

Article ID: 1001-0742(2000)02-0129-09

Suspended particulate and colloidal matter in natural waters

RAN Yong¹, FU Jia-mo¹, SHENG Guo-ying¹, R. Beckett², B. T. Hart²

(1. State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China; 2. Water Studies Center, Monash University, Caulfield East, Victoria 3145, Australia)

Abstract: The association of pollutants (nutrients, heavy metals and organic compounds) with colloidal and suspended particle matter (SPM) plays a dominant role in determining their transport, fate, biogeochemistry, bioavailability and toxicity in natural waters. A scheme for the fractionation and composition of colloidal and suspended particulate matter from river waters has been tested. Sieving, continuous flow centrifugation and tangential flow filtration were used to collect gram amounts of colloidal and particulate matters. The separation scheme was able to process large samples(100L), within reasonable times(1 day) and the apparatus was portable. The aquatic colloid was also separated with high resolution, and sized using sedimentation field-flow fractionation technique. The mass-based particle size distribution for the river water sample showed a broad size distribution between 0.05 and 0.4 μm with the maximum around 0.14 μm . There was a systematic increase in the content of organic carbon, Mg, Ca, Na, Cu and Zn with decreasing particle size, highlighting the importance of the colloidal(<1 μm) fraction.

Key words: suspended particulate; colloidal matter; natural waters; pollutants

CLC number: X132 **Document code:** A

Introduction

There is considerable evidence that partition between solid and aqueous phase has a major effect on the occurrence, transport, fate and biological effects of natural and anthropogenic chemicals in aquatic systems(Allan, 1986; Rees, 1991). A number of studies are now available that show the importance of particle-associated transport of contaminants such as trace metals, organic compounds and nutrients in natural waters, soils and groundwater(Koile, 1990; Wells, 1991; 1992; Orlandili, 1990; McCarthy, 1989; Chin, 1991). Unfortunately, many of these studies have used a two phase (membrane filtration) separation to produce “particulate”(i.e. >400 nm in size) and “dissolved” fractions, and by including the colloidal particles in the “dissolved” fraction, have neglected the role of colloids in any transfer processes occurring. This simple two-phase separation can hide the complexity of the interactions occurring and may even provide incorrect information on the speciation and bioavailability of a particular contaminant(Hart, 1993).

A considerable amount is known about the suspended particulate matter (SPM)-associated transport of contaminants in aquatic systems. SPM has the capacity to interact physico-chemically (surface complexation, ligand exchange, hydrophobic association) with a range of inorganic and organic contaminants. Additionally, SPM often contains higher concentrations of trace metals than bottom sediments(Juracic, 1987), with increased concentrations of trace metals being particularly under conditions where low SPM concentrations prevail (Baeyens, 1987). However, there is still much to be learned about the relative importance of the colloidal fraction in these processes. Colloidal particles are of particular importance due to their high specific surface area and, hence, high potential adsorptive capacity for natural macromolecules, organic contaminants(Chiou, 1987) and metal ions. Additionally, colloids will remain suspended until aggregation occurs and may

potentially facilitate the transport of adsorbed species over appreciable distances in both surface (Means, 1982) and groundwater (McCarthy, 1989). Under some circumstances, the binding of chemical species (e.g. actinides) to SPM can be reduced by orders of magnitude in the presence of colloidal organic matter (Orlandini, 1990). The behavior of colloidal material is also influenced by aggregation and disaggregation processes (Santschi, 1984).

Traditional SPM separation methods from natural water include settling, centrifugation, flocculation and membrane filtration, the latter commonly using 0.45 μm filters (Laxen, 1982; Horowitz, 1986). New methods such as ultrafiltration, reverse osmosis, tangential flow or cross-flow filtration (TFF) and field-flow fractionation (FFF) have been used to separate and characterize colloidal matter from natural waters (Beckett, 1989; Hart, 1993; Tanizaki, 1992; Kuwabara, 1990; Serkiz, 1990; Marley, 1991; Whitehouse, 1989; 1990).

In this paper we used sieving, continuous flow centrifugation, tangential flow filtration and field-flow fractionation to fractionate SPM in natural water. Geochemical analysis of the individual sample fractions was achieved using alkali fusion followed by determination using inductively coupled plasma atomic emission spectrometry (ICP-AES), which allows simultaneous analysis of the major elements including silicon.

1 Materials and methods

1.1 Sampling and fractionation

Surface water samples, usually 75–100 L, were collected in 25 L polyethylene drums from a transect across the water body in the Namoi River of the Murray-Darling River. The submersible plastic bilge pump (Rule 400 GPH Rule Industries) used to fill the drums was covered with a 1000 μm mesh prefilter to exclude any large debris. All equipment used in sampling and fractionation was acid washed (10% nitric acid) and rinsed (Milli Q) before use.

Coarse particulate matter: The initial fractionation step used nylon mesh (25 μm) to separate out material greater than 25 μm . The water sample was pumped at approximately 4 L/min using a peristaltic pump onto a flat 25 μm nylon mesh sieve 30 cm in diameter. All retained material was washed into a 1 L/polyethylene bottle using a known volume of deionized water.

Fine particulate matter: A continuous flow centrifuge was used to fractionate particles from 25 μm down to a density dependent size of approximately 1 μm . The filtrate from step (a) was pumped at approximately 4 L/min using peristaltic pump into a continuous flow centrifuge (Alfa Laval Model MAB 102B-25) operating at approximately 8200 r/min. The resultant slurry let in the centrifuge vessel was resuspended and washed into a 1 L polyethylene bottle with a known volume of deionized water.

Coarse, fine and ultrafine colloidal matters: Tangential flow filtration was used to separate and concentrate three fractions in the colloidal ($< 1 \mu\text{m}$) size range, namely: (1) coarse colloidal matter: 1–0.2 μm ; (2) fine colloidal matter: 0.2–0.006 μm (100000 MW); (3) ultrafine colloidal matter: 0.006–0.003 μm (10000 MW). The molecular weight (MW) equivalent spherical diameter was calculated assuming particle sphericity and an estimate of density obtained from the particle geochemistry. For the FFF size analysis, another portion of the water sample was fractionated and concentrate about one hundred-fold using the continuous centrifuge and tangential flow filtration. A nominal particle size cutoff of 0.2 μm was obtained using polysulphone membrane filters. The coarse colloidal matter for the FFF study was stored at 4 $^{\circ}\text{C}$ and prior to use was subject to ultrasound to break up any aggregates present.

The filtrate from step (b) and successive filtrates were separated and concentrated using a commercial tangential flow filtration system (Millipore-pellicon Model ON 141). The membranes are polysulphone filters.

The TFF fractionation process was taken to be completed when the retentate volume (suspension retained by the filter membrane) was about 500 ml. Two aliquots of deionized water were used to flush any residue from the system, with the retentate and washings transferred to a 1L-polyethylene bottle using a known volume of deionized water.

1.2 Sample analysis

After each fractionation step was completed, the particulate slurries and filtrate were refrigerated at 4 °C. Each of the particulate slurries was further concentrated to 50 ml using a rotary evaporator, dried in a vacuum oven (400 mm Hg/ 70 °C) and subsequently weighted to obtain the suspended matter concentration (SPM in mg/L).

Bulk chemical analysis for major elements (Si, Ti, Fe, Mn, Mg, Ca, Na and K) and trace elements (Cu and Zn) in the particulate matters was achieved using a lithium metaborate (LiBO_2) fusion technique with determination by ICP-AES (Perkin Elmer Model Plasma II emission spectrometer). Determination of Cu and Zn was by flame AAS (Perkin Elmer Model 1100 atomic absorption spectrophotometer). One whole rock standard (NBS Canada) was prepared identically as calibration standards for each element. Background correction for matrix effects due to the high salt concentration (9 g/L) was achieved using a Myers-Tracey signal compensation method with an internal Sc reference (Myers, 1983).

1.3 FFF size analysis

The sedimentation FFF apparatus (SedFFF) was essentially the same as described previously (Beckett, 1988). Clamping two concentric nickel-chromium rich alloy (Hastalloy C) rings with a 0.0254 cm thick mylar spacer (which had the channel shape cut out) sandwiches between them made the FFF channel. The channel was 93.1 cm long (inlet to outlet) and 2.1 cm in breadth. The channel void volume was 5.30 ml and detector dead volume was 0.54 ml. From these measurements, the channel thickness was calculated to be 0.0266 cm.

The channel was fitted inside a centrifuge basket so that its radius was 15.5 cm. O-ring seals at the ends of the axle allowed liquid to flow through the channel while the centrifuge rotated. A DC motor with speed controller (DPM-6130E, Bodine Electric Company) powered the centrifuge. Rotation speed was computer controlled using hardware and software from FFF, UT. The speed was measured by a photocell whose light path was interrupted as the rotor spun by a notched disc attached to the end of the centrifuge axle. This enabled the centrifuge speed to be kept constant or in the case of field programming, to be decayed during the run. For samples with a broad size distribution such as the suspended particulate matter used in this study it is almost mandatory to use

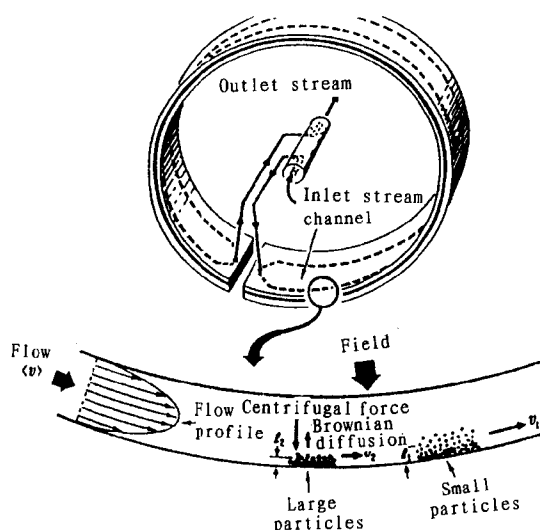


Fig.1 Diagram of a sedimentation FFF centrifuge with cross section of channel showing normal mode separation

some form of field decay during the run. Since laminar flow conditions prevail in the channel, a parabolic velocity profile is established across the thin dimension of the channel (Fig. 1). Sample particle forced to form more compact layers closer to the accumulation wall will migrate at a lower velocity than components whose center of mass is further from the wall where they can be carried by the faster moving fluid.

A Gilson minipuls 2 peristaltic pump pumped the carrier solution and the outlet stream from the channel was passed through a Waters 441 UV detector operating at 254 nm. The detector signal was monitored on an Omniscrite chart recorder (Houston Instruments).

An injection volume of 10 μl was introduced onto the channel through a septum. To relax the sample, an initial field of 1000 r/min was maintained for 20 min under stop-flow conditions. The channel flow was then started and the field decay program commenced according to the power program, using the following parameters. The initial field of 1000 r/min was held for a time lag of 10 min. A decay parameter of -80 min reduced the field to a hold value of 10 r/min at 205 min. It should be noted that the time required to reach the hold r/min was far in excess of that needed for the completion of these experiments.

An aqueous solution of 0.1% sodium dodecylsulphate and 0.02% sodium azide at a flow-rate of 2 ml/min was used as the carrier. Detector sensitivity ranged between 0.02 to 0.05 a. u. f. s. The chart recorder was maintained at 10 cm/h.

2 Results and discussion

2.1 The fractionation of SPM in natural water

Traditional methods of collection, fractionation and concentration for SPM are generally time consuming (e.g. settling, flocculation) or labor intensive (e.g. conventional membrane filtration). However, this has been partly redressed in the last decade by the use of continuous flow centrifugation although this device has limitation in the separation of the lower size particles due to mechanical specification of the centrifuge. Nevertheless, with the traditional methods generally only one particulate fraction is collected and there is a limited capacity to fractionate and concentrate colloidal material in any substantial amount on a time efficient basis.

The use of tangentially flow filtration overcomes many of the problem associated with classical filtration techniques. It allows large volume of water to be processed and can therefore produce relatively large masses (gram quantities) of colloidal particles. The entire fractionation system as outlined here is compact and highly portable, weighing less than 100 kg, facilitating on-site or laboratory fractionation of the water sample and hence minimizing storage and transportation effects.

The reproducibility of the continuous flow centrifugation and tangential flow filtration steps was assessed from the mass (dry weight) of each fraction collected. A 75L sample of natural water (Namoi River) was collected, thoroughly homogenized, and split into three equivalent 25L

Table 1 Fractionation steps and time

Fractionation step	Time taken, h/100L	Comments
Sieving-mesh	1	Rapid, efficient
Continuous flow centrifugation	1	Rapid, efficient
Tangential flow filtration		
$>0.2 \mu\text{m}$	5	Fractionation time increases
$>0.006 \mu\text{m}$	8	with decreasing porosity
$>0.003 \mu\text{m}$	10	
Total fractionation time	25	Approx. 2 days processing

aliquots. Each aliquot was then fractionated under identical experimental conditions as previously outlined.

The time taken for each fractionation step is given in Table 1. The total required for the entire fractionation scheme is around 25 h, with only infrequent monitoring of the process required in the last three tangential flow filtration steps.

The reproducibility of the mass recovered of each fraction (95% confidence limits) varied between 10% and 29% (Table 2), with the greatest variation in the smallest (0.006–0.003 μm) fraction, probably due to a combination of small sample size (a low concentration of SPM) and

Table 2 The mass and percentage of each SPM fraction separated

Fraction, μm	Number of replicates	Mean, mass, g	Percent of total SPM	95% confidence limits, % RSD
>25	1	0.31(75)*	6.1	—
25–1	3	0.23(25)	13.3	0.03(13)
1–0.2	3	0.98(25)	57.6	0.10(10)
0.2–0.006	3	0.25(25)	14.8	0.03(12)
0.006–0.003	3	0.14(25)	8.2	0.04(29)
Total SPM, mg/L	3	68		4.4(6)

* Number in parentheses is volume (liters) of water processed

cumulative errors from the preceding steps. The variation for the total combined mass of all the fraction was 6%.

2.2 Particle distribution of SPM

Fig.2 shows a SedFFF fractogram and the calculated particle size distribution of the coarse colloidal matter sample collected from the Namoi River. The methods to calculate particle size distribution from the fractogram were detailed by Beckett and Hart (Beckett, 1993). The two main uncertainties with these calculations are the need to know or assume a particle density (for mineral-rich samples a particle density of 2.5 g/cm³ is generally assumed) and the possible underestimation of the concentration of very small particles which are less than the wavelength of the radiation (254 nm) used in the detector.

The mass-based particle size distribution for the sample shows a broad size distribution between 0.05 and 0.4 μm . The upper limit is controlled by the continuous flow centrifuge conditions used to concentrate the sample from the water. The fact that particle less than the 0.2 μm filter cutoff are present is most likely due to partial blockage of the pores during filtration or perhaps variations in the particle density (assumed 2.5 g/ml). The maximum for the particle size distribution is around 0.14 μm .

2.3 Chemical composition of SPM

The chemical composition of each fraction is given in Table 3. The overall variation was up to 29% for the major elements and up to 48% for the trace elements at the 95% confidence limit, but in most instances the repeatability was less than 10%. This variability can be ascribed to three factors. First, a number of components, especially SiO₂, would be expected to have the largest variation in the 25–1 μm fine particulate fraction because resistant minerals such as quartz (which is difficult to grind) ensure that some inhomogeneities persist although each dried fraction was thoroughly homogenized before subsampling for analysis. Secondly, the variations in the mass of each fraction and the combined total mass of all fraction suggest that the fractionation process is not entirely uniform, especially where small 25L samples are fractionated, thus giving rise to a degree of geochemical variation. This might be reduced in actual field sampling when 100L samples are fractionated.

A third factor that may also explain some of the observed variation is the accuracy and

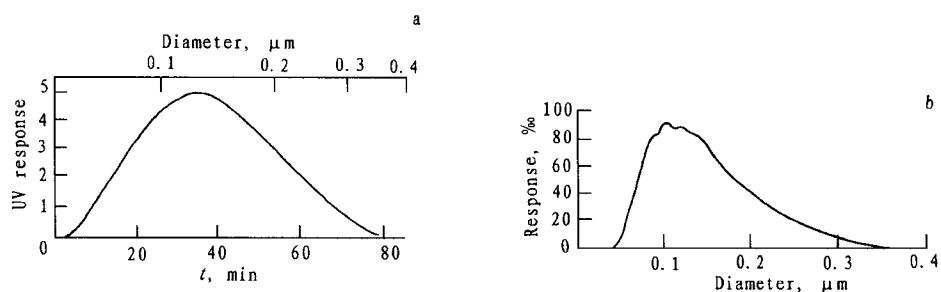


Fig. 2 (a) Sedimentation FFF fractogram of the coarse colloid fraction of Namoi River; (b) particle size distribution calculated assuming a particle density of 2.5 g/cm^3

precision of the analytical method used. To test this, a standard marine sediment sample (BCSS-1) was prepared as an unknown. The results (Table 4) indicate that accuracy is extremely good, with most elements falling within the quoted 95% confidence limits, the only exception being Fe_2O_3 , Cu and Zn. Precision of the analytical method is also extremely good, with the largest variations found for SiO_2 , Fe_2O_3 and Cu. These data show that most of the variation in the chemical analysis of the sample could be accounted for by variations in the analytical method rather than the fractionation procedures.

Table 3 Bulk chemical composition of SPM fractions separated from Namoi River. All elements are expressed as percentage oxides except Cu and Zn ($\mu\text{g/ml}$)

	Size fraction, μm					Total SPM composition
	>25 (<i>n</i> = 1)	25—1 (<i>n</i> = 3)	1—0.2 (<i>n</i> = 3)	0.2—0.006 (<i>n</i> = 3)	0.006—0.003 (<i>n</i> = 3)	(<i>n</i> = 3)
SiO_2	68.2	59.6(5.6) *	29.6(1.6)	17.4(0.5)	5.6(0.1)	32.2
TiO_2	1.1	1.21(0.01)	0.41(0.02)	0.22(0.02)	0.09(0.05)	0.5
Al_2O_3	11.7	15.3(1.5)	17.3(0.6)	9.1(0.5)	1.9(0.3)	14.2
Fe_2O_3	5.9	6.7(0.5)	10.4(0.2)	5.6(0.3)	1.3(0.1)	8.2
MnO	0.09	0.05(0.00)	0.03(0.00)	0.03(0.02)	0.01(0.02)	0.03
MgO	0.60	0.79(0.02)	1.5(0.4)	2.7(0.1)	4.2(0.6)	1.7
CaO	0.12	0.11(0.02)	1.4(0.4)	2.6(0.1)	4.3(0.6)	1.6
Na_2O	0.32	0.24(0.02)	1.29(0.07)	3.8(0.1)	5.3(2.4)	1.8
K_2O	1.43	1.6(0.2)	1.05(0.01)	0.92(0.05)	0.8(0.2)	1.1
Cu	52	80(6)	143(24)	279(19)	397(189)	170
Zn	86	86(11)	171(30)	215(8)	203(78)	164
Total	89.3	85.6(7.7)	63.0(2.6)	42.3(1.4)	23.4(2.7)	61.3
LOI**	10.7	14.4	37.0	57.7	76.6	38.7

* 95% confidence limits in parentheses; ** loss on ignition (%) (100—total%)

There was a noticeable variation in the elemental composition of the fractions with two largest fractions dominated by Si, Al and Fe, and the smaller size fractions enriched in organic carbon (estimated by loss on ignition (LOI)), Mg, Ca, Na, Cu and Zn (Fig. 1). An inverse relationship was found between SiO_2 and LOI with SiO_2 decreasing by over 10-fold and the LOI increasing by over seven-fold as the particle size decreased. There was a variation in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio with decreasing particle size, indicating the relative proportion of quartz to clay within the individual

SPM fractions. Not unexpectedly, Ti and Mn, which are probably associated with heavy mineral phases, either free or as inclusion in quartz, display a similar trend to SiO₂.

A significant correlation ($r = 0.9012$) was found between the clay component (estimated as Al₂O₃) and the Fe content (Table 5). This is not unexpected, as the association of Fe with clays either as an interlayer cation or as an oxide or hydroxide coating has been well documented.

A feature of the chemical composition of the different SPM fractions is the progressive enrichment of Mg, Ca, Na, Cu and Zn with decreasing particle size (Fig.3b, c). These elements are all highly correlated with each other and with organic carbon

Table 4 Reproducibility of standard marine sediment (BCSS-1). All elements expressed as percentage oxides except Cu and Zn (µg/g)

Elements	This work, n = 10	BCSS-1	Ratio of analysis
SiO ₂	66.3(2.6) *	66.10(1.00)	1.00
TiO ₂	0.72(0.03)	0.73(0.02)	0.99
Al ₂ O ₃	11.6(0.5)	11.83(0.41)	0.98
Fe ₂ O ₃	4.9(0.3)	4.70(0.14)	1.04
MnO	0.03(0.004)	0.03(0.00)	1.00
MgO	2.4(0.1)	2.44(0.23)	0.98
CaO	0.75(0.04)	0.76(0.07)	0.99
Na ₂ O	2.5(0.1)	2.72(0.21)	0.92
K ₂ O	2.15(0.03)	2.17(0.04)	0.99
Cu	22(5)	18.5(2.7)	1.19
Zn	103(11)	119(12)	0.87
Total	91.35(2.88)	91.48(-)	1.00

* 95% confidence limits in parentheses

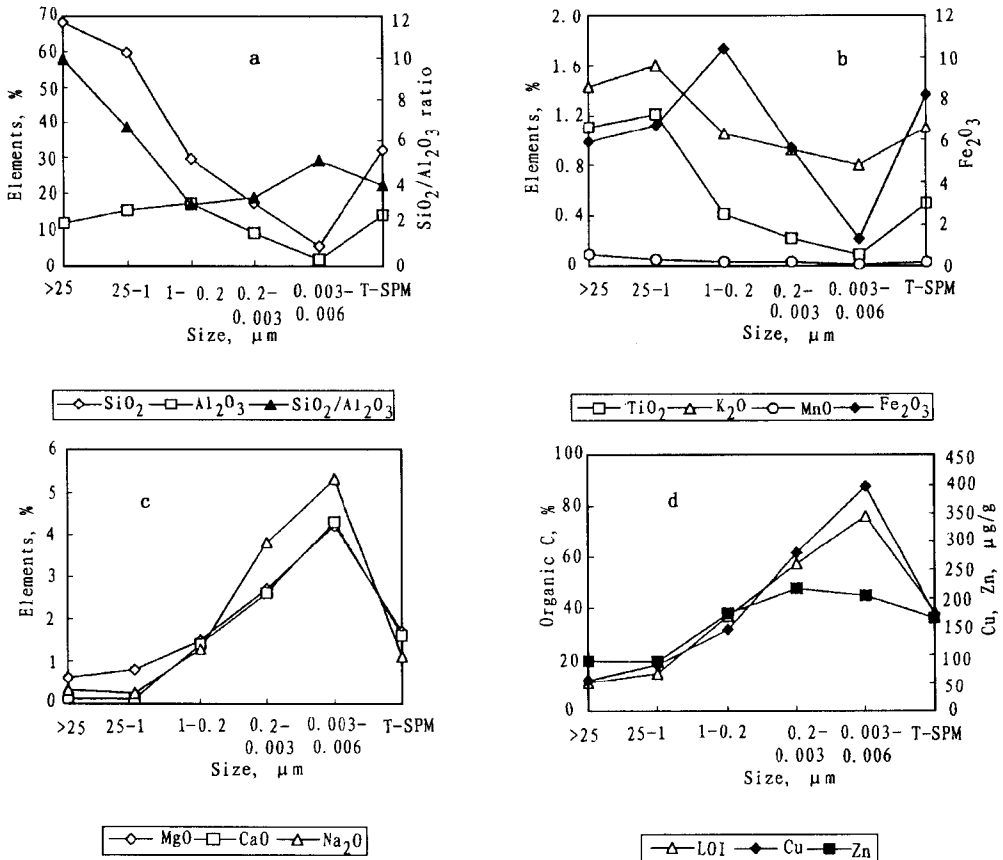


Fig.3 Changes of bulk chemical composition of SPM fractions from Namoi River

(LOI, Table 5). This relationship may be ascribed to three main factors. First, the surface area increases by many orders of magnitude as the particles decrease in size, resulting in the potential availability of many more cation binding sites per unit mass of particulate. Second, organic matter in most natural waters is negatively charged and has a high cation-exchange capacity. Thirdly, Fe oxide/hydroxide, which have the ability to bind both cations and anions via surface complexation, are also present. Therefore, considering these likely increases in surface area, organic carbon content and cation-exchange capacity with decreasing particle size, it is not surprising that colloidal ($<1 \mu\text{m}$) fractions have an enhanced ability to complex dissolved cations.

The presence of a significant component of clay may be precluded in the two smallest fractions, where the largest increase in complexing ions occurs. Simple mass balance calculations indicate that even if all the available Al_2O_3 and SiO_2 are used in a clay component, there is a large excess of Mg, Ca and Na over that required to satisfy a charge balance. Further evidence is provided by the fact that K, which is generally enriched in the clay phase during weathering, decreases with particle size and is negatively correlated with Mg, Ca and Na (and also Cu, Zn and LOI).

This study has shown that the filtrate (nominally $<0.45 \mu\text{m}$), which is nominally classified as the dissolved fraction, contains a range of colloidal species of diverse chemical compositions. Hence the working definition or nominal designation of material $<0.45 \mu\text{m}$ being truly "dissolved" species, as described in many reports, has been shown in this study to be incorrect.

Table 5 Correlation coefficients (r) between elements in the five SPM fractions

	MgO	CaO	Na ₂ O	Cu	Zn	LOI	K ₂ O
MgO	1.000						
CaO	0.9958**	1.0000					
Na ₂ O	0.9896**	0.9866**	1.0000				
Cu	0.9973**	0.9926**	0.9945**	1.0000			
Zn	0.8507	0.8819**	0.7769	0.8722	1.0000		
LOI	0.9841**	0.9920**	0.9822**	0.9887**	0.9295**	1.0000	
K ₂ O	-0.8869*	-0.9237*	-0.8991*	-0.8910*	-0.9657**	-0.9434	1.0000

Notes: *, ** represent significant and very significant correlation, respectively

3 Conclusions

Aquatic colloids are characteristically very small (1–1000 nm), have widely varying sizes and shapes, and a quite heterogeneous composition. The concentrations of colloids in rivers can be significant, and when this is coupled with their high specific surface area, large adsorptive capacity, and small tendency to settle out of solution, they are potentially very important in taking up and transporting contaminants. Unfortunately, many contaminant studies use a two-phase membrane filtration separation to produce "particulate" (i. e. $>450 \text{ nm}$ in size) and "dissolved" fractions, which will include the colloidal fraction in the "dissolved" fraction. This simple two-phase separation can hide the complexity of interaction occurring and may provide incorrect information on the speciation and bioavailability of a particular pollutant.

A fractionation scheme has been applied to separate and concentrate colloidal and suspended particulate matter from river waters. Five size particulate fractions were separated using sieving, continuous centrifugation and tangential flow filtration. Significant (gram) amounts of colloidal

matter ($< 1 \mu\text{m}$) in three size ranges, nominally 1—0.2, 0.2—0.006 and 0.006—0.003 μm were obtained. In terms of speed, efficiency, reproducibility, portability and ability to process large volumes of natural waters, tangential flow filtration was found to be extremely useful for separating colloidal matter from natural waters. The aquatic colloid was also separated with high resolution, and sized using sedimentation field-flow fractionation. The mass-based particle size distribution for the river water sample showed a broad size distribution between 0.05 and 0.4 μm with the maximum around 0.14 μm .

Bulk chemical analysis for major elements and trace elements in the particulate fractions was achieved using small (ca. 100 mg) amounts of sample. All major elements, including Si, were analyzed and a mass balance approach can be used to quantify the geochemistry of SPM. For the collected samples, it was found that the geochemical composition varied with particle size. This is particularly important in the colloidal size fractions, which appears to have large capacity to complex major and trace elements.

References:

- Allan R J, 1986. The role of particulate matter in the transport and fate of pollutants[M] (Ed. by B. T. Hart). Melbourne: Water Studies Center, Chisholm Institute of Technology.
- Baeyens W, G Gillain, G Decadt, I Elskens, 1987. *Oceanol Acta*[J], 10:169—179.
- Beckett R, B T Hart, 1993. Environmental particles[M](Ed. by J Buffle, H. P Van Leeuwen). London: Lewis Publishers, Vol. 2. 165—205.
- Beckett R, G J Nicholson, B T Hart *et al.*, 1988. *Water Res*[J], 22:1535—1545.
- Chin Y P, P M Gshwend, 1991. *Geochim Cosmochim Acta*[J], 55:1309—1318.
- Chiou C T, D E Kile, T I Brinton *et al.*, 1987. *Environ Sci Tech*[J], 21:1231—1234.
- Hart B T, Hines T, 1993. Biogeochemical cycling of elements in rivers[M] (Ed. by P. Benes, E. Steines). London: Lewis Publishers. 268—300.
- Hart B T, B B Douglas, R Beckett *et al.*, 1993. *Hydrol Processes*[J], 7:105—118.
- Horowitz A J, 1986. *Environ Sci Technol*[J], 20:155—160.
- Juracic M, L M Vitturi, S Rabitti *et al.*, 1987. *Estuar Coast Shelf Sci*[J], 24:349—362.
- Kuwabara J S, R W Harvey, 1990. *J Environ Quality*[J], 19:625—629.
- Koike I, S Hara, K Terauchi, K Kogure, 1990. *Nature*[J], 345: 242—244.
- Laxen D P H, I M Chandler, 1982. *Anal Chem*[J], 54, 1350—1355.
- Marley N A, J S Gaffney, K A Orlandini *et al.*, 1991. *Hydrol Processes*[J], 5:291—299.
- McCarthy J F, J M Zachara, 1989. *Environ Sci Technol*[J], 23:496—502.
- Means J C, R Wijayarathne, 1982. *Science*[J], 215:968—970.
- Myers S A, D H Tracey, 1983. *Spectrochim Acta*[J], 38B(9):1227—1253.
- Orlandini K A, W R Penrose, B R Harvey *et al.* 1990. *Environ Sci Technol*[J], 24:706—712.
- Rees T F, 1991. The handbook of environmental chemistry[M](Ed. by O Hutzinger). Heidelberg: Springer-Verlag. Vol. 2, 165—184.
- Santschi P H, 1984. *Oceanogr*[J], 29:1100—1108.
- Serkiz S M, E M Perdue, 1990. *Water Res*[J], 24:911—916.
- Tanizaki Y, T Shimokawa, M Nakamura, 1992. *Environ Sci Technol*[J], 26:1433—1444.
- Wells M L, E D Goldberg, 1991. *Nature*[J], 353:342—344.
- Wells M L, E D Golderberg, 1992. *Mar Chem*[J], 40:5—18.
- Whitehouse B G, R W McDonald, K Iseki, 1989. *Mar Chem*[J], 26:371—378.
- Whitehouse B G, P A Yeats, P M Strain, 1990. *Limnol Oceanogr*[J], 35:1368—1375.