CHARACTERIZATION OF SUBMICROMETRE COLLOIDS IN FRESHWATERS: EVIDENCE FOR THEIR BRIDGING BY ORGANIC STRUCTURES

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ABSTRACT

Colloidal particles play an important role in the distribution of pollutants in natural aquatic systems because they may sorb significant quantities of both inorganic and organic substances due to their large surface areas relative to their masses. Currently, only a limited amount of data is available on particle number and size distributions of natural submicron particles, owing to the many problems involved in their experimental determination. In the present paper, experimental results on particle size distribution and characterization of submicron colloidal particles from two different natural water systems will be discussed and compared with theoretical predictions based on a classical coagulation/sedimentation model. This theoretical model is well suited to describe the behaviour of particles greater than 100 nm but fails to predict the existence of colloids smaller than this. The existence of such small colloids have been observed by high resolution TEM. They seem to be embedded in large organic matrices, and probably for this reason they have neither been detected by other experimental techniques nor predicted by classical coagulation models. Improvement of the measurement techniques currently available as well as development of the theory necessary to describe this type of colloid-organic matrix associations are therefore definitely needed.

KEYWORDS

aggregation, aquatic colloids, bridging, coagulation/sedimentation, filaments, freshwaters, lake, organic matrices, river, submicron particles

INTRODUCTION

Particles are ubiquitous in all natural waters and play a recognized role in the control of the transport and fate of nutrients and pollutants (Baccini, 1984; Sigg, 1985; Whitfield and Turner, 1987). Submicron particles are especially important because, due to their small size, they have large specific surface areas and high surface free energies which facilitate sorption of significant quantities of substances. The fate of the compounds sorbed to particles is then directly linked to the fate of the particles, which, in turn, is a function of their size distribution, morphology, and composition, as well as of the chemistry and flow patterns of the water body. Many authors believe that submicron colloidal particles may be the main transport vehicle for heavy metals, hydrophobic organic materials and radioisotopes in surface waters and groundwater systems (Means and Wijayaratne, 1982; Salbu et al., 1985; Buddemeier and Hunt, 1988; Orlandini et al., 1990; Sigleo and Means, 1990; Honeyman and Santschi, 1992). The importance of the role played by these particles necessitates a better
understanding of the nature and behaviour of small size colloids in water treatment processes where the elimination of heavy metals and organic pollutants is of prime interest.

A limited amount of data is available on particle number and size distributions in natural aquatic systems, particularly in the submicrometer range (Laxen and Chandler, 1983; Gallegos and Menzel, 1987; Beckett et al., 1988; Nomizu et al., 1988; Buffe et al., 1989; Degueudre et al., 1989; Koike et al., 1990; Rees and Ranville, 1990; Wells and Goldberg, 1991). The determination of particle size distributions in natural systems is severely hampered by the low concentration of particles (<1 to 500 mg/l), the wide distribution of sizes (1 nm to >100 μm), the wide variation in particle morphology and nature, and the unstable nature of natural aggregates. The study of submicron particles is made even more difficult by the high probability of artifacts occurring during sampling, sample handling, storage, and analysis. Furthermore, most of the methods currently available do not allow direct characterization of small particles in the presence of a high proportion of larger particles, as it is often found in aquatic systems. In this instance, size fractionation procedures must be used with the subsequent possibility of perturbing the sample.

The nature of naturally-occurring colloids in freshwaters is discussed below. It is important to point out that, given the current state of knowledge, only a semi-quantitative approach to the problem can be undertaken, since most of the experimental techniques available either provide only qualitative information (e.g. Transmission Electron Microscopy (TEM)), or are subject to important limitations (e.g. filtration, Photon Correlation Spectroscopy (PCS) or Field Flow Fractionation (FFF)). The use of a multi-method approach is therefore strongly recommended in order to minimize the artifacts often encountered in the different techniques. This paper gives an example of the application of such an approach. First, the size distribution and chemical nature of Rhine River, Switzerland colloids is described. Then these experimental observations are compared with the results predicted by a classical theoretical model where the kinetics of coagulation is described by Smoluchowski's equations and sedimentation is characterized by Stokes' law. Finally, the possible reasons for some of the discrepancies observed will be discussed by studying the behaviour of well-characterized iron oxy(hydroxo)phosphate colloidal particles formed in a eutrophic lake (Lake Bret, Switzerland). The data discussed here give an overview of the results explained in detail elsewhere (Newman et al., in press; Perret et al., in press; Pizarro-Konsak et al., submitted).

RHINE RIVER COLLOIDS: STUDY OF THE WHOLE PARTICLE SIZE RANGE

Studies of particle size distributions in rivers are very scarce (Hoffmann et al., 1981; Karaiskakis et al., 1982; Gallegos and Menzel, 1987; Beckett et al., 1988; Nomizu et al., 1988; Van de Meent et al., 1983; Rees and Ranville, 1990; Waber et al., 1990). Most of these authors have used filtration and/or microscopy, both techniques involving significant sample handling and processing.

Particle size distribution in the nanometer-to-micrometer range was studied in the Rhine River near Basle, Switzerland for a period of over a year. Water samples were collected every six weeks. The sampling, fractionation and analysis procedures have been described in detail by Buffe et al. (1991), Newman et al. (in press), and Perret et al. (in press). Samples were fractionated by natural sedimentation followed by either sequential ultracentrifugation or sequential filtration (both techniques have been used in parallel for comparison purposes). The sedimentation and first centrifugation/filtration steps were carried out in the field immediately after sample collection to minimize coagulation prior to analysis. Particle size distributions were measured by PCS and samples were also examined by TEM.

A complete size distribution cannot be obtained from a single, unfractionated, sample due to the broad size distribution of natural colloids (from a few nm to >100 μm), the very low proportion of small size colloids compared to large ones, and the limitations inherent to PCS (Schurtenberger and Newman, 1992). The main limitations of this technique are a size resolution in a range of only one decade and a lower sensitivity in the small size range compared to the large size one. Therefore, a combination of the particle mass removed during the sedimentation step and mass weighted size distributions obtained from the sediments sample and the supernatant from the second
Submicrometre colloids

Fig. 1. Particle size distributions measured by PCS for a sample collected from the Rhine River on the 6th November 1990: a) raw sample, b) after a 2 hour sedimentation, c) after centrifugation for 1.5 hours at 4 000 rpm.

centrifugation step were used to make a composite distribution. For a detailed explanation on the calculation mode applied, refer to Newman et al. (in press).

PCS results may be summarized as follows. i) The range of particle sizes observed was continuous from 50 nm to well above the upper limit of PCS, 3 µm. Peaks in the size distribution were generally observed in the ranges 100 - 200 nm, 300 - 500 nm, and 1 - 3 µm (Figure 1). ii) The position of the observed peaks in the size distribution did not change appreciably over the year, no evident seasonal variation being observed. iii) The position of these peaks did not appear to be influenced by changes in the flow-rate. iv) The average percentage of the total particle mass concentration over the entire sampling period was:

<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>Mass % (mean ± 1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 3 000</td>
<td>59.1 ± 24.1</td>
</tr>
<tr>
<td>1 000 - 3 000</td>
<td>26.2 ± 22.0</td>
</tr>
<tr>
<td>500 - 1 000</td>
<td>4.5 ± 4.4</td>
</tr>
<tr>
<td>200 - 500</td>
<td>8.8 ± 3.6</td>
</tr>
<tr>
<td>&lt; 200</td>
<td>1.5 ± 1.1</td>
</tr>
</tbody>
</table>

ICP-AES analyses (Al, Ca, Fe, Mg, Si) indicated that the composition of the various colloidal size classes varied little with time or flow-rate. Figure 2 shows the results obtained for calcium and aluminium. It can be seen that all the curves are similar except the one corresponding to June 1991. At this date the flow-rate was more than 10 times greater than the average and the total load of the river was about 100 times greater than the usual load. The interesting feature of Figure 2 is that the concentration of large particles (separated by centrifugation for 0.5 hours at 30,000 rpm) is strongly influenced by river flow-rate while the concentration of smaller particles is much less affected.

High resolution TEM observation of Rhine River samples revealed some interesting, although contradictory, findings: while i) no particles smaller than 50 nm could be seen, either by PCS or by TEM, in the filtrates of 0.05 µm pore size membranes, ii) no particles smaller than 50 nm were observed by PCS even in the centrifugates where large particles had been eliminated but colloids smaller than 50 nm remained in suspension, and iii) particles of few nm in size were observed by high resolution TEM in all samples where most of the large particles (interfering in the small particle observations) had been removed by centrifugation.
Fig. 2. Mass concentration of a) calcium and b) aluminium measured by ICP-AES in the raw, sedimented and centrifuged fractions of the Rhine River samples for each sampling date.

Each of the individual observations reported above might be partly explained by certain limitations associated with the corresponding techniques used. Observation i) might be due to the coagulation of colloids at the membrane surface (Buffle et al., 1992), even if great care had been taken to avoid it. Observation ii) might be explained by coagulation of non centrifuged colloids with centrifuged ones during the centrifugation process, although this is inconsistent with observation iii). However, if the three observations are considered together, then it becomes difficult to interpret them solely on the basis of technique limitations. Furthermore, the findings of high resolution high contrast TEM provides an explanation for all these phenomena: this technique shows that the very small colloids are often embedded in organic matrices or in a mesh of filaments (Figure 3). The reason why such observations have not been reported until now is that it is very difficult to distinguish these organic matrices because: i) large particles (> 0.1 - 1.0 µm) tend to hinder the use of high resolution TEM which is required for observing very fine organic mesh, and ii) the organic mesh is not readily visible.

Fig. 3. High resolution TEM micrograph of a centrifuged Rhine River sample showing associations between small colloids and organic fibrils. Apart from one large fibril, an extremely fine mesh dominates the picture.
submicrometre colloids under the normal conditions used in TEM because organic and inorganic materials have extremely different electron densities.

The embedding of colloids smaller than 50 nm in much larger organic hydrophilic matrices may explain i) their retention by 0.05 µm filters, ii) the fact that PCS does not "see" them, but iii) that they are seen by TEM (sometimes the image looks as if they were isolated when the conditions are not good enough to visualize the organic matrix). The important debating question from these observations is whether or not significant concentrations of individual particles smaller than 50 nm are likely to exist in natural waters. In order to gain an insight into the nature and behaviour of such small colloids in natural aquatic systems, a two-fold approach has been followed. On the one hand, the study of the stability of such small colloids as predicted by the classical coagulation/sedimentation theory has been undertaken. On the other hand, the behaviour of a well characterized naturally-occuring colloid has been monitored under natural aquatic conditions.

**COMPARISON OF RHINE RIVER OBSERVATIONS WITH CLASSICAL COAGULATION THEORY PREDICTIONS**

A large body of theory and experience concerning particle interactions has been developed by aerosol physicists and by chemical engineers treating aqueous suspensions. Basic coagulation theory for hydrophobic colloids, which is largely based on the seminal work of Smoluchowski (1917), has been presented in detail elsewhere (Friedlander, 1977; O'Melia, 1980; Stumm and Morgan, 1981; Hirtzel and Rajagopalan, 1985) and will not be discussed here.

Combining the coagulation theory with Stokes' law for gravity yields the dynamic equation that describes the fate of particles in aquatic systems. For a particle of size k:

\[
\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} \alpha(i,j) \beta(i,j) n_i n_j - n_k \sum_{i=1}^{\infty} \alpha(i,k) \beta(i,k) n_i - \left( w_k / z \right) n_k
\]

where \( n_i, n_j, n_k \) denote the number concentration of particles of sizes \( i, j, k \) [L\(^{-3}\)]; \( \alpha \) is the collision efficiency [dimensionless]; \( \beta(i,j) \) is a collision frequency function, which depends upon the physical mode of interparticle approach [L\(^{-3}\)T\(^{-1}\)] (three particle collision mechanisms have been considered: Brownian motion, fluid shear and differential settling); \( w_k \) is the settling velocity of particles of size \( k \) assumed by Stokes' law [LT\(^{-1}\)], and \( z \) is the depth [L].

The left-hand side of equation (1) describes the rate at which the number concentration of particles of size \( k \) changes with time [L\(^{-3}\)T\(^{-1}\)]. The first term of the right-hand side expresses the rate of formation of particles of size \( k \) from smaller particles \( (i,j) \) having a total volume \( v_k \). The second term describes the loss of particles of size \( k \) by growth to form larger aggregates. The third term describes the loss of size \( k \) particles by settling.

No general analytical solution exists for equation (1): it must be solved either using simplified analytical solutions or numerically. In the present work the particle size distribution has been expressed as a finite number of size intervals and a set of differential equations of the form of equation (1) have been integrated numerically over time (Lawler et al., 1980; O'Melia and Bowman, 1984). For details on the selection of size intervals and the criteria followed for the assignation of new particles to standard particle size classes, refer to Lawler et al. (1980). The model has been previously applied to lakes by O'Melia and co-workers (O'Melia and Bowman, 1984; O'Melia et al., 1985; Ali et al., 1984; Wellenmann et al., 1989). The values of the parameters used in the model simulations are indicated in Table 1.

When comparing simulated predictions with experimental observations, it is important to keep in mind that in the development of the model the following assumptions are made: i) colloids are hydrophobic; ii) particles are of identical nature (chemically homogeneous); iii) particles before and after each aggregation are rigid spheres; iv) volume of solid particles is conserved during agglomeration; v) particles approach one another on rectilinear paths, the path of one particle not being affected by the presence of another; vi) collision functions for Brownian motion, fluid shear and differential settling are assumed to be additive; vii) only binary particle encounters are assumed to
## TABLE 1  System Properties Used in the Model Calculations

<table>
<thead>
<tr>
<th>Property</th>
<th>River</th>
<th>Lake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean depth (m)</td>
<td>2.5</td>
<td>1.0&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Water viscosity (g.cm&lt;sup&gt;-1&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>1.146.10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>1.515.10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Water density (g.cm&lt;sup&gt;-3&lt;/sup&gt;)</td>
<td>0.999</td>
<td>1.000</td>
</tr>
<tr>
<td>Velocity gradient (s&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.5&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>Coagulation efficiency (dimensionless)</td>
<td>0.05&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>Particle density (g.cm&lt;sup&gt;-3&lt;/sup&gt;)</td>
<td>1.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.0&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td>Initial particle concentration (mg.dm&lt;sup&gt;-3&lt;/sup&gt;)</td>
<td>Varied</td>
<td>0.492&lt;sup&gt;h&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Stumm and Morgan (1981).  
<sup>c</sup> Newman <i>et al.</i> (in press).  
<sup>d</sup> Redox boundary layer.  
<sup>e</sup> Weilenmann <i>et al.</i> (1989).  
<sup>f</sup> Tipping and Higgins (1982).  
<sup>g</sup> Schwertmann and Fisher (1973).  
<sup>h</sup> Experimentally measured value (Pizarro-Konsak <i>et al.</i>, submitted).

VII) breakup or dissolution of aggregates due to fluid shear or other processes are not included;  
ix) the water body is considered as an ideal settling basin.

The assumptions of such a coagulation/sedimentation model are not directly applicable to model  
colloid transport in the rivers since horizontal transport is not considered. However, the purpose  
of the present calculations is not to model such transport, but to explore semi-quantitatively the role  
of factors related to coagulation and sedimentation of hydrophobic colloids in controlling the observed  
size distributions of submicron particles.

Figure 4a shows the evolution with time of an initially tridisperse system of 10 nm, 200 nm and 4 µm  
particles having the same concentration (1.0 mg.dm<sup>-3</sup> each). Figure 4b shows the distributions  
obtained after 2 days for initially continuous particle size distribution (power law distribution with  
β = 4) ranging from 1 nm to 100 µm and various initial mass concentrations (varying over three orders  
of magnitude, from 0.01 to 10 mg.dm<sup>-3</sup>). Similar results as those depicted in Figure 4 have been  
obtained by using different initial particle size distributions, initial total particle concentrations and  
collision efficiency values (Newman <i>et al.</i>, in press). Computer simulation predictions corroborate  
partially the experimental findings, confirming a depletion in both small (fast coagulation by Brownian  
motion) and big (fast sedimentation) particles with a tendency of particles of intermediate sizes to  
remain in suspension due to their slow coagulation and sedimentation rates. The classical coagulation  
theory fails, however, to represent completely the behaviour of colloids in the lower size range  
(< 100 nm). Theory predicts extremely low concentrations of colloids in this range; e.g. only 4.3.10<sup>-9</sup>  
mg.dm<sup>-3</sup> and 2.9.10<sup>13</sup> mg.m<sup>-2</sup> are predicted to remain in suspension after 2 hours and 2 days,  
respectively, from an initial 0.01 mg.dm<sup>-3</sup> monodisperse suspension of 10 nm particles. At these  
concentrations particles should not be detected by any currently available technique. Therefore, even  
the small individual colloids formed <i>in situ</i> would not be detected since they would form aggregates  
immediately. However, high resolution TEM observations reveal that small colloids are present in  
significant concentrations. Although their corresponding proportion is presumably low with respect to  
the total particle mass concentration (< 200 nm colloids account for less than 1.5% of the total mass),  
surface area estimations show that they may represent an important percentage of the total surface  
area available for metal and organic compound binding (e.g. a 0.01 mg.dm<sup>-3</sup> suspension of 10 nm  
particles offers the same surface area as a 4.0 mg.dm<sup>-3</sup> suspension of 4 µm particles). Hence they may  
play a very important role in natural waters.
Fig. 4. Simulation results for: a) An initially tridisperse particle size distribution of 10 nm, 200 nm and 4 μm. Initial particle size concentration = 1 mg dm⁻³ for each size class. b) A continuous particle size distribution with β = 4 and size range from 1 nm to 100 μm at 2 days with different initial mass concentrations ranging from 0.01 to 10 mg dm⁻³. Values of other parameters as in Table 1.

LAKE BRET IRON OXY(HYDROXO)PHOSPHATE PARTICLES: STUDY OF THE SMALL PARTICLE SIZE RANGE

Lake Bret, Switzerland is a eutrophic lake where an oxic-anoxic boundary layer develops in summer at a depth of about 10 m (maximum depth of the lake 20 m). At this layer, iron oxy(hydroxo)phosphate particles are formed. They have been well characterized in the past in terms of their chemical composition and morphological structure as well as of the limnological process involved (De Vitre et al., 1988). In particular, detailed STEM/EDS studies of these iron particles (Buffle et al., 1989) have shown that: i) a well-defined chemical entity is formed at the redox interface in the water column, composed mostly of Fe(III), Fe(II), PO₄ and Ca (and probably OH⁻); ii) they have a globular or roughly spherical shape and a mean diameter smaller than one-third of a micron, most of them being close to 100 nm (Leppard et al., 1988); iii) the size of at least three-quarters of the iron particles is smaller than 130 nm, a significant fraction of them having sizes down to a few nm; iv) the size distribution of iron particles seems to follow a power law distribution with β = 4.

These iron-rich colloidal particles constitute an ideal model for studying submicron colloidal behaviour in natural waters because they are a well-characterized system and relatively homogeneous from a size and composition point of view. Furthermore, large particles entering the lake have been eliminated by sedimentation before reaching the sampling point and they do not interfere with the iron particle observations.

A very large number of samples containing iron-rich particles from the oxic-anoxic interface of Lake Bret has been collected and observed by TEM at high resolution (Pizarro-Konsak et al., submitted). Many pictures similar to that shown in Figure 5 were repeatedly obtained. They confirmed previous estimations on size and characteristics of the particles and revealed the frequent existence of small
particles (down to a few nm) associated with larger sponge-like networks or fibrils of organic nature and 10-100 times larger in size.

The evolution of the simulated size distribution with time of an initially monodisperse suspension of 10 nm particles as well as that of an initially continuous particle size distribution (power law with $\beta = 4$) ranging from 1 to 300 nm are depicted in Figures 6a and 6b, respectively. They have been calculated by means of the coagulation/sedimentation model discussed above using the parameters given in Table 1. These figures show that very small particles are predicted to coagulate rapidly; all 10 nm particles disappear very fast forming agglomerates of 100 - 300 nm which are much more stable. This particle size predicted by the model for the "stable" colloids agrees quite well with the observed one. But, again the model does not predict the presence of small colloids, observed by high resolution TEM, most probably because the aggregation of these small colloids with large organic matrices is not taken into account by the classical coagulation model.

An in situ study of the sedimentation rate of natural iron oxy(hydroxo)phosphate colloidal particles formed in the redox transition boundary layer of Lake Bret has been performed. Measurements have been made with a specially designed plexiglass sedimentation tube (120 cm x 13 cm) allowing one to sample lake particles at the desired depth and to record their concentration profiles as a function of time. (See Pizarro-Konsak et al. (1992), for a detailed description of the tube and of the methodology used.) The effect of large particles settling fast from the surface water on the sedimentation of iron particles has been tested by circulating water from the upper part of the lake into the tube.

Fig. 5. High resolution TEM micrograph of Lake Bret iron oxy(hydroxo)phosphate particles showing their association with organic matrices. Note the very small iron particles (few nm) embedded in organic gel in the lower left corner of the photograph with the 100 nm bar.
Submicrometre colloids

Fig. 6. Simulation results for a) an initially monodisperse 10 nm particle size distribution, b) an initially continuous particle size distribution with \( \beta = 4 \) and size range from 10 to 300 nm. Values of other parameters as in Table 1.

Summarizing, the following results have been found. i) The iron particle profiles obtained were always vertical, thus indicating a constant iron concentration with depth in the tube. ii) The average concentration significantly decreased with time, but the profiles remained vertical. A pseudo-first-order rate law of 0.033 h\(^{-1}\) was found (ca. 15% of the iron disappeared within the six hours of the experiment). iii) No differences were observed between the experiments with and without circulation of surface water, indicating that settling of large particles does not influence the fate of iron particles.

The high rate of iron disappearance observed in these experiments is not well explained by the computer simulation of the coagulation/sedimentation processes occurring in the sedimentation tube. In fact, the model does not predict any iron disappearance during the duration time of the experiment (6 hours). This is to be expected since the size of aggregates predicted to be formed by coagulation is not very different from the initial size and therefore the characteristics of settling are not significantly changed by the coagulation process. According to the time predicted by Stokes' law a 100 nm particle of density 3.0 g cm\(^{-3}\) would settle 5 cm in 80 days under the conditions of the lake.

There is a large gap between the model predictions and experimental observations in these sedimentation studies. In fact, the model predicts a general process involving an initial fast coagulation step (formation of intermediate size particles) followed by a very slow sedimentation which on the whole would give very long residence times for the iron particles in the lake. But, sedimentation experiments seem to favour the contrary, i.e. a slow coagulation step followed by fast settling resulting in an overall much faster cycling rate of iron in the lake. A possible explanation for this difference might be the entrapment of iron particles by organic matrices, as observed by TEM. The sedimentation of such entities requires an initial slow step, e.g. of coiling or biological degradation of the organic matrix. The large number of particles initially blocked by the matrix could only then form aggregates, large and dense enough to sediment quickly. For this hypothesis to be tested and quantified a new theory needs to be developed.
CONCLUSION

Experimental observations show that natural aquatic systems are depleted of both small and large independent particles. These results are qualitatively in agreement with classical theory predictions. Small particles and large particles seem to disappear very fast, the former due to efficient Brownian coagulation and the latter because they settle down faster than they are formed by coagulation. The existence in suspension of both, small and large particles, seems always to be linked to the proximity of an autochthonous production source of suspended matter (i.e. the case of iron-rich particles in the redox transition boundary layer of Lake Bret). The presence of stable intermediate size particles in solution (100 - 300 nm) also agrees well with model predictions. These particles may be expected to traverse long distances in rivers and groundwater systems and since they have high specific surface areas, they will carry associated pollutants and nutrients along with them. Similarly, they will be responsible for the maintenance in suspension of the associated pollutants and nutrients in these water bodies characterized by long mean residence times (lakes and oceans).

Classical theory, however, does not allow one to explain the relatively large concentration of colloids smaller than 100 nm in surface waters. The TEM results presented here strongly suggest that these colloids are associated with organic fibrils and networks or with larger clay flakes. To our knowledge, so far only Nomizu et al. (1988) have suggested the possible association of small colloids with biological material transparent to TEM in natural waters. But this was only based on the observation that inorganic colloids smaller than 100 nm from the Shonaiwaga River, Japan contained high phosphorous and calcium amounts. They have not reported direct observation of organic-inorganic associations.

Presumably, the existence of such associations has not been previously reported because their physical properties (size, density) lie closer to those of the organic matrices involved rather than to those of the small hydrophobic colloids. These agglomerates are then easily lost by adsorption during any type of fractionation treatment. Moreover, the low electron-density of the organic compounds in TEM makes their observation difficult.

Although it is impossible at present to quantify the extension of the association of small inorganic colloids with organic matrices, it is easy to foresee its importance since the maintenance of these very small colloids in suspension could greatly increase the total area available for binding trace compounds in the water body. This has obviously important consequences for water treatment strategies relevant to the elimination of trace adsorbed pollutants.

Stabilization of colloids by adsorption of natural or synthetic organic polymers has been well known in water treatment for a long time (Ruehrwein and Ward, 1952; La Mer, 1966; Kitchener, 1972; Gregory, 1978). Large polymers can form adsorbed segments on a solid surface with loops and tails extending into the solution (Lyklema, 1978). Long chains of polymers adsorbed onto more than one colloid act as bridges between the particles, such as in the aggregation of bacteria through exocellular polymers. Unfortunately, the characterization of such an interfacial region is difficult both theoretically and experimentally.

At the present state of the art, it is impossible to say whether the observed associations could be explained by the so-called bridging action or if the organic component just provides a sticking substrate for particle accumulation. Improvement in the measurement techniques available as well as developing the necessary theory to describe in a sound manner these inorganic-organic associations are definitely needed.

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