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PARTICLES IN NATURAL SURFACE WATERS: CHEMICAL COMPOSITION AND SIZE DISTRIBUTION

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The size distributions and chemical composition of particles in natural surface waters were studied using filtration and laser light scattering. An on-line tangential sequential-stage filtration system was tested using compounds of known particle sizes. With this filtration system six fractions of different particle sizes were obtained which could then be further analysed, *e.g.* by ICP-AES, resulting in the chemical composition of each particle size fraction. This technique was then applied to natural surface waters. Data were compared with parallel filtration results using three filters. In addition, the particle size distribution of several European river waters was measured by laser light scattering.

Keywords: Particles; size distribution; filtration; surface water; chemical composition

INTRODUCTION

In natural surface waters, metals can bind to particles such as clay minerals, iron- and manganese oxides and organic colloids including humic and fulvic acids. The presence of particles may result in variations with respect to the physico-chemical distribution of the trace metals with subsequent effects on their mobility and bioavailability. Therefore, in order to understand the fate of the trace metals, it is necessary to characterise the chemical composition, size, charge, and dissolution properties of the natural particles. If trace metals are bound to the particle surface, the surface area and therefore the particle size will play an important role in the binding capacity of that particle. Knowledge of the

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distribution of trace metals among the different size fractions can reflect the relative importance of these different metal species^[1].

Despite its potential for artefacts, filtration can be used to fractionate particles into fairly distinct particle size ranges. In combination with a sensitive detection technique like Inductively Coupled Plasma (ICP-AES/ICP-MS), it is possible to obtain information on the chemical composition of the various particle size fractions. Recently an on-line, tangential, sequential-stage filtration technique has been developed to separate particles with minimal artefacts^[2]. Although the applicability of this technique has been demonstrated for several aquatic humic substances^[2-5], data for natural aquatic systems are very scarce^[6-7]. This technique is promising since it should have several advantages over conventional filtration techniques including the reduction of both concentration polarisation and the clogging of the membranes.

Laser light scattering in combination with photon correlation spectroscopy (PCS) can also be used to determine the size distribution of particles in natural waters^[8-9]. Although this method does not disturb the sample, it does not isolate the fractions. The measurement procedure is fast and relatively simple to perform. Because the theory for the calculations is based on spherical particles, the interpretation of measurements for "well-defined" particles such as polystyrene latex is not difficult. Unfortunately, particles in natural systems are chemically heterogeneous and not necessarily spherical, which makes interpretation of the measurements much more difficult. A comparison of the advantages and disadvantages of filtration and light scattering is given in Table I. The techniques are generally complementary to each other since light scattering gives information on the particle size distribution in very narrow size bands whereas filtration gives information on both size distributions and chemical composition in discrete fractions.

TABLE I Comparison of the advantages and disadvantages of filtration and laser light scattering techniques

	<i>Advantages</i>	<i>Disadvantages</i>
Filtration	Proper fractionation of sample Information on particle size and chemical composition	Time consuming Sample disturbed Discrete, large fractions
Light scattering	Fast technique Sample undisturbed "Continuous" distribution (very small size fractions)	Calculations based on spheres No fractionation of sample

The aim of the research was to obtain better insight into the applicability of the combined methods for the characterisation of particles in natural aquatic systems. In this study, samples with known particle sizes and/or compositions (latex, hematite, clay and fulvic acids) were first used to test and equilibrate the filtration and light scattering equipment prior to the application of the techniques to natural surface water samples.

EXPERIMENTAL

Particle size distribution by tangential sequential-stage filtration

The filtration system used is an on-line tangential sequential-stage filtration unit, developed at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow. The system is described and illustrated in detail in Burba *et al.*^[2]. In brief, the system consists of five stages into which 47 mm diameter membranes of several pore sizes are inserted. In this filtration system, the sample flow is upwards, contrary to conventional systems. The lowest membrane in the system has the largest pore size, with the pore size decreasing as the filtrate passes from one level to the next. The sample is fed from a reservoir to the lowest stage where a portion of the sample moves in parallel to the membrane surface, *i.e.* the tangential flow, and a portion of the sample passes through the membrane, *i.e.* the filtration flow. The filtrate penetrates into the chamber of the next stage, where it is also partially filtered and partially recirculated. This process is repeated for each of the decreasing pore sizes. In principle, both the tangential flow and the successive removal of the larger particle fractions should reduce concentration polarisation and clogging of the membranes. The flow is maintained by a 6 channel peristaltic pump (Gilson Minipuls 3). At the end of the procedure, the filtration chambers are emptied with 5 mL disposable syringes. The resulting solutions were acidified with nitric acid (*supra pure*).

In Table II, the used membranes are listed. Initially, tubing (Elkay and Bran & Luebbe) with an internal diameter (I.D.) of 1.42 mm was used on the peristaltic pump. Later, this was replaced by 2.06 mm I.D. tubing in order to obtain higher flow rates and, hence, shorter filtration times.

In order to reduce trace metal contamination, the membranes were shaken with 0.01 mol L⁻¹ HNO₃ for at least 1 hour followed by a minimum of a 4 hour MilliQ water ($R > 18 \text{ M}\Omega$; dissolved organic carbon (DOC) $< 5 \mu\text{g C L}^{-1}$) rinse, with water renewal each hour. The 1 and 10 kD membranes did not resist the nitric acid treatment and thus were only thoroughly shaken with MilliQ water to remove the organic surfactant layer. The filtration system (without the mem-

branes) was flushed with $0.01 \text{ mol L}^{-1} \text{ HNO}_3$, then with MilliQ for at least 4 hours. After inserting the membranes into the filtration apparatus, the whole system was rinsed with MilliQ water overnight. The efficiency of the cleaning procedure was verified by monitoring Fe, Al, Mn, Na and DOC concentrations in the final fraction of the MilliQ rinse. If these concentrations were above detection limits, a correction was applied to the data.

TABLE II Types of membranes used with filtration system

<i>pore size</i>	<i>Brand</i>	<i>Type</i>
1.2 μm	Millipore	Mixed cellulose ester
1.2 μm	Millipore	Polycarbonate
0.45 μm	Millipore	Mixed cellulose ester
0.4 μm	Millipore	Polycarbonate
0.22 μm	Millipore	Polyvinylidene fluoride
0.2 μm	Schleicher & Schuell	Regenerated cellulose
0.05 μm	Millipore	Polycarbonate
0.025 μm	Millipore	Mixed cellulose ester
10 kD	Millipore	Regenerated cellulose, Low binding
1 kD	Millipore	Regenerated cellulose, Low binding

About 50 mL of sample solution was filtered with the filtration time depending on, among other things, the types of membranes used. Due to the size of the sample, a closed loop system was applied in the filtration procedure. This means that the final filtrate was reintroduced into the sample flow. In this way, the whole sample will pass the system allowing complete fractionation of the sample.

Particle size distributions by laser light scattering

A continuous particle size distribution was measured with a Malvern Mastersizer Microplus system with a He-Ne laser (min. 2 mW, 633 nm wavelength). The size distribution of the sample, from 50 nm to 550 μm , was calculated from the scattered light on the basis of Mie theory^[10] using the software supplied by Malvern. It should be noted that Mie theory has been developed for small, spherical particles. This implies that the size distribution of non-spherical particles will provide an approximation of the equivalent hydrodynamic radius. In addition, even where Mie theory is valid, scattering varies as a function of radius to the sixth

power. This means that in the presence of large particles, the contribution to the scattering signal by small particles will be too small to be detected^[11].

The sample (minimum volume of 80 mL) was pumped by an external dispersion unit through an internal cell. Triplicate measurements of 30 seconds each were performed. In-between measurements, the sample unit was rinsed with MilliQ water. Well-defined polystyrene latex spheres (Duke Scientific Corporation) of particle sizes of 0.084 μm ($\pm 9\%$), 1.11 μm ($\pm 1.0\%$) and 102 μm ($\pm 11.3\%$) were used to check the equipment. Our results of the two larger size standards were in excellent agreement with the data given by the manufacturer. For the smallest size standard, a slightly overestimated size of 0.11 μm was found. We assume that this small discrepancy is due to a lower accuracy near the lower detection limit of the instrument.

Particle size distributions by classical filtration

Surface water samples of approximately 10 mL were also filtered in a parallel set-up using a coarse paper filter (Schleicher & Schuell) and syringe filters with pore sizes of 0.45 μm and 0.2 μm (both from Millipore). The filters were used without pre-treatment. Blanks were carried out to check for contamination.

Analyses

Since some of the experiments were performed in Geneva and others in Bilthoven, the (fractionated) samples were analysed with respect to metals and organic matter using different but equivalent instruments. Metal concentrations were determined by ICP-MS (Geneva, Hewlett Packard 4500 ICP-MS), ICP-AES (Geneva, Perkin Elmer 1000 ICP spectrophotometer; Bilthoven, Optima XL 3000), and Flame-AAS (Geneva, Philips-Pye-Unicam SP9). Organic material was characterised with respect to (i) total organic carbon (TOC) using a Shimadzu TOC 5000 analyser (Geneva), or (ii) dissolved organic carbon (DOC) using a Skalar Continuous Flow Analyser (Bilthoven). Finally, UV absorbance of the fulvic acid solution was measured at different wavelengths, i.e. 254, 280 and 330 nm (Geneva, Perkin Elmer Lambda 2 UV-VIS spectrophotometer).

Samples

Size distribution measurements were performed on:

- i. **Several well-defined solid mineral systems, such as hematite and clay-particles** The hematite suspension was prepared (in Geneva) according

to the method of Penners and Koopal^[12] and is composed of particles of an average diameter of 70 nm at pH 3^[13]. The size distribution was measured independently using transmission electron microscopy (Zeiss EM 109) and photon correlation spectroscopy (Malvern). A Na-montmorillonite suspension, from Crook County, Wyoming, USA (Source Clays Repository, Dept. of Geology, University of Missouri, Columbia, MO, 65211, USA), was prepared by suspending the clay particles in MilliQ water with 1 mmol L⁻¹ NaCl at pH 9.6. The suspension was centrifuged at 3700 × g for at least 20 min. to remove the largest particles and aggregates. The supernatant was neutralised with HCl to near neutral pH.

- ii. **Commercially available fulvic acid** Suwannee River fulvic acid^[14] was obtained from the International Humic Substances Society. The fulvic acid solution was prepared by dissolving a few mg in 50 mL MilliQ water without further treatment.
- iii. **Dextran blue** Dextran blue (Sigma) is a dyed, globular polysaccharide with a molecular weight of about 2x10⁶ Daltons and a corresponding hydrodynamic diameter of about 80 nm^[15].
- iv. **Natural surface water samples** Surface waters were sampled in rivers and lakes in Spain, Sweden, Finland, The Netherlands and Switzerland. The chemical composition of some of these surface waters is described in more detail in Buykx *et al.*^[16]. Samples were stored at about 7°C in the dark prior to use. For the fractionation with the sequential-stage filtration system, rivers were selected for their high metal concentration (Kromme Rijn and Nant Chatillon).

RESULTS AND DISCUSSION

In this section, we first describe the discrete size distributions obtained by both the tangential, sequential-stage filtration and by classical filtration. Secondly, continuous particle size distributions measured by laser light scattering are shown. Finally, results from the different approaches are compared.

Tangential sequential-stage and classical filtration

Six filter determined fractions were obtained with the tangential sequential-stage filtration system. Analyte concentrations in each of the fractions were calculated as percentages of the original concentration in the sample. These were corrected for the amount of “dissolved” element in the fraction with the smallest particle

size, which was assumed to be present in all fractions. The mass balance was determined as the ratio of the sum of the amounts of analyte in all fractions to its initial amount in the corresponding water sample.

Hematite

For the sequential filtration of the hematite suspension, membranes with pore sizes of 1.2, 0.45, 0.2, 0.05 and 0.025 μm were used. Since the particle size of the hematite is about 70 nm, all hematite was expected in the 0.05 – 0.2 μm fraction. Contrary to this expectation, it was found that nearly all hematite was adsorbed to the first membrane (1.2 μm). This result can be explained by considering the charge of the particles, which is positive at pH 3. Since the membrane is negatively charged, the hematite particles are likely to be retained under these conditions. In another experiment, citric acid was added at a concentration of 1 mmol L^{-1} in order to modify the charge of the hematite. Electrophoretic mobility measurements confirmed that the colloids were negatively charged under these conditions. For a hematite concentration of 10 mg $\text{Fe}_2\text{O}_3\text{L}^{-1}$ at pH 5.7, the filtration process was monitored visually due to the bright red colour of the hematite. A long filtration time (6h15') was needed to obtain a clear solution in the largest particle size fraction, indicating a significant decrease in the hematite concentration. At this point in the experiment, only the 0.05 – 0.2 μm fraction was red: all other solutions were clear. Nonetheless, adsorbed hematite was apparent on the 0.05 μm , and, to a lesser extent, the 0.2 μm membranes. Fe concentrations were analysed by ICP-AES and mass balances were calculated (Figure 1). Total recovery on the filters and in the different fractions was only 60 %, with the remainder of iron losses occurring on the drainage pads behind the membranes (on the basis of visual observation) and to a lesser extent to the plexiglass system itself.

Suwannee River fulvic acid

For the filtration of Suwannee River fulvic acid (23 mg L^{-1}) membranes with smaller pore sizes (1.2 μm , 0.4 μm , 0.05 μm , 10 kD, 1 kD) were used since fulvic macromolecules are much smaller than hematite^[17]. Fulvic acid concentrations were determined by spectrophotometry at 3 different wavelengths, 254, 280 and 330 nm, which are commonly used to detect various forms of natural organic material^[18]. The amount of the Suwannee River fulvic acid in the various fractions (in %) was expressed by the ratio of measured absorbance in the particular fraction and the original sample, assuming a linear absorbance-to-concentration relationship. In addition, less sensitive, total organic carbon (TOC) measure-

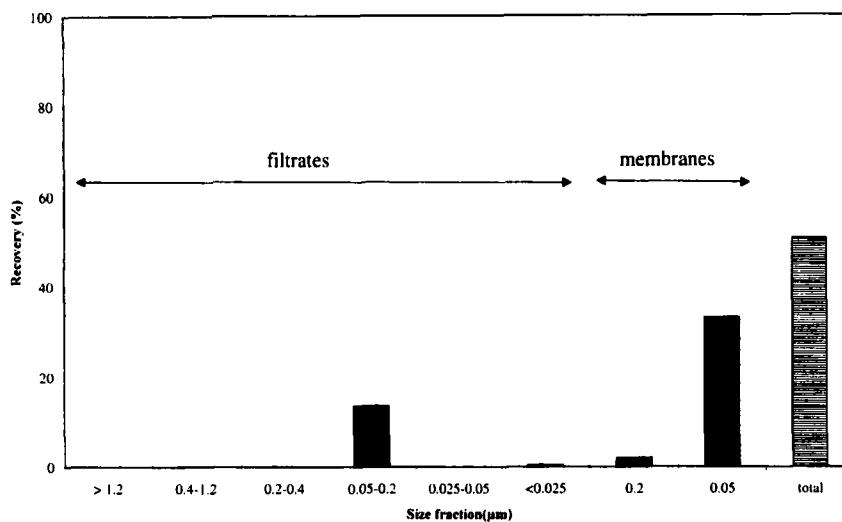


FIGURE 1 Distribution of hematite (measured as Fe) in the presence of 1 mmol L⁻¹ citric acid (filtration time 6 hrs. 15 min.)

ments were made for all of the fractions. In Figure 2, the size distribution of fulvic acid is presented using the different detection methods. The highest concentrations were found in the fraction < 1 kD, in line with the expectations^[19]. A smaller amount was found in the 1 – 10 kD fraction whereas no significant concentrations of fulvic acid were found in the remaining fractions. The fractionation pattern as observed by spectrophotometry is similar for the three wavelengths, which might indicate that the various forms of organic matter are equally distributed within the original sample. Total recovery of the UV-absorbance was 25 to 32 %. Although the recovery of TOC in the 1–10 kD fraction was similar to the data obtained by spectrophotometry (about 5 %), recovery in the < 1 kD fraction was about four times higher, resulting in a total recovery of about 100 %. At this stage, we can only speculate as to the possible reasons for this discrepancy. For instance, it is likely that the highly UV absorbing components of the fulvic acids are more hydrophobic than the bulk organic matter and thus more likely to be adsorbed to the membranes and filtration system. Furthermore, although organic carbon contamination by the membranes was not detected, the surfactants on the membrane surfaces, especially on the ultrafiltration membranes, are likely highly aliphatic and weakly absorbing. We note that contamination of filtrates by surfactants coating the membranes is a well-documented problem^[20].

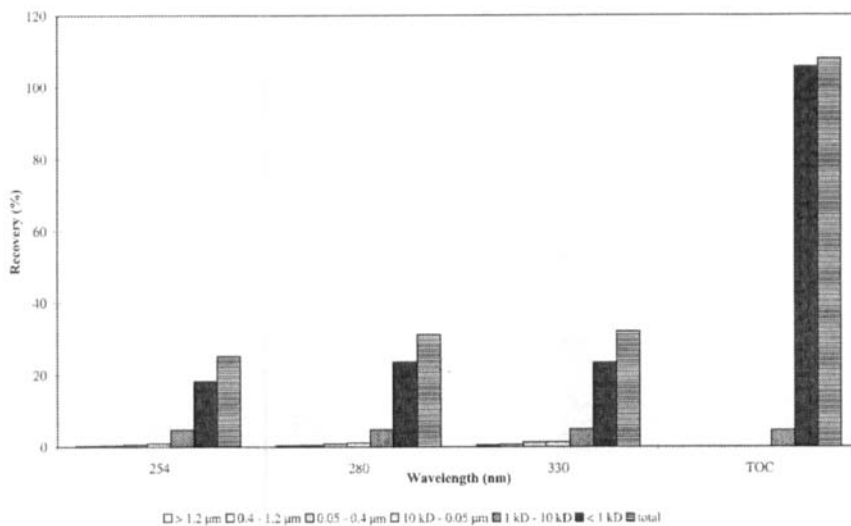


FIGURE 2 Distribution of Suwannee River fulvic acid (23 mg L^{-1} , filtration time 21 hrs. 30 min.) measured spectrophotometrically at 3 different wavelengths and as TOC

Clay minerals

In Figure 3, results for the sequential multi-stage filtration of a colloidal montmorillonite clay suspension are presented in terms of the clay components Al, Si and Fe as measured after acidification with nitric acid (pH 2) and sonication prior to ICP-AES. In a previous study, we have determined that metal concentrations measured in this manner are representative of the colloidal and dissolved elemental concentrations in the samples^[21]. In the present case, about 25% of the metals were found in the first fraction ($>1.2 \mu\text{m}$) and less than 10% in the following three fractions, resulting in a total recovery of approximately 50%. No Al, Si or Fe were found in the fractions $<0.05 \mu\text{m}$. A thin clay cake was observed on the $0.2 \mu\text{m}$ membrane and an even thicker one on the $1.2 \mu\text{m}$ membrane, which appeared to be responsible for the lower total recovery. The average particle size of the colloidal suspension as measured by photon correlation spectroscopy was 273 nm ($n=46$ measurements) with a fairly wide distribution (polydispersity index 0.451), which corresponds quite well with the distribution found within the filtrates. Furthermore, the concentration ratios of the metals appear to be similar in these 4 fractions. The results suggest that clay particles are uniform in composition but different in size.

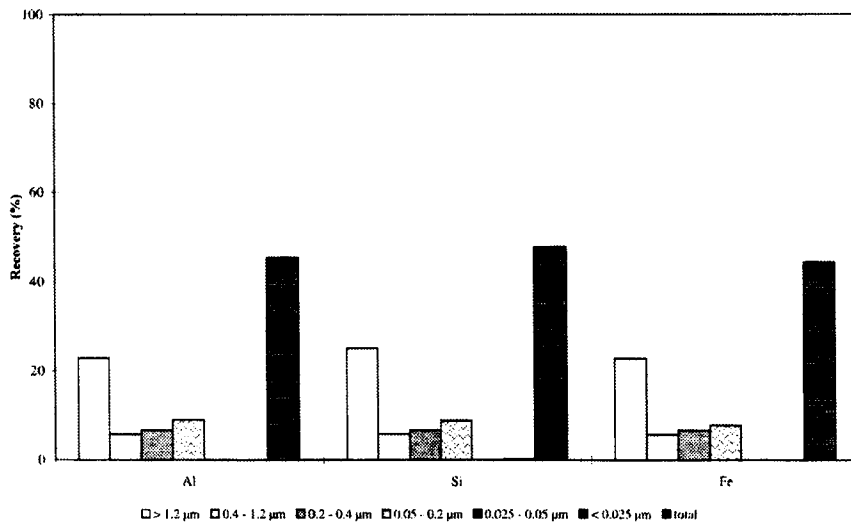


FIGURE 3 Distribution of clay particles (Na-montmorillonite) quantified as Al, Si and Fe (filtration time 11 hrs.)

Dextran blue

Additional performance characteristics of the sequential multi-stage filtration system were determined using the model compound dextran blue. Here the membranes were the same as for the fulvic acid experiment. The presence of dextran blue in the fractions was easily visible and was quantified by spectrophotometry at 620 nm. Considering the size of dextran blue (hydrodynamic diameter of approximately 80 nm), it was expected to end completely in the fraction 0.05 – 0.4 µm. Contrary to the hematite experiment, however, even after 28 hours of filtration, not all dextran blue had gone through the larger pore size membranes. The >1.2 µm fraction contained 9% of the absorbance, the 0.4–1.2 µm fraction 17% and the 0.05 – 0.4 µm fraction 63% of the original dextran blue solution. Only trace amounts of dextran blue were detected in the 10 kD–0.05 µm fraction (2%) and the 1–10 kD fraction (1%). Two explanations can be invoked to explain the presence of dextran blue in the larger size fractions: either the size distribution of dextran blue was not as narrow as assumed, or the filtration time was not long enough to obtain complete fractionation. Total recovery of dextran blue (92%) was satisfactory. The membranes were also visually clean, indicating that little or no dextran blue was adsorbed. The filtration of dextran blue indicates that when using a 1 kD membrane, very long filtration times are required to attain steady-state conditions. The filtration time was clearly dependent upon the pore sizes of the membranes, especially when using small pore size membranes.

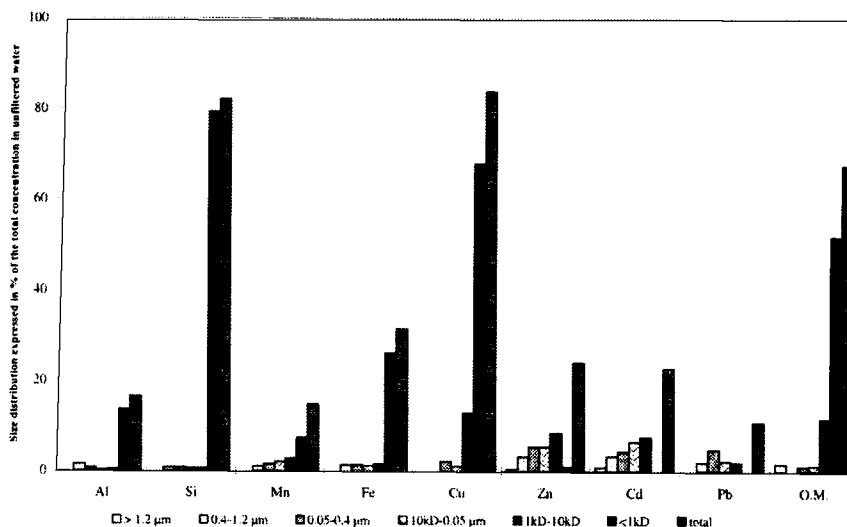


FIGURE 4 Fractionation of river Nant Chatillon (Switzerland), size distribution of several metals and organic matter (O.M.; filtration time 49 hrs. 25 min.)

Natural surface waters

The fractionation of the Nant Chatillon and Kromme Rijn rivers were examined using the 1.2 μm , 0.4 μm , 0.05 μm , 10 kD and 1 kD membranes (Figures 4 and 5). For the Nant Chatillon sample, total recovery was quite low, only Si and Cu had a total recovery >80%. Most of the Mn and Al and some of the Fe was found on the 1.2 μm membrane, but even when the metal contents on the membranes were taken into account (measured after digestion of the membranes with HNO_3), recovery of Al, Mn, Fe, Zn and Cd remained less than 100%. Some portion of these metals is probably adsorbed by the plexiglass filtration system itself. On the other hand, greater than quantitative recovery (160%) was observed for Cu when Cu on the membranes was taken into account. This was most likely due to accumulated errors of the Cu concentrations, which were near the detection limit. Cu was found mainly in the <1 kD fraction and on the 1.2 and 0.4 μm membranes. Cd was added as a spike, but its total recovery was low, as was observed for Zn. For both elements, the smaller size fractions were more important, as was adsorption to the 1.2 μm membrane. In addition, the largest amount of Pb was found on the 1.2 μm membrane with smaller amounts found on the 0.4 and 0.05 μm membranes. Organic matter measured by UV-absorbance (at 280 nm) showed somewhat lower recovery (68%), of which most was found in the <1 kD fraction. The fractionation pattern of Cu and organic matter was very similar, indicating a possible binding or complexation of Cu to organic matter^[22].

TABLE III Results of classical parallel filtration for several European rivers: Total concentrations and concentrations in the filtrates (na-not analysed, NL=The Netherlands, SF=Finland, S=Sweden)

	$\mu\text{mol L}^{-1}$				mmol L^{-1}						
	Al	Fe	Mn	Zn	Si	Ca	Mg	K	Na	DOC	
Maas	4.34	6.91	1.58	0.40	0.076	1.63	0.37	0.19	2.21	0.33	
K'veer	0.74	0.50	0.10	0.24	0.070	1.61	0.37	0.19	2.30	na	
(NL)	<0.50	<0.20	<0.04	0.20	0.069	1.62	0.37	0.19	2.21	0.34	
	<0.50	0.26	<0.04	0.29	0.071	1.62	0.36	0.19	2.20	na	
Maas	0.58	0.64	0.68	0.47	0.11	1.67	0.39	0.14	1.52	0.34	
Eysden	<0.50	<0.20	<0.04	0.36	0.11	1.64	0.40	0.14	1.64	na	
(NL)	<0.50	<0.20	0.04	0.38	0.11	1.67	0.39	0.14	1.52	0.34	
	<0.50	<0.20	<0.04	0.40	0.11	1.67	0.39	0.15	1.52	na	
Geul	1.19	3.74	2.19	6.88	0.16	2.01	0.55	0.13	1.02	0.26	
(NL)	0.65	0.74	<0.04	5.38	0.16	1.99	0.56	0.14	1.08	na	
	0.58	<0.20	<0.04	5.77	0.16	2.01	0.55	0.13	1.02	0.28	
	<0.50	<0.20	<0.04	5.91	0.16	2.02	0.55	0.13	1.02	na	
Pielinen	2.34	1.78	0.08	<0.10	0.053	0.05	0.029	0.017	0.05	0.59	
(SF)	2.10	1.20	<0.04	<0.10	0.051	0.05	0.027	0.017	0.10	na	
	1.90	1.14	<0.04	<0.10	0.051	0.05	0.029	0.016	0.05	0.61	
	1.60	1.30	<0.04	<0.10	0.053	0.05	0.030	0.017	0.06	na	
Pielisjoki	2.92	5.47	0.33	0.11	0.054	0.06	0.030	0.018	0.13	0.67	
(SF)	1.95	3.26	0.06	<0.10	0.052	0.06	0.029	0.019	0.21	na	
	1.75	2.95	0.04	<0.10	0.052	0.06	0.029	0.018	0.13	0.65	
	1.50	2.55	<0.04	<0.10	0.054	0.06	0.029	0.019	0.18	na	

	$\mu\text{mol L}^{-1}$				mmol L^{-1}							DOC
	Al	Fe	Mn	Zn	Si	Ca	Mg	K	Na			
Koitajoki (SF)	Total	2.74	4.81	0.24	0.19	0.051	0.06	0.029	0.018	0.14	0.73	
	coarse	2.33	3.31	0.06	0.11	0.050	0.06	0.028	0.018	0.19	na	
	0.45 μm	2.00	3.10	0.05	0.16	0.050	0.06	0.028	0.019	0.14	0.72	
Göta Älv I (S)	0.20 μm	1.72	2.98	0.05	0.12	0.051	0.06	0.028	0.018	0.14	na	
	Total	4.89	1.67	0.09	<0.10	0.022	0.20	0.073	0.035	0.33	0.36	
	coarse	3.35	0.87	0.05	<0.10	0.020	0.19	0.075	0.043	0.46	na	
Hiihta- Bäcken I (S)	0.45 μm	2.01	0.54	<0.04	0.14	0.017	0.20	0.072	0.036	0.33	0.36	
	0.20 μm	1.04	0.47	0.27	<0.10	0.015	0.20	0.073	0.035	0.34	na	
	Total	5.88	2.69	0.08	<0.10	0.077	0.22	0.062	0.030	0.32	0.61	
Lärjeån I (S)	coarse	5.76	2.14	<0.04	<0.10	0.077	0.21	0.067	0.081	0.39	na	
	0.45 μm	4.31	1.78	<0.04	<0.10	0.075	0.22	0.062	0.029	0.32	0.63	
	0.20 μm	3.15	1.36	<0.04	<0.10	0.074	0.22	0.062	0.029	0.33	na	
Lärjeån I (S)	Total	34.49	14.81	0.39	0.11	0.17	0.27	0.16	0.098	0.85	0.64	
	coarse	32.02	12.15	0.18	<0.10	0.17	0.27	0.15	0.107	0.91	na	
	0.45 μm	22.45	8.24	0.20	<0.10	0.15	0.27	0.15	0.096	0.84	0.61	
0.20 μm	9.07	4.03	0.05	<0.10	0.12	0.27	0.15	0.093	0.85	na		

Recoveries were low for all elements from the Kromme Rijn river except for DOC which showed a slight contamination (recovery 114 %). In this case, most of the metals were found in the <1 kD fraction except for Al, Mg and K, which were found mainly in the >1.2 μm fraction. For Al this is a reasonable result since some particles remained in this first stage even after the system was emptied (with a resulting total low recovery). The findings for Mg and K are most likely due to artefacts. For other river samples, Mg and K were always found in the fraction with the smallest pore size. Cu was mainly present in the <1 kD fraction, suggesting its association to dissolved organic matter in the same fraction, as was obtained for the Nant Chatillon sample.

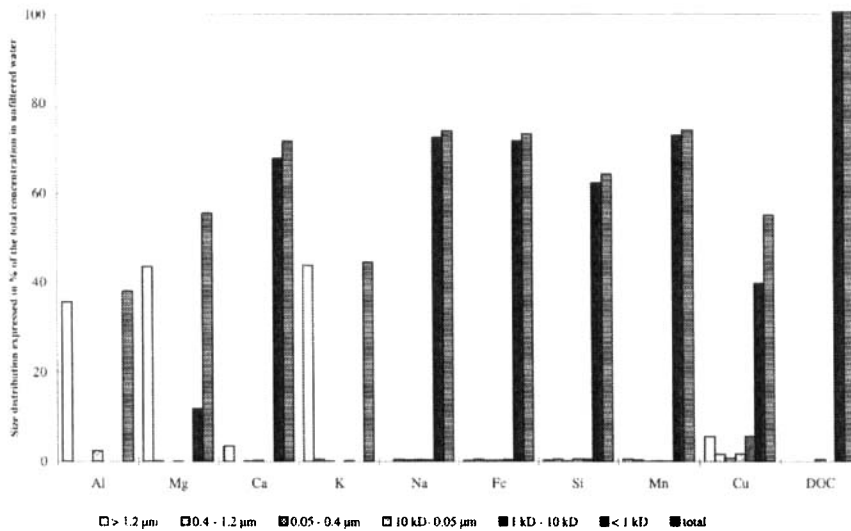


FIGURE 5 Fractionation of river Kromme Rijn (The Netherlands), size distribution of several metals and dissolved organic carbon (DOC; filtration time 40 hrs. 30 min.)

Results of the classical parallel filtration of several European surface waters over a coarse paper filter and 0.45 μm and 0.20 μm syringe filters are given in Table III. In addition, total concentrations in the samples are listed. The data show that Al, Fe and Mn are increasingly retained by the filters with concentrations in the filtrates decreasing in the order coarse > 0.45 μm > 0.20 μm . For Si, this tendency is to a lesser extent only observed for the rivers Göta Älv and Lärjeån. The observation that Ca, Mg, K and Na concentrations are similar in the filtered and unfiltered water is expected since these elements will mainly be present in their free ionic form. DOC was only measured in the filtrates of the 0.45 μm filter and was not retained, in line with the results obtained from the tangential

filtration experiments. No clear tendency for Zn can be deduced since Zn concentrations in most samples or filtrates were below or just above the detection limit. In the samples from The Netherlands, Zn seems to be partly retained by the filters. In summary, one can conclude that in the studied rivers, particles larger than $0.20\ \mu\text{m}$ contained Al, Fe and Mn, and in a few rivers, Si or Zn.

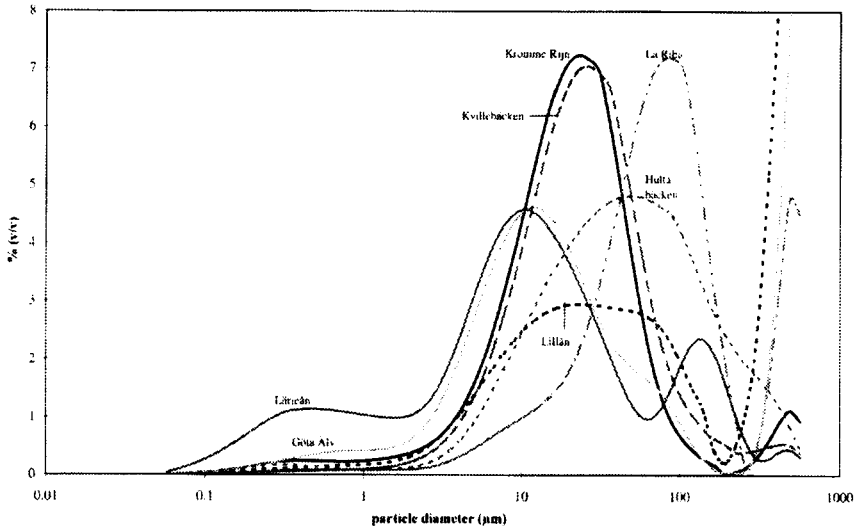


FIGURE 6 Particle size distribution in several European rivers by laser light scattering

Laser light scattering

Results of the particle size distribution obtained by light scattering of several European rivers are given in Figure 6. The size distribution is based on volume calculations. The main problem with the measurement of these samples is their small particle concentration. Nevertheless, it is still possible to compare the data from one river to another. Total concentrations of the particle-building elements Al, Fe, Mn and Ca in the samples are given in Table IV. The particle concentrations are given in two units: (i) mass concentrations obtained by filtration and (ii) a particle concentration calculated from the values obtained by laser light scattering (in % (v/v)). Most rivers have one typical particle size range with the exception of river Lärjeån (which has three: around $0.45\ \mu\text{m}$, $9.7\ \mu\text{m}$ and $125\ \mu\text{m}$). The middle size range is comparable to the pattern observed for Göta Älv. The size distribution of Kromme Rijn is comparable to that of Kvillebäcken. Hulta-Ås-Ån and Lillaån have a wider size distribution than the other rivers. In a previous study^[16], it was found that differences with respect to the chemical composition

between rivers from the same country appeared to be small, but differences between countries are obvious. Nonetheless, there is no clear trend for the samples from the different countries with respect to their particle size distributions. Among others, the source and hydrological flow of the river, erosion and run-off material are expected to contribute to the measured particle size distributions, which however, were outside the scope of the present paper. Within the detection limits of the instrument, the particle size distributions of the studied rivers fall between 3 and 300 μm . Hence, in order to obtain additional information of the smaller particles (tangential sequential-stage or classical) filtration experiments should be carried out.

Comparison between filtration and light scattering

For the Kromme Rijn sample, the particle size distribution was measured both by sequential filtration and by laser light scattering. Corresponding size bands were chosen for the particle sizer. As shown in Figure 7, the results for Al (a "particle building element") are in good agreement for the two techniques. The other elements were mainly found in the $<0.05 \mu\text{m}$ fraction, which can't be measured with the light scattering apparatus, so a comparison is not possible. For Cu, the comparison was not useful since Cu is mainly bound or adsorbed to the smallest particles, such as organic matter.

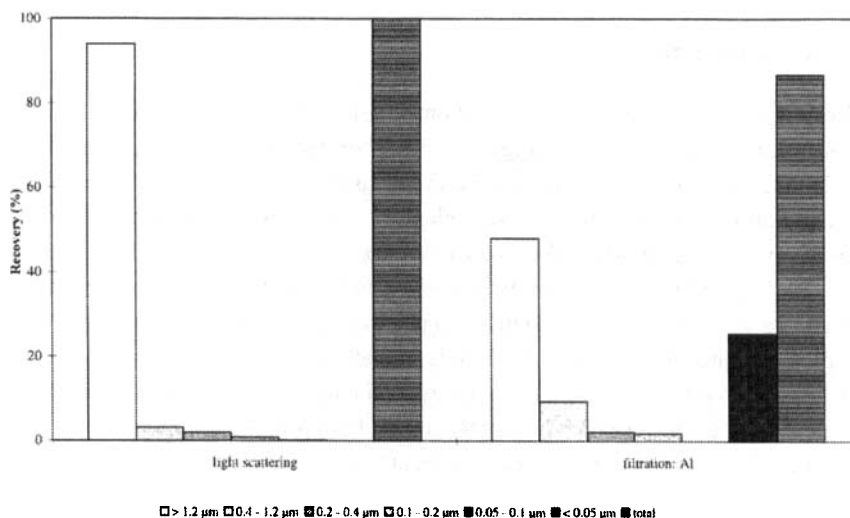


FIGURE 7 Comparison of size distribution by laser light scattering and tangential filtration

TABLE IV Characteristics of surface waters analysed by light scattering (NL=The Netherlands, E=Spain, S=Sweden)

	Al $\mu\text{mol L}^{-1}$	Fe $\mu\text{mol L}^{-1}$	Mn $\mu\text{mol L}^{-1}$	Ca mmol L^{-1}	Particle conc. > 0.45 $\mu\text{m mg L}^{-1}$	Particle Conc. % (v/v)
Kromme Rijn (NL)	5.36	8.93	1.61	1.72	30.6	0.0068
La Riba (E)	18.96	0.44	4.21	2.52	15.4	0.0039
Göta Älv II ^a (S)	6.20	3.61	0.22	0.20	4.8	0.0009
Lillån (S)	1.46	7.62	0.62	0.23	3.1	0.0017
Lärjeån II ^a (S)	51.61	40.22	1.45	0.23	34.7	0.0025
Hultabäcken II ^a (S)	10.09	17.83	1.32	0.14	10.2	0.0020
Kvillebäcken (S)	3.01	18.49	6.08	1.11	10.0	0.0047

a. Samples II were collected at a later stage than samples I in table III

CONCLUSIONS

Tangential sequential-stage filtration

Filtration results are in good agreement with expectation based on known particle size distributions of well-defined systems. Further development of the filtration system is necessary in order to reduce adsorption and contamination of membranes and equipment. With a 1 kD membrane in the system, filtration times to attain equilibrium are very long (>30 hours) which could lead to important modifications of the sample. With this filtration system, six separate size fractions can be obtained which can be analysed further.

Compounds of a known particle size can be employed to calibrate the system in order to determine the optimal filtration time for a complete fractionation with a given set of membranes. Coloured materials (*e.g.* hematite and dextran blue) may be of help, because the fractionation process can be followed visually.

In natural samples, Al, Fe and Mn are mainly present in the larger particle size fractions. Mg, Ca, K and Na are found in the smallest fractions, likely representing their ionic forms. Cu and DOC are often found together in the "dissolved" (<1 kD) fraction, suggesting that Cu may be bound to organic matter.

Laser light scattering

Although this technique is very fast and simple to operate, no fractionation of the sample is obtained, as is the case for the tangential sequential-stage filtration system. On the other hand, no sample perturbation occurs. For natural river systems, particle concentrations are generally very low, which limits the reliability of the particle size distributions. Another complication is that calculations are based on the equivalent diameters for spherical particles, which is seldom the case in natural river waters. In spite of these complications, the results suggest that different rivers may be compared with each other and that particles are important in a variety of rivers from a broad spectrum of geographical regions. For natural samples, good agreement was obtained between observed particle size distributions (>0.05 μm) obtained by laser light scattering and tangential filtration.

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