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Department of Chemical Engineering

Charge and Size of Particles in Surface Waters

Master's Thesis by

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Picture on front page:

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1. Surface water, jar tests of surface water, the cell for zeta potential measurements and the instrument Malvern Nano ZS.

   Photo: A. Peternelj

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SUMMARY

Size and surface charge of small particles in natural surface waters has been studied in the literature and in the laboratory by the instrument Malvern Nano Zetasizer. Also the effect of pH on surface charge of particles was measured and furthermore the size and charge of particles in water treated with aluminum sulfate.

According to literature surface waters contain particles with a broad size range. The size distribution of the particles (PSD) in natural water usually follows power law distribution (Pareto's law). With decreasing size of particles the number of the particles is increasing exponentially.

The surface charge of particles in surface waters is negative and the charge usually become less negative with decreasing pH. Since the particles have negative charge they repel each other and remain suspended in water for long time. The surface charge of particles in natural waters also depends on the composition of particles (mineral detritus, organic detritus or a living cell), the concentration of positively charged ions in the water (particularly Ca^{2+}, Mg^{2+}) and the DOC-concentration of the water. The negative charge of some particles in surface waters is often caused by coating of negatively charged natural organic material onto the particles.

The size and charge of particles was measured in five surface waters. Some waters were pH adjusted and the charge of the particles was measured. Also the effects of different doses of aluminum sulfate on size and zeta potential of particles in water was evaluated. The charge of particles was measured as zeta potential (mV).

Malvern Nano Zetasizer uses dynamic light scattering (DLS) for measuring size and laser doppler velocimetry (LDV) for measuring charge of particles. It can measure the size of particles in a size range 0.6 nm – 6 µm and the charge of particles in a size range 5 nm – 10 µm.

In size measurements DLS measures the Brownian motion of the particles which is related to the size of them. The sample is illuminated by a laser beam and the intensity fluctuations in the scattered light are analyzed. Brownian motion is a random movement of particles caused by thermal motion of molecules of the liquid in which particles are suspended. Larger particles are moving slowly and the intensity of the scattered light will also fluctuate slowly. On the contrary the small particles give greater fluctuations.

Most size measurements did not fulfill Malvern's Quality Criteria. Dynamic light scattering (DLS) is not a suitable method for measuring sizes of particles in samples with a broad particle size distributions. When the DLS is used in studies of surface waters the sample should be fractionated in order to make PSD narrower. Fractionation could be performed by filtration or centrifugation. However, such pretreatment methods were not developed in this study. DLS also assumes that particles are spheres and that is seldom the case in surface waters.

The charge of the particles was determined by subjecting the particles to electric field and measure their velocity.

The measurements of zeta potential of particles in water samples were possible, but the repeatability was not always good. The zeta potential of particles in the studied water samples was between approximately -16 mV and -22 mV. Hard water had a less negative zeta potential than the soft waters. The zeta potentials became less negative with decreasing pH.

The zeta potential of particles after having added aluminum sulfate to the water became less negative with increasing doses of added aluminum sulfate.

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Lund, January 2009

Andreja Peternelj

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1 INTRODUCTION

1.1 Background

In many parts of the world it is common to produce drinking water from surface water taken from a river or a lake. Before distributing water to the citizens, the impurities in the source water have to be removed.

Impurities in natural surface waters can be divided in two main groups, suspended matter and dissolved matter. Suspended matter are microorganisms and other particles, while dissolved matter are for instance humic substances, giving water the characteristically light brown color. Often the surface water is chemically treated by adding metallic salts, e.g. aluminum sulfate. The impurities in surface waters are usually having a negative charge; they are repeling each other and remaining suspended in water for a long time. After adding a metallic salt with di- or trivalent positively charged ions, the impurities can aggregate and sediment or be removed by flotation. Additionally the positive ions of the metal salt will precipitate the dissolved matter in water.

Kemira Kemi AB in Helsingborg is producing chemicals for drinking water treatment, as well as developing and researching on chemicals for drinking water treatment. Despite of many years of experiences and research on drinking water chemicals there are still some unknowns and challenges remaining. Like for instance the knowledge about size and charge of particles and molecules after chemical water treatment. The initiative for this master thesis came from this lack of knowledge.

When treating water with aluminum or iron salts, the pH of the treated water will be reduced. The extent of the pH reduction depends on the type and amount of salt added and the buffer capacity of the water. The charge of particles in water depends on the pH. With decreasing pH the surface charge will be less negative and that could possibly lead to coagulation. Therefore the question is if some particles are removed only as a result of pH decrease and not because of metal ions, and in such case how big are the particles which coagulate only because of pH decrease.

Furthermore it should be studied how some metal salts, commonly used in drinking water treatment, affect size and charge of particles in water. Are there small or larger particles coagulating first and is this effect different for various metal salts and with different doses?

Malvern Nano Zetasizer, an instrument available at Kemira Kemi Helsingborg, can measure the size of particles in a size range 0.6 nm – 6 µm and the charge of particles in a size range 5 nm – 10 µm, by dynamic light scattering method. This instrument could be used for the studies mentioned above and this possibility is evaluated in the current master thesis.

1.2 Objectives

There are three main objectives with this master thesis:

1. To measure the size and surface charge of small particles in surface water samples by the instrument Malvern Nano Zetasizer.
2. To measure the effect of pH on surface charge of particles in surface waters.
3. To measure the size and charge of particles in surface water treated with aluminum sulfate.

1.3 Limitations

A lot of work was put into trying to understand how to make a good measurement with Malvern Nano Zetasizer and how to interpret the results of the measurements. Because of a lack of experience with this kind of measurements the experimental course of events was not optimal and there was some uncertainty in performing the measurements and interpreting the results.

1.4 Thesis outline

This report starts with a short description of the origin and nature of particles in surface waters and continues with detailed literature review of the size and charge of particles in surface waters. Several methods for measuring particle size are described, but the focus is on dynamic light scattering, a technique used by Malvern Nano Zetasizer. The section for surface charge of particles introduces zeta potential concept and how it is measured. Also results of various studies of zeta potential of particles in surface waters are shown.

The experimental part of this study describes the water samples used and how the measurements of surface charge and size of particles were performed. Furthermore it is explained how the pH of samples was adjusted and how the jar tests with aluminum sulfate were carried out. Repeatability of the measurements and ageing of water samples are also included in the practical part which is concluded with the results and discussion.

Finally conclusions and recommendations for future work are given.

2 PARTICLES IN SURFACE WATERS

2.1 Origin and nature

Aquatic particles are of many different kinds and origin, and have sizes over a very wide range. Studies of particles in water are challenging because besides the large variety among them they are also involved in many different chemical and physical processes. When producing drinking water particles can be seen as impurities in natural waters.

Contaminants in surface waters are humic substances, mineral particles, organic contaminants, bacteria, viruses, parasites and algae (Gillberg et al., 2003).

Weathering of rocks and soils via runoff is the main source of impurities in natural waters. However a very important group of constituents of natural waters is also aquatic life. Furthermore in many cases human activities are a significant contributor of contaminants, especially by discharging domestic and industrial wastewaters to the surface waters (Gregory, 2006).

Water is a good solvent and the majority of dissolved matters in water are inorganic salts (90 % of all dissolved matter in most fresh waters). However on the other hand there are also relatively insoluble substances in water, i.e small particles which remain suspended for days or weeks. Suspended particles in natural waters can be divided in three main groups:

- Inorganic
- Organic, including macromolecules
- Living and dead organisms (Gregory, 2006).

Inorganic suspended particles are principally a product of natural weathering processes. In this group there are clays (like kaolinite and montmorillonite), oxides (for instance various iron oxides), silica, calcite and several other minerals.

Organic matter origins mainly from biological degradation of plant and animal remains (Gregory, 2006). These impurities are called natural organic matter (NOM) and are measured as total organic carbon (TOC). Soluble components of NOM, mainly humic substances are defined as dissolved organic carbon (DOC). 10-20% of the DOC is present as polysaccharides and 5-10% of the DOC is present as proteinaleous compounds. The rest and the major proportion of DOC in natural waters are humic and fulvic acids giving the water yellowish-brown color. Organic molecules can be quite large (macromolecules) and in some aspects they can be considered as particles as well. Nevertheless cell debris is an example of “real” organic particles (Gregory, 2006).

Although different forms of aquatic life are some kind of “particles” in water, usually only single-celled microorganisms are classified as particles. In order of increasing size these “living particles” are viruses (even though they are not cells), bacteria, algae (also diatoms) and protozoa (Gregory, 2006). They are present in water as single cells or as larger colonies.

Several kinds of microorganisms in surface waters are pathogenic and have to be removed in drinking water treatment otherwise such water would be hazardous to human health. Furthermore the particles in surface waters have relatively high surface area and they absorb contaminants from water, as for instance humic substances or heavy metals, which are also not wanted in drinking water.

2.2 Size of particles

The description of particle size measuring is based on Gregory (2006).

2.2.1 Background theory for measuring particle size

Particles can be transported in water by convection, diffusion or sedimentation (Gregory, 2006). The movement of particles with water flow is called convection whereas diffusion is a result of Brownian motion and sedimentation is result of gravity.

Convection (fluid drag)

When a particle moves in a fluid it undergoes a drag force, F_D. The drag force is a product of a force term and a dimensionless *drag coefficient*, C_D. The force term is the dynamic pressure ($\rho_L U^2/2$) multiplied by an effective area of the particle, S:

$$F_D = \frac{1}{2}\rho_L S U^2 C_D$$

Where ρ_L is the density of the fluid and U is the velocity.

Furthermore the drag coefficient, C_D, is a function of Reynolds number, Re:

$$\mathrm{Re} = \frac{\rho_L l U}{\mu}$$

Where l is a characteristic length (as for instance the diameter of a spherical particle) and μ is the viscosity of the fluid.

It is important to choose an appropriate effective area, S, especially if particles have asymmetric shapes, like fibers (Gregory, 2006). S can be defined as the projected area of the particle on a plane normal to the direction of flow. For a sphere with diameter d, S would be $\pi d^2/4$. Low Re values means that viscous effects dominate over inertial effects and flows are “in order” and laminar. When fluid velocity or the size of particle increases the Reynolds number increases also and inertial forces becomes more important than viscous effects. This leads to vortices and to turbulence.

When $\mathrm{Re} < 0.1$ the drag coefficient of a sphere is:

$$C_D = \frac{24}{\mathrm{Re}}$$

and this formula is usually useful for most particles in natural waters. However when Re is 1-100 this formula is of interest:

$$C_D = \frac{24}{\mathrm{Re}} + \frac{6}{1+\mathrm{Re}^{1/2}} + 0.4$$

Diffusion

Particles of a few microns in size or less are in constant random motion, some kind of endless “jiggling” (Gregory, 2006). It is called *Brownian motion* and can be observed in microscope. This random movement of particles is caused by thermal motion of molecules of the liquid in which they are suspended. Water molecules are in continuous chaotic motion because of their kinetic energy, and they constantly collide with the particles suspended in water. The kinetic energy is passed on to the particles and that results in Brownian motion. In average water molecules hit the particles in all directions, but under a very short time more molecules will hit from one side which gives the particle a “kick” in one direction.

In a given time, t, the particle will move a certain distance from its starting point, as described in the following equation:

$$\bar{x} = \sqrt{2Dt}$$

where D is the *diffusion coefficient* of the particle. The diffusion coefficient of a spherical particle, with a diameter d, is described by *Stokes-Einstein equation*:

$$D = \frac{k_B T}{3\pi d\mu}$$

where k_B is the Boltzmann constant and T is the absolute temperature.

Diffusion is very significant phenomena for colloidal particles and it is important for particle aggregation (Gregory, 2006).

Sedimentation

Particles in water undergo gravitation which causes their movement. However this motion is retarded by fluid drag, i.e. convection. The gravitational force depends on the particle volume and the difference in density between the particle and fluid. Gravitational force for a sphere is given by this equation:

$$F_g = \frac{\pi d^3}{6}(\rho_S - \rho_L)g$$

where ρ_S is the density of the particle and ρ_L is the density of the fluid. At very low Reynolds numbers (i.e. for small particles) the sedimentation velocity is calculated with the Stokes law:

$$U = \frac{gd^2}{18\mu}(\rho_S - \rho_L)$$

Diffusion and sedimentation differ greatly in their dependence on particle size. The characteristic time for a particle to move a distance equal to its own diameter is for diffusion much shorter than that for sedimentation when particles are small (Gregory, 2006), see Figure 1.

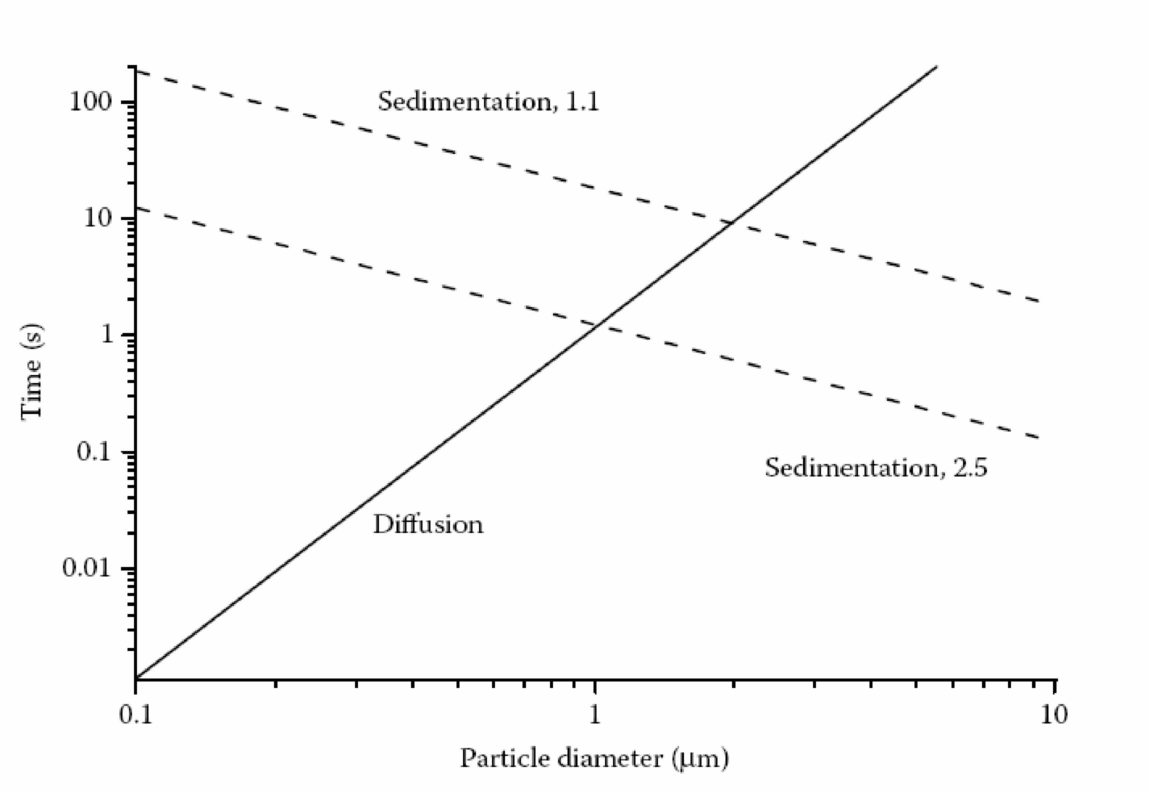


Figure 1. Characteristic diffusion or sedimentation times needed for a particle to move a distance equal to its own diameter, as a function of particle diameter. Sedimentation is shown for particles having density 1.1 and 2.5 g/cm^3. (Gregory, 2006. With permission).

The crossover point of the lines in the Figure 1 above depends on the particle density. Usually is this point of the order of 1µm. For smaller particles, i.e. particles below this crossover point, diffusion is more important than sedimentation and therefore these particles tend to remain in suspension. This is one explanation why 1 µm is normally taken as the upper limit of the colloidal size range (Gregory, 2006).

Light scattering and turbidity

When a suspension of particles is illuminated by a light beam some light is scattered and some adsorbed, and that results in a reduced intensity of the transmitted beam.

In some cases adsorption of light by particles in water may be significant but this will not be discussed here because it is complex. Light scattering is generally a more important effect. All particles in water are scattering light and that does not cause any net loss of energy from the beam. A light beam "hitting" a particle induces displacements of electrons and hence fluctuating dipoles within the particle. As a consequence the energy is radiated in all directions at the same frequency as the incident radiation. The interference of the radiated and incident light result in the observed scattering behavior. The *polarizability* of the material and hence on the *refractive index* are the characteristics which affect the intensity of the induced dipoles. The only condition for light scattering is that the particle has different refractive index than water (Gregory, 2006).

Water containing particles is not clear and it is more or less cloudy. This cloudiness of water is called turbidity. Turbidity is a direct consequence of light scattering and it can be measured in two different ways. One way is to measure a reduction in intensity of the transmitted light and the other way is to measure an increase in scattered light intensity at a chosen angle (often 90 degrees) to the beam.

Light scattering depends on the size of the particles, their shape and their refractive index (Gregory, 2006).

Light transmission

According to the *Beer-Lambert law*, the intensity of the transmitted light depends exponentially on the concentration of particles in a suspension and the optical path length, L:

$$I=I_0 \exp(-NCL)$$

Where I is the intensity of light transmitted through the suspension, I_0 is the intensity of the incident light (i.e. the intensity of light transmitted through a fluid without any particles), N is the particle number concentration and C is the *light scattering cross-section* of a particle, i.e. an area of the incident beam that is "blocked" by a particle. Beer-Lambert law does not depend on the assumption that all the particles have the same size, but it is convenient to assume that (Gregory, 2006). Light scattering or adsorption by the fluid or the optical cell is considered under I_0.

The Beer-Lambert law can also be written like this:

$$\ln(\frac{I}{I_0}) = -NCL$$

Or in terms of turbidity, τ:

$$\tau = NC$$

This equation is valid if all particles have the same scattering cross-section, otherwise this equation has to be used

$$\tau = \sum N_i C_i$$

These equations are useful for turbidity measured by transmission. For turbidity obtained from measurements of scattered light there are no equivalent definitions, and calibration standards have to be used (Gregory, 2006).

2.2.2 Measuring particle size

Particle size can be determined by various measuring techniques. None of the methods for determining particle size covers all size ranges and a suitable method has to be chosen depending on the nature of the suspension. The problem of particle shape is a big issue when determining particle size. A very convenient way is to report particle size as a single diameter, as "an equivalent diameter". In case of a nonspherical particle this does not give any information of the true shape (Gregory, 2006).

Direct methods (microscopy)

Microscopic observation is an old and the most direct method of determining particle size and shape (Gregory, 2006). The sample is viewed at some magnification and the size of individual particles is examined by comparing them to a suitable scale or by using an automated image analysis method.

Optical microscopy is limited by the wavelength of visible light and discerning particles that are smaller than about 1µm is difficult. Reliable particle sizes can be obtained only for particles larger than about 5 µm (Gregory, 2006). *Ultramicroscope* can resolve smaller particles, although deriving reliable particle size is remaining a problem. Ultramicroscope is basically a light scattering method, using dark-field illumination, where particles are seen as points of light against a dark background.

In *confocal laser scanning microscope* a small sample is illuminated by a laser beam. The suspension sample is scanned point by point and layer by layer and the scattered light is monitored by a detector, resulting in a three-dimensional image. This microscope gives a much higher resolution than a conventional light microscope (Gregory, 2006).

Electron microscope is capable of a much higher resolution than an optical microscope. Errors introduced by sample preparation are possible (Gregory, 2006). There are two main sorts of electron microscopy, *transmission electron microscopy (TEM) and (SEM).* TEM provides observation of fine structures down to nanometer level (Perret et al., 1994). SEM can not provide observations on so small particles but it can give information on the 3D structure of the sample. TEM is a frequently used method when studying particles in natural waters.

A great advantage of direct microscopic observation is that particle shapes can be examined in details, but anyway usually particle size is reported as an equivalent diameter. Gregory (2006) describes three possible ways of reporting equivalent diameter (see Figure 2):

- *The projected area diameter:* the diameter of a circle having the same area as the projected area of the particle.
- *The Feret diameter:* the perpendicular distance between two parallel tangents, in a fixed direction, to the projected outline of the particle.
- *The Martin diameter:* the length of a chord, in a fixed direction, dividing the project area into two equal parts.

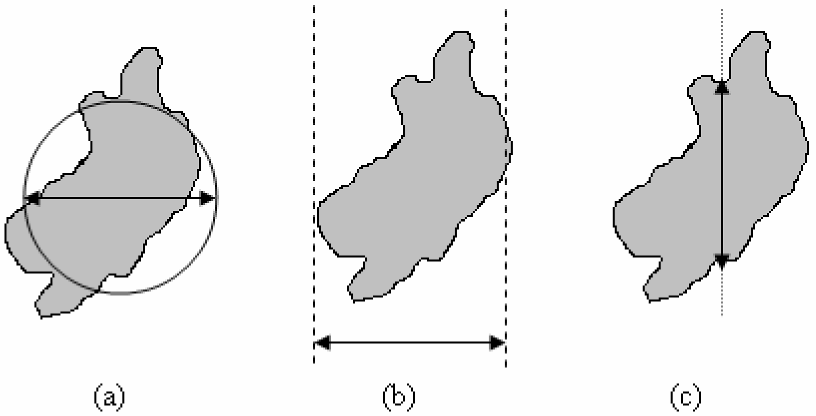


*Figure 2. Three possible ways of deriving a "equivalent diameter" while viewing nonspherical particles under a microscope. **(a)** Project area diameter (the diameter of a circle having the same area as the projected area of the particle; **(b)** Feret diameter (the perpendicular distance between two parallel tangents, in a fixed direction, to the projected outline of the particle); **(c)** Martin diameter (the length of a chord, in a fixed direction, dividing the project area into two equal parts). (modified Gregory, 2006)*

Particle counting and sizing

In some instruments particles are passing one by one through a zone where their presence can be detected by a sensor. The detector gives response on particles as a series of pulses which can be counted. The pulse height is dependent on size of the particles in case when the sensor response depends on particle size (Gregory, 2006).

When measuring particles by this technique it is important that particles are passing the sensing zone one by one, otherwise two or more particles could give only one pulse and they could be interpreted as one (larger) particle (Gregory, 2006). This is called *coincidence effect* and it is possible to correct it by a statistical method. However it is better to ensure that sample is sufficiently diluted. When the sample has to be diluted in high degree, changes in particle size distribution are possible, especially for aggregated particles.

Two commonly used detection techniques in particle counting are:

- Electrical sensing zone (electrozone)
- Optical sensing zone (light scattering).

Both have advantages and disadvantages. Electrozone counters are commercially available as *Coulter counter*. They are based on a principle developed by Wallance Coulter. Its main concept is that particles in an electrolyte solution cause a momentary change in electrical resistance when they are passing through an orifice. That gives a voltage pulse, provided that the basic voltage between the two electrodes is maintained constant. The electrodes sit on both sides of the orifice and when a particle is passing through, a volume of electrolyte equal to the particle volume is displaced. The obtained voltage pulse is proportional to particle volume.

The Coulter technique has been widely used, as for instance for rapid counting of blood cells. It can count 5000 or more particles per second and discern small differences in size.

An important advantage of electrozone method is that it is almost independent of the shape or composition of the particles. The obtained pulse depends only on the volume of the particle (Gregory, 2006). For an aggregate the pulse height is proportional to the sum of volumes of particles in the aggregate, excluding the included liquid in the aggregate. However the aggregate can break when passing through the orifice, because of possible high shear rates.

The samples are often diluted with a particle-free salt solution (usually 2% NaCl) and that may affect the colloidal stability of particles, resulting in their aggregation. However the sample has to be diluted to a very low concentration, i.e. under 10^6 particles/mL, and aggregation is very slow at such low particle concentrations.

The electrozone method measures only a narrow range of particle sizes. In order to get reliable detection of particles, the orifice diameter may not be larger than 50 times the particle size. Furthermore is the electrozone technique not optimal for colloids because it has difficulties in monitoring particles smaller than about 0.5 μm. Orifice blockage can also be a problem, especially for particles larger than about 40% of the orifice diameter. Thus, for measuring the size range of 1-20 μm, a 50-μm orifice is needed. In case of wider size ranges 2 or more orifices have to be used which makes the measurements less convenient (Gregory, 2006).

The second commonly used detection technique for particle counting and sizing is light scattering. Particles are one by one passing through a focused light beam, usually a laser beam, and subsequently either the transmitted light or scattered light intensity is measured. When a particle is passing through the beam the intensity of the transmitted light is reduced while the intensity of the scattered light is increased. The smallest particle size that accurately can be measured is around 1 µm when measuring transmitted light (*light blockage method*) and around 0.2 µm when measuring scattered light (Gregory, 2006). Light scattering depends on refractive index of particles which is very influenced by the shape and composition of the particles. This means that the results obtained are difficult to interpret for natural waters or other suspensions with particles of various compositions.

Another method for counting and sizing particles is *focused beam reflectance measurement* (FBRM). A suspension of particles is illuminated by a laser beam which is projected into the sample through a window. The laser beam is focused to a small spot close to the window and this spot is rotating at high speed (approx. 2 m/s). When a particle passes by the window, some of the light of the focused beam will be backscattered. From the backscattered light and the speed of the rotating light spot the particle size can be derived. FBRM can measure particles over the size range (0.5 µm – 2.5 µm), the suspensions can be more concentrated compared to techniques described above and particle properties do not affect the result as in the case of light scattering techniques (Gregory, 2006).

An important advantage of the particle counting and sizing methods is that these methods derive particle size distribution directly, without any assumptions about the form of the particle distribution (Gregory, 2006).

Static light scattering

Particle size can be studied by measuring scattered light as a function of scattering angle, but it is difficult to derive information on the size distribution out of the scattered light. Usually a mathematical form, as for instance the log-normal distribution, is used as an assumption and fitted to the experimental scattering data (Gregory, 2006).

Light-scattering methods need also the refractive index of particles which means that the suspensions have to be of the same material (Gregory, 2006).

Fraunhofer diffraction

A spherical particle, much larger than the light wavelength, i.e. much larger than 750 nm, can be seen as a circular disc in the light beam. The diameter of the disc is the same as the diameter of the sphere. Light diffracted at the edge of the disc gives a characteristic pattern of light and dark rings called *Fraunhofer diffraction*. These light and dark bends are observed at a plane far from the particle and they represent maxima and minima in the intensity of the diffracted light. The positions of the bends are a function of the light wavelength and the particle diameter and they are not dependent on other particle properties (Gregory, 2006).

Optical wavelengths and particles larger than 10 µm give bands at low angles. Fraunhofer theory is not applicable for small particles, i.e. particles being smaller than the light wavelength (Gregory, 2006).

Sedimentation methods

Techniques based on sedimentation methods are used widely. Sedimentation rate in diluted solutions is dependent on particle size and therefore it can be even used for size determination. The particle size obtained by such method gives equivalent Stokes diameter. The methods using gravitational settling measure particles larger than a few µm. Small particles settle too slowly. However the sedimentation technique can be used for submicron particle size if a centrifugation technique is used (Gregory, 2006).

Photosedimentation device combines gravitational settling with light transmission measurements. To obtain particle size, the density and light-scattering properties of particles have to be known (Gregory, 2006).

2.2.3 Dynamic light scattering (DLS)

The description of dynamic light scattering is based on Malvern user manual (2005).

Dynamic light scattering (DLS), also called *photon correlation spectroscopy (PCS)* or *quasi-elastic light scattering (QELS)* (Gregory, 2006), is based on Brownian motion and it measures this random motion of small particles. The extent of Brownian motion is related to the size of the particles. When a small particle is illuminated by laser light, the light is scattered in all directions. In a sample there are thousands of particles and not only one. Let us consider that these particles are stationary and that there is a screen close to these particles. The screen would be illuminated by the scattered light and the speckle pattern would consist of areas of bright light and dark areas without any light detected. Where the light scattered by the particles arrives at the screen with the same phase and interferes constructively, it forms the bright areas of light on the screen. Where the phase additions are mutually destructive and cancel each other out, the dark areas appear. As the particles in the sample were considered to be stationary, this means that even speckle pattern would be stationary, i.e. having retaining the same speckle position and size.

However particles suspended in a liquid are never stationary and they are constantly moving due to Brownian motion. DLS technique makes use of the fact that small particles move quickly and large particles move slowly. The relationship between the size of a particle and its speed of movement due to Brownian motion is defined by Stokes-Einstein equation (Malvern, 2005):

$$D = \frac{k_B T}{3\pi d \mu}$$

Since the particles are constantly moving the speckle pattern will also appear to move and the intensity appears to fluctuate. Malvern Nano Zetasizer which has been used in this master thesis measures the rate of the intensity fluctuation and from this it calculates the size of the particles. In the instrument there is a component which is called a *digital correlator*. A correlator basically measures the degree of similarity between two signals over a period of time (Malvern, 2005).

For instance when the intensity signal of a particular part of the speckle pattern at time t is compared to the intensity signal a very short time later, $t + \delta t$, it can be seen that these two signals are very similar, i.e. strongly correlated. If the original signal is then furthermore compared to an even later signal ($t + 2\delta t$) the comparison would still be relatively good, but not as good as in $t + \delta t$. Hence the correlation is reducing with time (Malvern, 2005).

If the intensity of the signal at time t is compared to the intensity at a much later time, the signals would not have any relation to each other because the particles have been moved in random direction due to the Brownian motion. After a certain time has passed there is no correlation between the signals (Malvern, 2005).

Perfect correlation is when signals are identical (Malvern, 2005). In the Figure 3 below a typical correlation function is shown. It can be seen that perfect correlation is reported as 1 and no correlation as 0.

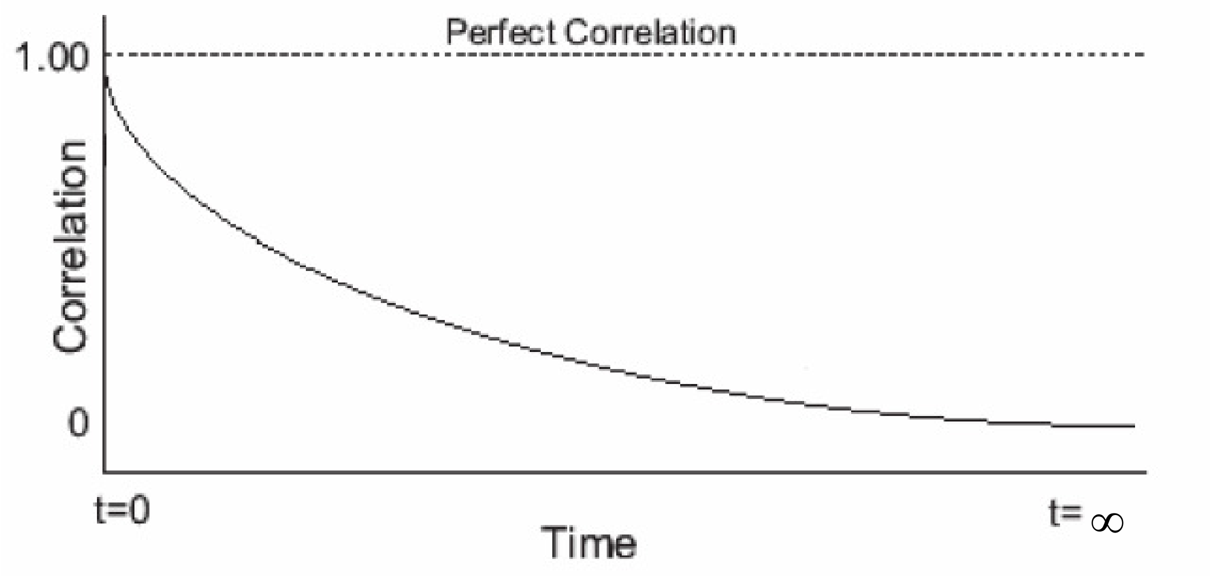


Figure 3. Correlation function over time scale. At 1 there is a perfect correlation and with time the correlation will be approaching 0 because after some time has passed there will be no correlation left. y-axis shows correlation. (Malvern, 2005. With permission).

DLS technique is dealing with extremely small time scales (Malvern, 2005). The time it takes for a correlation to reduce to zero is in order of 1 to 10´s of milliseconds. The “short time after time t” (*t* + *δt*), when correlation is still over zero, is in order of nanoseconds or microseconds.

Next step is how to use the correlation function to obtain particle size. As mentioned before, according to Stokes-Einstein equation the speed of particles being moved by Brownian motion is related to the size of the particles. Large particles move slowly and small particles move quickly. This will affect the speckle pattern in the following way:

- Large particles are moving slowly and the intensity of the speckle pattern will also fluctuate slowly
- Small particles are moving quickly and than the intensity of the speckle pattern will fluctuate quickly (Malvern, 2005).

In the Figure 4 the correlation functions for large and small particles are shown.

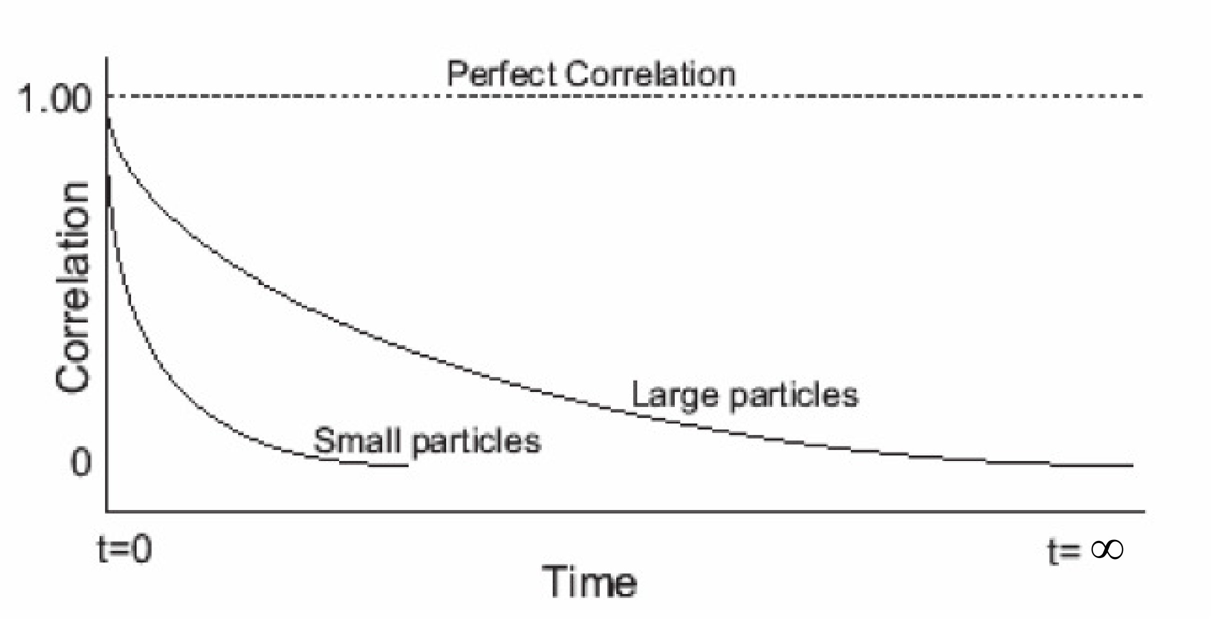


Figure 4. The correlation function for large and small particles. y-axis shows correlation. (Malvern, 2005. With permission).

According to Figure 4 above the rate of decay for the correlation function is related to particle size and the rate of decay is much slower for larger particles than for small ones.

When the correlation function has been measured it is used to calculate the size distribution. The software in the instrument uses algorithms to extract the decay rate for a number of size classes to produce a size distribution. In this way the intensity distribution is obtained. The graph of intensity distribution shows the relative intensity of the scattered light as a function of particle size. Thus fundamental size distribution generated by DLS is an intensity distribution. The intensity distribution can be converted to a volume distribution, by using a very advanced theory, called Mie theory. The volume distribution can be further converted to number distribution but the last one is of very limited use since small errors in gathering data for the correlation function will result in huge errors in distribution by number (Malvern, 2005).

Dynamic light scattering is not suitable for polydisperse samples because derivation of particle size is mathematically difficult in that case. Commercial instruments usually report a mean size of particles in the sample, but also a “polydispersity index”. The polydispersity index is a measure of size distribution in the sample (Gregory, 2006).

2.2.4 Particle size in surface waters

Sizes of aquatic constituents vary a lot, from some tens of nano-meters and up to sizes of sand grains. In Figure 5 the variation of sizes is shown schematically with a logarithmic scale ranging from 1 Ångstrom (1 Å = 10^{-10} m) to 1 mm. The diagram shows the typical sizes for a certain type of particles, as for instance viruses, and the wavelengths of different electromagnetic radiations. Moreover the defined boundary between colloidal and suspended matter are shown and suitable separation processes for certain size of particles.

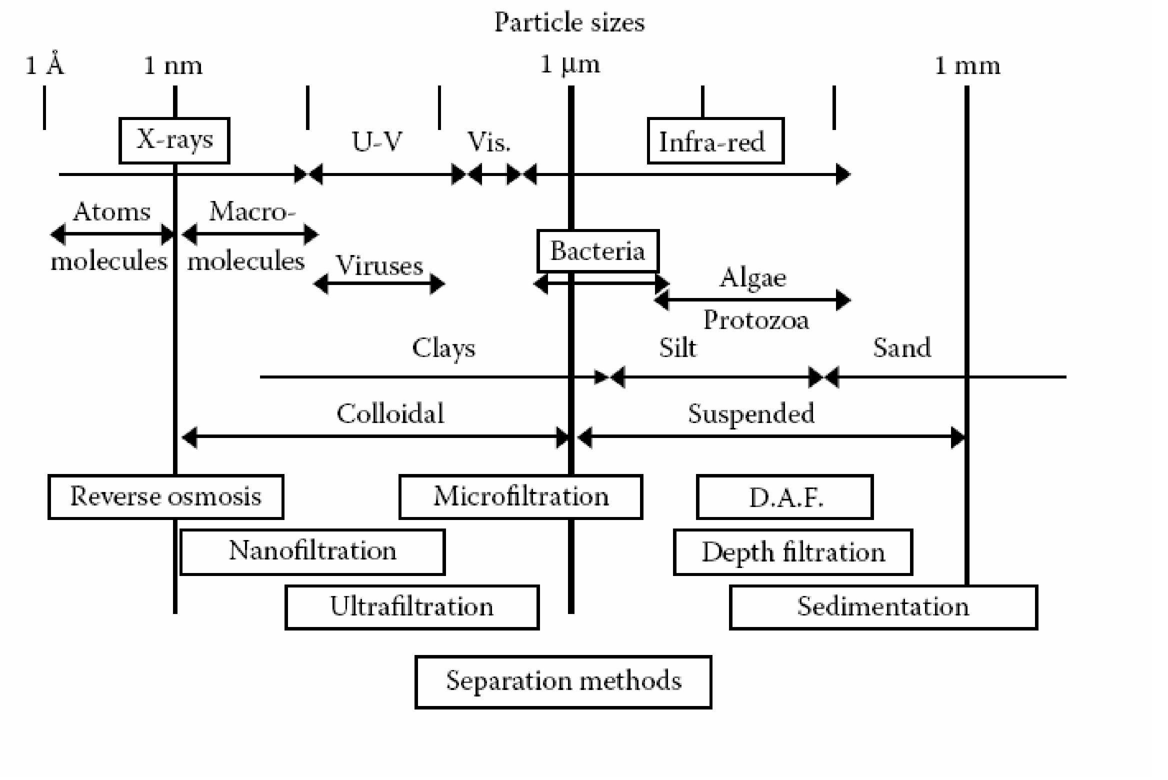


Figure 5. Different groups of aquatic constituents, their size ranges and corresponding wavelengths of electromagnetic radiation. Also shown are the possible particle separation processes for various size ranges. (Gregory, 2004. With permission).

Natural particles have different sizes and different shapes. It is often difficult to determine their size. Most instruments measuring particle size give the particle size as one length and the instruments assume that the particles have spherical form. Some instruments (e.g. light blocking instruments) measure the size of rotating particles and therefore report larger particle volumes than the true particle volume. Most natural particles have no spherical form (Gregory, 2006).

However if the particles are considered to be spherical, then the diameter is the only size parameter needed and it is easier to discuss hydrodynamic properties. Therefore the concept of “equivalent sphere” is an ordinary way to make measurements of size of particles easier (Gregory, 2006). If a certain property of an irregular particle, for instance surface area, is known then the equivalent sphere is a sphere having the same surface area as the irregular particle. When the surface area is known the diameter (d) of the equivalent sphere can be calculated, as the surface area of a sphere is πd^2.

Anyway when studying natural aquatic particles one has to take into account that these particles are usually nonspherical.

Equivalent spherical diameter can be calculated also from sedimentation velocity and density of a particle, and that gives the so called “Stokes equivalent diameter” (Gregory, 2006). In this case, the sphere is of the same material and it is having a diameter which gives the same sedimentation velocity as the particle has. Although most of real particles are not spherical, they are often studied as equivalent spheres in order to simplify the observations.

Particle size distributions (PSD)

In natural waters there is a wide range of particle sizes. One way of presenting particle size distribution is the number of particles within a certain size range. Also mass (or volume) distribution, i.e. the fraction of particle mass or volume within a given size range, can also be used. If the particles are of same material, then is mass distribution the same as volume distribution. When different kinds of particles are present in water, it is difficult to compare number and mass distributions.

Nature is many times following normal or Gaussian distribution, but for natural aquatic particles a power law distribution is often more suitable. In differential form the power law distribution, also called *Pareto's law* looks like this:

$$\frac{dN}{dx} = n(x) = Zx^{-\beta}$$

where N is the number of particles with sizes less than x, and Z and β are empirical constants. Z describes the total amount of material and β the width of the distribution (or the slope in log-log plots). Usually is β between 3 and 5 (Gregory, 2006). Figure 6 is showing some examples of the power law distributions of particle size in natural water.

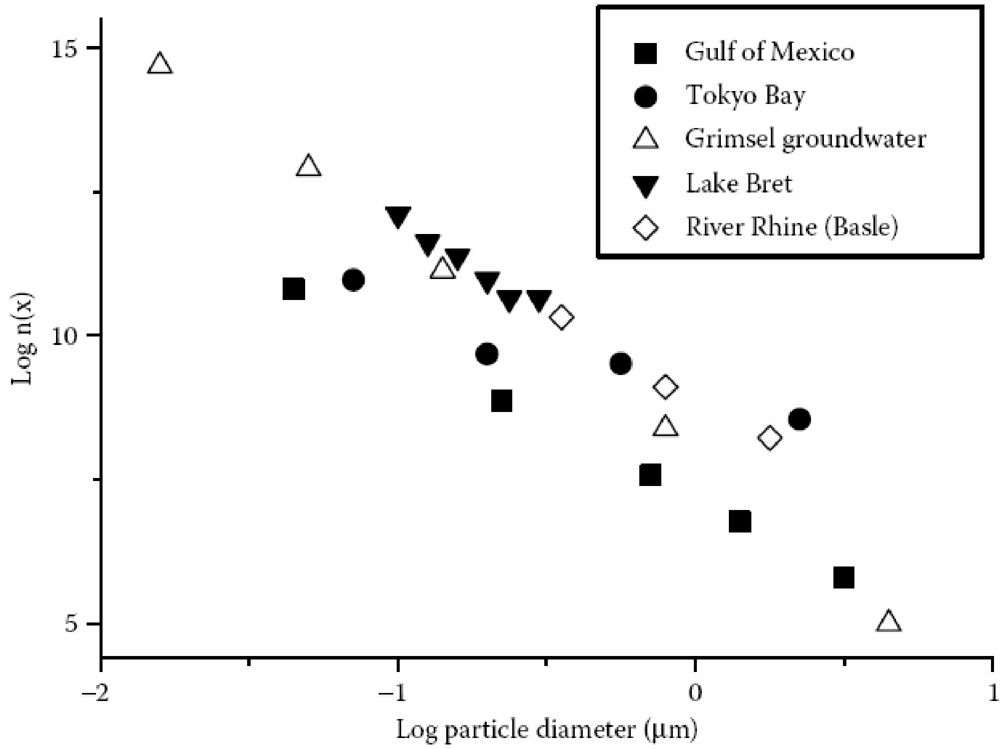


Figure 6. Particle size distributions for five natural waters, n(x) = dN/dx according to equation for Pareto's law. (Gregory, 2006. With permission).

According to Figure 6 particles in surface waters are legibly following the power law distribution.

Buffle and Leppard (1995) concluded that in aquatic systems the size distribution based on particle number follows Pareto´s law. All colloidal material in natural waters is following this law and similar distributions have been obtained when studying only a specific type of colloids, like polysaccharides, iron oxyhydroxides, proteins, fulvics and humics. Since Pareto´s law is valid in most water samples, it can be assumed that the number of small particles in general is much greater than the larger ones, e.g 10^6 times more 10-nm particles than 1-µm particles. However the size distribution based on mass looks completely different, i.e. the mass proportion of large particles is much higher than that of the smaller ones (Buffle and Leppard, 1995).

Same more examples of aquatic particles following the power law distribution are shown in Figure 7. Most of presented results in this graph are the same as in Figure 6, but Figure 7 is showing four additional studies of particles in water. Again the particles from various natural waters are shown to follow the power law distribution.

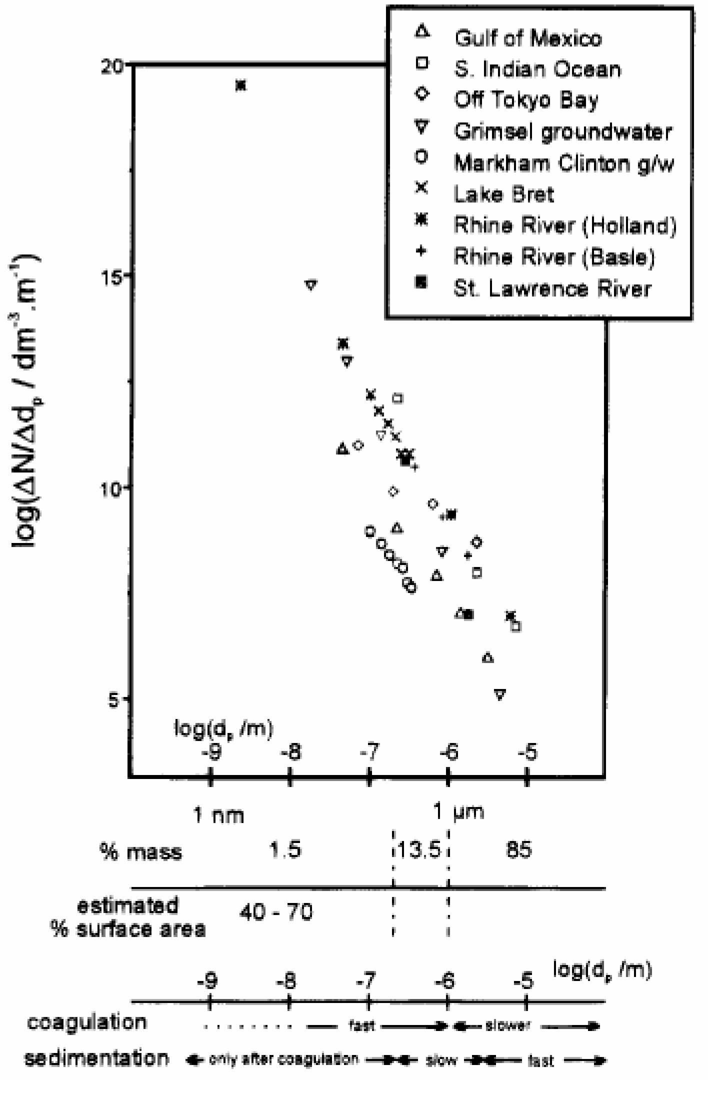


Figure 7. Size distribution of particles in several natural waters, based on particle number distribution. Below are shown also proportions of mass and estimated surface areas. The bottom scale indicates the nature of the slower processes leading to particle settling. d_p *is particle diameter. (Buffle and Leppard, 1995. With permission).*

Human eye can see particles larger than 40µm. Smaller particles have to be observed microscopically. A common light microscope is useful down to 1µm and for smaller particles electron microscope has to be used (Gregory, 2006).

It is difficult to define exactly the boundary between dissolved and particulate impurities in water. Dissolved macromolecules have similar size as very small particles, about 20 nm or less. Particles are often separated from the liquid in which they are suspended. In practice this means that a sample is filtered through a filter with pore size 0.45µm, and impurities passing the filter are regarded as dissolved matter while impurities retained by the filter are characterized as particulate. By this definition even viruses and clays are defined as dissolved components.

Furthermore it is also very important to make a distinction between colloidal and suspended (dispersed) material.

Buffle and Leppard (1995) define colloids and macromolecules as any organic or inorganic component in the size range of 1nm to 1µm. Chanudet and Fiella (2007) refer the term colloid to entities between 0.1 and 2 µm. There is no concrete size limit for a definition of a colloid. Colloidal particles are particles which do not settle with time and the sedimentation properties are density dependent. Thus sometimes also larger particles can be seen as colloids if they remain suspended in the solution.

The behavior of submicron colloids is difficult to predict (Buffle and Leppard, 1995). It is easier to estimate what happens with large particles (10µm and larger) in water since they are filtered away in porous media and settle to sediments in surface waters. Colloids are too small and they can not settle on their own, unless they form aggregates large enough.

Fulvics, humics, and proteins are typically smaller than tens of nanometers, while cellular debris, polysaccharides, clays, carbonates, and MnO_2 are usually larger (Buffle and Leppard, 1995). Iron hydroxide colloids may have sizes from nanometers to microns (Buffle and Leppard, 1995).

Buykx el al (1999) studied particle size in water samples from rivers and lakes in Spain, Sweden, Finland, The Nederlands and Switzerland. The measurements were done with laser light scattering which could be problematic because of the low particle concentration in the samples. However according to the authors it is possible to compare the results from the rivers as shown in Figure 8.

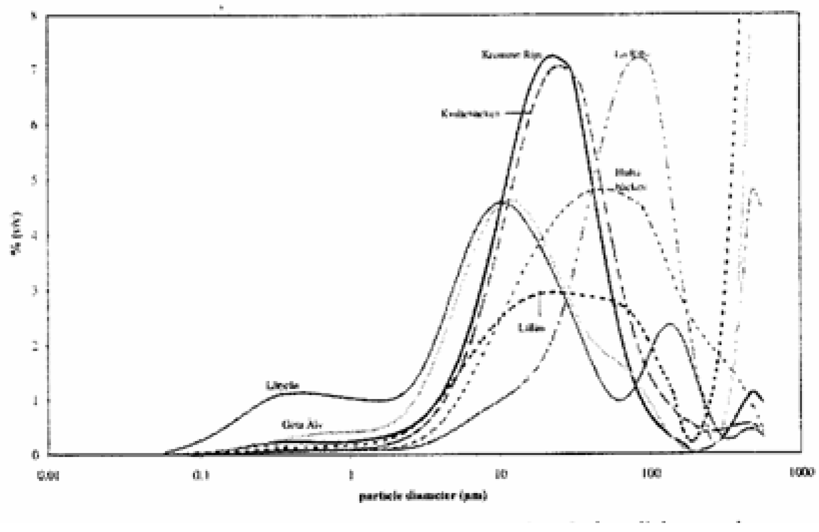


*Figure 8. Particle size distribution in some European rivers, obtained by laser light scattering. %(v/v) is shown as a function of particle diameter (**µm**). (Buykx et al, 1999. With permission).*

The size distribution in Figure 8 is based on volume calculations. Except from river Lärjeån, have all studied rivers one typical particle size range. Lärjeån has three tops: around 0.45 µm, 9.7 µm and 125 µm. Typical particle size range of Göta Älv is at 9.7 µm, while size distribution of Kromme Rijn and Kvillebäcken is mostly around 20 µm. Hültabäcken and Lillån have a broader size distribution than other rivers in this study.

Chanudet and Fiella (2007) have been studying colloidal particles in Lake Brienz in Switzerland. Colloidal particles, i.e. the size distribution between 0.1 – 2 µm, represented from 11 to 29 % of the total mass of particles in samples collected over several months.

Lartiges et al (2000) made a study on size distribution of particles in the Rhine River, using a Malvern MasterSizer particle size analyzer. Their results are shown in Figure 9.

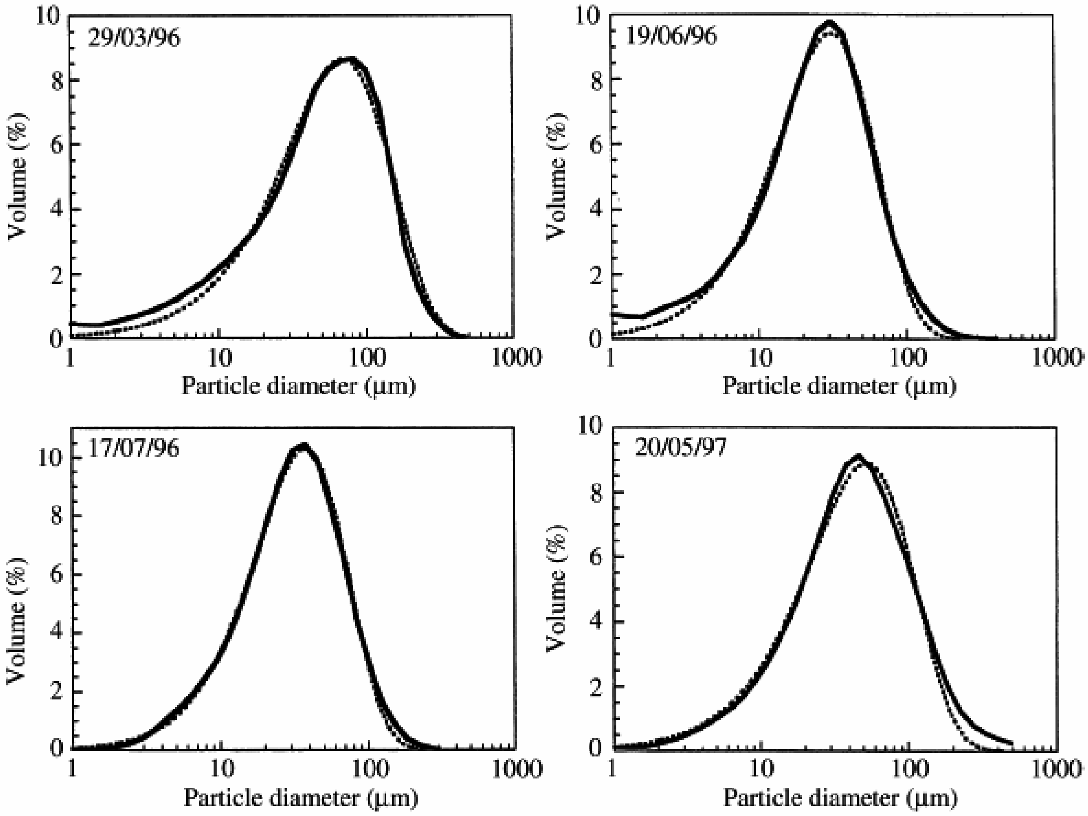


Figure 9. Particle size distribution in river Rhine at different seasons. Natural distribution is shown with solid line and a fit with gamma curve is shown by the broken line. Gamma curve: $y = kx^{a}e^{-bx}$*, where k, a, b are constants, y the particle volume and x the particle diameter. (Lartiges et al, 2000. With permission).*

In the summer the volume of smaller particles was larger that in the spring (see Figure 9).

Walther et al (2006) were measuring particle size in water of Lake Brienz (Switzerland) and River Pfinz (Germany), and it was found that the particle size distributions follow Pareto´s law even down to 15 nm in both cases. These results are presented in Figure 10 and Figure 11. It is not possible to cover a complete size range with one method and therefore several size measuring techniques has to be combined if the whole size range is needed.

Filella and Buffle (1993) concluded that most of the size measuring techniques do not enable direct measuring of size of small particles in the presence of high proportion of large particles, which is usually the case in natural waters. Therefore size fractionation procedures have to be used. As this is giving risk of perturbing the sample a combination of different fractionation and measuring techniques is recommended.

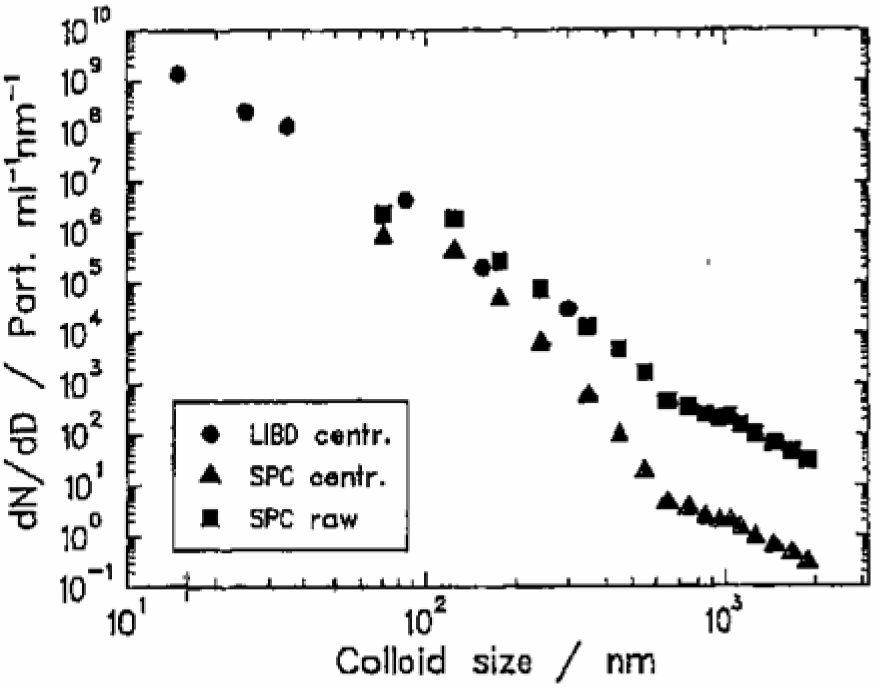


Figure 10. The size distribution of particles in water sample from Pfinz channel close to Karlsruhe (Germany). Particle size was measured by SPC (single-particle counter) in raw sample, in the diagram as SPC raw, and in centrifuged sample (SPC centr.). Particles larger than 80nm are removed by centrifugation. Centrifuged sample was measured also by LIBD (laser-induced brake-down detection), LIBD centr. in the diagram. (Walther et al, 2006. With permission).

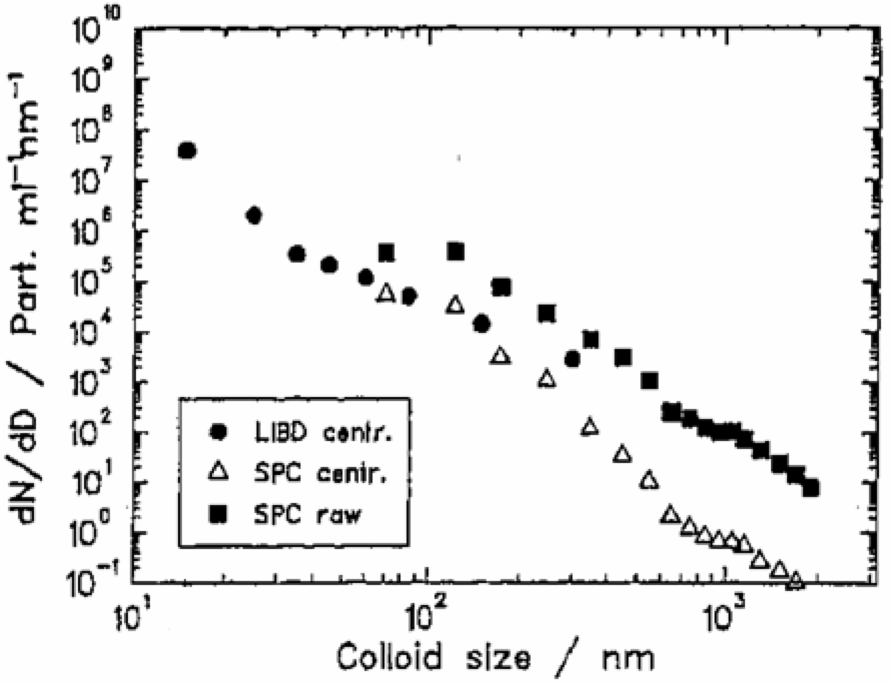


Figure 11. The size distribution of particles in water sample from Lake Brienz (Switzerland), measured as described for Figure 10. (Walther et al, 2006. With permission).

Veber, Bergant and Marsel (1986) have measured particle sizes in the River Sava in Slovenia, and in the Table 1 below it can be seen that most of the particles were in the range of 0 - 10 µm. The size of particles was measured microscopically, and the percentage in the table below is likely aiming at the number % of all particles in the sample, but the authors have not explained that in the article.

Table 1. Particle size distribution in river Sava (Veber et al, 1986).

	Particle size			
	0-10 µm	**20-30 µm**	**20-30 µm**	**30-40 µm**
Sample	Distribution (%)			
1	90.1	5.6	2.7	1.6
2	90.7	8.1	0.9	0.3
3	86.5	11.3	1.7	0.5
4	90.3	9	0.6	0

Atteia et al. (1998) have studied natural colloids and particles in a karstic aquifer. They have used three methods for size determination and they also showed that PDS (particle size distributions) can be described by Pareto's law (see Figure 12). Based on the amount of colloidal/particulate matter, this study is an intermediate between deep groundwaters and large rivers. In the study particles smaller than 5µ (defined as colloidal phase) constitute about 10% of the total particle mass. In terms of surface area (if they are spheres) this corresponds to 40% of all surface area and if one takes into account the clay nature of particles then the actual specific surface area reaches more than 95% of the total surface area of particulate matter. Atteia et al. (1998) pointed out that colloid and particle distributions are entirely multidispersed and therefore they must be analyzed in terms of PSD.

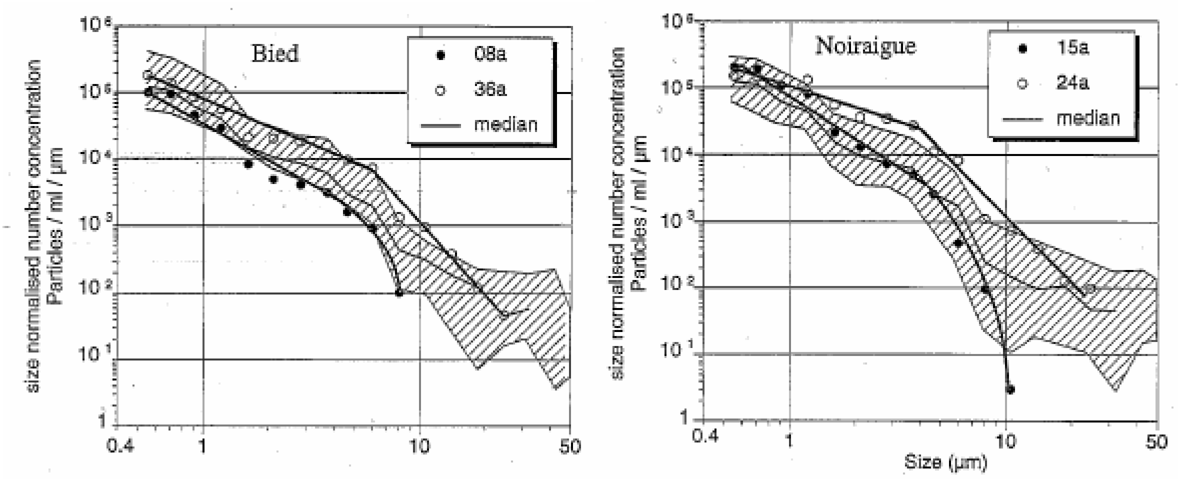
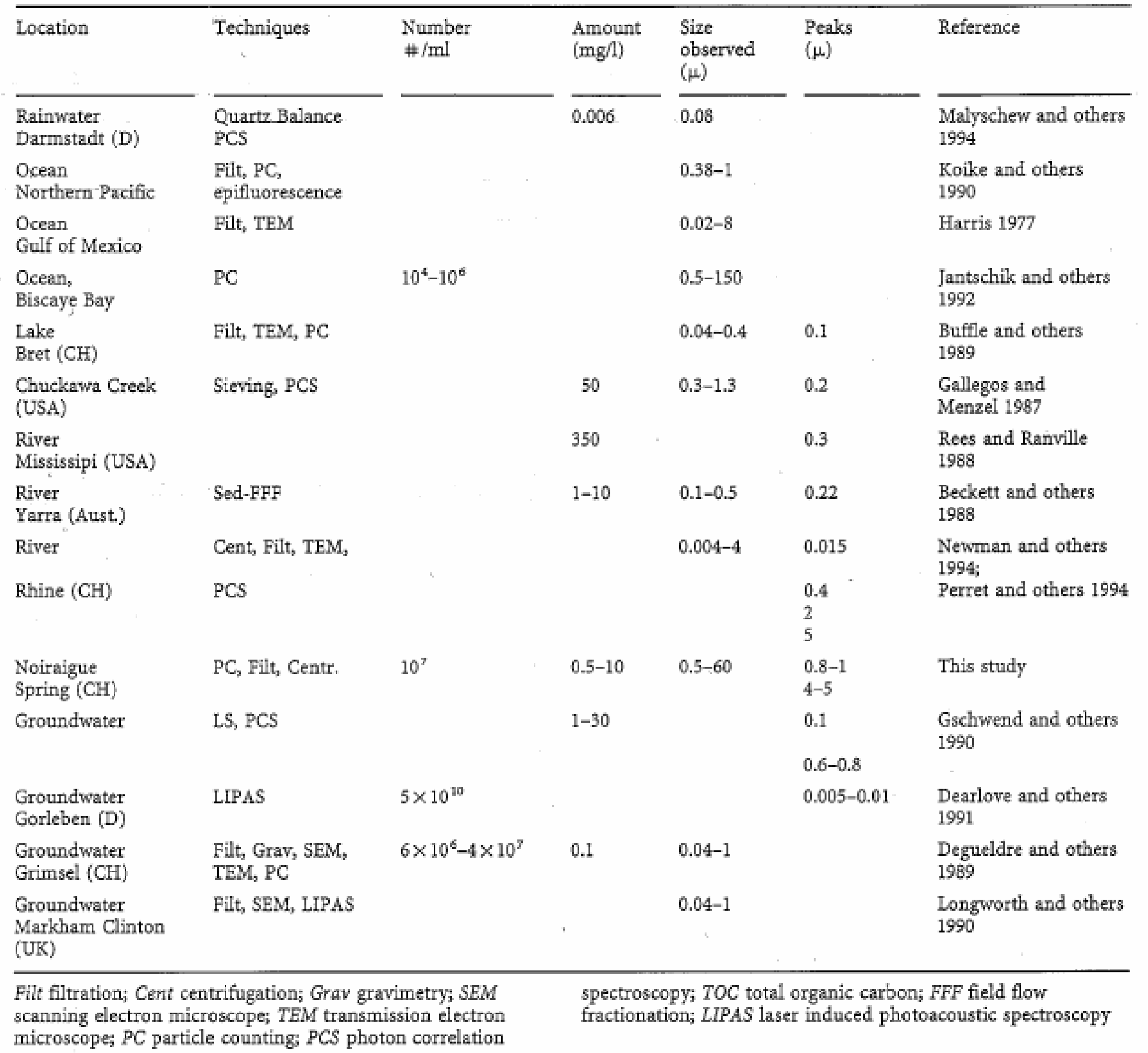


Figure 12. PDS for Noiraigue Spring and Bied Book. 08a, 36a, 15a and 24a are sampling events numbers. The graphs include fitted Pareto or exponential law (▬) and median (–) plus 10 and 90 % percentiles (marked with ///) of the number values. Bied had 35 samples and Noiraigue had 50 samples. (Atteia et al., 1998. With permission).

In Table 2 it can be seen that there is a wide variation in size of particles in different types of natural waters. The comparisons of various studies should be careful. It is difficult to compare results from different methods because of the lack of standardization (Atteia and Kozel, 1997).

Table 2. Sizes of colloidal particles in various natural waters observed by different measuring techniques (Atteia et al., 1998. With permission).



Location	Techniques	Number #/ml	Amount (mg/l)	Size observed (μ)	Peaks (μ)	Reference
Rainwater Darmstadt (D)	Quartz Balance PCS		0.006	0.08		Malyschew and others 1994
Ocean Northern Pacific	Filt, PC, epifluorescence			0.38–1		Koike and others 1990
Ocean Gulf of Mexico	Filt, TEM			0.02–8		Harris 1977
Ocean, Biscaye Bay	PC	10^4–10^6		0.5–150		Jantschik and others 1992
Lake Bret (CH)	Filt, TEM, PC			0.04–0.4	0.1	Buffle and others 1989
Chuckawa Creek (USA)	Sieving, PCS		50	0.3–1.3	0.2	Gallegos and Menzel 1987
River Mississipi (USA)			350		0.3	Rees and Ranville 1988
River Yarra (Aust.)	Sed-FFF		1–10	0.1–0.5	0.22	Beckett and others 1988
River	Cent, Filt, TEM,			0.004–4	0.015	Newman and others 1994;
Rhine (CH)	PCS				0.4 2 5	Perret and others 1994
Noiraigue Spring (CH)	PC, Filt, Centr.	10^7	0.5–10	0.5–60	0.8–1 4–5	This study
Groundwater	LS, PCS		1–30		0.1 0.6–0.8	Gschwend and others 1990
Groundwater Gorleben (D)	LIPAS	5×10^{10}			0.005–0.01	Dearlove and others 1991
Groundwater Grimsel (CH)	Filt, Grav, SEM, TEM, PC	6×10^6–4×10^7	0.1	0.04–1		Degueldre and others 1989
Groundwater Markham Clinton (UK)	Filt, SEM, LIPAS			0.04–1		Longworth and others 1990

Filt filtration; *Cent* centrifugation; *Grav* gravimetry; *SEM* scanning electron microscope; *TEM* transmission electron microscope; *PC* particle counting; *PCS* photon correlation spectroscopy; *TOC* total organic carbon; *FFF* field flow fractionation; *LIPAS* laser induced photoacoustic spectroscopy

Perret el al. (1994) made a very thorough study of particles in Rhine River. They have used three fractionation methods: sedimentation, centrifugation and filtration, many analytical techniques: PCS - photon correlation spectroscopy, i.e. DLS, ME – micro-electrophoresis, TEM – transmission electron microscopy, LS – light scattering, ICP-AES – inductively coupled plasma-atomic emission and TOC – total organic carbon. Fractionation of the raw water was necessary because large particles hamper DLS and TEM. DLS analyses over the entire year showed the existence of three major particle size classes:

- Larger than 1 μm (two classes: 1-3 μm and larger than 3 μm)
- Comprised between 0.2 and 0.7 μm
- Smaller than 0.2 μm.

This is shown in Figure 13.

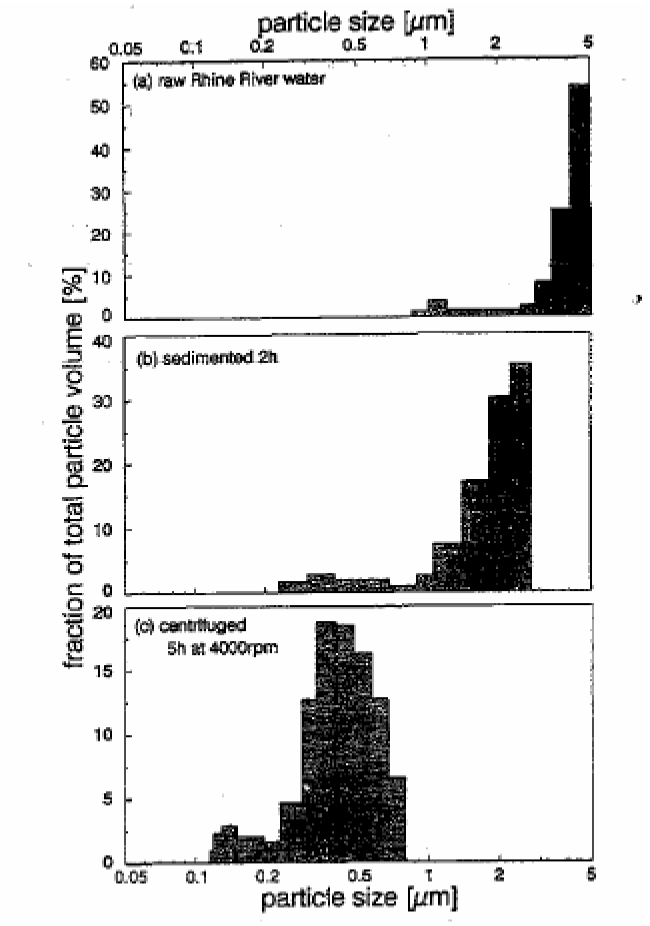


Figure 13. Volume particle size distributions (a) in raw Rhine River water, (b) after 2h sedimentation of same raw water and (c) after centrifugation of the sedimented raw water. After fractionation the size shifts towards smaller sizes. The size distribution in (a) is only indicative and does not show the true distribution since the upper size limit is imposed by the DLS instrument. (Perret el al., 1994. With permission).

Particles smaller than 0.2 µm contribute a negligible proportion (less than 2%) of the total particle volume and mass. But they may represent a dominant proportion of the available surface area for adsorption of pollutants. The largest particles (>1 µm) contributed to majority of the total mass, while the smallest particles (0.05-0.2 µm) are present in the greatest number. High resolution TEM showed that all samples contained many “large” (50-300 nm) organic fibrils, filaments or spongy networks. A large fraction of the inorganic microcolloids (< 50 nm) was associated with larger organic matrices. (Perret et al., 1994)

The majority of submicrometer inorganic particles were composed of clays, silica and iron oxyhydroxides, the sizes of which are sometimes as small as a few nanometers. Inorganic particles can be divided in three groups:

- Larger than 1-3 µm, sediment quickly
- Between 100 nm and 1 µm, sediment slowly
- Smaller than 100 nm, associated with, and stabilized by, organic matrices.

According to Figure 14 there are particles with diameter 200-300 nm remaining in solution even after 10000 h sedimentation, i.e after 5 h centrifugation at 3700 g. Particles must be largely organic ($\rho \approx 1.1$ g/cm^3) in order to remain suspended under such conditions. (Perret et al., 1994)

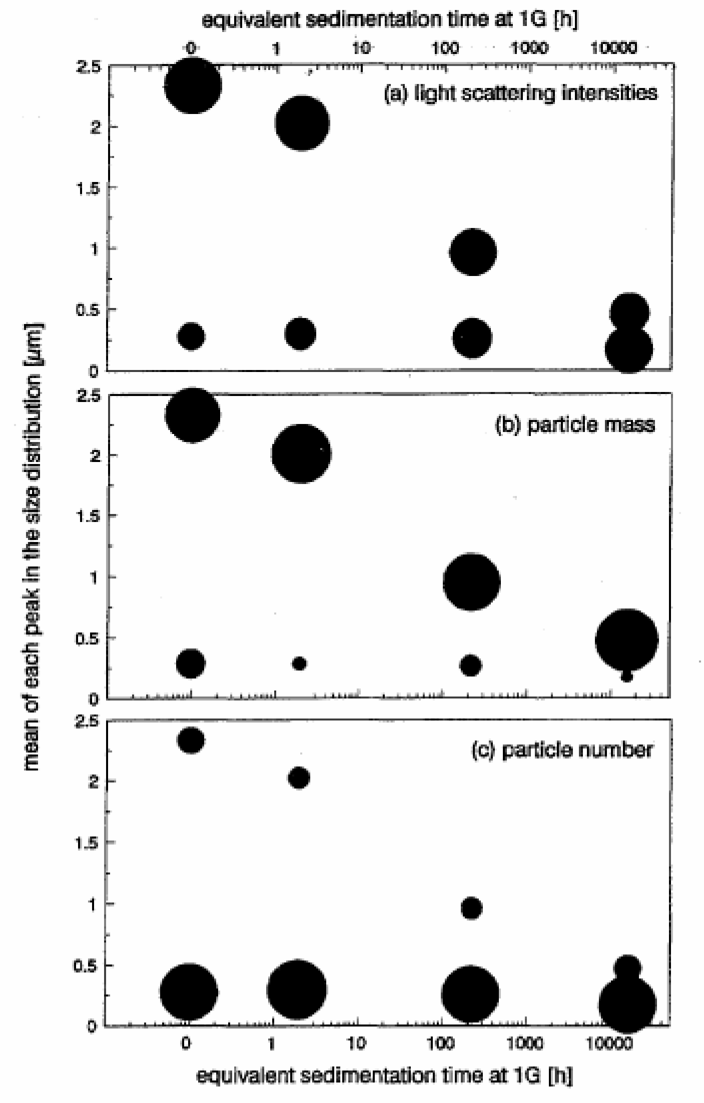


Figure 14. DLS results for mean of each peak in the size distribution for raw, sedimented and centrifuged sample of Rhine River water. Results are presented as (a) light scattering intensities, (b) particle mass (proportional to particle volume) and (c) particle number. Centrifugation times are given in equivalent sedimentation times at 1g. Surfaces of circles show the proportion of particles of the certain size. For (a) and (b) are variabilities of these proportions 10-15 % while for (c) variability is about 50 %. (Perret el al., 1994. With permission).

Weilenmann et al. (1989) have studied diameter of particles in a lake as a function of depth. Their results are shown in Figure 15.

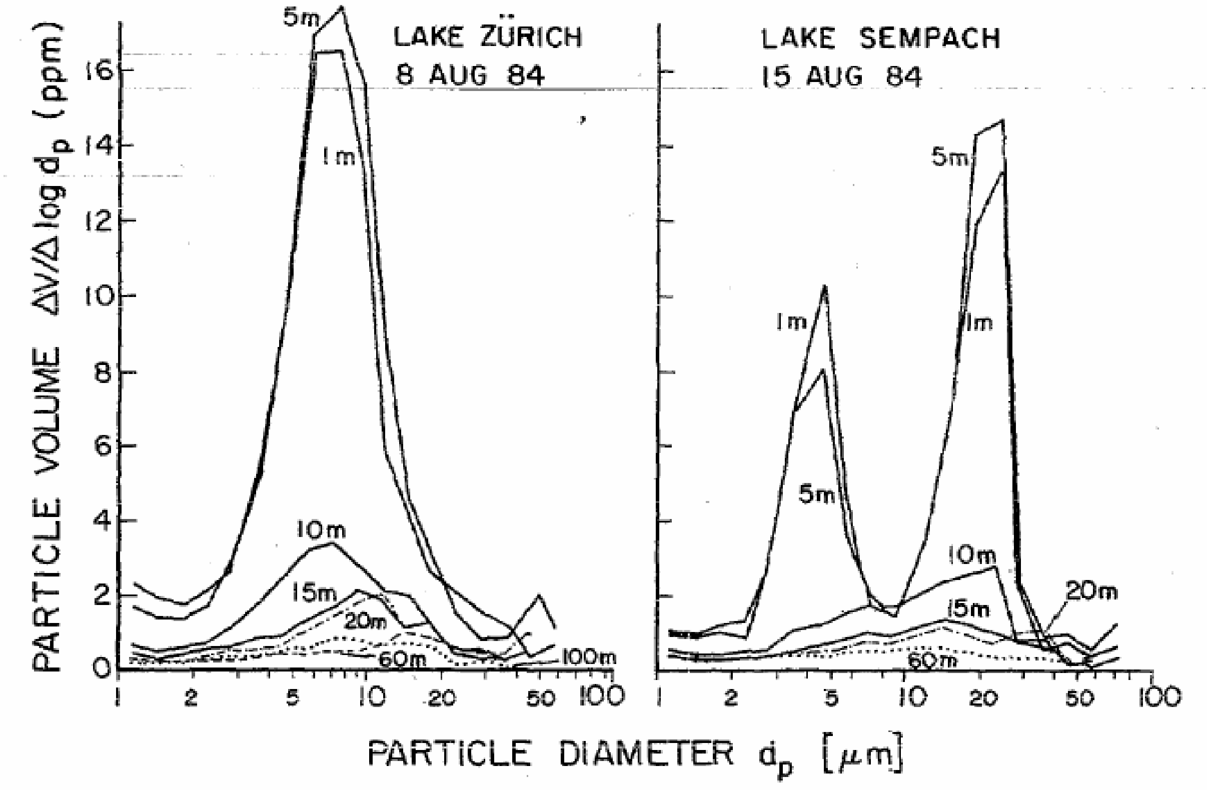


Figure 15. Particle volume concentration distribution of samples obtained at various depths in Lakes Zürich and Sempach (Weilenmann et al., 1989. With permission).

In the study of particles in Lake Brienz, performed by Chanudet and Filella (2008), could the power-law distribution describe the dependence of the colloid concentration numbers on colloid diameters in all cases (see Figure 16). They pointed out that in the rivers, where almost no aggregates were observed, particle size distribution (PSD) would be mostly the result of the nature (particle formation and mineralogy) of the colloids, whereas in the lake, the measured PSD is a result of the original colloid sizes but also of aggregation and sedimentation processes, particularly in the summer.

Generally surface waters are polydispersed solutions, i. e. they contain a broad range of size and shape characteristics. The particle size distributions (PSD) in natural water usually follow the Pareto's law, i. e. the power law distribution. The smaller the particles are the larger is the number of them and this correlation is exponential. When measuring the size of particles in surface waters several methods should be combined in order to get correct results.

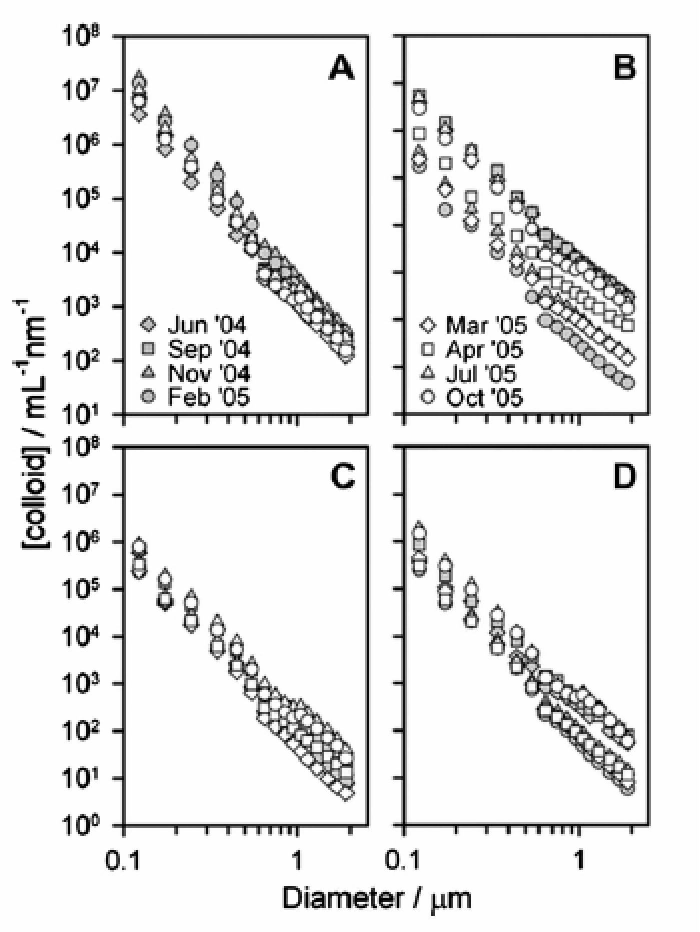


Figure 16. Particle size distributions. (A) in the River Aare, (B) in the River Lütschine and (C) Lake Brienz. The samples for A, B and C were taken 1m deep. D is showing the PDS at the turbidity peak when present, otherwise the sample was taken at 1om depth. (Chanudet and Filella, 2008. With permission).

2.3 Surface charge of particles

Most of particles in contact with an aqueous solution have a surface charge. The surface of particles has chemical groups that can ionize in water and leave a residual negative or positive charge on the surface (Gregory, 2006).

2.3.1 Zeta potential and electrophoretic mobility (EM)

This section is based on Malvern user manual (2005).

A charged particle suspended in a liquid is surrounded by ions of an opposite charge. Cations and anions are present in the most liquids and they are attracted to the surface of the suspended particles. Negatively charged particles attract positive ions from the liquid and on the opposite positive charged particles attract negative ions from the liquid. There is an electrical double layer around particles. The first layer around a suspended particle, close to the surface of the particle, consists of strongly bound ions. This layer is called *Stern layer*. Ions further away from the surface of the particle are more loosely bound and the layer of these loosely attached ions is called a *diffuse layer* (see Figure 17). Inside this layer there is an imaginary boundary called the *Slipping plane*. When the suspended particle surrounded by attached ions is moving in the liquid, all ions within the slipping plane boundary are moving with the particle and all ions outside this boundary will not move with the particle. There is a potential between the particle and the liquid. At the slipping plane this potential is called *Zeta potential*.

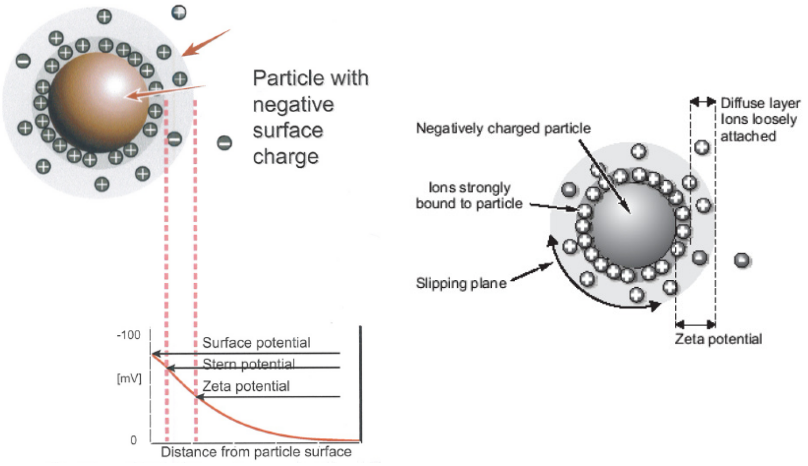


Figure 17. Ions around a particle with a negative surface charge forming diffuse layer and slipping plane (Malvern, 2005. With permission).

Zeta potential can not be measured directly. However it can be calculated from its electrophoretic mobility by applying Henry equation. Electrophoresis is “the movement of charged particle relative to the liquid it is suspended in under the influence of an applied electric field” (Malvern, 2008). If we apply electric field across an electrolyte, charged particles suspended in the electrolyte will be attracted towards the electrode of opposite charge. This will be opposed by viscous forces of the liquid in which the particles are suspended. When equilibrium is reached between the opposing viscous forces and the dragging force against the opposite electrode, the particle will move with constant velocity.

The velocity of the particle in an electric field is called electrophoretic mobility and it is dependent on these factors:

- Strength of electric field or voltage gradient
- The dielectric constant of the medium
- The viscosity of the medium
- The zeta potential

Henry equation is describing the relationship between the zeta potential and the electrophoretic mobility.

Henry equation:

$$U_E = \frac{2\varepsilon z f(Ka)}{3\eta}$$

Where z is zeta potential, U_E is electrophoretic mobility, ε is dielectric constant, η is viscosity and $f(K_a)$ is Henry´s function. K_a is the ratio of particle radius to double layer thickness (Debye length). Two values are usually used as approximations of $f(K_a)$, namely 1.5 or 1.0. When we are dealing with aqueous media $f(K_a)$ would be 1.5, according to Smoluchowski approximation. Smoluchowski model is suitable for particles larger than 0.2 microns and dispersed in electrolytes containing more than 10^{-3} moles of salt. $f(K_a)$ 1.0 is used for small particles or non-aqueous measurements. In this case the Hückel approximation is used (Malvern, 2005).

2.3.2 Measuring electrophoretic mobility (EM)

This section is based on Malvern user manual (2005).

The electrophoretic mobility is measured in a cell with electrodes on both ends (see Figure 18). A potential is applied to the sample in the cell and particles move towards the electrode of the opposite charge. The instrument Malvern Nano Zetasizer measures the velocity of particles with Laser Doppler Velocimetry (LDP). Light scattered from a moving particle causes a frequency shift. The scattered light is combined with a reference beam. In the produced fluctuating intensity signal the rate of fluctuation is proportional to the speed of particles.

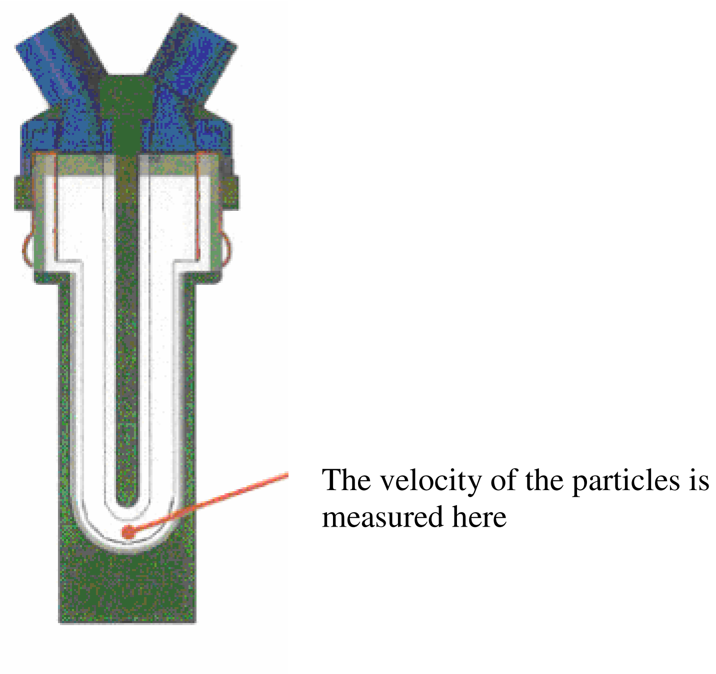


Figure 18. The cell for measuring the electrophoretic mobility (Malvern, 2005. With permission).

2.3.3 Zeta potential of particles in surface waters

Perret et al. (1994) reported that mean zeta potential of sedimented samples and centrifuged samples from River Rhine were -21.3 (±13.1) and -17.6 (±6.9) mV. That is similar to other reported values in the literature. These values correspond to the slightly negative electrophoretic mobilities observed for natural particles with organic surface coatings.

Gerritsen J. and Bradley S. (1987) measured electrophoretic mobility (EM) of natural particles in 11 lakes and streams in southeastern U.S. and also EM of living cells. Surfactants (e.g. organic coatings on natural particles), with a polar end in the water phase, increased the size of the counter-ion cloud. Increased concentration of electrolytes (i.e. increased hardness or salinity) increases the concentration of positive counter-ions and reduces the size of the counter-ion cloud, making the particle less repulsive. EM is decreasing with increasing conductivity, but on the contrary it is increasing with DOC concentration and pH. EM of particles is mostly dependent on:

- Their composition (mineral detritus, organic detritus or a living cell)
- Concentration of metallic cations in the water (particularly divalent ions, Ca^{2+}, Mg^{2+})
- DOC-concentration
- pH of water.

In Figure 19, taken from the study of Gerritsen J. and Bradley S. (1987), the EM of natural particles as a function of DOC-concentration and conductivity are presented. Each point presents mean value of measurements for a certain water sample.

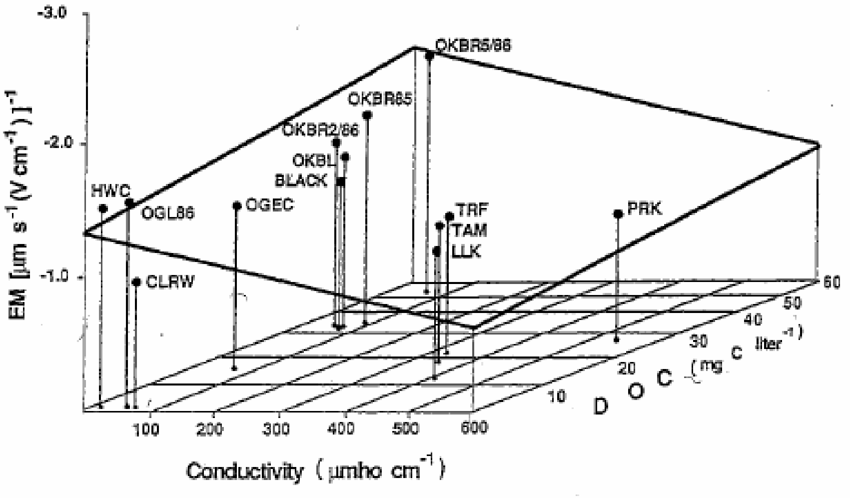


Fig. 1. Electrophoretic mobilities of natural particles at each site and two-way regression plane of EM on conductivity and DOC. Each point represents the mean of at least 100 observations. OKBR5/86—Okefenokee, Buzzard's Roost Lake, sampled May 1986; OKBR85—same, June 1985; OKBR2/86—same, February 1986; OKBL—Okefenokee, Billy's Lake; BLACK—Black Creek; OGEC—Ogeechee River; OGL86—Lake Oglethorpe, sampled 1986; HWC—Hugh White Creek; CLRW—Clearwater Lake; TRF—Lake Trafford; TAM—Tamiami Canal; LLK—Lettuce Lake; PRK—Lake Parker.

Figure 19. EM of natural particles as a function of DOC and conductivity (Gerritsen J. and Bradley S., 1987. With permission).

Several authors (Gibbs, 1983; Loder and Liss, 1985; Beckett and Le, 1990; Mosley and Hunter, 2003) have shown that the charge of natural particles in surface waters is negative due to the natural organic coatings on particles. Suspended particles in natural waters have in most cases negative surface charge even though one should expect that certain mineral particles (e.g. iron oxides/hydroxides) should have positive surface charge. Loder and Liss (1985) broke down organic material in a water sample by UV irradiation and they measured EM of particles before and after this treatment. The water sample was natural surface water containing many suspended particles composed of iron oxide/hydroxide. Their results provided strong indications that the break down of organic coatings leads to more positive surface charge of particles in a iron-rich system. Afterwards they have resuspended these particles in same natural water (with particles removed) and the surface charge of particles has changed from positive to negative values. This was explained to occur due to uptake of organic material from the natural water onto the particle surface. According to Figure 20 the change of charge from positive to negative values is complete within minutes, but it takes several hours to reach the charge of natural particles.

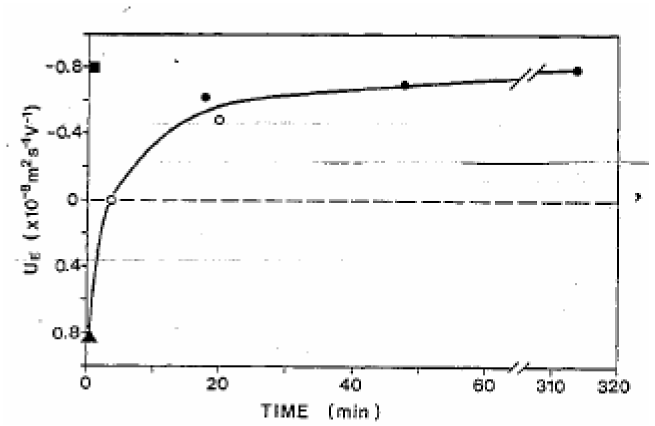


Figure 20. Electrophoretic mobility of particles without organic coatings resuspended in natural water. The open circles shows EM for more dilute suspensions while the closed circles represent less dilute suspensions. Closed triangle shows EM for particles without organic coating suspended in organic-free water. Closed square indicates EM for natural (untreated) particles from Keithing Burn. (Loder and Liss, 1985. With permission).

The negative charge of particles affects the coagulation process of particles. Gibbs (1983) made an interesting study by comparing coagulation process of natural particles with organic coatings and particles from which these organic coatings have been removed by oxidizing with sodium hypochlorite. He found out that natural particles with organic coatings coagulate slower than particles without these natural organic coating. This effect of organic coatings was higher at low salinity in water, while DOC-concentration in water did not did not have any significant effect on the results in this experiment. However Gibbs results show indirectly that particles with organic coating have higher surface charge.

Several studies (cited in Loder and Liss, 1985) have shown that the electrophoretic mobility, and hence the surface charge, of suspended particles in estuaries is always negative and falls in the range -0.7 to -2.0×10^{-8} m^2 s^{-1} V^{-1}, that is zeta potential from -8.96 to -25.6 mV. According to Loder and Liss (1985) even the surface charge of particles in fresh waters and seawater is similar to that in estuaries. Furthermore they cited that also plankton in natural waters has negative surface charge.

Beckett and Le (1990) were measuring EM of natural suspended particles in river water and EM of organic coated goethite colloid. The aim of the study was to investigate how organic matter and ionic composition of water affect the charge of natural particles in water. The surface charge was always negative and it decreased in magnitude in samples with higher ionic strength. Their study showed that surface charge of particles was relatively similar for all particles even though the particles were very different (se Figure 21). After the addition of Ca^{2+} and Mg^{2+} the surface charge became less negative. EM of natural particles is very affected by presence of divalent cations and not as much affected when Na^+- ions are present in water. They concluded that the absorbed layer of natural organic matter (particularly the humic substance component) is the most important factor for the surface charge of particles in water. This charge is furthermore modified mostly by the concentration of divalent ions in water, and in minor extent by pH.

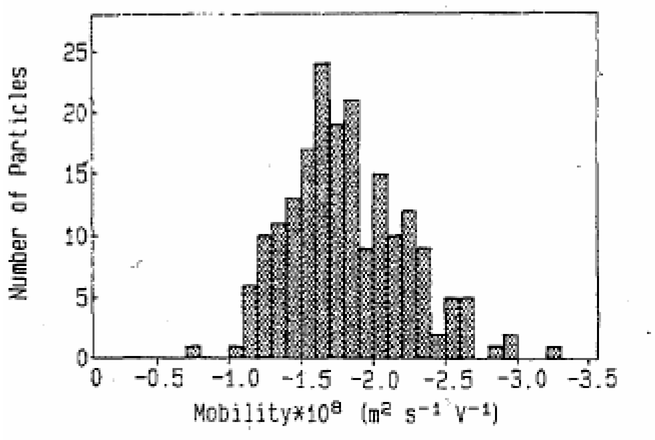


Figure 21. Frequency histogram showing the electrophoretic mobility of 200 particles in a water sample from Yarra River (Beckett and Le, 1990. With permission).

2.3.4 Zeta potential as a function of pH

In the study by Gerritsen J. and Bradley S. (1987), already mentioned above, also electrophoretic mobility of particles in samples with adjusted pH was measured (see Figure 22). pH was adjusted in a range between 3 and 10. It was shown that an increase in pH will increase the net charge of the particle, making it more repulsive. EM of particles in hard water do not change much if pH changes. However in soft waters changes EM a lot if pH changes, i.e. EM increases if pH increases. Highest EM was measured in soft waters with high DOC-concentration, like for instance blackwater. EM of living cells is more stable and it varies less than EM of other particles. This because of the phenomena of homeostasis which is the ability of cells to neutralize their surface charge to a certain extent.

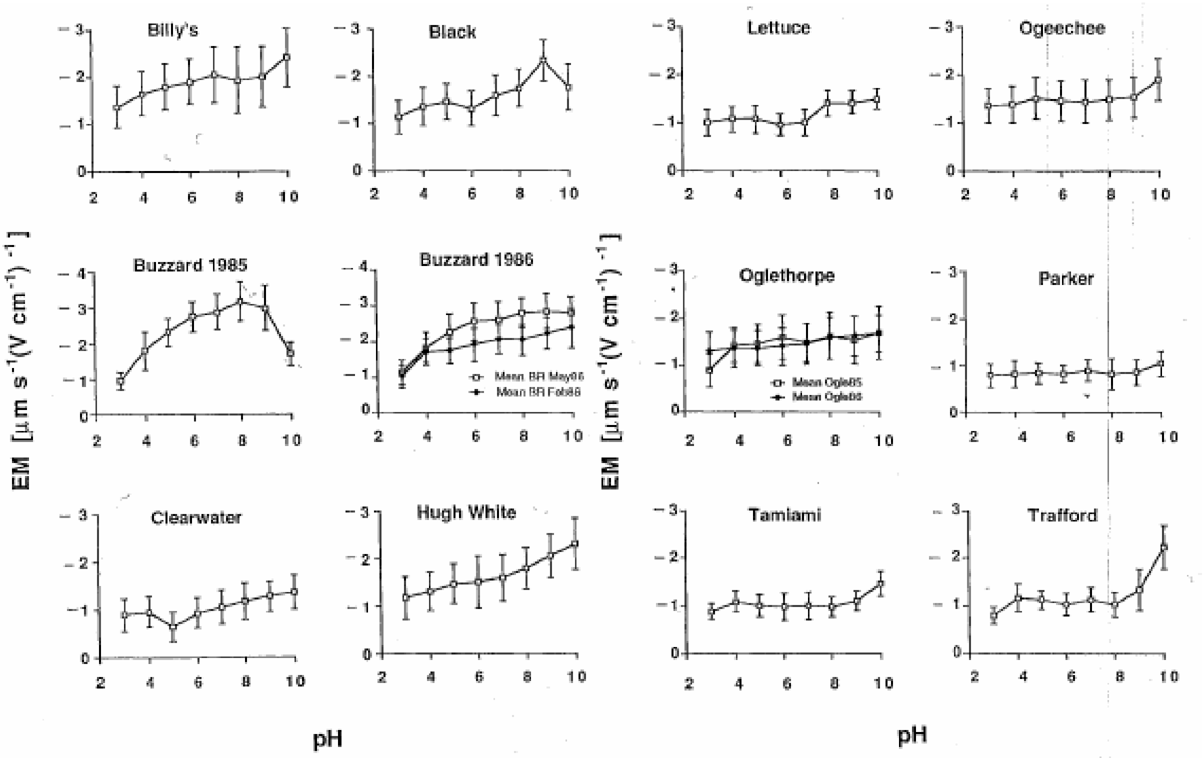


Figure 22. EM of natural particles in various water samples as a function of pH (Gerritsen J. and Bradley S., 1987. With permission).

Beckett and Le (1990) has also shown that with increasing pH the surface charge of particles will be more negative (se Figure 23).

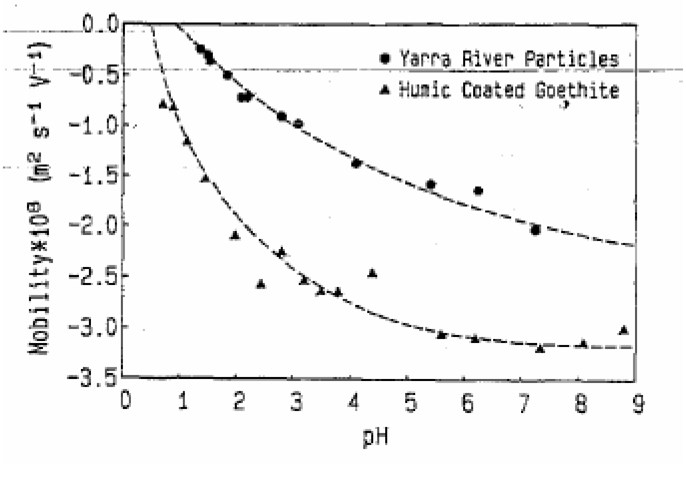


Figure 23. Electrophoretic mobility of Yarra River colloidal particles and electrophoretic mobility of goethite colloid (20 mg l^{-1}) coated with Aldrich humic acid (10 mg l^{-1}) as a function of pH which was adjusted with HNO_3 (Beckett and Le, 1990. With permission).

Tripping (1980) showed that adsorption of humic substances to iron oxides is decreasing with increasing pH.

2.4 Coagulation of particles by chemical treatment

The coagulation of particles by chemical treatment will be described here only shortly to give some understanding to why the size and charge of particles are important for coagulation processes and furthermore for drinking water treatment. The size of particles and their density are crucial factors for the sedimentation process of particles. Larger and heavier particles will settle fast, while small particles, colloids will remain suspended in water for very long time. Since they almost all have negative surface charge they repel each other when they approach. If they would not repel each other they would aggregate, become larger with time and finally settle. A rule of thumb is that suspensions, with particles having charge + 30 mV or more positive, or – 30 mV or more negative, are stable with particles remaining in suspension. In natural waters the charge of particles is negative, but not that negative as – 30 mV. This means that natural water suspensions are not completely stable, and there is aggregation occurring. However the aggregation is not fast enough and therefore chemical treatment is needed.

There are three ways by which iron and aluminum salts clean water, namely by sweep coagulation, patch coagulation and by charge neutralization of dissolved matter.

Sweep coagulation

When adding an aluminum salt to water small sized positively charged aluminum hydroxide is formed that adsorbs to the surface of particles or dissolved substances and to other aluminum hydroxide flocks. Layers of aluminum hydroxide start growing and when they are big enough they sink. While sinking they sweep down the remaining impurities in the water (Gillberg et al., 2003). Most Al^{3+} and Fe^{3+} salt clean water by sweep coagulation.

Patch coagulation

Especially when adding high basicity polyaluminum chlorides to water polymeric aluminum ions are formed in the water. These can aggregate particles through a mechanism called patch coagulation. In this case the added chemical adsorb on to patches on the particles and works like a sort of glue between particles (Gillberg et al., 2003).

Charge neutralization

Addition of positive ions can also precipitate the dissolved matter, e. g. the dissolved phosphate, by charge neutralization.

3 MATERIALS AND METHOD IN LABORATORY EXPERIMENT

The practical part of this master thesis was performed at Kemira Kemi AB's laboratories in Helsingborg. The size and zeta potential of the particles in five water samples were measured by Malvern Nano Zetasizer. Measurements were done in raw samples and in pH adjusted samples. Furthermore the effects of different doses of aluminum sulfate on size and zeta potential of particles in three waters was measured.

3.1 Five surface waters: source and characterization

3.1.1 Water samples

Samples of four surface waters were collected in the South of Sweden and one sample was obtained from the River Neva in Russia. Two 25 liters cans were sampled from each water source. They were stored at 4°C and in darkness.

Neva water

Water from River Neva was sampled in St Petersburg in Russia. One sample of Neva water, called Batch 2, was taken in the summer 2007 and one sample, called Batch 3, was taken in November 2007.

Ödåkra water

A sample from a small stream running into Vegeå stream was sampled in Ödåkra, close to Helsingborg, on the 15th of April 2008.

Småland water

On the 20th of April 2008 a water sample was taken from the small lake Ljusgöl, situated 30 km south of Västervik in Småland.

Stehags water

The water was fetched at Ringsjö water treatment plant at Stehag on the 19th of May 2008. This water came through a tunnel from Lake Bolmen in the south of Småland. Before entering the tunnel, the larger particles were removed.

Pinnå water

Water was taken from the Pinnå stream at Stidsvik on the 19th of May 2008. The Pinnå stream is running into Rönne stream in the east part of Skåne.

3.1.2 Characterization of water samples

All samples were characterized by analyzing calcium, magnesium and iron concentrations, pH, alkalinity, turbidity, color, UV absorbance and DOC concentration.

Calcium, magnesium and iron

Calcium, magnesium and iron were analyzed by ICP (Inductively Coupled Plasma Spectroscopy). From the calcium and magnesium concentrations the hardness of the waters was calculated. The total hardness of water is the sum of concentration of calcium and magnesium salts expressed as mg Ca/l or as German degree of hardness (°dH). One °dH is equivalent to 10 mg CaO/l or to 7.14 mg Ca^{2+}/l. There are no standard levels for what is hard or soft water and in the current work the water hardness has been compared according to Table 3.

Table 3. The characteristics of water in the aspect of total water hardness expressed as mg Ca/l or German degree of hardness.

Water description	Total hardness (mg Ca/l)	German degree of hardness (°dH)
Very soft	0 - 15	0 - 2.1
Soft	15 - 35	2.1 - 4.9
Moderately hard	35 - 70	4.9 - 9.8
Hard	70 - 150	9.8 - 21
Very hard	> 150	> 21

Turbidity

Turbidity was measured by a HACH 2100N turbidimeter.

pH

pH was measured by a WTW 323 pH-meter using a Hamilton Polilyte bridge lab electrode being calibrated at the temperature of the sample.

Titration with HCl and NaOH and alkalinity

Water samples (0.5 l) were titrated by 0.5 M HCl and 0.2 M NaOH respectively. The pH was measured after every addition of the acid or base. These results were used for pH adjustments in the later experiment. From the volume of acid needed to get pH 5.4 the alkalinity was calculated by this equation:

HCO_3^- (mg/l) = 2 × mmol HCl (used for titration of 0.5 l water to pH 5.4) × 61 g/mol.

Filter used

Before the analysis of DOC, color and UV absorbance water samples were filtered through cellulose nitrate filters with openings of 0.45 µm.

DOC (Dissolved organic carbon)

The concentration of organic carbon in filtered samples was analyzed by a Shimadzu TOC-5000 instrument.

Color

Color was analyzed in filtered samples by absorbtion at 455 nm by Dr Langes Dr 2800 instrument. There are three main causes for color of natural waters, namely the presence of humic and fulvic acids and iron.

UV absorbance

UV absorbance was analyzed in filtered samples at 254 nm by Shimadzu UVmini-1240, UV-VIS spectrophotometer. Aromatic rings present in e.g. humic and fulvic acids absorb UV light.

SUVA

SUVA is the Specific Ultraviolet Absorbance calculated by dividing the normalized UV absorbance (m^{-1}) at 245 nm by the DOC concentration (mg/l). SUVA value gives a simple characterization of the nature of the natural organic matter (NOM) in water as shown in Table 4.

Table 4. Nature of natural organic matter (NOM) based on SUVA value (Modified Edzwald and Tobiason, 1999).

SUVA	Water composition
< 2	Mostly non-humics Low hydrophobicity Low molecular weight
2 - 4	Mixture of aquatic humics and other NOM Mixture of hydrophobic and hydrophilic NOM Mixture of molecular weights
> 4	Mostly aquatic humics High hydrophobicity High molecular weight

3.2 Measuring particle size

An instrument Malvern Nano Zetasizer was used that can measure size of particles in size range 0.6 nm – 6 µm.

The water in a can was mixed by shaking and ca 200 ml was poured into a glass beaker and stirred by a magnet bar. A small portion of the sample was taken by a syringe. A polystyrene cuvette (see Figure 24) was filled with this sample 7-15 mm high and placed in the instrument for measurements. It is important to avoid getting air bubbles in the sample when filling the cuvette.

Figure 24. Polystyrene cuvette for particle size measurements with Malvern Nano Zetasizer.

The software of Malvern Nano Zetasizer, DTS gives possibility to use a Standard Operating Procedure (SOP) where the parameters and various settings can be saved. When the measurement is performed one can just choose a suitable SOP and does not have to fix settings for each measurement. Of course the settings can be done also for each measurement and that is called “Manual measurement”. However whereas the measurement is done by SOP or "manually" the following settings have to be done (in parenthesis are settings used in this study):

- Material of the particles ("*Protein*" with refractive index (RI) 1.450 and adsorption 0.001)
- Liquid media (water)
- Temperature (22°C)

  The instrument can perform measurements at different temperatures and in this study the measurements were made at 22°C.
- Equilibration time (5 minutes)

  The time between when the "Start" button has been pressed and the real beginning of the measurement is called equilibration time. This is the time needed for a sample to achieve the set temperature. The instrument can adjust the wanted temperature around the sample and measure it, but it can not measure the temperature exactly in the sample. Therefore one has to estimate the time needed for the sample to get the wanted temperature.
- Sort of cuvette used (a polystyrene cuvette)
- Measurement duration (number of sub-runs was set to be automatic)
- Number of measurements: 5
- For data processing a "*General Purpose (normal resolution)*" was chosen

The size of particles can also be measured in the green cell intended for zeta potential measurements but the polystyrene cuvette was preferred in this study.

Only results meeting "Malverns quality criteria" were used. "Malverns quality criteria" are some general quality parameters for dynamic light scattering checked by the software.

The size of particles was measured in all raw water samples, in some pH-adjusted samples and in samples of water from Pinnå treated with aluminum sulfate.

3.3 Measuring zeta potential

The zeta potential was measured by Malvern Nano Zetasizer which can measure zeta potential of particles in size range 5 nm – 10 µm.

The can with water sample was mixed and ca 200 ml was poured in a glass beaker containing a magnet bar used for stirring the sample. A small portion of this sample was taken by a syringe, transferred to green capillary cell (see Figure 25) and placed in the instrument for measurements. Air bubbles in the cell have to be avoided.

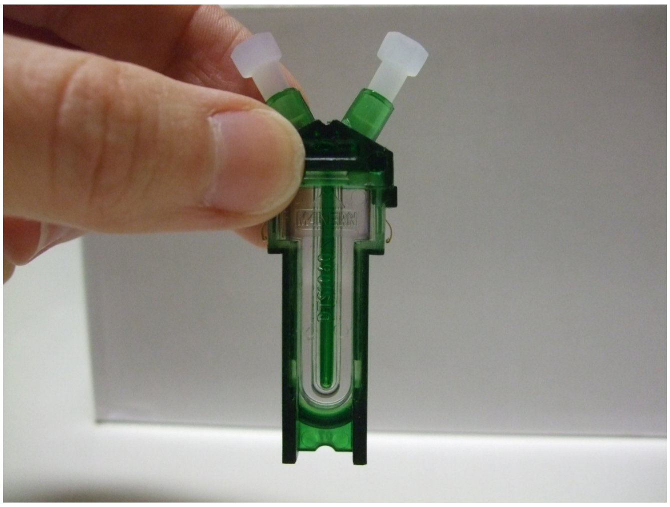


Figure 25. Green cell for zeta potential measurements with Malvern Nano Zetasizer.

Standard Operating Procedure (SOP) can be used for zeta potential measurements as well or the measurement can be done by manual settings. For zeta potential measurements the following settings have to be done (in parenthesis are settings used in this study):

- Material of the particles

  For the zeta potential measurements the choice of material is not important since the refractive index is not needed for data processing.

- Liquid media (water)

  The dispersant was water and the software automatically give the viscosity of water at the set temperature of measurements.

- Smoluchowski or Hückel approximation (Smoluchowski was used)
- Temperature (22°C)

  The instrument can perform measurements at different temperatures and in this study the measurements were made at 22°C.

- Equilibration time (5 minutes).
- Sort of cuvette used (a green or white disposable cell)
- Measurement duration (automatic, but minimum 25 sub-runs and maximum 100 sub-runs)
- Number of measurements: 10

Only results meeting “Malvern quality criteria” were used.

The number of sub-runs was set to be automatic. Sub-runs are multiple measurements of same sample, e.g. a reported result of one measurement is a mean value of results of for instance 22 measurements (sub-runs). If the measured value is not stable with time the instrument will increase the number of sub-runs until a stable result is obtained but not using more than 100 sub-runs.

Each sample was set in the SOP to be measured 10 times after each other and each of these measurements had for instance 22 sub-runs. After the measurement the quality report was checked to be “results meets quality criteria” for all 10 measurements. If the quality criteria were acceptable the *mean value* was calculated for the 7 last measurements.

The temperature to which the instrument preheated the sample was set to 22°C in most cases.

The instrument can measure zeta potential at different temperatures. Zeta potential is very dependent on viscosity which is a function of temperature. In order to see how temperature affects the results measurements of one sample were performed at various temperatures.

The zeta potential of particles was measured in all raw water samples, in pH-adjusted samples and in some samples of water treated with aluminum sulfate

3.4 Quality of measurements

Kemira Kemi AB had not previously used the Malvern Nano Zetasizer for measuring size or charge of particles in natural waters. Therefore repeatability of the measurements was followed in order to see the precision of measurements. Standard solutions were measured as well.

3.4.1 Standard solutions

Measurements of standard solutions can give an indication of a systematic error in the results.

Zeta potential measurements

“Zeta Potential Transfer Standard”, a latex standard having a zeta potential -50 mV ± 5 mV was used as zeta potential standard.

Size measurements

The standard for particle size measurements was a suspension of polymeric microspheres in water *(Nanosphere^{TM} Size Standards)* containing particles with a mean diameter of 60 ± 2.7 nm and size distribution 8.0 nm (CV 13.3 %).

3.4.2 Repeatability of measurements

The repeatability of size and zeta potential measurements by Malvern Nano Zetasizer have been studied.

According to Håvard et al. (2007, pp. 30) repeatability is “The degree of agreement between independent test results of repeated determinations of a sample with the same method and under identical conditions, *e.g. same instrument, operator and within a short interval of time.* The whole procedure should be repeated from taking a new test portion of a sample to the final reading or calculation of result.”

In this study some “real” repeatability measurements were done according to the definition above by filling the cell or cuvette with a new portion of the sample before each measurement. However most of the repeatability studies were done by repeating the measurement having the same sample in the cell or cuvette. When measuring zeta potential each sample was measured 10 times, i.e. there was the same sample portion in the cell under 10 measurements. When measuring size each sample was measured 5 times. These results are reported as repeatability in this report while the real repeatability results are reported as “real” repeatability. Repeatability was expressed as standard deviation or as a *coefficient of variation* (CV) calculated by this equation:

$$CV(\%) = \frac{100 \cdot s}{\bar{x}}$$

where s is the standard deviation and $\bar{x}$ is the mean value of the measurements.

3.5 Adjusting the pH

The influence of pH on size and charge of particles was studied. The pH was adjusted by adding a certain amount of HCl (0.5M) or NaOH (0.2M) to 200 ml of sample under mixing with a magnetic bar (100 rotations per minute). Appendix A illustrates the influence of added acid/base volume on the pH. The pH of the sample was measured before and after addition of acid or base. For each pH adjusted a new portion of sample was taken, i.e. to each 200 ml of sample the acid or base was added only once.

When pH was adjusted the sample was taken by a syringe and transported to the green cell or polystyrene cuvette. The zeta potential or size was measured by using same SOP as for raw samples as described under section 3.2 and 3.3.

3.6 Effect of aluminum sulfate on size and zeta potential of particles

Before the start of this study the ambition was to make coagulation experiments, i.e. jar tests for all water samples, using different doses of various metal salts. However after measuring size and zeta potential of non-treated water it turned out that dynamic light scattering method is not very suitable method and gives bad repeatability for natural water samples. Therefore only some jar tests with aluminum sulfate (ALS) were done on Ödåkra, Småland and Pinnå water.

The ALS used for coagulation contained 4.30% Al, had a molar OH/Al ratio of 0.08 and a density of 1.32 g/ml.

Before coagulation the soft waters, i.e. Småland and Pinnå water, were pre-treated by adding $NaHCO_3$, in order to increase their buffer capacity.

To water from Ödåkra and Småland 0.110 mmol Al/l and 0.150 mmol Al/l was added. To water from Pinnå these concentrations were added: 0.050, 0.075, 0.100, 0.125, 0.150 and 0.180 mmol Al/l. Repeatability was done for jar tests with water from Pinnå, i.e. same jar tests were done at two occasions.

Coagulation procedure

Kemira Flocculator 2000 was used for the jar tests (see Figure 26). The ALS was added to 1 liter water sample with a micro-pipette while rotating the propeller for 10 seconds with a speed of 350 rpm. pH was measured. Coagulation was carried out for 10 minutes with a propeller speed of 40 rpm. Then flocks were allowed to settle for 15 minutes and the flock size was observed. Sample for analysis was withdrawn 3 cm below the water surface.

Figure 26. The device for the jar tests.

In the sample of the treated water the turbidity, zeta potential and size of particles were measured. Then the sample was filtered through 0.45 µm cellulose nitrate filter and turbidity, color, DOC, UV-absorbance and size of particles were measured.

3.7 Ageing of water samples

Water samples could be changing with time and therefore the ageing of water samples was studied from the aspect of zeta potential.

The zeta potential of water samples was measured while the samples were getting older. In between the samples were stored at 4°C in dark and the samples were always mixed before the measurement.

Ödåkra water was measured at several occasions under a period of 69 days and Småland water under a period of 246 days. Pinnå and Stehags water were measured at some occasions under a period of 217 days.

Size measurements gave generally bad results hence the size was not followed as a function of sample ageing.

4 RESULTS AND DISCUSSION

4.1 Characterization of sampled surface waters

The results of characterization of the water samples are shown in Table 5. Titrations with HCl respectively NaOH are presented in Appendix A. The water from Ödåkra was hard, had high alkalinity and pH around 8 while the other Swedish waters were very soft, had low alkalinity and pH around 7. Water from Stehag and Neva had low turbidity compared to the other three samples. Turbidity of the filtered samples was highest for the water from Småland indicating that this sample was containing more small colloid particles. The water from Ödåkra had lowest turbidity of the filtered sample, color and DOC concentration. Hard waters are usually less colored and have lower amount of humic and fulvic substances than soft waters.

Table 5. The results of characterization of water samples.

	Ödåkra water	**Småland water**	**Stehags water**	**Pinnå water**	**Neva water (Batch 3)**
Raw sample					
Ca (mg/l)	83	3.3	6.5	9.1	/
Mg (mg/l)	7.7	1.9	1.5	2.8	/
Fe (mg/l)	0.3	0.3	0.6	1.8	/
Hardness (ºdH)	13.4	0.91	1.26	1.95	/
	Hard	Very soft	Very soft	Very soft	
HCO_3^- (mg/l) pH = 5.4	240.1	6.71	15.86	19.37	/
pH	8.19 (14ºC) 8.55 (22ºC)	6.76 (15ºC) 7.07 (22ºC)	6.54 (14ºC) 7.06 (20ºC)	6.82 (13ºC) 7.24 (21ºC)	7.46 (10°C)
Turbidity (NTU)	4.01	3.52	0.75	4.16	0.764
Filtered sample**					
Turbidity (NTU)	0.132	0.531	0.220	0.385	0.176
Color (PtCoU)	13	42	94	106	27
DOC (mg/l)	8.566	12.57	13.23	12.08	8.404
UV abs (cm^{-1})	0.148	0.274	0.457	0.47	0.218
SUVA*	1.73	2.18	3.45	3.89	2.86

**SUVA = UV abs (cm^{-1}) / (0.01 * DOC (mg/l)), UV absorbance was measured at 254nm.*

***The samples were filtered through 0.45 µm cellulose nitrate filter.*

The SUVA value of water from Ödåkra was < 2, meaning that the natural organic matter consisted mostly of non-humics and had low hydrophobicity. The other waters had SUVA values between 2 and 4, indicating that the NOM in water was a mixture of aquatic humics and other NOM, both hydrophobic and hydrophilic. Humic substances are giving water brown color and that agrees well with the results for the water from Ödåkra which had least color and lowest SUVA value.

4.2 Particle size

Measurements of particle size in most water samples generally were not acceptable according to Malvern quality criteria.

However, it was possible to measure the size of particles in water from Pinnå filtered through 8 µm filter and the repeatability was good. The average size of the particles was 144 ± 6 nm (CV = 4.3 %).

The size of particles could also be measured in water from Pinnå treated with aluminum sulfate (ALS). These results are shown in section 4.5 (Effect of metal salt), in Figure 39.

Dynamic light scattering (DLS) is not a suitable method for measuring size of particles in raw surface water samples since they contain many different kinds of particles of various sizes. DLS is most appropriate for measuring monodisperse solutions, i.e. solutions containing particles of one size and shape. Malvern Nano Zetasizer can measure particle size in size range 0.6 nm – 6 µm. This range is only one part of the whole particle size distribution in surface waters and larger particles are disturbing the measurements. Therefore the samples have to be fractionated by filtration, centrifugation or some other procedure. Such pretreatment can affect particles in the sample and particles can for instance coagulate (Comba and Kaiser, 1990; Buffle and Leppard, 1995). In the water from Pinnå larger particles (> 8 µm) were removed by filtration and the measurement of particle size was possible. When the water from Pinnå was treated with ALS it might be that the sample was less polydisperse and could thus be measured.

Furthermore it has to be taken into account that DLS method does not measure the size of a particle directly, but it measures its movement in the liquid (hydrodynamic diameter) and in calculations it assumes that the particle is a sphere.

4.3 Zeta potential

Zeta potentials of particles in the raw water samples are shown in Table 6. The repeatability of the measurements on the water from Ödåkra was acceptable, i. e. CV = 6 %. The zeta potentials of particles in water from Småland varied more and CV of the measurements was 8 %. The CV of measurements of the water from Pinnå was 9 %. The CV of zeta-potential measurements on the water from Stehag was highest of all waters. As the measured zeta potential varied a lot this water was not used for further measurements with pH adjustments etc. The results for zeta potential of particles in water from Neva, Batch 2 were not acceptable according to Malvern quality criteria. The software reported that the count rate was too low, which means that the concentrations of particles might have been too low. However water from Neva, Batch 3 could be measured and CV of the measurements was 10.5%.

Table 6 summarizes the zeta potential and coefficient of variation of the measurements on the raw waters.

Table 6. Zeta potential in raw water sample and repeatability.

	Zeta potential (mV)	Standard deviation (mV)	CV%	Repeatability
Ödåkra water	-16.5	0.99	6.0	acceptable
Småland water	-18.4	1.47	8.0	not good
Pinnå water	-21.8	1.96	9.0	not good
Stehags water	-19.7	3.58	18.2	bad
Neva water (Batch 3)	-19.9	2.08	10.5	not good

The results indicate that particles in the water from Ödåkra had highest zeta potential. This may be due to the shielding effect of the relatively high concentrations of calcium and magnesium ions in the water. It has been statistically verified that water from Ödåkra had less negative zeta potential when compared with water from Småland.

On the water from Småland the influence of the water temperature on the zeta potential of the particles was measured. The results are shown in Figure 27. From the diagram it can be seen that the zeta potential was not very dependent on the temperature at which the measurement is performed.

For all other measurements of zeta potential in this study the water was having a temperature of 22°C.

However it is very important that the temperature set in the software is same as actual temperature of the sample in the cell. The viscosity is needed for the calculations of the zeta potential and the software uses viscosity corresponding to the set temperature.

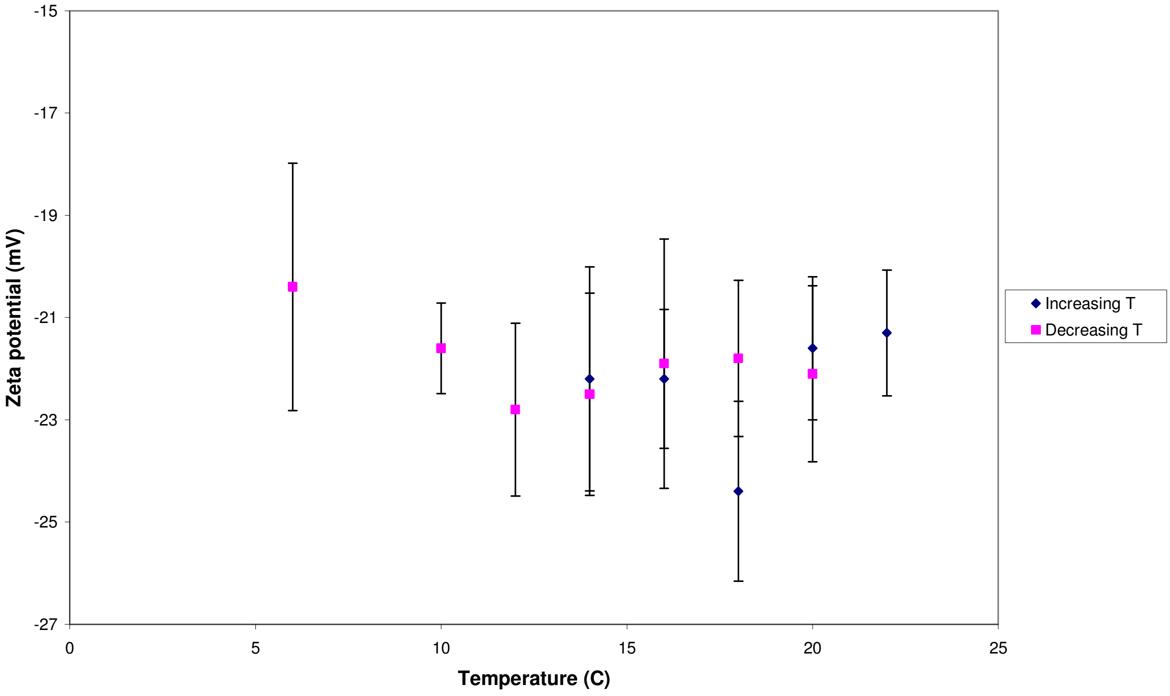


Figure 27. Zeta potential of particles in Småland water as a function of temperature. Through all measurements there was the same sample in the cell. The instrument was first increasing temperature from 14°C to 22°C and than decreasing it from 22°C to 6°C.

4.4 Zeta potential as a function of pH

In the Figure 28 the results for zeta potential of particles in Ödåkra water as a function of pH. The two lines are showing that the "real" repeatability of the measurements was not very good. Zeta potential might be increasing slightly with decreasing pH, but even at pH 3.8 the zeta potential is still about -14 mV. Repeatabilities among single measurements are shown as standard deviations in Figure 29.

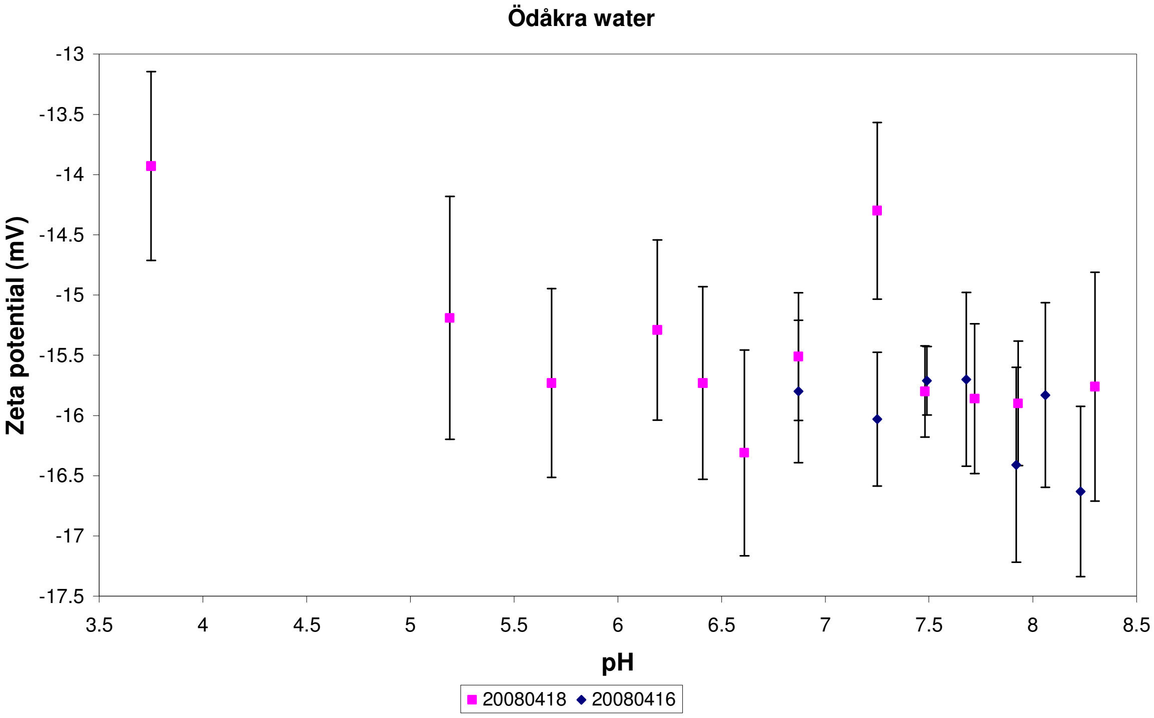


Figure 28. Zeta potential in Ödåkra water as a function of pH. Real repeatability was done for some pH adjustments.

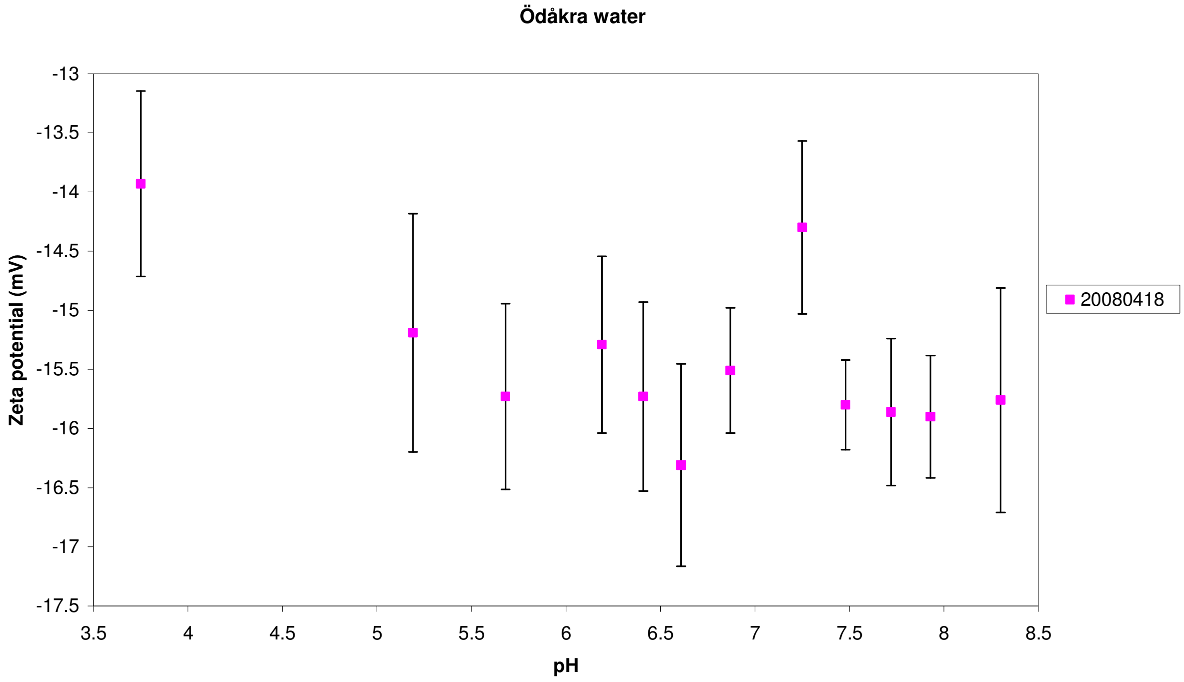


Figure 29. Zeta potential with standard deviations in Ödåkra water as a function of pH.

The influence of pH on the zeta potential in water from Småland is shown in Figure 30. The zeta potential was increasing slightly with decreasing pH.

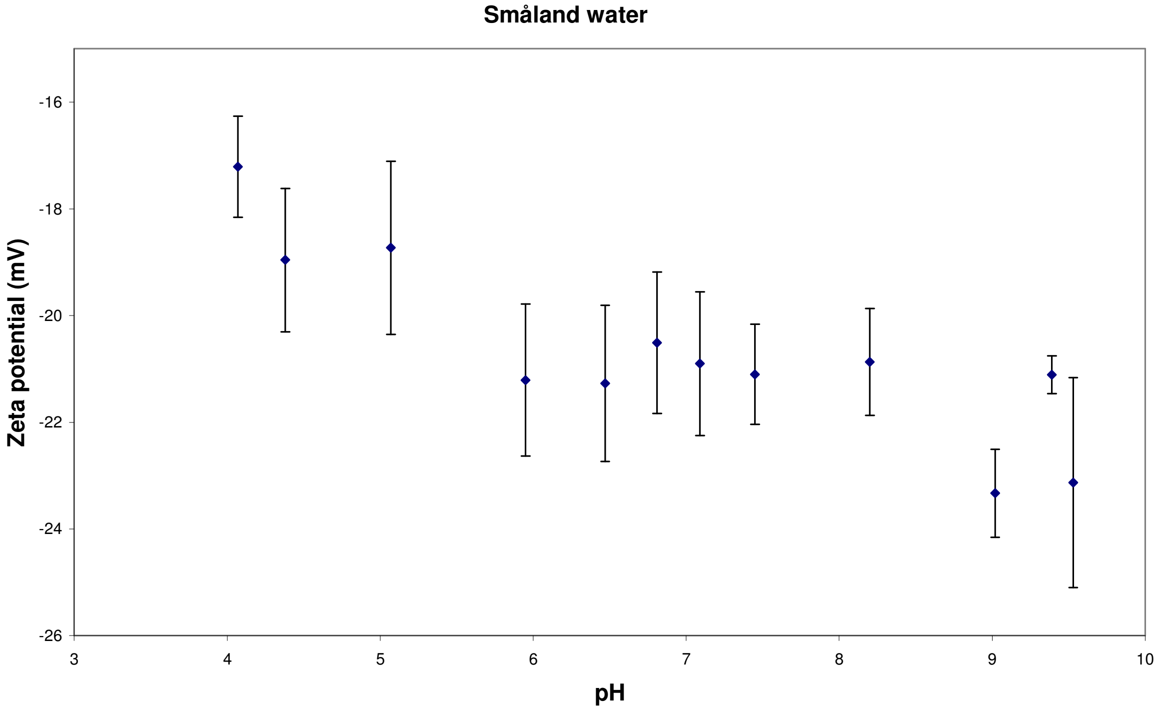


Figure 30. Zeta potential with standard deviation in Småland water as a function of pH.

The influence of pH on the zeta potential of particles in water from Pinnå is shown in Figure 31.

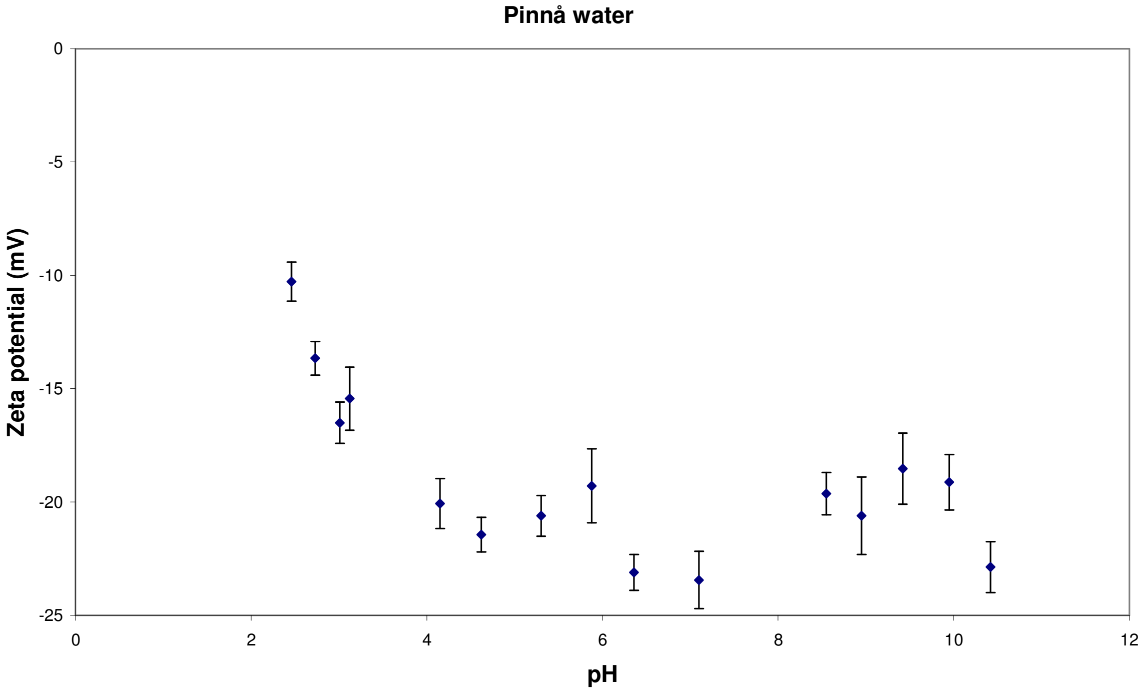


Figure 31. Zeta potential of particles in Pinnå water as a function of pH.

From the diagram it can be seen that the zeta-potential started to increase when the pH became lower than 4. This effect probably is due to neutralization of carboxylic groups. The zeta-potential still was negative when the pH was close to 2. This indicates that the particles contain other charged groups than carboxylic groups. The particles could e.g. contain sulfate or phosphate groups.

The zeta potential of particles in pH-adjusted water from Stehag was not measured because water from Stehag had bad repeatability of the results for zeta-potential measurements.

4.5 Effect of metal salt

In Table 7 the results of jar test for water from Ödåkra and Småland are presented.

Table 7. Results of the jar tests for Ödåkra water and Småland water, coagulated with two doses of aluminum sulfate (ALS).

	Ödåkra water		**Småland water**	
ALS dose (mmol/l)	**0.110**	**0.150**	**0.110**	**0.150**
In the glass beaker				
pH (9ºC)	8.11	8.11	6.80	6.80
pH (17ºC)	8.19	8.16	6.91	6.91
pH (after addition of 0,1 g/l NaHCO3, 17ºC)	-	-	7.89	7.87
pH (after coagulation, 10 min)	7.52	7.37	6.92	6.72
Flock size (mm)	~ 0.5	0.5-0.75	0.75-1	1.5
Unfiltered sample				
Turbidity (NTU)	1.61	1.12	3.06	1.05
Zeta potential (mV)	-10.89 ± 0.34	-9.90 ± 0.83	-16.91 ± 0.89	-12.70 ± 0.43
CV (%) of zeta potential	3.11	8.40	5.28	3.40
Filtered sample				
Turbidity (NTU)	0.137	0.121	0.123	0.117
DOC (mg/l)	8.144	7.989	9.297	10.02
Color (PtCoU)	9	8	9	6

In Figure 32 the zeta potential of particles in the treated water from Ödåkra and Småland are plotted. Zeta potential was less negative after the addition of higher dose of ALS, especially in the case of water from Småland.

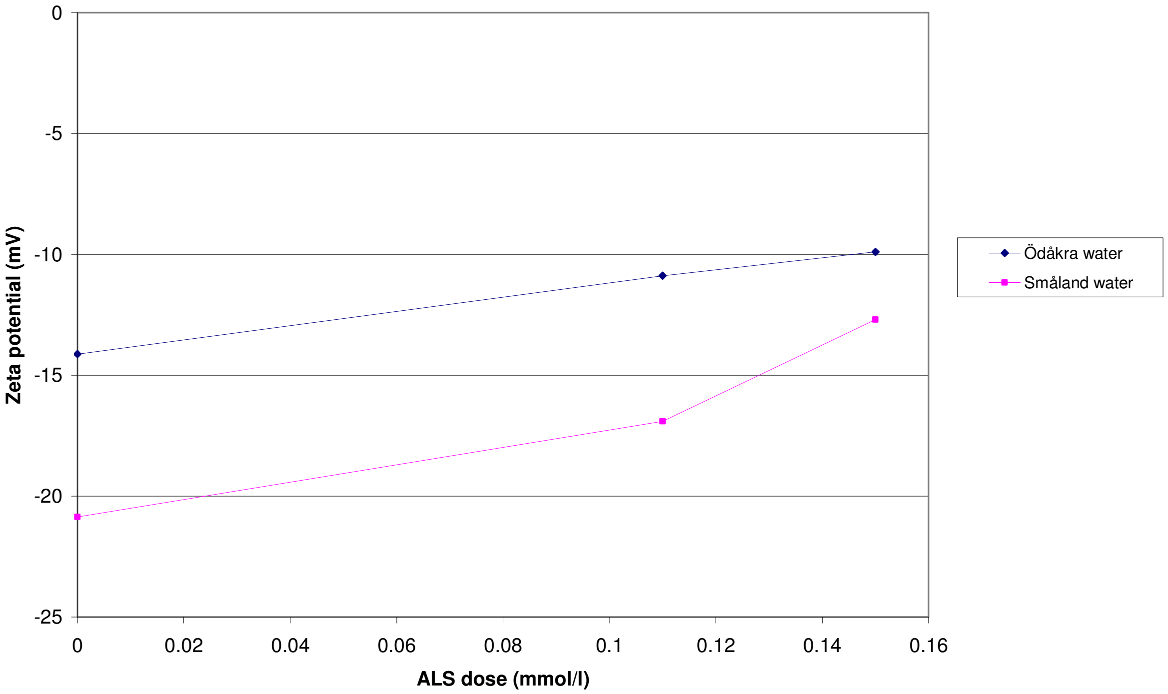


Figure 32. The results of jar tests for Ödåkra water and Småland water, coagulated with 110 mmol/l and 150 mmol/l aluminum sulfate. Standard deviations were small and are therefore not shown in the graph.

Figure 33 is showing how the treated water from Pinnå looked like after addition of different doses of ALS. Results of the jar tests of the water from Pinnå are presented in Appendix B.

Figure 33.Treated Pinnå water in a jar test. Increasing concentration of aluminum salt was added. From the left: 0.050, 0.075, 0.100, 0.125, 0.150 mmol Al/l.

The zeta potentials of particles in treated buffered water from Pinnå are shown in Figure 34. Same jar test were done at two occasions (20080609 and 20090616) and the diagram is showing the repeatability of the jar test. One jar test was made on not buffered water from Pinnå with addition of 0.150 mmol Al/l.

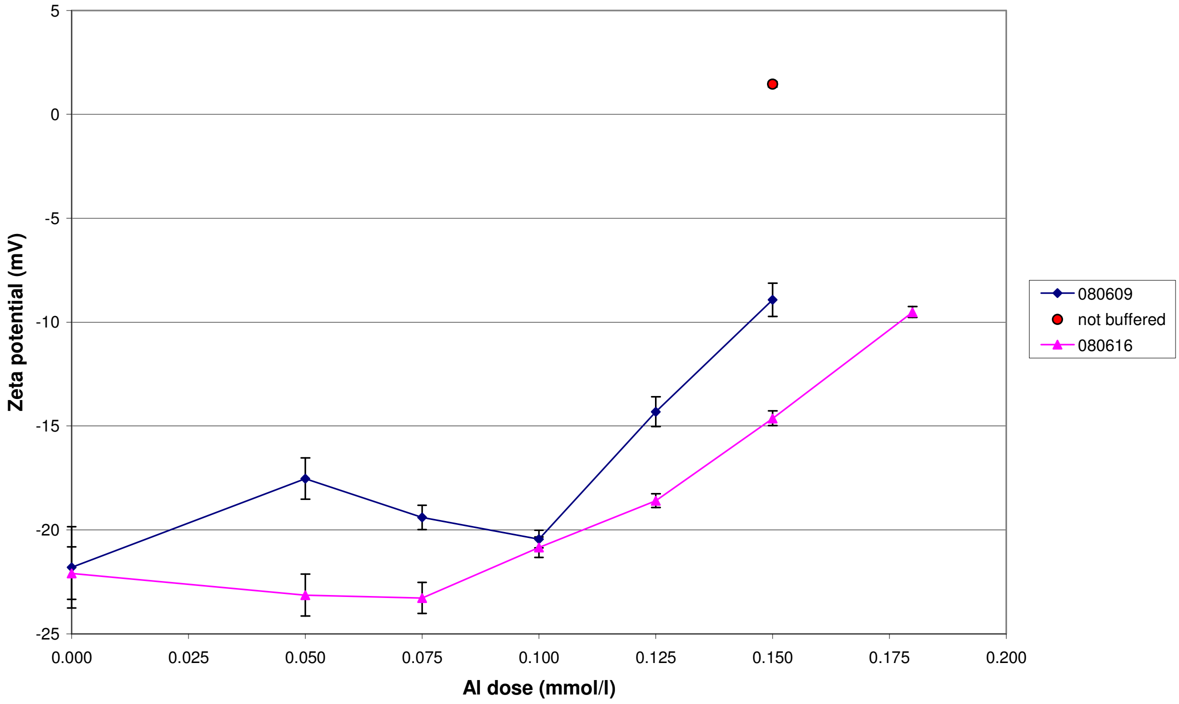


Figure 34. Zeta potential of particles in the buffered water from Pinnå as a function of Al-dose added in the jar test. The diagram shows repeatability of the jar tests. One jar test with 0.150 mmol/l ALS added was made on not buffered water.

The "real" repeatability of zeta potentials of particles from the jar tests was not very good (see Figure 34), but CV of the zeta-potential measurements of treated water was quite good and under 5 % in most cases (see Figure 34 and Appendix B). Zeta potential of particles was increasing with the increasing aluminum dose. Only in case of not buffered water the zeta potential of particles was positive.

In the Figure 35 the turbidity as a function of ALS-dose in the jar tests of the water from Pinnå is presented. Real repeatability of turbidity in jar tests is also shown. As it can be seen in the diagram the turbidity was first increasing with the increasing dose of ALS. The flocks were still too small to settle. But over 0.100 mmol Al/l the turbidity decreased.

Real repeatability of turbidity was quite good.

Corresponding results for turbidity of the filtered samples are shown in Figure 36. Real repeatability for the turbidity of filtered samples was less good, but typical trends can be seen anyway. Turbidity of the filtered sample increased first and over 0.075 mmol Al/ l it started to decrease.

Results for color and DOC concentration of the ALS-treated water from Pinnå are presented in Figure 37 and 38.

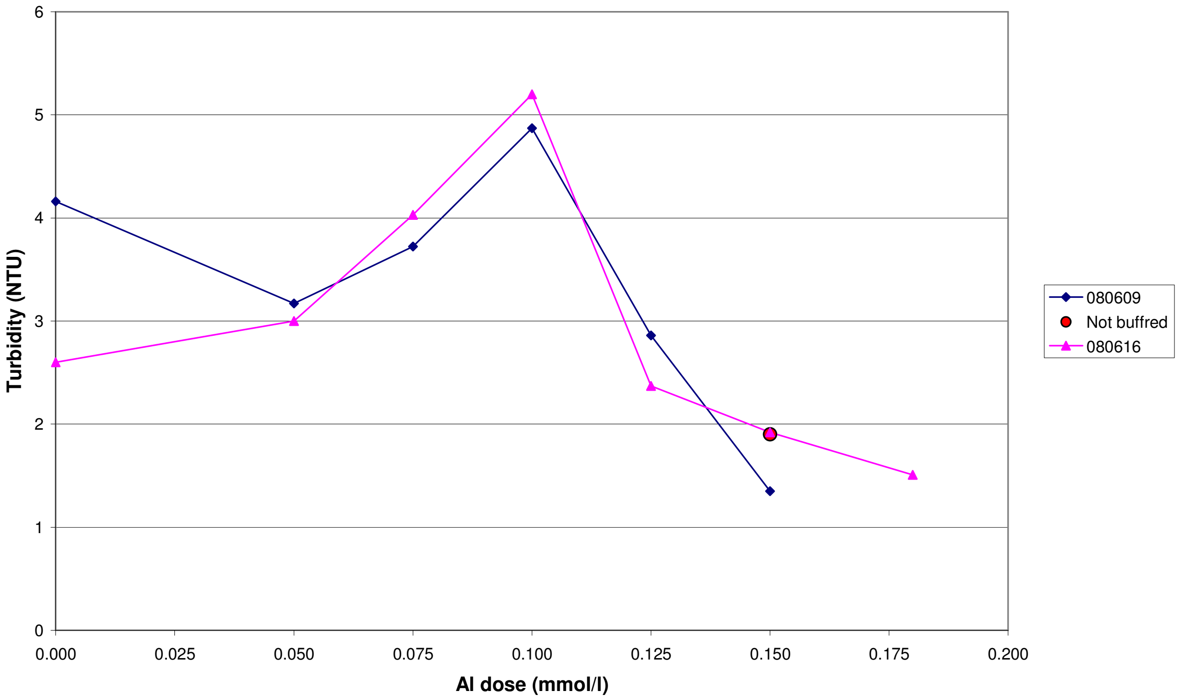


Figure 35. Turbidity in the buffered water from Pinnå as a function of Al-dose added in the jar test. The diagram shows repeatability of the jar tests. One jar test with 0.150 mmol/l ALS added was made on not buffered water.

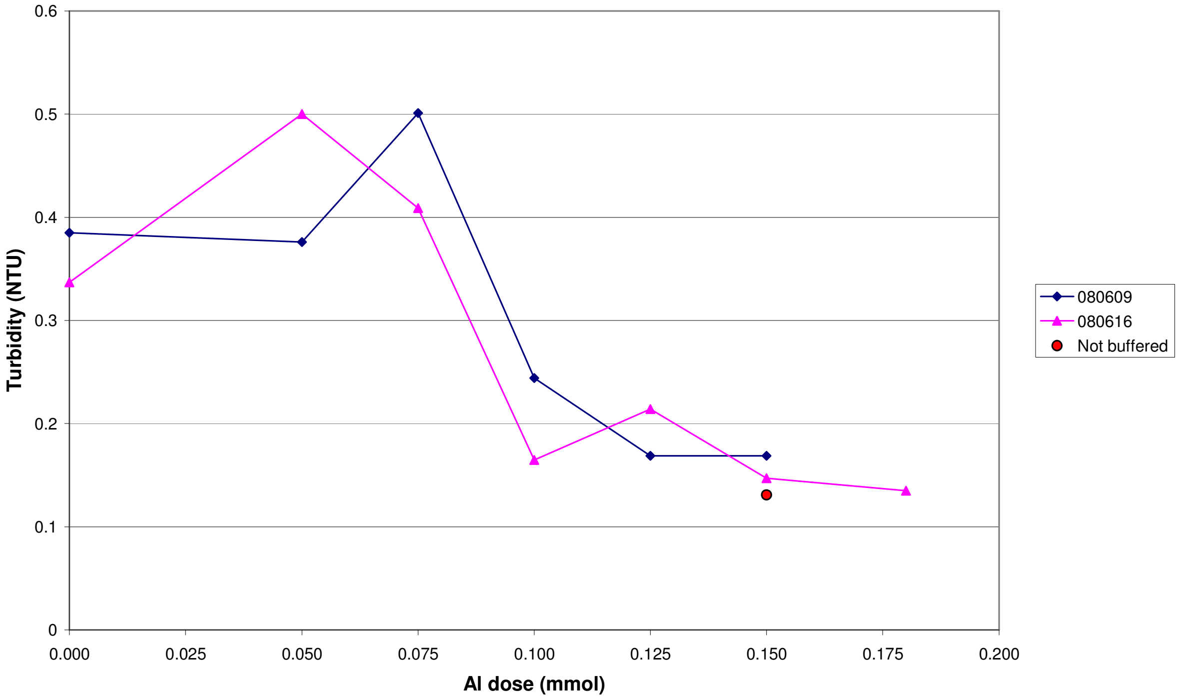


Figure 36. Turbidity of the filtered samples as a function of Al-dose added to buffered Pinnå water. The diagram shows repeatability of the jar tests. One jar test with 0.150 mmol/l ALS added was made on not buffered water.

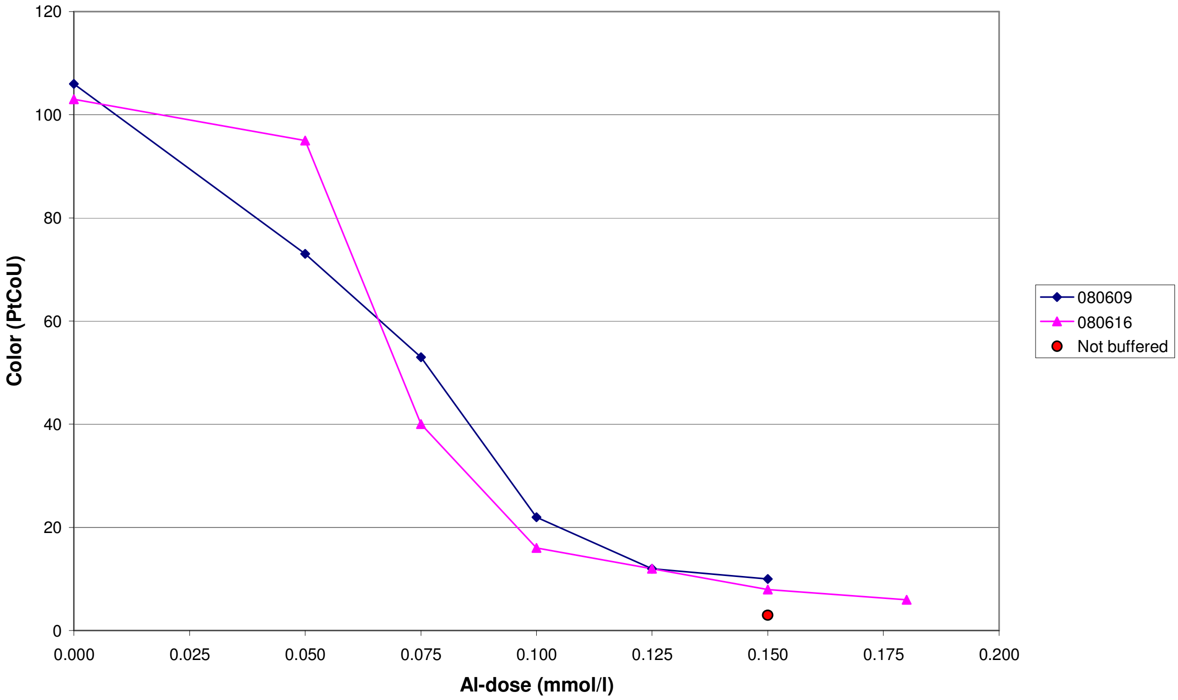


Figure 37.Color in the buffered water from Pinnå as a function of Al-dose added in the jar test. The diagram shows repeatability of the jar tests. One jar test with 0.150 mmol/l ALS added was made on not buffered water.

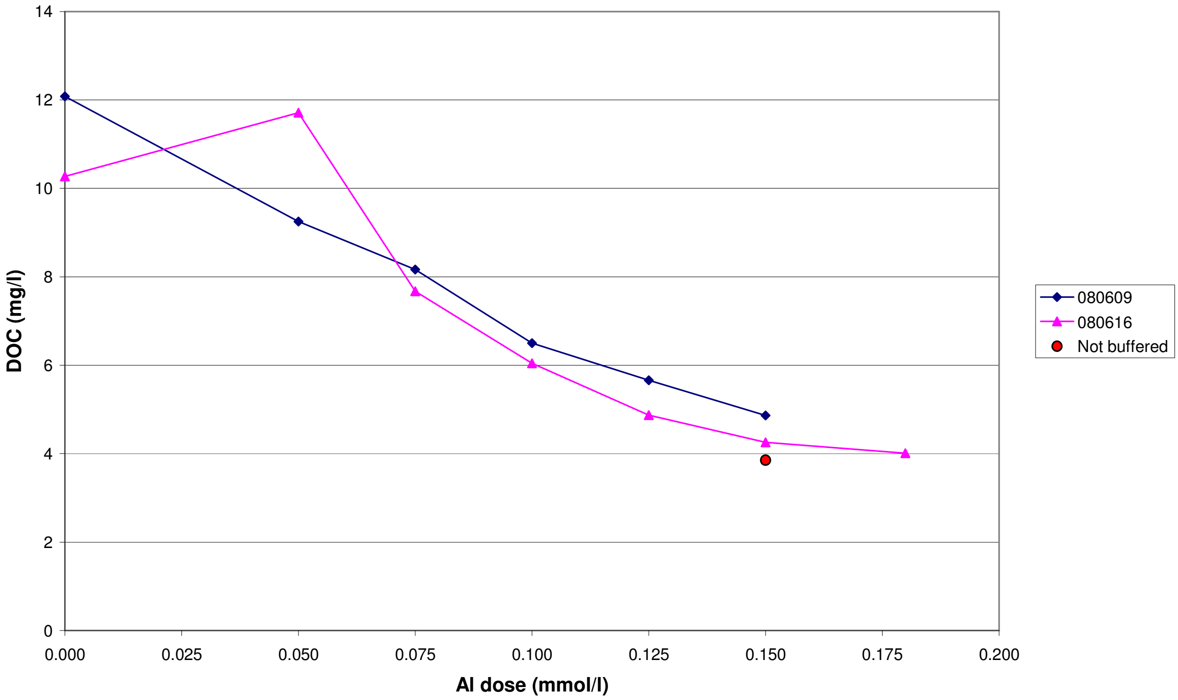


Figure 38. DOC in the buffered water from Pinnå as a function of Al-dose added in the jar test. The diagram shows repeatability of the jar tests. One jar test with 0.150 mmol/l ALS added was made on not buffered water.

The results for particle size in the water from Pinnå treated with ALS are shown in Appendix D. Average sizes of the measurements meeting Malvern quality criteria are plotted in Figure 39. Size of particles was increasing with the ALS-dose. In the sample treated with 0.150 mmol Al/l more particles have been removed and therefore size measurements were not good.

The filtered samples gave acceptable results up to the dose of 0.075 mmol Al/l. For higher doses the size measurements were not good because there were too little particles left. This agrees well with the results in Figure 36 where if can be seen that the turbidity of the filtered samples was low at the dose of 0.100 mmol Al/l.

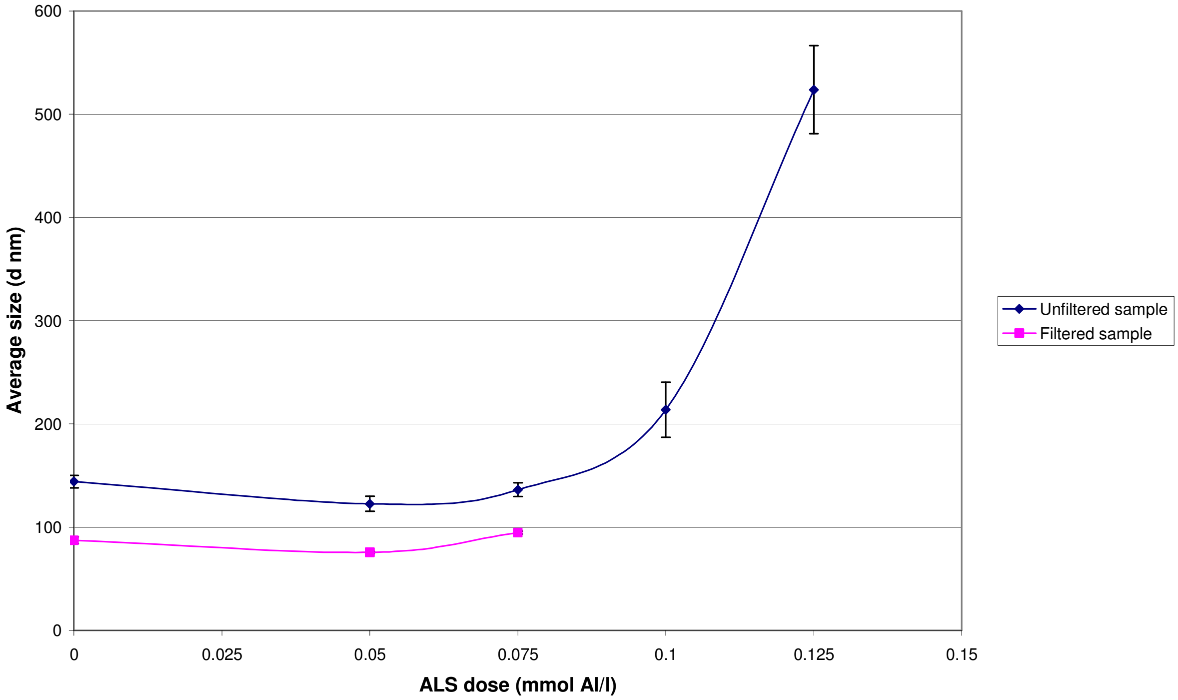


Figure 39. The average size of particles in the treated water from Pinnå as a function of ALS dose, both in unfiltered samples and in samples filtered through 0.45 µm cellulose nitrate filter. Standard deviations for the filtered samples can not be seen because they are very small.

4.6 Quality of the measurements

4.6.1 Standard solutions

The results for standard solutions were satisfactory both for zeta potential and for size measurements and also repeatability of these results was good.

The latex standard was stated to have zeta potential of -50 ± 5 mV. The results for zeta potential standard were:

- 53.03 ± 0.87 mV (CV = 1.64 %),

- 51.30 ± 0.83 mV (CV = 1.62 %),

- 50.53 ± 0.34 mV (CV = 0.66 %),

- 51.84 ± 0.57 mV (CV = 1.10 %).

The size of particles in the size standard (60 ± 2.7 nm) measured in the polystyrene cuvette was:

61.68 ± 0.48 nm (CV = 0.77 %),

62.11 ± 0.72 nm (CV = 1.16 %).

4.6.2 Repeatability of the measurements

According to the representative for Malvern in Sweden, Ulf Willén (2007), a good zeta potential measurement should be determined with repeatability of **5% (CV).**

The repeatability of zeta-potential measurements of standard solution was very good, highest CV was 1.64 %. But the repeatabilities of the measurements of the natural waters were not very good. In Appendix C the results of many measurements of zeta potential of particles in raw water samples are presented. Repeatabilities of zeta potential measurements are summarized in Table 8.

Table 8. Repeatabilities of several measurements of raw water, of pH-adjusted water and of ALS-treated water.

Water sample	Repeatability (CV%)
Ödåkra water (raw)	≈ 5 % under the first two weeks The repeatability became worse as the sample was getting older
Småland water (raw)	2.31 - 10.54 % under the first weeks 6.85 - 19.13 % later on
Pinnå water (raw)	3.92 - 13.59 % under the first weeks 3 % after several months
Stehags water (raw)	3.44 - 29.42 %
pH adjusted Ödåkra water	1.81 - 6.02 %
pH adjusted Småland water	1.67 - 8.65 %
pH adjusted Pinnå water	3.46 - 9.06 %
ALS-treated water from Pinnå	1.77 - 9.02 %
ALS-treated water from Ödåkra	3.11 and 8.40 %
ALS-treated water from Småland	3.40 and 5.28 %

The water from Ödåkra had best repeatability, usually around 5 % under the first two weeks. However the repeatability became worse as the sample was getting older.

Zeta-potential measurements of pH adjusted and ALS-treated waters had good repeatability in some cases, but not always.

However the “real” repeatability was not so good for pH-adjusted water (see Figure 28) and jar tests with ALS (see Figure 34).

4.7 Ageing of water samples

In the beginning of measurements with Malvern Nano Zetasizer the measurements were done on Neva water, Batch 2, which was 6 months old by then. The results for zeta potential and size were not acceptable according to Malvern quality criteria and the software reported that the “count rate” was too low. When the count rate is too low then the concentration of particles in the sample is usually too low.

The other sample of water from Neva (Batch 3) was measured when it was 4 months old. The measurements of zeta potential were acceptable according to Malvern quality criteria, but when same water was measured again after two months, i. e. 6 months old, the results did not meet Malvern quality criteria.

That suggested that water samples are changing with time and therefore the ageing of water samples was studied.

In the Figure 40 it is shown how zeta potential of particles in Ödåkra water had changed with time. After about two months the zeta potential was getting less negative and repeatability was worse. The phase plots in the results of 58 and 69 days old sample were not very good meaning that these results are less reliable. When the sample was that old some measurements were reported as “The count rate is too low”.

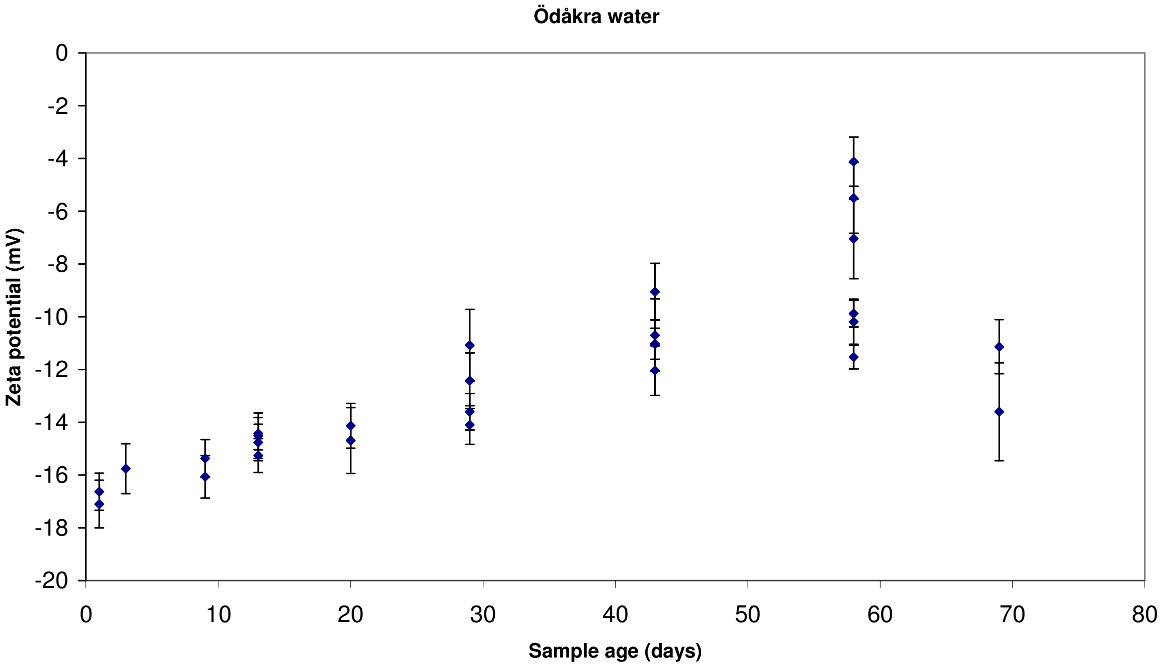


Figure 40. Ageing of Ödåkra water sample.” Real” repeatability is also shown as well as standard deviation of every measurement of zeta potential.

Zeta potential of water from Småland did not change much with time (see Figure 41). Last measurements were done when the sample was 246 days old (about 8 months) and the zeta potential could still be measured and was not less negative.

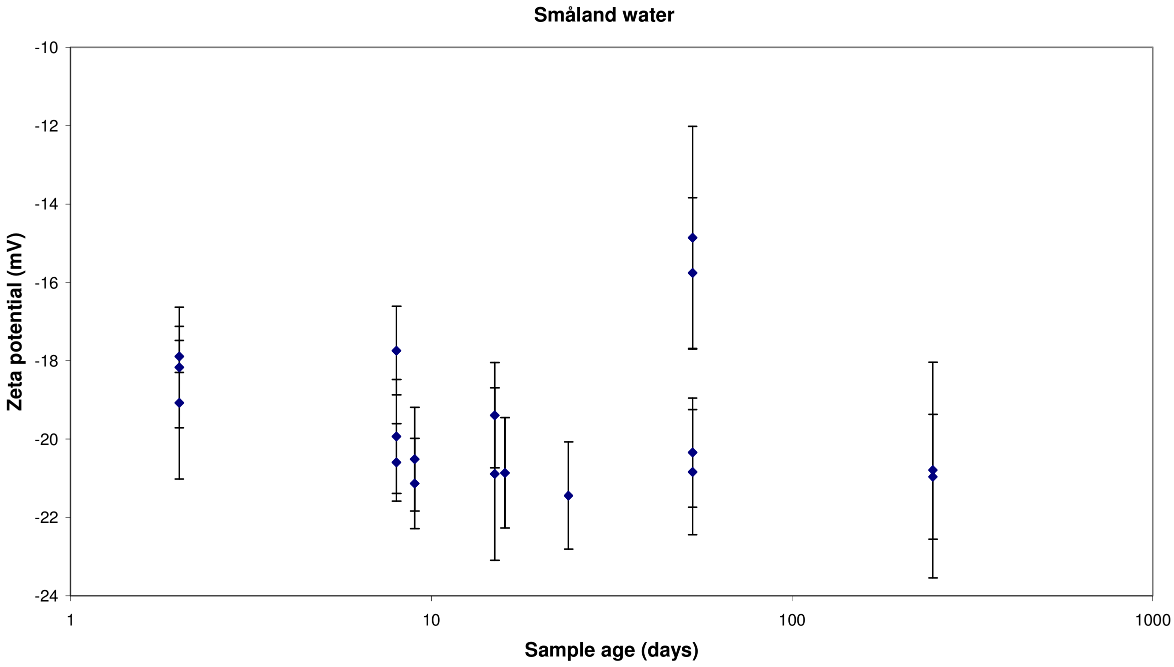


Figure 41. Ageing of Småland water sample." Real" repeatability is also shown as well as standard deviation of every measurement. Time in days is on a logarithmic scale.

Zeta potential of ageing water from Pinnå is shown in Figure 42. This sample did not change much in the aspect of zeta potential.

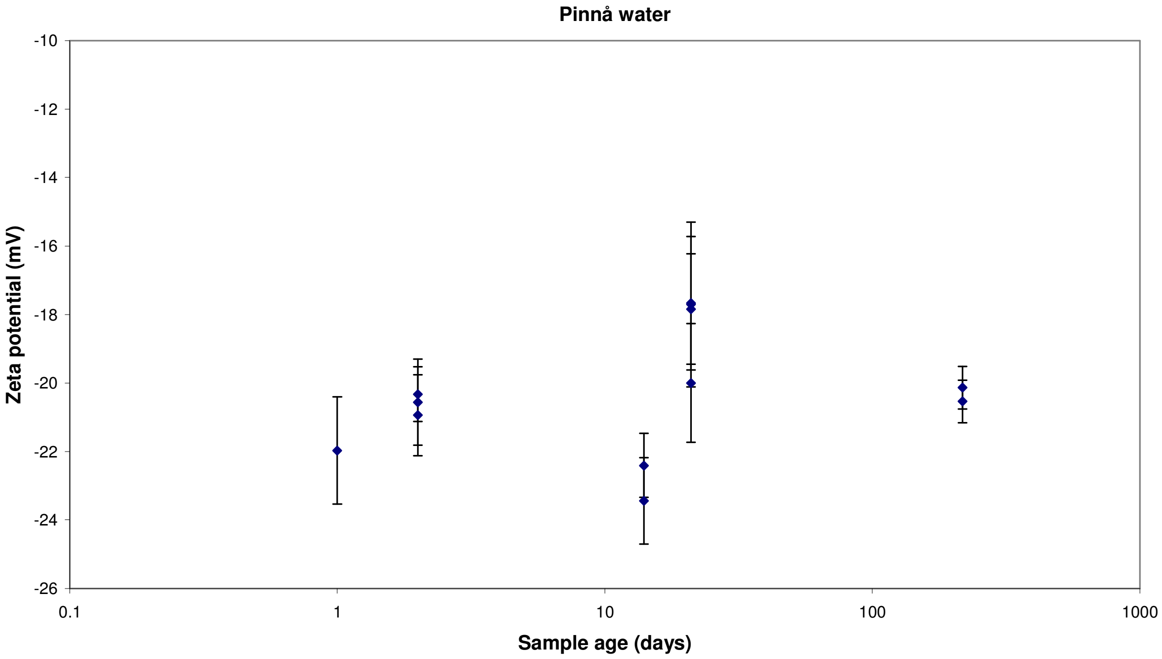


Figure 42. Ageing of Pinnå water sample. Real repeatability is also shown as well as standard deviation of every measurement. Time in days is on a logarithmic scale.

Results for zeta potential of ageing sample of water from Stehag are shown in Figure 43. Also in this case the zeta potential did not change much.

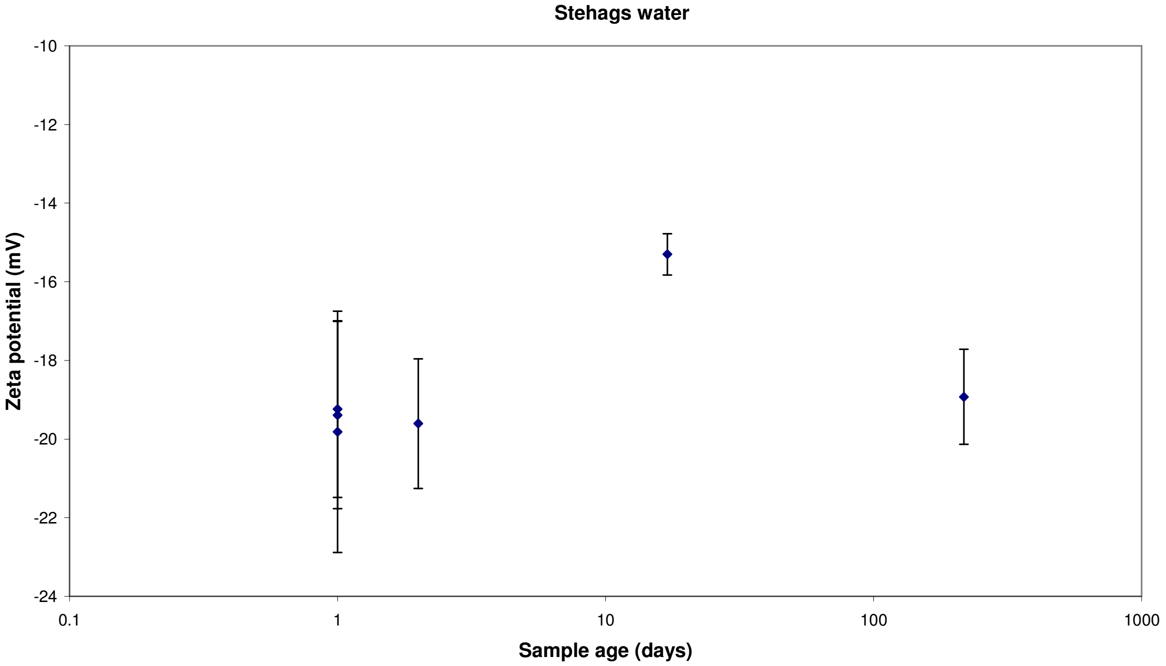


Figure 43. Ageing of Stehags water sample. Real repeatability is also shown as well as standard deviation of every measurement. Time in days is on a logarithmic scale.

Soft waters, i. e. water from Småland, Pinnå and Stehag, did not change noticeably with time in the aspect of the surface charge. On the other hand Ödåkra water, which is hard water, changed evidently. When Ödåkra water was getting older the surface charge of particles became less negative and after about two months the measurements were less reliable. Also visibly Ödåkra water changed with time.

According to several authors (Buffle and Leppard, 1995; Perret et al., 1994; Atteia et al., 1998) water samples are changing with time and the question is in which extent.

Perret et al. (1994) found that water from River Rhine could be stored at 4°C in darkness up to 4 days without any obvious change in size distribution, bacteria concentration, or morphology of particles. According to Buffle and Leppard (1995) measurements of aquatic colloids has to be carried out within 2-3 days after sampling in order to obtain reliable results. Under 2-3 days storage at 4°C and in darkness there are no significant changes by coagulation or bacterial activity in the sample.

Considering zeta potential of particles in this study only the water from Ödåkra changed with time. Changes in the size of particles with time should also be studied. The particles usually coagulate a bit and some aggregates settle. When such sample is analyzed it is mixed and particles are resuspended, but the question is if the resuspended particles are of same size as original particles. In many studies (Walther et al., 2006; Chanudet and Filella, 2007; Weilenmann et al., 1989; Perret et al., 1994) measurements of size of particles in natural waters are done within hours or at the most within some days.

5 CONCLUSIONS

Measurements of particle size with Malvern Nano Zetasizer were not acceptable according to Malvern quality criteria for most water samples in this study.

Dynamic light scattering (DLS) is not a suitable method for measuring sizes of particles in samples with a broad particle size distributions. As surface waters usually contains particles with a broad particle size distribution DLS is not a suitable method for measuring the size of particles in natural waters. When the DLS is used in such studies of surface waters the sample should be fractionated in order to make particle size distribution (PSD) narrower. Fractionation could be performed by for instance filtration or centrifugation. Nevertheless the pretreatment of samples was not developed in this study. DLS also assumes that particles are spheres and that is seldom the case in surface waters.

According to the literature the charge of particles in surface waters is negative and is usually increasing with decreasing pH. This was found to be the case in this study.

The measurements of zeta potential with Malvern Nano Zetasizer were possible, but the repeatability was not always good. The zeta potential of particles in the studied water samples was between approximately -16 mV and -22 mV. Hard water had higher zeta potential, i. e. less negative, than the soft waters.

The zeta potential of particles after the addition of aluminum salt in a jar test was increasing with an increasing dose of aluminum sulfate.

When Ödåkra water, which is hard water, was getting older the surface charge of particles became less negative. Soft waters, i. e. water from Småland, Pinnå and Stehag, did not change noticeably with time in the aspect of the surface charge.

6 RECOMMENDATIONS FOR FUTURE WORK

6.1 Develop a method for pretreatment of water samples

It was found that when particle size is measured by dynamic light scattering (DLS) the sample should only contain particles with a limited size range. If the sample contains particles with a wider size range the sample should be fractionated. Appropriate fractionation techniques were not developed in this study and that could be an objective of a coming study. The work should start by doing a detailed literature study, followed by various fractionation experiments in the laboratory.

6.2 Measure size of particles as a function of pH and time

With decreasing pH the surface charge of particles become less negative. With decreasing pH particles in natural waters would self-aggregate (coagulate). One can ask oneself if some particles are removed only as a result of pH decrease in chemical water treatment. It would be interesting to study the speed by which particles in natural waters with time self-aggregate at different pH's. It would also be interesting to see if tendency to self-aggregation varies with the water temperature. The tendency for particles to aggregate depends on the likelihood by which they collide, i.e. they depend on stirring intensity or on time when the water is not agitated. Therefore it would be useful to study the phenomena as a function of time.

6.3 Jar test with several metal salts

Zeta potential and size of particles in water treated with different metal salts should be measurement, i.e. the comparison between the effects of different metal salts on charge and size of particles should be studied.

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APPENDIX A – TITRATION OF WATER SAMPLES WITH ACID/BASE

Småland water, T = 22ºC

ml HCl (0.5 M) added to 0.5 l Småland water	HCl (mmol)	pH
0	0	7.07
0.030	0.015	6.71
0.055	0.028	6.24
0.080	0.040	5.95
0.090	0.045	5.74
0.110	**0.055**	**5.39**
0.130	0.065	5.01
0.140	0.070	4.81
0.150	0.075	4.67
0.160	**0.080**	**4.55**
0.170	0.085	4.43
0.180	0.090	4.33

04/23/2008

ml NaOH (0.2 M) added to 0.5 l Småland water	NaOH (mmol)	pH
0	0	7.16
0.028	0.006	7.46
0.058	0.012	7.92
0.088	0.018	8.48
0.122	0.024	8.90
0.156	0.031	9.10
0.186	0.037	9.25
0.218	0.044	9.38
0.252	0.050	9.49
0.284	0.057	9.59
0.320	0.064	9.67
0.356	0.071	9.75
0.390	0.078	9.80
0.420	0.084	9.86
0.456	0.091	9.91
0.488	0.098	9.96

04/24/2008

Ödåkra water, T = 22ºC

ml HCl (0.5 M) added to 0.5 l Ödåkra water	HCl (mmol)	pH
0	0.000	8.55
0.015	0.008	8.53
0.040	0.020	8.47
0.050	0.025	8.45
0.085	0.043	8.36
0.120	0.060	8.31
0.160	0.080	8.20
0.195	0.098	8.12
0.215	0.108	8.04
0.240	0.120	7.97
0.270	0.135	7.90
0.300	0.150	7.80
0.320	0.160	7.76
0.340	0.170	7.72
0.365	0.183	7.67
0.380	0.190	7.64
0.415	0.208	7.58
0.490	0.245	7.46
0.540	0.270	7.39
0.580	0.290	7.34
0.650	0.325	7.28
0.740	0.370	7.19
0.810	0.405	7.13
0.855	0.428	7.11
0.925	0.463	7.05
1.045	0.523	6.97
1.190	0.595	6.88
1.360	0.680	6.78
1.500	0.750	6.72
1.720	0.860	6.61
1.990	0.995	6.49
2.210	1.105	6.40
2.480	1.240	6.28
2.530	1.265	6.26
2.645	1.323	6.22
2.860	1.430	6.12
3.150	1.575	5.98
3.500	1.750	5.79
3.795	1.898	5.58
3.935	**1.968**	**5.44**
4.055	2.028	5.29
4.200	2.100	5.03
4.340	2.170	4.58
4.365	**2.183**	**4.48**
4.390	2.195	4.38
4.415	2.208	4.27

04/23/2008

ml NaOH (0.2 M) added to 0.5 l Ödåkra water	NaOH (mmol)	pH
0	0.000	8.49
0.035	0.007	8.52
0.104	0.021	8.57
0.254	0.051	8.67
0.428	0.086	8.77
0.668	0.134	8.89
0.810	0.162	8.95
1.054	0.211	9.04
1.194	0.239	9.09
1.220	0.244	9.11
1.212	0.265	9.14
1.324	0.287	9.14
1.468	0.316	9.18
1.682	0.359	9.22
1.860	0.394	9.28
1.960	0.414	9.30
2.306	0.484	9.38
2.514	0.525	9.42
2.630	0.548	9.42
2.668	0.556	9.35
2.874	0.597	9.37
3.228	0.668	9.44
3.566	0.736	9.50
3.954	0.813	9.56
4.360	0.894	9.63
4.942	1.011	9.73
5.214	1.065	9.76
5.554	1.133	9.80
5.734	1.169	9.81
6.110	1.244	9.88
6.434	1.309	9.93
6.592	1.341	9.95

04/23/2008

Over the pH 9.42 the water was turbid and "milky".

Stehags water, T = 20ºC

ml HCl (0.5 M) added to 0.5 l Stehags water	HCl (mmol)	pH
0	0.000	7.06
0.030	0.015	6.90
0.075	0.038	6.62
0.150	0.075	6.22
0.175	0.088	6.07
0.215	0.108	5.79
0.260	**0.130**	**5.36**
0.305	0.153	4.77
0.330	**0.165**	**4.54**
0.355	0.178	4.34
0.375	0.188	4.20
0.400	0.200	4.10
0.425	0.213	3.99
0.445	0.223	3.92
0.470	0.235	3.86
0.490	0.245	3.81
0.535	0.268	3.70
0.555	0.278	3.67
0.575	0.288	3.63
0.630	0.315	3.55
0.675	0.338	3.49
0.700	0.350	3.46
0.770	0.385	3.38
0.920	0.460	3.26
1.065	0.533	3.16
1.240	0.620	3.07

05/29/2008

ml NaOH (0.2 M) added to 0.5 l Stehags water	NaOH (mmol)	pH
0	0	7.10
0.038	0.008	7.25
0.108	0.022	7.70
0.140	0.028	8.04
0.176	0.035	8.46
0.210	0.042	8.73
0.282	0.056	9.09
0.390	0.078	9.39
0.466	0.093	9.55
0.578	0.116	9.73
0.680	0.136	9.87
0.790	0.158	9.99
0.862	0.172	10.04

05/29/2008

Pinnå water, T = 21ºC

ml HCl (0.5 M) added to 0.5 l Pinnå water	HCl (mmol)	pH
0	0.000	7.24
0.055	0.028	6.92
0.105	0.053	6.64
0.150	0.075	6.43
0.200	0.100	6.21
0.220	0.110	6.11
0.245	0.123	5.99
0.270	0.135	5.86
0.295	0.148	5.71
0.340	**0.170**	**5.28**
0.365	0.183	5.00
0.390	0.195	4.71
0.415	**0.208**	**4.46**
0.440	0.220	4.27
0.465	0.233	4.14
0.555	0.278	3.80
0.585	0.293	3.74
0.655	0.328	3.60
0.750	0.375	3.47
0.850	0.425	3.36
1.005	0.503	3.24
1.135	0.568	3.16
1.280	0.640	3.08

05/29/2008

ml NaOH (0.2 M) added to 0.5 l Pinnå water	NaOH (mmol)	pH
0	0	7.12
0.094	0.019	7.53
0.126	0.025	7.72
0.158	0.032	7.98
0.194	0.039	8.28
0.230	0.046	8.52
0.268	0.054	8.70
0.304	0.061	8.84
0.342	0.068	8.96
0.376	0.075	9.05
0.450	0.090	9.22
0.526	0.105	9.35
0.634	0.127	9.51
0.778	0.156	9.68
0.928	0.186	9.82
1.070	0.214	9.94
1.206	0.241	10.04

05/29/2008

APPENDIX B – RESULTS FOR JAR TESTS OF WATER FROM PINNÅ

Jar tests with the water from Pinnå:

ALS dose (mmol/l)		pH before coagulation	pH after coagulation	Floc size (mm)	Zeta potential (mV)	Standard deviation (mV) of zeta potential	CV % of zeta potential	Turbidity (FTU)	Turbidity (FTU)	Color (PtCoU)	DOC (mg/l)	UA-abs, 254 nm (cm-1)	SUVA
									Filtered sample				
0.000		7.24	-	-	-21.8	1.96	9.0	4.16	0.385	106	12.08	0.470	3.89
0.050	+ 0,05 g/l NaHCO3	7.79	7.13	0.3-0.5	-17.53	0.99	5.65	3.17	0.376	73	9.247	0.387	4.19
0.075		7.77	6.94	0.5	-19.40	0.58	2.99	3.72	0.501	53	8.162	0.312	3.82
0.100		7.77	6.83	0.5-0.75	-20.45	0.42	2.07	4.87	0.244	22	6.500	0.184	2.83
0.125		7.77	6.66	1.5-2.25	-14.31	0.72	5.01	2.86	0.169	12	5.658	0.133	2.35
0.150		7.77	6.52	1.5-2.25	-8.93	0.80	8.92	1.35	0.169	10	4.867	0.102	2.10
0.150		7.38	5.21	-	1.45	0.13	9.02	1.90	0.131	3	3.852	0.073	1.90

T = 22 ºC

Repeatability of same jar tests with the water from Pinnå (2008-06-16):

ALS dose (mmol/l)		pH before coagulation	pH after coagulation	Floc size (mm)	Zeta potential (mV)	Standard deviation (mV) of zeta potential	CV % of zeta potential	Turbidity (FTU)	Turbidity (FTU)	Color (PtCoU)	DOC (mg/l)	UA-abs, 254 nm (cm-1)	SUVA
									Filtered sample				
0.000	+ 0,05 g/l NaHCO3	7.18	/	< 0.3	-22.09	1.26	5.72	2.60	0.337	103	10.27	0.473	4.61
0.050		7.60	7.04	0.3-0.5	-23.14	1.01	4.38	3.00	0.500	95	11.71	0.445	3.80
0.075		7.62	6.88	0.5	-23.27	0.75	3.21	4.03	0.409	40	7.671	0.248	3.23
0.100		7.60	6.73	0.5-0.75	-20.84	0.49	2.35	5.20	0.165	16	6.048	0.151	2.50
0.125		7.61	6.62	1.5-2.25	-18.59	0.33	1.77	2.37	0.214	12	4.874	0.120	2.46
0.150		7.60	6.47	1.5	-14.63	0.35	2.42	1.92	0.147	8	4.257	0.096	2.26
0.180		7.60	6.34	1.5	-9.52	0.26	2.77	1.51	0.135	6	4.009	0.078	1.95

T = 22 ºC

APPENDIX C – ZETA POTENTIALS OF PARTICLES IN AGEING RAW WATER SAMPLES AND REPEATABILIES

Zeta potential (ZP) of particles under a period of several months. St. dv. is standard deviation.

Date	Ödåkra water			Småland water			Pinnå water			Stehags water		
	ZP (mV)	St.dv. (mV)	CV%	ZP (mV)	St.dv. (mV)	CV%	ZP (mV)	St.dv. (mV)	CV%	ZP (mV)	St.dv. (mV)	CV%
16/04/2008	-16.63	0.71	4.25									
	-17.10	0.90	5.27									
18/04/2008	-15.76	0.95	6.02									
22/04/2008				-17.89	0.41	2.31						
				-18.17	1.54	8.45						
				-19.07	1.95	10.22						
24/04/2008	-15.37	0.71	4.62									
	-16.07	0.81	5.01									
28/04/2008	-15.26	0.64	4.21	-17.74	1.13	6.37						
	-14.43	0.61	4.25	-19.93	1.45	7.27						
	-14.51	0.86	5.91	-20.59	0.99	4.80						
	-14.76	0.69	4.68									
29/04/2008				-21.13	1.15	5.45						
				-20.51	1.32	6.46						
05/05/2008	-14.13	0.85	5.99	-19.39	1.35	6.94						
	-14.69	1.25	8.52	-20.89	2.20	10.54						
06/05/2008				-20.86	1.41	6.75						
14/05/2008	-12.43	1.05	8.48	-21.44	1.37	6.38						
	-11.08	1.36	12.30									
	-14.10	0.73	5.20									
	-13.60	0.69	5.08									
19/05/2008							-21.67	1.82	8.41	-21.89	6.44	29.42
							-21.70	2.64	12.16	-18.17	1.90	10.48
20/05/2008							-21.97	1.57	7.13	-19.82	3.07	15.48
										-19.24	2.25	11.68
										-19.39	2.38	12.29
21/05/2008							-20.56	1.26	6.12	-19.61	1.65	8.40
							-20.94	1.19	5.66			
							-20.33	0.80	3.92			
28/05/2008	-11.03	0.59	5.33									
	-12.04	0.94	7.83									
02/06/2008	-10.70	1.37	12.83				-23.44	1.26	5.38			
	-9.05	1.07	11.86				-22.41	0.93	4.16			
05/06/2008										-15.3	0.53	3.44
09/06/2008							-17.67	1.95	11.01			
							-20.00	1.74	8.68			
							-17.71	2.41	13.59			
							-17.84	1.61	9.02			
12/06/2008	-5.50	1.34	24.41	-15.76	1.92	12.20						
	-7.05	1.51	21.45	-14.86	2.84	19.13						
	-9.88	0.51	5.21	-20.34	1.39	6.85						
	-11.53	0.45	3.90	-20.84	1.60	7.67						
	-4.12	0.93	22.65									
	-10.19	0.85	8.38									
23/06/2008	-11.14	1.03	9.21									
	-13.6	1.86	13.64									
22/12/2008				-20.79	2.75	13.21	-20.54	0.62	3.01	-7.75	1.02	13.15
				-20.96	1.59	7.57	-20.14	0.62	3.09	-18.93	1.21	6.37

For the measurements in red the results had bad phase plots.

APPENDIX D – RESULTS FOR SIZE MEASUREMENTS OF TREATED PINNÅ WATER

PdI is polydispersity index.

Record	**Sample Name**	**Measurement Date**	**PdI**	**Z-Average (d.nm)**	**Size Peak 1 (d.nm)**	**Size Peak 2 (d.nm)**	**Size Peak 3 (d.nm)**	**Malvern quality criteria**
111	Pinnå + 0.150 mmol ALS, not buffered	den 9 juni 2008 15:59:53	1	5690	78.82	0	0	not OK
112	Pinnå + 0.150 mmol ALS, not buffered	den 9 juni 2008 16:03:09	0.786	2654	1002	0	0	not OK
113	Pinnå + 0.150 mmol ALS, not buffered	den 9 juni 2008 16:06:25	0.898	2412	900.1	0	0	not OK
114	Pinnå + 0.150 mmol ALS, not buffered	den 9 juni 2008 16:09:41	0.512	1662	1108	0	0	not OK
115	Pinnå + 0.150 mmol ALS, not buffered	den 9 juni 2008 16:12:58	0.564	2115	1346	0	0	not OK
116	Pinnå + 0.050 mmol ALS, buffered	den 9 juni 2008 16:22:13	0.429	283.2	150.6	39.07	0	not OK
117	Pinnå + 0.050 mmol ALS, buffered	den 9 juni 2008 16:25:29	0.342	219.8	90.22	283	0	not OK
118	Pinnå + 0.050 mmol ALS, buffered	den 9 juni 2008 16:28:45	0.385	151	171.5	38.38	0	not OK
119	Pinnå + 0.050 mmol ALS, buffered	den 9 juni 2008 16:32:02	0.56	120.7	165.2	4962	0	**OK!**
120	Pinnå + 0.050 mmol ALS, buffered	den 9 juni 2008 16:35:18	0.424	125	171.1	4635	0	**OK!**
121	Pinnå + 0.075 mmol ALS, buffered	den 9 juni 2008 16:42:33	0.611	147.1	240.8	3246	17.31	**OK!**
122	Pinnå + 0.075 mmol ALS, buffered	den 9 juni 2008 16:44:57	0.596	144.2	268.8	3587	0	**OK!**
123	Pinnå + 0.075 mmol ALS, buffered	den 9 juni 2008 16:47:22	0.601	144.6	274.6	3895	22.74	**OK!**
124	Pinnå + 0.075 mmol ALS, buffered	den 9 juni 2008 16:49:47	0.517	135.6	215.8	3509	20.24	**OK!**
125	Pinnå + 0.075 mmol ALS, buffered	den 9 juni 2008 16:52:12	0.543	135.9	292.1	78.17	4675	**OK!**
126	Pinnå + 0.100 mmol ALS, buffered	den 9 juni 2008 16:58:21	0.355	214.5	192.1	56.58	0	not OK
127	Pinnå + 0.100 mmol ALS, buffered	den 9 juni 2008 17:00:36	0.365	191.5	219.4	5134	0	**OK!**
128	Pinnå + 0.100 mmol ALS, buffered	den 9 juni 2008 17:02:50	0.36	182.3	215.3	4363	0	**OK!**
129	Pinnå + 0.100 mmol ALS, buffered	den 9 juni 2008 17:05:05	0.369	186.4	239.6	5369	0	**OK!**
130	Pinnå + 0.100 mmol ALS, buffered	den 9 juni 2008 17:07:19	0.444	183.3	281	4896	29.94	**OK!**
131	Pinnå + 0.125 mmol ALS, buffered	den 9 juni 2008 17:15:41	0.529	527.3	545.1	120.9	0	**OK!**
132	Pinnå + 0.125 mmol ALS, buffered	den 9 juni 2008 17:19:59	0.498	508.5	654.5	5117	61.83	**OK!**
133	Pinnå + 0.125 mmol ALS, buffered	den 9 juni 2008 17:24:17	0.472	465.3	973.7	0	0	**OK!**
134	Pinnå + 0.125 mmol ALS, buffered	den 9 juni 2008 17:28:36	0.476	468.8	687.7	141.1	4801	**OK!**
135	Pinnå + 0.125 mmol ALS, buffered	den 9 juni 2008 17:32:55	0.457	488.3	734.3	4088	72.6	**OK!**
136	Pinnå + 0.150 mmol ALS, buffered	den 10 juni 2008 08:27:53	0.86	1388	595.5	0	0	not OK
137	Pinnå + 0.150 mmol ALS, buffered	den 10 juni 2008 08:30:39	0.489	1294	970.4	122.8	0	not OK
138	Pinnå + 0.150 mmol ALS, buffered	den 10 juni 2008 08:33:25	0.488	1135	942.9	5256	0	**not OK**
139	Pinnå + 0.150 mmol ALS, buffered	den 10 juni 2008 08:36:10	0.558	947.4	1103	169.5	5560	not OK
140	Pinnå + 0.150 mmol ALS, buffered	den 10 juni 2008 08:38:55	0.406	949.9	949.3	130.4	5406	not OK

REPEATABILITY OF THE JAR TEST

Record	Sample Name	Measurement Date	PdI	Z-Average (d.nm)	Size Peak 1 (d.nm)	Size Peak 2 (d.nm)	Size Peak 3 (d.nm)	Malvern quality criteria
121	Pinnå + 0.050 mmol ALS, buffered	den 16 juni 2008 16:05:13	0.389	132.7	150.3	38.04	0	not OK
122	Pinnå + 0.050 mmol ALS, buffered	den 16 juni 2008 16:07:47	0.576	115.5	112.6	446.3	5179	**OK!**
123	Pinnå + 0.050 mmol ALS, buffered	den 16 juni 2008 16:10:23	0.587	118.8	205	4614	0	**OK!**
124	Pinnå + 0.050 mmol ALS, buffered	den 16 juni 2008 16:12:58	0.423	114.7	158.7	4531	0	**OK!**
125	Pinnå + 0.050 mmol ALS, buffered	den 16 juni 2008 16:19:49	0.652	134.8	134.5	591.1	5150	**OK!**
126	Pinnå + 0.050 mmol ALS, buffered	den 16 juni 2008 16:22:03	0.559	126.9	172.6	4780	0	**OK!**
127	Pinnå + 0.050 mmol ALS, buffered	den 16 juni 2008 16:24:18	0.445	117	175.6	4406	0	**OK!**
128	Pinnå + 0.050 mmol ALS, buffered	den 16 juni 2008 16:26:33	0.642	131.6	221.6	4540	22.67	**OK!**
129	Pinnå + 0.050 mmol ALS, buffered	den 16 juni 2008 16:28:47	0.415	134.1	234.5	3515	22.1	not OK
130	Pinnå + 0.075 mmol ALS, buffered	den 16 juni 2008 16:34:00	0.382	135.9	106.7	324.3	5240	**OK!**
131	Pinnå + 0.075 mmol ALS, buffered	den 16 juni 2008 16:36:25	0.353	129.5	330.6	0	0	**OK!**
132	Pinnå + 0.075 mmol ALS, buffered	den 16 juni 2008 16:38:50	0.347	130.4	167.1	4568	0	**OK!**
133	Pinnå + 0.075 mmol ALS, buffered	den 16 juni 2008 16:41:15	0.354	130.2	188.8	5007	0	**OK!**
134	Pinnå + 0.075 mmol ALS, buffered	den 16 juni 2008 16:43:39	0.343	129.9	191.2	3896	0	**OK!**
135	Pinnå + 0.100 mmol ALS, buffered	den 16 juni 2008 16:52:55	0.414	239.4	342.3	4244	0	**OK!**
136	Pinnå + 0.100 mmol ALS, buffered	den 16 juni 2008 16:55:10	0.423	236.8	634.6	148.3	0	**OK!**
137	Pinnå + 0.100 mmol ALS, buffered	den 16 juni 2008 16:57:24	0.418	230.7	474.9	39.07	0	**OK!**
138	Pinnå + 0.100 mmol ALS, buffered	den 16 juni 2008 16:59:39	0.447	238.6	595.4	16.23	0	**OK!**
139	Pinnå + 0.100 mmol ALS, buffered	den 16 juni 2008 17:01:53	0.448	234.6	370.3	4778	0	**OK!**
140	Pinnå + 0.125 mmol ALS, buffered	den 16 juni 2008 17:06:20	0.522	652.4	842.3	154.3	5520	not OK
141	Pinnå + 0.125 mmol ALS, buffered	den 16 juni 2008 17:08:34	0.63	568.8	764.4	185.9	5167	**OK!**
142	Pinnå + 0.125 mmol ALS, buffered	den 16 juni 2008 17:10:49	0.449	558.8	817	167.9	5394	**OK!**
143	Pinnå + 0.125 mmol ALS, buffered	den 16 juni 2008 17:13:03	0.488	574.1	912.9	4369	110.1	**OK!**
144	Pinnå + 0.125 mmol ALS, buffered	den 16 juni 2008 17:15:18	0.463	552.9	814.2	175.9	5379	**OK!**
145	Pinnå + 0.150 mmol ALS, buffered	den 16 juni 2008 17:19:49	1	1895	611	0	0	not OK
146	Pinnå + 0.150 mmol ALS, buffered	den 16 juni 2008 17:22:14	0.993	1599	632.1	0	0	not OK
147	Pinnå + 0.150 mmol ALS, buffered	den 16 juni 2008 17:24:38	0.495	1139	876.9	5184	0	not OK
148	Pinnå + 0.150 mmol ALS, buffered	den 16 juni 2008 17:27:03	0.627	1040	887.8	0	0	not OK
149	Pinnå + 0.150 mmol ALS, buffered	den 16 juni 2008 17:27:45	0.528	1028	918.6	121.6	0	not OK
150	Pinnå + 0.000 mmol ALS, buffered	den 16 juni 2008 17:32:53	0.471	279.5	299.2	86.12	0	not OK
151	Pinnå + 0.000 mmol ALS, buffered	den 16 juni 2008 17:35:39	0.54	206.8	285.9	73.53	0	not OK
152	Pinnå + 0.000 mmol ALS, buffered	den 16 juni 2008 17:38:24	0.577	162.7	247.3	50.98	4743	**OK!**
153	Pinnå + 0.000 mmol ALS, buffered	den 16 juni 2008 17:41:10	0.425	191.4	253.2	56.59	5560	not OK
154	Pinnå + 0.000 mmol ALS, buffered	den 16 juni 2008 17:43:55	0.566	149.2	208.4	43.72	4645	**OK!**

	Type	Sample Name	Measurement Date	PdI	Z-Average (d.nm)	Size Peak 1 (d.nm)	Size Peak 2 (d.nm)	Size Peak 3 (d.nm)	Malvern quality criteria
1	Size	Pinnå water + 0.050 mmol ALS, filtered	den 17 juni 2008 14:48:46	0.3	76.05	82.42	16.61	0	**OK!**
2	Size	Pinnå water + 0.050 mmol ALS, filtered	den 17 juni 2008 14:50:50	0.26	75.34	97.95	0	0	**OK!**
3	Size	Pinnå water + 0.050 mmol ALS, filtered	den 17 juni 2008 14:52:54	0.27	75.61	106.5	0	0	**OK!**
4	Size	Pinnå water + 0.050 mmol ALS, filtered	den 17 juni 2008 14:54:57	0.25	75.07	96.97	4906	0	**OK!**
5	Size	Pinnå water + 0.050 mmol ALS, filtered	den 17 juni 2008 14:57:01	0.28	73.62	116.8	0	0	**OK!**
6	Size	Pinnå water + 0.075 mmol ALS, filtered	den 17 juni 2008 15:14:23	0.24	96.54	114.9	4948	0	**OK!**
7	Size	Pinnå water + 0.075 mmol ALS, filtered	den 17 juni 2008 15:16:47	0.22	95.23	125.6	0	0	**OK!**
8	Size	Pinnå water + 0.075 mmol ALS, filtered	den 17 juni 2008 15:19:12	0.2	95.28	122	0	0	**OK!**
9	Size	Pinnå water + 0.075 mmol ALS, filtered	den 17 juni 2008 15:21:37	0.2	95.73	115.2	4772	0	**OK!**
10	Size	Pinnå water + 0.075 mmol ALS, filtered	den 17 juni 2008 15:24:02	0.21	93.6	123.2	0	0	**OK!**
11	Size	Pinnå water + 0.100 mmol ALS, filtered	den 17 juni 2008 15:42:31	0.31	177.1	194.1	4905	0	not OK
12	Size	Pinnå water + 0.100 mmol ALS, filtered	den 17 juni 2008 15:48:32	0.32	177.5	152.1	4837	0	not OK
13	Size	Pinnå water + 0.100 mmol ALS, filtered	den 17 juni 2008 15:54:33	0.27	171.2	179.2	4819	0	not OK
14	Size	Pinnå water + 0.100 mmol ALS, filtered	den 17 juni 2008 16:00:34	0.26	167.2	133.7	4919	0	not OK
15	Size	Pinnå water + 0.100 mmol ALS, filtered	den 17 juni 2008 16:06:35	0.3	196.1	141	5157	0	not OK
16	Size	Pinnå water, filtered	den 17 juni 2008 16:20:52	0.28	89.38	128.5	0	0	**OK!**
17	Size	Pinnå water, filtered	den 17 juni 2008 16:23:37	0.28	83.19	117.3	0	0	**OK!**
18	Size	Pinnå water, filtered	den 17 juni 2008 16:26:22	0.29	89.69	124.8	18.67	4302	**OK!**
19	Size	Pinnå water, filtered	den 17 juni 2008 16:29:08	0.28	82.6	127	0	0	**OK!**
20	Size	Pinnå water, filtered	den 17 juni 2008 16:31:53	0.29	84.03	129.3	15.02	0	**OK!**
1	Size	Pinnå water + 0.050 mmol ALS, filtered	den 18 juni 2008 10:25:35	0.32	76.85	93.82	5229	0	**OK!**
2	Size	Pinnå water + 0.050 mmol ALS, filtered	den 18 juni 2008 10:27:39	0.32	76.79	95.59	19.03	4876	**OK!**
3	Size	Pinnå water + 0.050 mmol ALS, filtered	den 18 juni 2008 10:29:43	0.33	76.66	93.3	4744	0	**OK!**
4	Size	Pinnå water + 0.050 mmol ALS, filtered	den 18 juni 2008 10:31:47	0.26	74.38	104.9	12.27	0	**OK!**
5	Size	Pinnå water + 0.050 mmol ALS, filtered	den 18 juni 2008 10:33:51	0.26	75.68	104.7	4388	0	**OK!**
6	Size	Pinnå water + 0.075 mmol ALS, filtered	den 18 juni 2008 10:52:34	0.22	96.97	112.8	5012	0	**OK!**
7	Size	Pinnå water + 0.075 mmol ALS, filtered	den 18 juni 2008 10:54:49	0.2	93.01	115.1	18.96	0	**OK!**
8	Size	Pinnå water + 0.075 mmol ALS, filtered	den 18 juni 2008 10:57:03	0.21	93.24	120.9	0	0	**OK!**
9	Size	Pinnå water + 0.075 mmol ALS, filtered	den 18 juni 2008 10:59:18	0.21	93.38	121.4	0	0	**OK!**
10	Size	Pinnå water + 0.075 mmol ALS, filtered	den 18 juni 2008 11:01:32	0.2	95.05	121.1	0	0	**OK!**
11	Size	Pinnå water + 0.100 mmol ALS, filtered	den 18 juni 2008 11:24:34	0.45	378	202.9	73.1	5560	not OK
12	Size	Pinnå water + 0.100 mmol ALS, filtered	den 18 juni 2008 11:31:16	0.37	301.1	127.1	416.4	5377	not OK
13	Size	Pinnå water + 0.100 mmol ALS, filtered	den 18 juni 2008 11:37:57	0.76	198.6	123.2	2848	26.83	not OK
14	Size	Pinnå water + 0.100 mmol ALS, filtered	den 18 juni 2008 11:44:39	0.5	174.4	169.4	4452	0	not OK
15	Size	Pinnå water + 0.100 mmol ALS, filtered	den 18 juni 2008 11:51:21	0.9	237.2	101.8	4526	583.9	not OK
16	Size	Pinnå water, filtered	den 18 juni 2008 12:43:55	0.41	92.07	112.8	4547	14.92	**OK!**
17	Size	Pinnå water, filtered	den 18 juni 2008 12:46:30	0.33	90.82	111	4704	17.02	**OK!**
18	Size	Pinnå water, filtered	den 18 juni 2008 12:49:05	0.29	85.9	123.8	0	0	**OK!**
19	Size	Pinnå water, filtered	den 18 juni 2008 12:51:40	0.27	89	117.6	4418	0	**OK!**
20	Size	Pinnå water, filtered	den 18 juni 2008 12:54:15	0.29	86.95	128	4234	0	**OK!**

APPENDIX E - THE ARTICLE

Size and charge of particles in surface waters

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Abstract

Size and surface charge of small particles in five surface waters has been studied by the instrument Malvern Nano Zetasizer. Also the effect of pH on surface charge of particles was measured and furthermore the size and charge of particles in water treated with aluminum sulfate. The instrument can measure the size of particles in a size range 0.6 nm – 6 µm and the charge of particles in a size range 5 nm – 10 µm. Most size measurements were not acceptable. Dynamic light scattering (DLS) used by this instrument is not a suitable method for measuring sizes of particles in raw samples with a broad particle size distribution (PSD). DLS also assumes that particles are spheres and that is seldom the case in surface waters. The zeta potential of particles in the studied water samples was between approximately -16 mV and -22 mV. The repeatability was not always good. Hard water had a less negative zeta potential than the soft waters. The zeta potentials became less negative with decreasing pH. The zeta potential of particles after having added aluminum sulfate to the water became less negative with increasing doses of added aluminum sulfate. Ageing of samples in the aspect of zeta potential was also studied. The zeta potential of the particles in the soft waters has not changed much with time, while zeta potential of hard water changed.

Keywords: size, surface charge, particles, surface waters, Malvern Nano Zetasizer

Introduction

Surface waters contain many kinds of particles and in a broad size range. The size of particles is often studied as particle size distributions (PSD) and in natural water it usually follows power law distribution (Pareto's law): with decreasing size of particles the number of the particles is increasing exponentially (Buffle and Leppard, 1995; Gregory, 2006; Lartiges et al., 2001). The surface charge of particles in surface waters is negative (Perret et al., 1994) and the charge usually become less negative with decreasing pH (Gerritsen and Bradley, 1987). This study was conducted in order to learn more about the size and charge of particles in surface waters. Knowledge of this kind would help understanding the processes of chemical water treatment.

The size and zeta potential of the particles in five water samples were measured by Malvern Nano Zetasizer. Measurements were done in raw samples and in pH adjusted samples. Furthermore the effects of different doses of aluminum sulfate on zeta potential of particles in three waters were measured.

Materials and methods

Samples of four surface waters were collected in the South of Sweden and one sample was obtained from the River Neva in Russia. Two 25 liters cans were sampled from each water source and stored at 4°C and in dark.

Neva water: Water from River Neva was sampled in St Petersburg in Russia. One sample of Neva water, called Batch 2, was taken in the summer 2007 and one sample, called Batch 3, was taken in November 2007.

Ödåkra water: A sample from a small stream running into Vegeå stream was sampled in Ödåkra, close to Helsingborg, on the 15th of April 2008.

Ljusgöl water: On the 20th of April 2008 a water sample was taken from the small lake Ljusgöl, situated 30 km south of Västervik in Småland.

Stehags water: The water was fetched at Ringsjö water treatment plant at Stehag on the 19th of May 2008. This water came through a tunnel from Lake Bolmen in the south of Småland.

Pinnå water: Water was taken from the Pinnå stream at Stidsvik on the 19th of May 2008. The Pinnå stream is running into Rönne stream in the east part of Skåne.

The samples were characterized by calcium, magnesium and iron concentrations, pH, alkalinity, turbidity, color, UV absorbance and DOC concentration.

Calcium, magnesium and iron were analyzed by ICP (Inductively Coupled Plasma Spectroscopy). From the calcium and magnesium concentrations the hardness of the waters was calculated. ***Turbidity*** was measured by a HACH 2100N turbidimeter. ***pH*** was measured by a WTW 323 pH-meter using a Hamilton Polilyte bridge lab electrode being calibrated at the temperature of the sample. ***Titration with HCl/NaOH and alkalinity:*** Water samples (0.5 l) were titrated by 0.5 M HCl and 0.2 M NaOH respectively. These results were used for pH adjustments in the later experiment. ***Filter used:*** Before the analysis of DOC, color and UV absorbance water samples were filtered through cellulose nitrate filters with openings of 0.45 µm. ***DOC (Dissolved organic carbon):*** The concentration of organic carbon in filtered samples was analyzed by a Shimadzu TOC-5000 instrument. ***Color*** was analyzed in filtered samples by absorbtion at 455 nm by Dr Langes Dr 2800 instrument. ***UV absorbance*** was analyzed in filtered samples at 254 nm by Shimadzu UVmini-1240, UV-VIS spectrophotometer. Aromatic rings present in e.g. humic and fulvic acids absorb UV light. ***SUVA*** is the Specific Ultraviolet Absorbance calculated by dividing the normalized UV absorbance (m^{-1}) at 245 nm by the DOC concentration (mg/l).

Measuring particle size

Malvern Nano Zetasizer uses dynamic light scattering (DLS) technique for measuring the size of particles. It can measure in size range 0.6 nm – 6 µm. Size measurements were done at the temperature of 22°C. The water in a can was mixed by shaking and a small portion of the sample was taken by a syringe. The number of sub-runs was set to be automatic and there were five measurements of each sample. For data processing a "*General Purpose (normal resolution)"* was chosen. Only results meeting "Malvern quality criteria" were used. "Malvern quality criteria" are some general quality parameters for dynamic light scattering checked by the software. DLS measures the Brownian motion of the particles which is related to the size of them. DLS technique is described elsewhere (Gregory, 2006; Perret et al., 1994). The size of particles was measured in all raw water samples, in some pH-adjusted samples and in samples of water from Pinnå treated with aluminum sulfate.

Measuring zeta potential

The zeta potential of particles was measured in all raw water samples, in pH-adjusted samples and in some samples of water treated with aluminum sulfate. Malvern Nano Zetasizer is measuring zeta potential by using laser doppler velocimetry (LDV). The instrument measures the velocity of a particle in an electric field, i.e. electrophoretic mobility. It can measure zeta potential of particles in size range 5 nm – 10 µm. The water sample was mixed and a small portion was taken by a syringe, transferred to green capillary cell and placed in the instrument for measurements done at 22°C. Equilibration time was 5 minutes. Measurement duration was set to be automatic, but with a minimum of 25 sub-runs. There were ten measurements of each sample. Only results meeting "Malvern quality criteria" were used. Sub-runs are multiple measurements of same sample, e.g. a reported result of one measurement is a mean value of results of for instance 22 measurements (sub-runs). If the measured value is not stable with time the instrument will increase the number of sub-runs until a stable result is obtained but not using more than 100 sub-runs. If the quality criteria were acceptable for all 10 measurements the *mean value* was calculated for the 7 last measurements.

Quality of measurements

"Zeta Potential Transfer Standard", a latex standard having a zeta potential -50 mV ± 5 mV was used as zeta potential standard. The standard for particle size measurements was a suspension of polymeric microspheres in water *(Nanosphere^{TM} Size Standards)* containing particles with a mean diameter of 60 ± 2.7 nm and size distribution 8.0 nm (CV 13.3 %). The repeatability of size and zeta potential measurements by Malvern Nano Zetasizer has been followed and it was expressed as standard deviation or as a *coefficient of variation* (CV %).

Adjusting the pH

The pH was adjusted by adding a certain amount of HCl (0.5M) or NaOH (0.2M) to 200 ml of sample under mixing with a magnetic bar (100 rotations per minute). For each pH adjustment a new portion of sample was taken.

Jar tests with aluminum sulfate

Jar tests with aluminum sulfate (ALS) were done on Ödåkra, Ljusgöl and Pinnå water. The ALS used for coagulation contained 4.30% Al, had a molar OH/Al ratio of 0.08 and a density of 1.32 g/ml. Before coagulation the soft waters, i.e. Ljusgöl and Pinnå water, were pre-treated with $NaHCO_3$, in order to increase their buffer capacity. To water from Ödåkra and Ljusgöl 0.110 mmol Al/l and 0.150 mmol Al/l was added. The water from Pinnå was treated with: 0.050, 0.075, 0.100, 0.125, 0.150 and 0.180 mmol Al/l. Repeatability was done for jar tests with water from Pinnå, i.e. same jar tests were done at two occasions.

Coagulation procedure: Kemira Flocculator 2000 was used for the jar tests. The ALS was added to 1 liter water sample with a micro-pipette while rotating the propeller for 10 seconds with a speed of 350 rpm. pH was measured. Coagulation was carried out for 10 minutes with a propeller speed of 40 rpm. Then flocks were allowed to settle for 15 minutes. Sample for analysis was withdrawn 3 cm below the water surface. In the sample of the treated water the turbidity, zeta potential and size of particles were measured. Then the sample was filtered and turbidity, color, DOC, UV-absorbance and size of particles were measured.

Ageing of water samples

Water samples could be changing with time and therefore the ageing of water samples was studied from the aspect of zeta potential. The zeta potential of water samples was measured while the samples were getting older. Ödåkra water was measured at several occasions under a period of 69 days and Ljusgöl water under a period of 246 days. Pinnå and Stehags water were measured at some occasions under a period of 217 days.

Results and discussion

The results of characterization of the water samples are shown in Table 1. The water from Ödåkra was hard while the other Swedish waters were very soft. The SUVA value of water from Ödåkra was < 2 $cm^{-1}/(0.01*mg/l\ DOC)$, meaning that the natural organic matter consisted mostly of non-humics and had low hydrophobicity (Edzwald et al., 1985; Edzwald and Tobiason, 1999). The other waters had SUVA values between 2 and 4, indicating that the NOM in water was a mixture of aquatic humics and other NOM, both hydrophobic and hydrophilic (Edzwald and Tobiason, 1999). Humic substances are giving water brown color and that agrees well with the results for the water from Ödåkra which had least color and lowest SUVA value.

Particle size

Measurements of particle size in most water samples generally were not acceptable according to Malvern quality criteria. However, it was possible to measure the size of particles in water from Pinnå filtered through 8 μm filter and the repeatability was good. The average size of the particles was 144 ± 6 nm (CV = 4.3 %). The size of particles could also be measured in water from Pinnå treated with aluminum sulfate (ALS) (see Figure 2).

Dynamic light scattering (DLS) is not a suitable method for measuring size of particles in raw surface water samples since they contain many different kinds of particles of various sizes. DLS is most appropriate for measuring monodisperse solutions, i.e. solutions containing particles of one size and shape. Malvern Nano Zetasizer can measure particle size in size range 0.6 nm – 6 μm. This range is only one part of the whole particle size distribution in surface waters (Buffle and Leppard, 1995) and larger particles are disturbing the measurements. Therefore the samples have to be fractionated by filtration, centrifugation or some other procedure. Such pretreatment can affect particles in the sample and particles can for instance coagulate (Comba and Kaiser, 1990; Buffle and Leppard, 1995).

Table 1. The results of characterization of water samples.

	Ödåkra water	Ljusgöl water	Stehags water	Pinnå water	Neva water
Raw sample					
Ca (mg/l)	83	3.3	6.5	9.1	/
Mg (mg/l)	7.7	1.9	1.5	2.8	/
Fe (mg/l)	0.3	0.3	0.6	1.8	/
Hardness (ºdH)	13.4, Hard	0.91, Very soft	1.26, Very soft	1.95, Very soft	/
HCO_3^- (mg/l) pH = 5.4	240.1	6.71	15.86	19.37	/
pH	8.19 (14ºC) 8.55 (22ºC)	6.76 (15ºC) 7.07 (22ºC)	6.54 (14ºC) 7.06 (20ºC)	6.82 (13ºC) 7.24 (21ºC)	7.46 (10°C)
Turbidity (NTU)	4.01	3.52	0.75	4.16	0.764
Filtered sample					
Turbidity (NTU)	0.132	0.531	0.220	0.385	0.176
Color (PtCoU)	13	42	94	106	27
DOC (mg/l)	8.566	12.57	13.23	12.08	8.404
UV abs (cm^{-1})	0.148	0.274	0.457	0.47	0.218
SUVA*	1.73	2.18	3.45	3.89	2.86

**SUVA = UV abs (cm^{-1}) / (0.01 * DOC (mg/l)), UV absorbance was measured at 254nm.*

In the water from Pinnå larger particles (> 8 μm) were removed by filtration and the measurement of particle size was possible. When the water from Pinnå was treated with ALS it might be that the sample was less polydisperse and could thus be measured.

Furthermore it has to be taken into account that DLS method does not measure the size of a particle directly, but it measures its movement in the liquid (hydrodynamic diameter) and in calculations it assumes that the particle is a sphere.

Zeta potential

Zeta potentials of particles in the raw water samples are shown in Table 2. The measured zeta potential of the water from Stehag varied a lot and therefore this water was not used for further measurements with pH adjustments etc. The results for zeta potential of particles in water from Neva, Batch 2 were not acceptable according to Malvern quality criteria. The software reported that the count rate was too low, which means that the concentrations of particles might have been too low. However water from Neva, Batch 3 could be measured.

The results indicate that particles in the water from Ödåkra had highest zeta potential. This may be due to the shielding effect of the relatively high concentrations of calcium and magnesium ions in the water (see Table 1). It has been statistically verified that water from Ödåkra had less negative zeta potential when compared with water from Ljusgöl.

Zeta potential as a function of pH

The results for zeta potential of particles in the water from Ödåkra, Ljusgöl and Pinnå as a function of pH are shown in the Figure 1. The zeta potential was slightly increasing with decreasing pH. In the case of the water from Pinnå it can be seen that the zeta-potential started to increase when the pH became lower than 4.

This effect probably is due to neutralization of carboxylic groups. The zeta-potential was still negative when the pH was close to 2.

Table 2. Zeta potential in raw water sample and repeatability.

	Zeta potential (mV)	Standard deviation (mV)	CV%	Repeatability
Ödåkra water	-16.5	0.99	6.0	acceptable
Ljusgöl water	-18.4	1.47	8.0	not good
Pinnå water	-21.8	1.96	9.0	not good
Stehags water	-19.7	3.58	18.2	bad
Neva water (Batch 3)	-19.9	2.08	10.5	not good

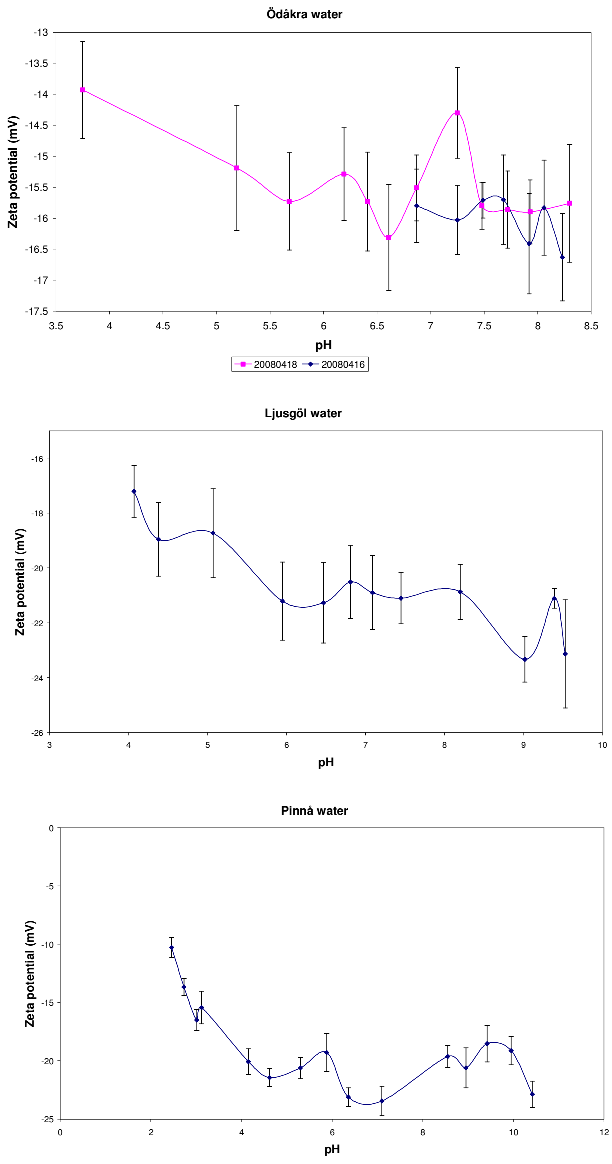

Figure 1. Zeta potential of particles in the water from Ödåkra, Ljusgöl and Pinnå. Some samples of Ödåkra water have been pH-adjusted twice - repeatability was not very good.

This indicates that the particles contain other charged groups than carboxylic groups. The particles could e.g. contain sulfate or phosphate groups.

Effect of metal salt

In Table 3 the results of jar test for water from Ödåkra and Ljusgöl are presented. Zeta potential was less negative after the addition of higher dose of ALS, especially in the case of water from Ljusgöl.

The results of jar tests with the water from Pinnå are shown in Figure 2. Most jar tests were done at two occasions (20080609 and 20090616) and the diagram is showing the repeatability of the jar tests. One jar test was made on not buffered water from Pinnå with addition of 0.150 mmol Al/l. Zeta potential of particles was increasing with the increasing aluminum dose. Only in case of not buffered water the zeta potential of particles was positive. In the diagram for turbidity (Figure 2) it can be seen that the turbidity was first increasing with the increasing dose of ALS. The flocks were still too small to settle. But over 0.100 mmol Al/l the turbidity decreased.

The size measurements meeting Malvern quality criteria are plotted in one diagram in Figure 2. Size of particles was increasing with the ALS-dose. In the sample treated with 0.150 mmol Al/l more particles have been removed and therefore size measurements were not good (results are not shown). The filtered samples gave acceptable results up to the dose of 0.075 mmol Al/l. For higher doses the size measurements were not good because there were too little particles left. This agrees well with the results shown in the diagram for filtered turbidity where it can be seen that the turbidity was low at the dose of 0.100 mmol Al/l.

Table 3. Results of the jar tests for Ödåkra water and Ljusgöl water, coagulated with two doses of aluminum sulfate (ALS).

	Ödåkra water		Ljusgöl water	
ALS dose (mmol/l)	**0.110**	**0.150**	**0.110**	**0.150**
Turbidity (NTU)	1.61	1.12	3.06	1.05
Zeta potential (mV)	-10.89 ± 0.34	-9.90 ± 0.83	-16.91 ± 0.89	-12.70 ± 0.43
CV (%) of zeta potential	3.11	8.40	5.28	3.40
Turbidity (NTU), filtered	0.137	0.121	0.123	0.117

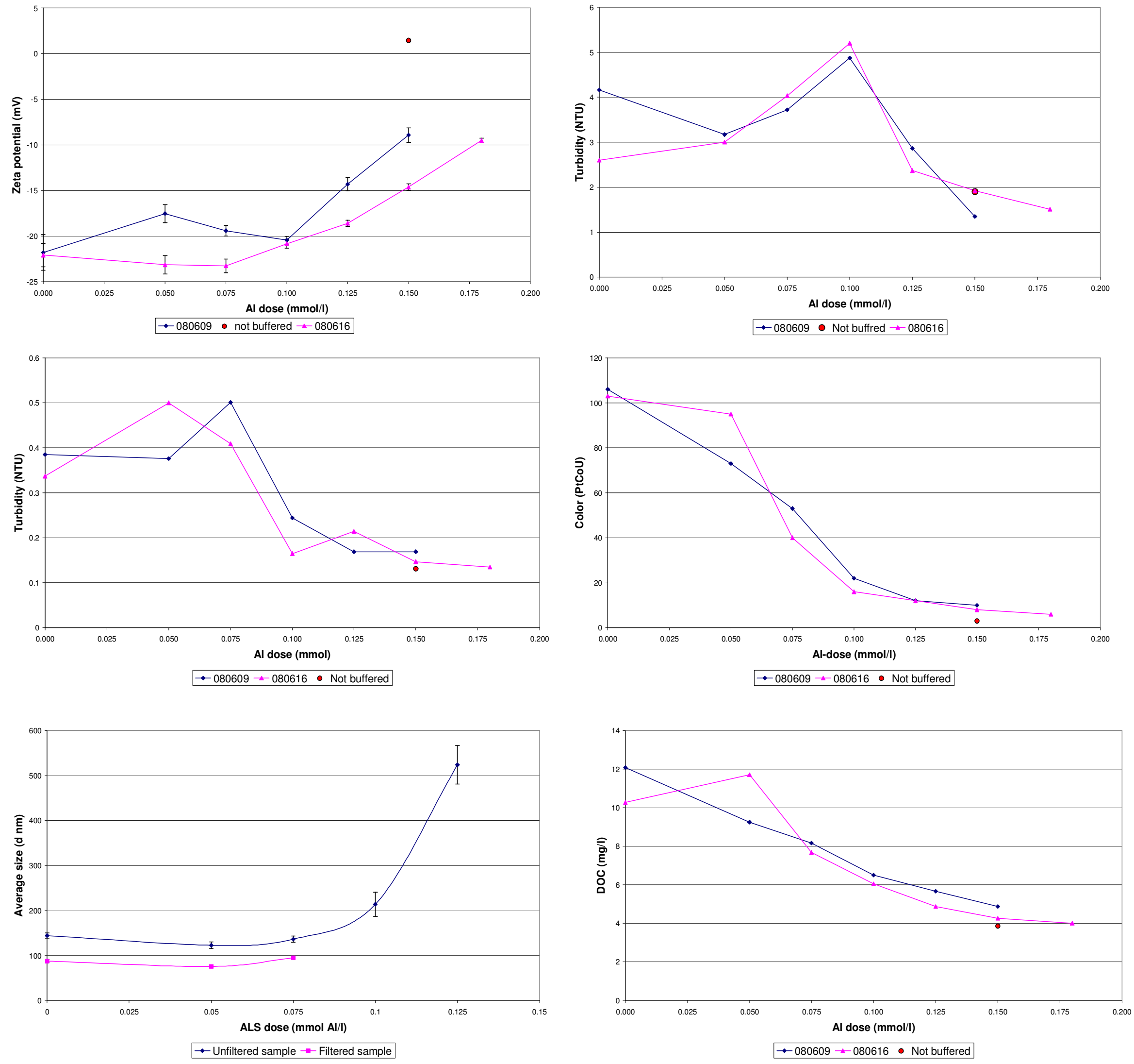

Figure 2.The results of the jar tests of the water from Pinnå. Repeatabilities are shown, zeta potential and size measurements, turbidity of filtered and unfiltered samples, and DOC and color of filtered samples.

Quality of the measurements

The results for standard solutions were satisfactory both for zeta potential and for size measurements and also repeatability of these results was good. The latex standard was stated to have zeta potential of -50 ± 5 mV. The results for zeta potential standard were: - 53.03 ± 0.87 mV (CV = 1.64 %), - 51.30 ± 0.83 mV (CV = 1.62 %), - 50.53 ± 0.34 mV (CV = 0.66 %) and - 51.84 ± 0.57 mV (CV = 1.10 %). The size of particles in the size standard (60 ± 2.7 nm) measured in the polystyrene cuvette was: 61.68 ± 0.48 nm (CV = 0.77 %), 62.11 ± 0.72 nm (CV = 1.16 %). A good zeta potential measurement should be determined with repeatability of **5% (CV).** The repeatabilities of the measurements of the natural waters were not very good. The water from Ödåkra had best repeatability, usually around 5 % under the first two weeks. However the repeatability became worse as the sample was getting older. Zeta-potential measurements of pH adjusted and ALS-treated waters had good repeatability in some cases, but not always.

Ageing of water samples

The measurements of zeta potential and size done on Neva water, Batch 2, which was 6 months old by then were not acceptable according to Malvern quality criteria and the software reported that the "count rate" was too low, indicating too low concentration of particles in the sample. The other sample of water from Neva (Batch 3) was measured when it was 4 months old. The measurements of zeta potential were acceptable according to Malvern quality criteria, but when same water was measured again after two months the results did not meet the criteria. That suggested that water samples are changing with time and therefore the ageing of water samples was studied (see Figure 3). The water from Ödåkra did change with time. When the sample was 58 and 69 days old the phase plots of the measurements were looking worse and the results were less reliable. The soft waters, i.e. water from Ljusgöl, Pinnå and Stehag did not change much with time in the aspect of zeta potential.

According to several authors (Buffle and Leppard, 1995; Perret et al., 1994; Atteia et al., 1998) water samples are changing with time and the question is in which extent. Perret et al. (1994) found that water from River Rhine could be stored at 4°C in darkness up to 4 days without any obvious change in size distribution, bacteria concentration, or morphology of particles. According to Buffle and Leppard (1995) measurements of aquatic colloids has to be carried out within 2-3 days after sampling in order to obtain reliable results.

Considering zeta potential of particles in this study only the water from Ödåkra changed with time. Changes in the size of particles with time should also be studied. The particles usually coagulate a bit and some aggregates settle. When such sample is analyzed it is mixed and particles are resuspended, but the question is if the resuspended particles are of same size as original particles. Usually the measurements of size of particles in natural waters are done within hours or at the most within some days (Walther et al., 2006; Chanudet and Filella, 2007; Weilenmann et al., 1989; Perret et al., 1994).

Conclusions

Measurements of particle size with Malvern Nano Zetasizer were not acceptable according to Malvern quality criteria for most water samples in this study. Dynamic light scattering (DLS) is not a suitable method for measuring sizes of particles in samples with a broad particle size distributions. As surface waters usually contains particles with a broad particle size distribution the sample should be fractionated before measurements in order to make PSD narrower.

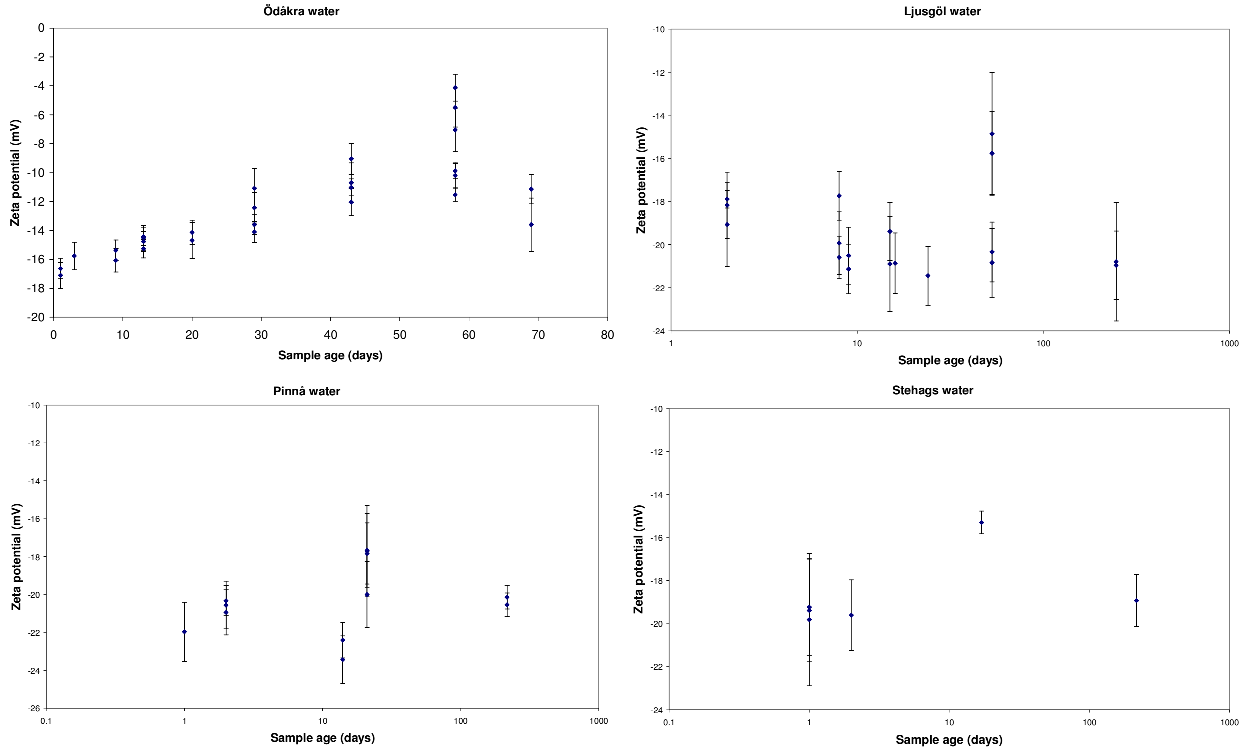

Figure 3. Zeta potential of ageing water from Ödåkra, Ljusgöl, Pinnå and Stehag.

Fractionation could be performed by for instance filtration or centrifugation. Nevertheless the pretreatment of samples was not developed in this study. DLS also assumes that particles are spheres and that is seldom the case in surface waters.

According to the literature (Gerritsen and Bradley, 1987; Perret et al., 1994; Gibbs, 1983; Gregory, 2006) the charge of particles in surface waters is negative and is usually increasing with decreasing pH. This was found to be the case in this study. The zeta potential of particles in the studied water samples was between approximately -16 mV and -22 mV. The repeatability was not always good. Hard water had less negative zeta potential than the soft waters. The zeta potential of particles after the addition of aluminum salt in a jar test was increasing with an increasing dose of aluminum sulfate. When Ödåkra water, which is hard water, was getting older the surface charge of particles became less negative. Soft waters, i. e. water from Småland, Pinnå and Stehag, did not change noticeably with time in the aspect of the surface charge.

Acknowledgement

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