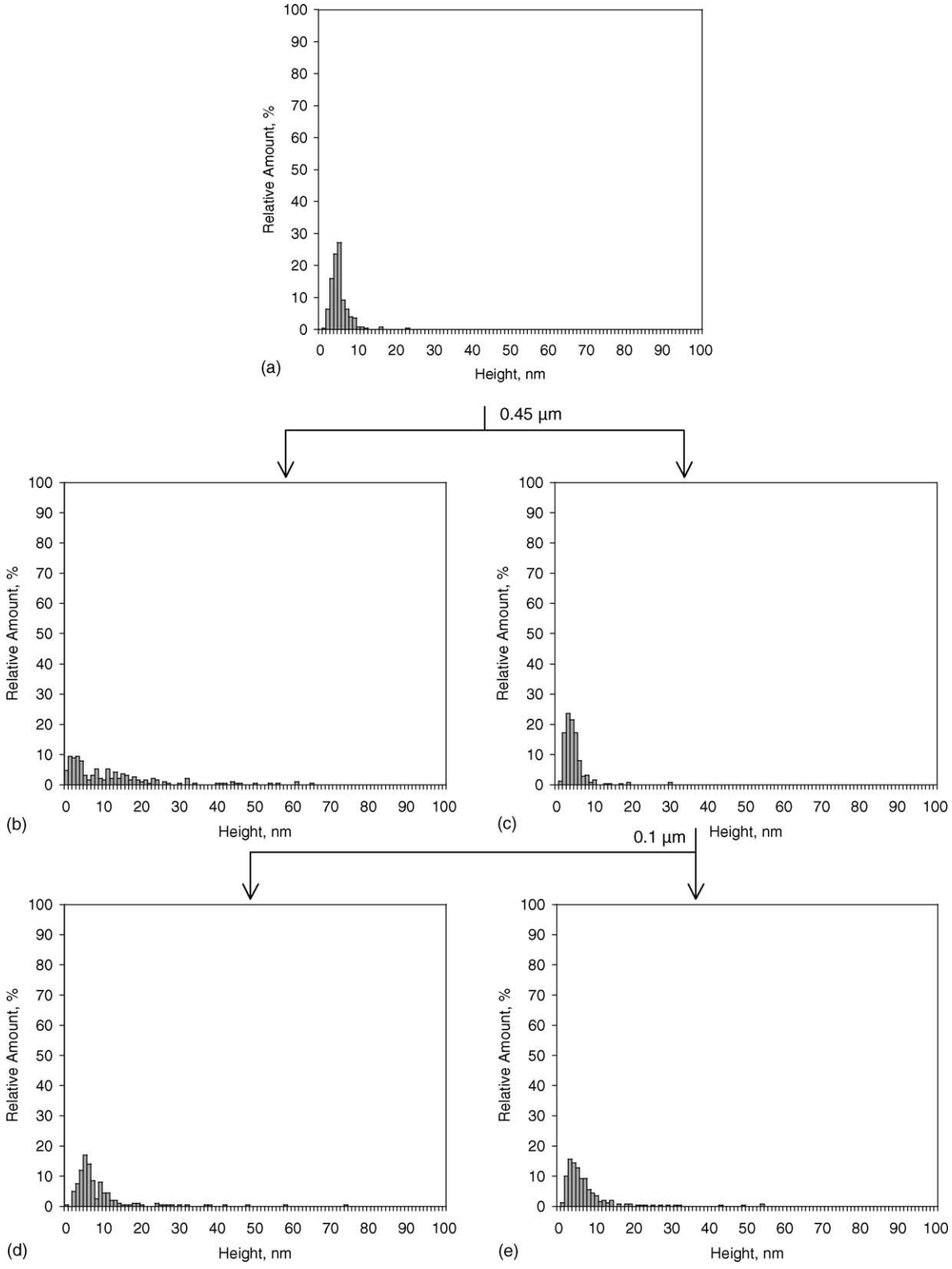

Fig. 5. Size distribution histograms from AFM analysis: (a) River Cole, (b) retentate R_1, (c) permeate P_1, (d) retentate R_2 and (e) permeate P_2.

tributions (PSD) obtained by AFM were similar for all size fractions and only included colloids smaller than a few tens of nanometers (Fig. 5). The PSD results and the observation of only small colloids were consistent with previous findings on lake water [23]. However, the high sensitivity of AFM for the visualisation of very small colloids was very useful since it permitted the identification of the presence of large amounts of small material (<50 nm) in all retentates and permeates, obtained from both 0.1 and 0.45 μm nominal pore size membranes. These results confirmed the SEM observation that very fine colloids smaller than the nominal cut-off were retained by the membrane. These findings may have important

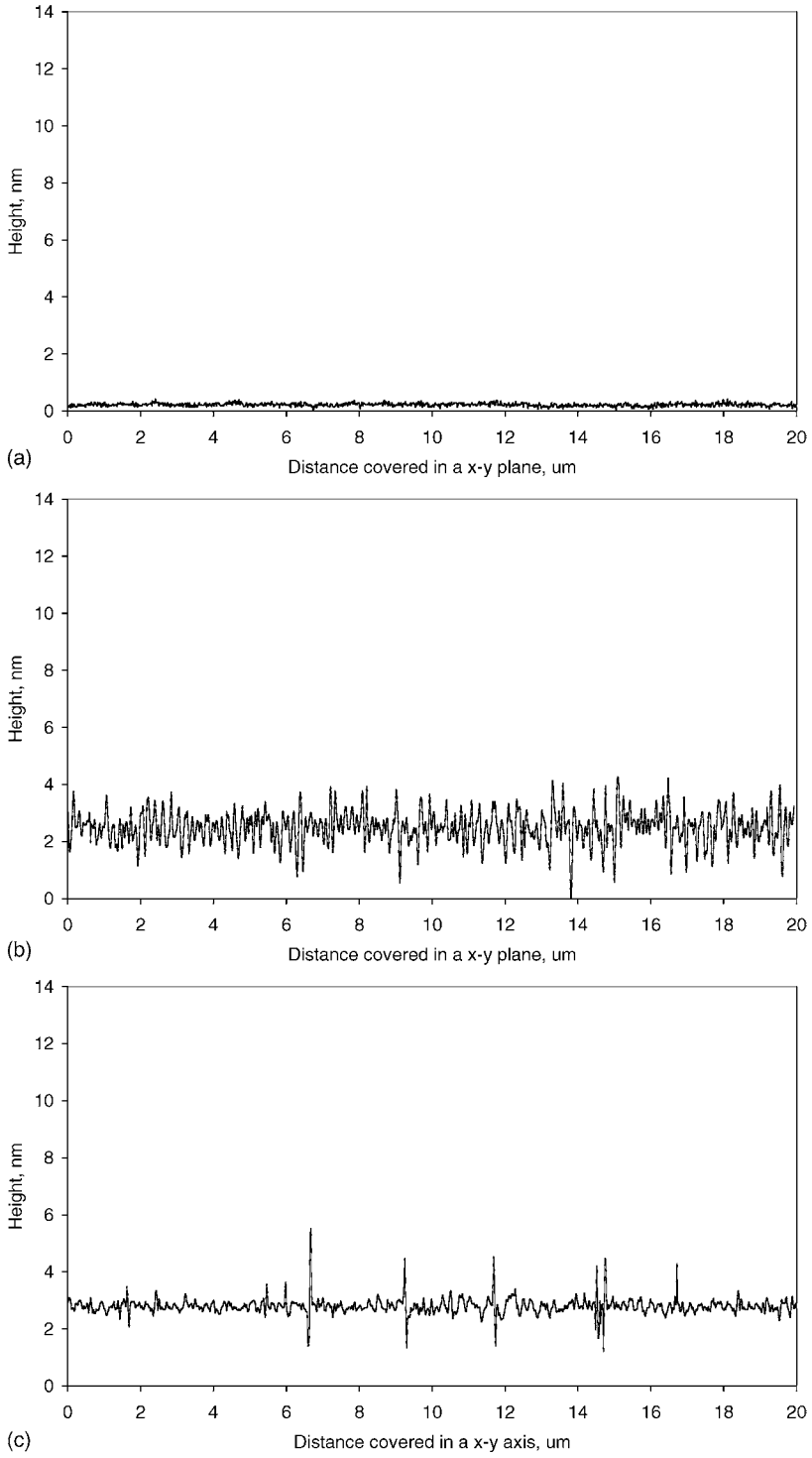

Fig. 6. Comparison of surface variability between (a) bare mica and mica sheets that have been immersed in (b) River Cole and (c) permeate P_1, respectively, for a 30 min period.

implications for studies that have used CFF fractionation to estimate trace element partitioning in natural waters. Clearly, the retention of colloids smaller than the nominal pore size of the membrane will lead to retention of much or all of the metals bound to these small colloids. If the CFF fractionation occurred ideally, then all of this material (<0.45 or 0.1 μm) would have been included in the 'dissolved' fraction, i.e. in the membrane permeate. The common assumption, based on geometrical arguments and an assumption of spherical shape, is that the smaller colloids will have a higher specific surface area and will thus be able to bind greater metal fractions than the larger sized colloids and particles [37]. Some recent research [7] suggests that indeed this fraction is responsible for the majority of metal binding. This being the case, the retention of even small amounts of colloids smaller than the nominal pore size will lead to a significant error in our understanding of metal speciation in natural waters. Based on these results, we suggest that colloid-bound metal is severely underestimated. However, to be definitive, clearly this analysis needs to be extended into the ultra-filtration range, carried out at a variety of concentration factors and include metal analyses, with mass balances.

Significant variability of the AFM background (expressed in terms of height, in nanometer) adsorbed onto the mica sheets (i.e. ca. 2.5 and 2.8 nm for the River Cole and the permeate P_1, respectively, not including discrete sorbed colloids) (Fig. 6b and c) was observed compared to the variability of the background measurement of untreated mica (ca. 0.3 nm) (Fig. 6a). Analysis of all AFM images obtained for other samples showed similar changes in the variability of the background (results not shown) when natural colloids had been deposited onto mica. This difference in background variability between clean and exposed mica sheets was indicative of the presence of a surface layer. This confirms similar observations made in our previous studies that reported the use of AFM for the visualisation of aquatic colloids from lake, river and glacial waters [23,27,29]. The entire surface of the mica was covered with this layer after insertion in the water and the layer showed prominent features, such as troughs and peaks. This sorbed layer was presumably composed of humic-like macromolecules and possibly oxide material [27], although further analysis will be required to fully elucidate their structures. AFM was also very useful in discriminating between the surface roughness characteristics (defined as root mean square roughness) of whole mica sheets that had been covered with different CFF fractions and the river water (Fig. 7). In particular, the root mean square roughness was found to increase from clean bare mica (0.11 ± 0.09) < P_2 (1.3 ± 0.1) < P_1 (1.6 ± 0.2) < R_2 (3.4 ± 0.2) < R_1 (8.5 ± 1.1) < River Cole (11.9 ± 1.8). This was consistent with a previous study [23], and measurement of surface roughness by AFM has also already been used successfully to study protein deposition onto different CFF membranes [38]. Determination of a variation of this parameter between the size fractions was therefore an indication that some fractionation occurred by CFF but it was not fully

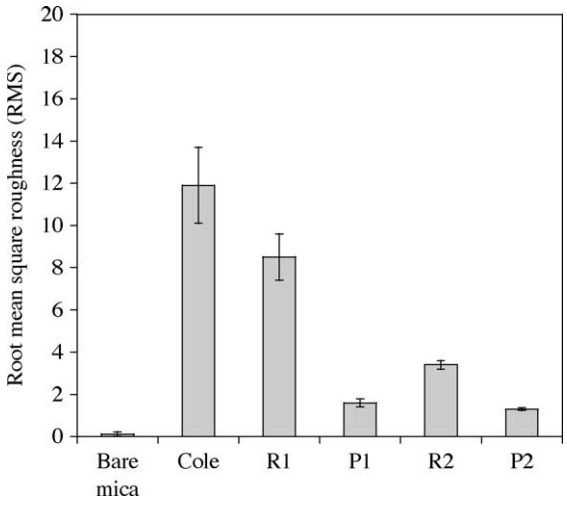

Fig. 7. Roughness analysis histogram from AFM analysis of natural aquatic colloidal material from the River Cole and the corresponding CFF-generated fractions.

quantitative and not in line with the expected sizes based on the nominal pore size. The observation that ultra-fine colloidal material strongly interacts with and completely coats mica (an extremely smooth and negatively charged surface) within as little as 30 min again has important potential implications for our understanding of the behaviour of trace elements in aquatic systems. The results strongly suggest that clean, 'pure' surfaces are unlikely to exist in the natural environment. As surface binding of trace elements is of great importance, the nature of this layer may dominate trace element partitioning, rather than the nature of the bulk particle. This result is consistent with previous data on electrophoretic mobility of particles in the absence or presence of humic substances [39] and models of particle structures [40].

4. Conclusion

The combined use of SEM and AFM demonstrated the inability of CFF to make accurate size fractionation of aquatic colloids and particles. Retentates (in principle containing particles greater than the nominal pore size) were substantially contaminated with small colloids. These observations have important implications for the interpretation of speciation data from CFF. This study therefore shows that unconstrained use of the CFF may lead to uncertain and misleading results. Ideally, microscopy and perhaps other techniques need to be used to provide an independent measure of the success of size fractionation. SEM showed the presence of colloids and particles larger than the nominal pore size in the permeate, although drying artefacts may be responsible for this. In addition, AFM allowed the observation and quantification of very fine scale material (<20 nm in size), which was present in all fractions, including the retentates. The validity of the use of CFF for the size fractionation of aquatic colloids and particles

is therefore questionable, although future extensive studies are required, especially in the ultra-filtration size range.

Acknowledgments

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