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COAGULATION/SEDIMENTATION OF SUBMICRON IRON PARTICLES IN A EUTROPHIC LAKE

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Abstract—*In situ* measurements of the coagulation/sedimentation of natural submicron iron particles in the oxic-anoxic interface of a eutrophic lake are described. Such measurements allow to understand the scavenging role of iron oxyhydroxide particles and give an insight on the role of organic matter on the coagulation of submicron colloids. A special sedimentation tube has been designed and built for this purpose. Experimental conditions have been determined to avoid artifacts during sedimentation measurements. An order of magnitude for the sedimentation rate of iron particles in lakes has been determined. Theoretical predictions have been made based on a classical coagulation/sedimentation model where the kinetics of coagulation is described by Smoluchowski's equations and sedimentation is characterized by Stokes' law. The nature and morphology of submicron colloid aggregates, in particular of those containing lake-born iron oxyhydroxides, have been investigated by Transmission Electron Microscopy in conjunction with Energy Dispersive Spectroscopy. Experimental sedimentation results are discussed and compared both to model predictions and Transmission Electron Microscopy observations. Both sedimentation rates and Transmission Electron Microscopy results emphasize the important role of organic matter present in lakewaters, particularly of non fulvic organic macromolecules, on the coagulation/sedimentation processes of iron particles.

Key words—aquatic colloids, clays, coagulation, eutrophic lake, iron oxyhydroxide, organic matter, organic macromolecules, sedimentation, sedimentation tube, transmission electron microscopy

NOMENCLATURE

Superscripts

i = input
o = output

Subscripts

i, j, k = particle size class
m = box
p = particle

Latin

A = coefficient in empirical power-law size distribution function ($\mu m^{(\beta-1)} \cdot cm^{-3}$)
d_p = diameter of a suspended particle (nm, μm)
$\bar{d}_p$ = average diameter of all particles at time t (nm, μm)
G = velocity gradient (s^{-1})
k' = first-order sedimentation rate constant (h^{-1})
n_i = number concentration of particles of size i (cm^{-3})
$n(d_p)$ = size distribution function ($dm^{-3} \cdot \mu m^{-1}$)
q = areal hydraulic loading ($cm \cdot s^{-1}$)
t = time(s)
v_i = volume of particles of size i (μm^3)
V = volume concentration of particles ($\mu m^3 \cdot cm^{-3}$)
w_i = settling velocity of particles of size i in a quiescent medium ($cm \cdot s^{-1}$)
W_i = rate of production or destruction of particles of size i ($cm^{-3} \cdot s^{-1}$)
z = depth of vertical compartment box in settling tank (cm)

Greek

$\alpha(i, j)$ = coagulation efficiency for collisions between particles of sizes i and j (dimensionless)
$\beta(i, j)$ = collision frequency function for particles of sizes i and j ($cm^{-3} \cdot s^{-1}$)
β = exponent in empirical power-law size distribution function (dimensionless)

INTRODUCTION

The purpose of this paper is to shed some light on the factors affecting coagulation and sedimentation of submicron colloids in surface waters, by combining *in situ* measurements of sedimentation rates of colloids with Transmission Electron Microscopy (TEM) characterization of the aggregates formed during the sedimentation process. Aggregates of well characterized iron oxyhydroxide particles formed at the oxic-anoxic boundary of a eutrophic lake are described in detail.

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Although submicron colloids in surface waters often represent only a few percent in mass of the total particulate concentration, they may play a very important role in the transport of pollutants, due to their very large specific surface areas, and their significant potential adsorbing capacity (Filella *et al.*, 1993; Newman *et al.*, 1994). Submicron colloids show peculiar behaviour, for instance, they may either remain in the "dissolved" form in which case the pollutants associated with them are eliminated by outflowing via lake outlets or coagulate to form larger aggregates in which case the pollutants are removed by entrapment into the sediments. In order to discriminate between these two types of behaviour, a better understanding of the factors influencing the coagulation/sedimentation of submicron inorganic colloids is required.

The importance of particle interactions for the transport of pollutants have long been recognized (Stumm and Morgan, 1981; Means and Wijayaratne, 1982; O'Melia *et al.*, 1985; Sigg, 1987; Honeyman and Santschi, 1992). Metal-to-ligand ratio calculations in Swiss lakes (Sigg *et al.*, 1987) have laid emphasis on the strong interaction between metals and biogenic material. On the other hand, two factors, i.e. the concentration of calcium and the presence of dissolved organic carbon, suspected of influencing coagulation processes in freshwaters have been studied in detail (Tipping and Higgins, 1982; Gibbs, 1983). Gibbs (1983) showed that the coagulation rates of organic-coated clays are significantly lower than those for uncoated particles. Stabilization by organic matter was also observed by Tipping and Higgins (1982) in their study with haematite particles and humic substances; they also observed that dissolved calcium causes the opposite effect (i.e. to destabilize particles and favour coagulation). Similar conclusions were drawn by other authors (Jekel, 1986; Dowbiggin and Singer, 1989; Ledin *et al.*, 1993). These laboratory studies seem to support the fact that the solution chemistry can control the colloidal stability of natural particles. Ali *et al.* (1984), Gallegos and Menzel (1987) and Weilenmann *et al.* (1989) have reported some measurements of coagulation efficiency, α (defined as the ratio of collisions producing aggregates to the total number of collisions), for lake particles as a whole (i.e. without discriminating different coagulation rates of chemically-different particles). They report that the α value increases with increasing calcium concentration and decreases with increasing fulvic and dissolved organic matter concentration. A detailed investigation by Liang and Morgan (1990a, 1990b) on the effect of the nature of organic coating on colloid stability indicated that long chain organic molecules with long carbon chains (laurate, caprate) have stronger stabilization effect on suspended haematite particles than the smaller chained ones.

Until now, two aspects in relation with colloid-organic matter interaction, however, have severely limited the understanding of colloid stability in surface waters: (i) the ill-defined nature of natural organic matter (NOM), which has been considered to be composed of only one type of compound in most of the reported studies, and (ii) the wide variation in the nature and morphology of inorganic colloids which has also generally been considered to show a single type of behaviour.

Aquagenic and pedogenic NOM

On our previous paper (Zumstein and Buffle, 1989), we showed that two types of "dissolved" NOM can be discriminated in the eutrophic lake studied therein viz: (i) the pedogenic NOM (similar to soil fulvic acids), primarily aromatic, originating from the leaching of soils, which are mostly eliminated at the outflow of the lake, with very little being removed from sedimentation in the lake, and (ii) the aquagenic NOM, essentially aliphatic, originating from lake primary productivity, which are mostly eliminated by sedimentation in the lake. Owing to the marked differences in properties and behaviour (degree of hydrophilicity and size) between these two types of NOM, one would expect them to play a very different role on the stability of inorganic colloids. As most of the investigations reported on NOM-colloid interactions have been done with the pedogenic type fulvic and humic type compounds (Tipping and Higgins, 1982; Ali *et al.*, 1984; Jekel, 1986; Dowbiggin and Singer, 1989; Ledin *et al.*, 1993), which appear to hardly sediment in the lake, nothing is known about the role of aquagenic compounds.

Inorganic colloids

Until now, all the above-mentioned studies have been performed either in the laboratory with well-characterized simple components (Tipping and Higgins, 1982; Jekel, 1986; Dowbiggin and Singer, 1989; Ledin *et al.*, 1993) or in the field by considering only the average behaviour of the aquatic particles as a whole (Ali *et al.*, 1984; Gallegos and Menzel, 1987; Weilenmann *et al.*, 1989). Considering the wide chemical and physical diversity of lacustrine components, it is difficult to extend either type of study to investigate the real behaviour of specific chemical constituents of the lake, e.g. iron oxyhydroxides.

Fig. 1. (*Facing page*) High resolution TEM micrographs of small homogeneous aggregates of colloidal iron oxyhydroxide particles. These iron-rich globules are visualized here as whole mounts within a Nanoplast film and are accompanied by an EDS spectrum which is typical for the individual globules comprising them. The copper peak results from the copper grid upon which the Nanoplast film is mounted.

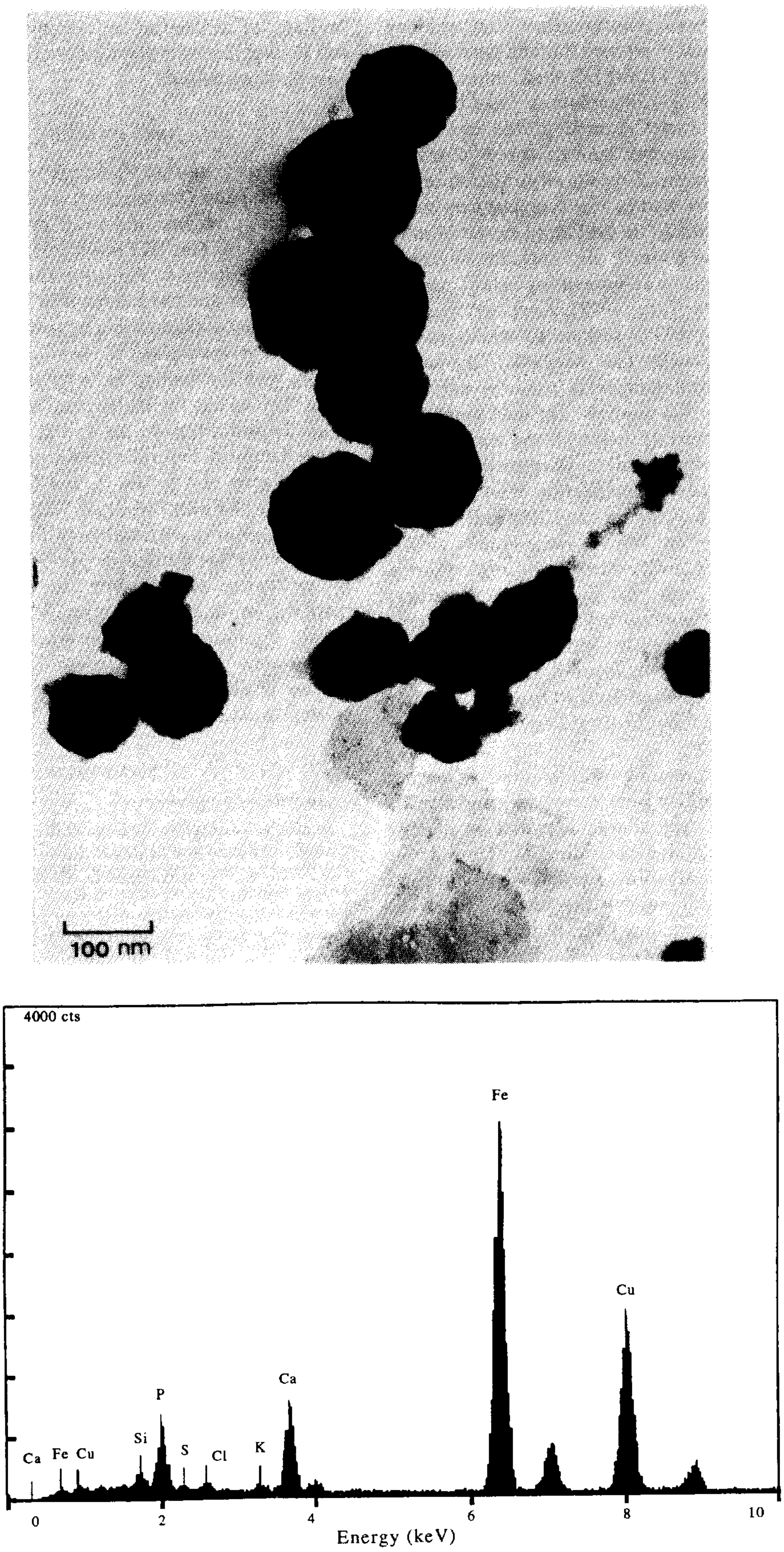

Fig. 1

In this paper, *in stiu* measurements of coagulation/sedimentation rates of iron-containing particles have been combined with TEM-EDS observation of aggregates formed during sedimentation. Lake-born iron oxyhydroxide particles formed at the oxic-anoxic interface of the eutrophic lake have been studied in detail. A comparison of results of field studies with those of laboratory studies with synthetic iron oxyhydroxides is also made. It should be borne in mind, however, that lake water also includes significant concentrations of iron-containing clay particles (Davison and De Vitre, 1992). Since wet chemical methods are not 100% specific to lake-born iron oxyhydroxide particles (see Methods), the contribution of iron-containing clay particles has to be considered in the data analysis. The term globule will be used in the text to refer to the more or less spherical lake-born iron oxyhydroxide particles (Fig. 1). A detailed characterization of these globules has been reported (Leppard *et al.*, 1988; De Vitre *et al.*, 1988; Buffle *et al.*, 1989). These studies showed that the globules are formed from association of smaller units (1–2 nm) and that they can aggregate between themselves or with other colloids or larger particles. The predominant globule type is a well-defined chemical entity composed mainly of Fe(III), Fe(II) (30–50% of total Fe), PO_4 and Ca of size 100–300 nm (maximum of the size distribution) (Buffle *et al.*, 1989).

Based on the foregoing consideration, an attempt has been made in this work to get an insight on the role of aquagenic type of organic matter on aggregation of iron-containing colloids. For this purpose, experimental observations have been compared with mathematical model predictions based on "hard sphere" interactions. The results suggests that bridging of submicron colloids by very large, non-fulvic, organic macromolecules plays an important role on coagulation.

AREA OF STUDY

Lake Bret is located 10 km east of Lausanne in the canton of Vaud (Switzerland). It has a surface area of 0.5 km^2, a volume of $4.6 \cdot 10^6$ m^3 and a maximum depth of 20 m. This lake is a drinking water reservoir and is not polluted by industry. The main input is the Grenet River and the output flow is controlled by a water treatment plant. It is a eutrophic lake as a result of a heavy phosphorous loading of agricultural origin, with the loading of heavy metals being negligible. The lake is thermally stratified during summer (Fig. 2) and develops an anoxic hypolimnion for about 4 months. Several studies have been carried out on the cycles of Fe, Mn, S, and P (Zali, 1983), the speciation of Fe and Mn (De Vitre *et al.*, 1988), the morphological characteristics of iron globules (Leppard *et al.*, 1988; Buffle *et al.*, 1989; Perret, 1989) and the circulation of pedogenic and aquogenic organic matter (Zumstein, 1989; Zumstein and Buffle, 1989). Total organic carbon concentration is about 4.0 mg · dm^{-3}, dissolved organic carbon concentration is about 3.5 mg · dm^{-3}, and the dissolved calcium concentration is around 1.5 mM.

METHODS

Sedimentation measurements

In situ sedimentation measurements were made using a specially-designed sedimentation tube [Fig. 3(a)]. It consists of a plexiglass tube (120 cm long, 13 cm diameter) equipped with sampling septa at different levels. The two lids at the extremities can be closed *in situ* by applying pressure by means of a pump or a gas cylinder. Sampling septa are

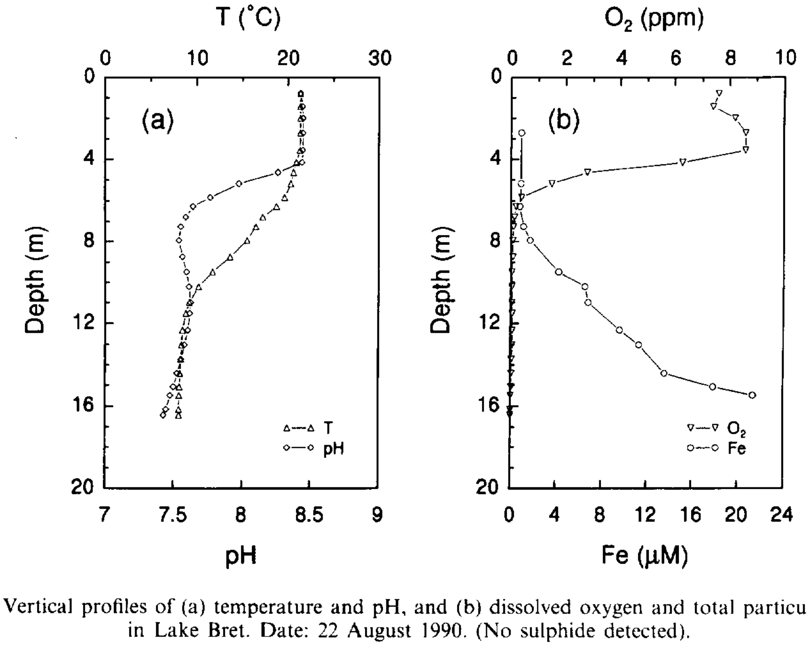

Fig. 2. Vertical profiles of (a) temperature and pH, and (b) dissolved oxygen and total particulate iron in Lake Bret. Date: 22 August 1990. (No sulphide detected).

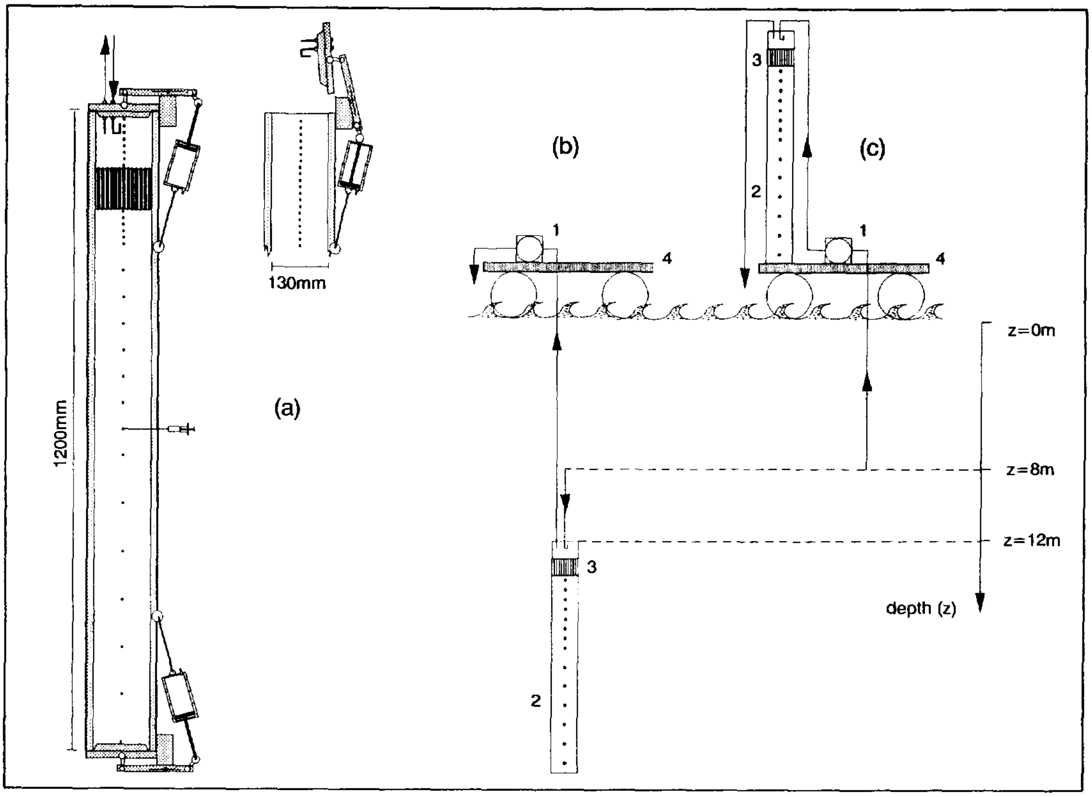

Fig. 3. Schematic representation of the sedimentation tube (a), at depth (b) and on the platform (c). (1) Peristaltic pump. (2) Sedimentation tube. (3) Turbulence breaker. (4) Platform.

placed at 5 cm intervals in the upper part of the cell, and at 10 cm intervals in the lower part. The different particle settling rates were taken into account while designing the apparatus. Thus better vertical resolution of slow sedimentation rates can be obtained with the system.

Sedimentation studies were made by submerging the tube with both lids open in water, at a depth corresponding to the zone where lake-born iron oxyhydroxides are formed, but no Fe(II) is present (*ca* 12 m, $[O_2] < 0.05$ ppm and $T \simeq 8°C$). The tube was allowed to attain thermal stability for 1 h [Fig. 3(b)], then the lids were closed and the filled tube was gently raised to the platform for withdrawing samples [Fig. 3(c)]. To prevent mixing problems, the water in the tube was kept continuously full by replacing the volume of water withdrawn by an equivalent volume of 0.2 μm filtered lake water sampled at the same depth as the water under study. For this purpose, a Tygon tube was passed through the entrance port of the top lid and water was pumped through this tube by means of a peristaltic pump (1 in Fig. 3). A filtration device was incorporated into the system prior to entry into the tube. In the sedimentation column a plexiglass mesh (3 in Fig. 3) was placed to break any turbulence that could be induced by the circulation of water in the upper part of the tube. For the same reason the inflow tubing, in the upper lid, has a U-shape.

The influence of the coagulation of the submicron iron colloids with larger, fast sedimenting particles (hereafter called large particles) coming from the upper part of the lake (metalimnion) was tested using the same procedure as described except that the filtration system was omitted in this case (1 in Fig. 3). A flow rate of $4\ \text{cm}^3 \cdot \text{min}^{-1}$ was used because preliminary tests indicated that at this flow rate, the flow of large particles in the tube is analogous to that found in the lake. Care was taken to avoid turbulence at the sampling points in the tube. The areal hydraulic loading calculated in the tube is $5 \cdot 10^{-4}\ \text{cm} \cdot \text{s}^{-1}$. For comparison, the areal hydraulic loading of lake Bret is $2.9 \cdot 10^{-5}\ \text{cm} \cdot \text{s}^{-1}$ (only input considered: Grenet river inflow = $4.6 \cdot 10^6\ \text{m}^3 \cdot \text{year}^{-1}$ and lake Bret surface area = $0.5\ \text{km}^2$). The lower size limit of the large particles sedimenting after being injected in the top of the tube by the unfiltered circulating water was estimated to be *ca* 2.6 μm (assuming a particle density of $3\ \text{g} \cdot \text{cm}^3$) based on sedimentation properties of aquatic particles and the above flow-rate.

Water samples for chemical analyses and TEM observations of iron globules were withdrawn every hour for several hours of experiment by means of plastic syringes fitted with stainless steel needles.

The following tests were performed with the tube, before recording sedimentation data:

Perturbation due to water circulation. Optimal conditions, e.g. the position and shape (geometry) of the input and output tubings on the top lid; and the characteristics of the plexiglass mesh (turbulence breaker), were designed for obtaining a solution as homogeneous as possible in the portion of the tube above the mesh and no turbulence below the mesh. This was achieved by circulating a solution with coloured indicator in the top portion of the tube above the mesh and determining the optimum height (10 cm) and section (1 × 1 cm) of the internal channels of the mesh at which the forementioned criteria are fulfilled.

Temperature regulation. Initially, sedimentation experiments were done over 6–8 h on the platform with the sedimentation tube fixed on it. Any increase in the temperature of water in the tube due to ambient temperature changes will lead to thermal convection of the water in the tube and perturb the sedimentation process. Therefore, attempts were made to keep the temperature of the water in the tube constant by pumping water at the depth at which sampling was done (*ca* 12 m) and spraying it on the tube. Even strong spraying did not allow to keep the temperature of water inside the tube constant and within few hours the temperature increased causing the iron particles to be forced out of the tube by the water circulating in the top portion of the sedimentation tube. Hence, to avoid these mixing effects, sampling intervals on the platform were shortened (10–15 min) and between each sampling the sedimentation tube was immersed in the lake water at the depth at which the water was collected (every hour). Tests with dyes have been performed to check that no mixing effect occurs under these conditions (see following section).

Diffusion and convection in the tube. The possible mixing effect of the sample solution in the tube was checked by the following method: after filling the tube at the desired depth, it was brought to the platform, a dye was introduced at the bottom of the tube by injecting it through the septa, and lowered again into the water at the same depth as before. The dipping and raising the tube was repeated 10 times. The thickness of dye layer was measured each time. The results indicated that the mixing effect and diffusion of the dye occur over a distance of less than 20 cm during the period of handling (8 h). Similarly the effect of convection due to external heating was tested and it was found to have no effect during the time scale of the measurements (always less than 15–20 min).

Reproducibility and precision of measurements. After filling the tube with water sample at the desired depth, it was brought to the platform. Then the tube with the water sample was immersed in the water at the same depth at which the sample was collected and brought back to the platform. This was repeated eight times within 30 min. During this period of time the iron concentration of the water in the tube does not decrease significantly. Water samples were withdrawn from the sedimentation tube at three different depths (top, middle, bottom) (Fig. 4) prior to immersing into the lake and the iron concentration determined. This allows to assess the repeatability of the method including precision of the chemical method of analysis, reproducibility of the sampling procedure, and effect of possible mixing processes taking place inside the tube during its handling for temperature regulation. The precision in concentration measurements is 0.16 μM (standard deviation) or 14% (relative standard deviation). Peaked profile such as that observed in Fig. 4 arises probably from sampling of iron-containing particles much larger than the average size. About 10–15% of the samples exhibit this feature. These can be easily detected and can be rejected when a large number of samples are measured.

Adsorption of iron particles on the walls of the sedimentation tube. In order to ascertain that no iron was lost through adsorption on to the container walls, mass balance calculations were done with data obtained from iron collected at the bottom of the tube, iron collected on the walls after emptying it, and iron concentration profile measurements made after 10 h contact with the container (i.e. maximum duration of a long term experiment). Experiments were done with: (i) synthetic iron hydroxide globules suspended in synthetic lake solution (containing only the right concentration of $Ca(HCO_3)_2$) and (ii) natural iron particles suspended in lake water. In both cases, the adsorption of iron on to the walls was found to be <2% of the sedimented iron and hence was neglected in subsequent calculations and interpretation of data.

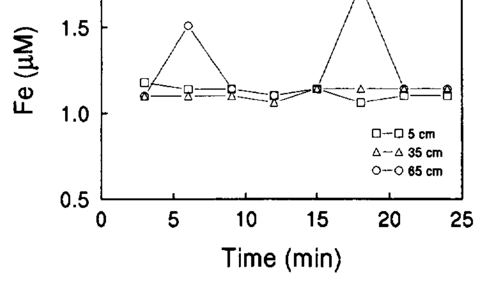

Fig. 4. Repeatability experiments performed in the sedimentation tube in Lake Bret. Samples taken at 5 cm, 35 cm, and 65 cm depth. Date: 17 June 1992.

Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS)

For microscopy, 20 cm^3 of sample were transferred to a centrifugation tube containing copper grids fixed on a plastic holder at the bottom of the tube. The grids were prepared previously according to a non-perturbing technique for TEM observations (Perret *et al.*, 1991). These samples were kept for less than 6 h in a cold box for their transport to the laboratory where they were centrifuged at 30,000 rpm (124,000 *g*) for 2 h at 10°C, with a Beckman Ultracentrifuge L7-55. The electron microscope used for examination and documentation was a JEOL 1200 ExII Temscan equipped with a Princeton Gamma Tech Si[Li] X-ray detector used for energy dispersive spectroscopy. Morphological measurements were made in transmission mode at accelerating voltages of 60 and 80 kV. The EDS provided a spectrum of all elements with an atomic number greater than 10; it was equipped with a PGT Imix multichannel analyser.

Chemical analyses

For particulate iron analyses, the samples (10 cm^3) were transferred to polypropylene tubes containing 0.15 cm^3 of a hydroxylamine hydrochloride solution (10% w/v) and heated in a water bath at 70°C for 15 min for reducing particulate Fe(III) to Fe(II). After cooling the sample to room temperature, Fe(II) concentration was determined by spectrophotometry using Ferrozine as the complexing agent (λ = 462 nm) (Stookey, 1970; Gibbs, 1979; Thompson and Mottola, 1984). It should be noted that this method is perhaps not uniquely selective to lake-born iron oxyhydroxide globules. In fact, an iron concentration of 1 μM [Fig. 2(b)] observed at depth <6 m, i.e. above the thermocline, may be attributed either to the upward diffusion of iron oxyhydroxide globules or to the fact that a small proportion of iron included in clays is also determined by the method. The contribution of iron from the latter is insignificant provided that one is interested only in the concentration of iron globules present in the water column, but it becomes significant when the data is used for interpretation of sedimentation (See Discussion).

Coagulation/sedimentation calculations

Combining basic coagulation theory for hydrophobic colloids with Stokes' law for gravitational settling yields the dynamic equation that describes the behaviour of hydrophobic particles in aquatic systems (von Smoluchowski, 1918; Lawler *et al.*, 1980; O'Melia and Bowman, 1984; O'Melia *et al.*, 1985). In the model used here, the water body (lake, sedimentation tube) is segmented into several overlying boxes, with particle suspension assumed to be spatially homogeneous within each box. The rate at which the number concentration of particles of size k in box m changes with time is dependent on (i) the rate of formation of particles of size k from smaller particles (i, j) that have a total volume v_k in box m, (ii) the loss of particles of size k by growth to form larger aggregates in box m, (iii) the loss of particles of size k from box m by settling into the box below, (iv) the gain in particles of size k in the box m by settling from above, (v) the input and output of size k particles by hydraulic inflow and discharge, and (vi) the production or destruction of particles of size k in the box m

$$\frac{\mathrm{d}n_{\mathrm{k,m}}}{\mathrm{d}t} = \left[\frac{1}{2} \sum_{(vi+vj=vk)} \alpha(i,j) \cdot \beta(i,j) \cdot n_i \cdot n_j - n_k \cdot \sum_{(i=1,\infty)} \alpha(i,k) \cdot \beta(i,k) \cdot n_i \right]_{\mathrm{m}} + \frac{w_{k,\mathrm{m}-1}}{z_{\mathrm{m}}} n_{k,\mathrm{m}-1} - \frac{w_{k,\mathrm{m}}}{z_{\mathrm{m}}} n_{k,\mathrm{m}} + \frac{q^{i}_{\mathrm{m}}}{z_{\mathrm{m}}} n^{i}_{k,\mathrm{m}} - \frac{q^{0}_{\mathrm{m}}}{z_{\mathrm{m}}} n^{0}_{k,\mathrm{m}} \pm W_{k,\mathrm{m}} \quad (1)$$

where n_i, n_j, n_k denote the number concentration of particles of sizes i, j, k; $\alpha(i,j)$ is the coagulation efficiency; $\beta(i,j)$ is a collision frequency function per unit volume per unit time, which depends upon the physical mode of interparticle approach (three particle collision mechanisms have been considered: Brownian motion, fluid shear and differential settling); $w_{k,\mathrm{m}}$ is the settling velocity of particles of size k in box m assumed by Stokes' law; z_{m} is the depth of box m; $W_{k,\mathrm{m}}$ is the rate of production or destruction of particles of size k in box m; q^{i}_{m}, q^{0}_{m} are the input and output areal hydraulic loadings of box m; $n^{i}_{k,\mathrm{m}}$, $n^{0}_{k,\mathrm{m}}$ are the number concentrations of particles of size k in the water flowing in and out of box m.

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 for assigning new particles to standard particle size classes, refer to Lawler *et al.* (1980). O'Melia and co-workers (O'Melia and Bowman, 1984; O'Melia *et al.*, 1985; Ali *et al.*, 1984; Weilenmann *et al.*, 1989) have applied this model to lakes. The values of the parameters used in the model simulations are indicated in Table 1. It should be noted that in simulation of the sedimentation experiments, the exact size and geometry of the sedimentation tube as well as the exact position of the sampling septa were considered.

When comparing simulated predictions with experimental observations, it should be borne in mind that the development of the model is based on the following assumptions: (i) colloids are hydrophobic; (ii) particles are of identical nature (chemically homogeneous); (iii) particles before and after each aggregation are rigid spheres; (iv) the volume of solid particles remains constant during agglomeration; (v) particles approach one another in rectilinear paths and the path of one particle is not 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 occur; (viii) breakup or dissolution of aggregates due to fluid shear or other processes are absent; (ix) the water body is an ideal settling basin. Most of the assumptions are valid for the interactions of iron particles between themselves but probably may not hold for the interaction of these with other lake particles. Nevertheless, they may be used as a first approximation for semi-quantitatively exploring the relative importance of the various factors affecting coagulation (Weilenmann *et al.*, 1989).

Table 1. Properties used in the model calculations

Property	Value
Mean depth (m)	1.0
Temperature (°C)	5
Water viscosity ($\mathrm{g \cdot cm^{-1} \cdot s^{-1}}$)	$1.515 \cdot 10^{-2}$
Water density ($\mathrm{g \cdot cm^{-3}}$)	1.000
Velocity gradient ($\mathrm{s^{-1}}$)	
lake	0.5[a]
tube	0.0
Coagulation efficiency, α	0.01[b]
Particle density ($\mathrm{g \cdot cm^{-3}}$)	3.0[c]
Initial particle distribution	Varied
Initial particle concentration ($\mathrm{mg \cdot dm^{-3}}$)	0.535

[a] Weilenmann *et al.* (1989).
[b] Tipping and Higgins (1982).
[c] Schwertmann and Fisher (1973).

RESULTS

Three types of sedimentation experiments were performed in the sedimentation tube:

(i) Type 1 experiments: iron oxyhydroxide globules prepared in the laboratory by slow oxidation of a ferrous salt in the presence of low oxygen concentration (≃ 1 ppm), at constant pH (7.4 ± 0.1) and temperature (10 ± 1°C) were used in synthetic lakewater containing 1.5 mM of $\mathrm{Ca^{2+}}$ as $\mathrm{Ca(HCO_3)_2}$. Preliminary tests showed that the results obtained by adding synthetic iron oxyhydroxide globules to natural lakewater samples filtered through 0.2 μm filter instead of synthetic lakewater were similar.
(ii) Type 2 experiments: *in situ* measurements in the lake following sedimentation of natural iron particles in lakewater.
(iii) Type 3 experiments: same as type 2 except that large particles present in the upper layer of the lake were pumped and circulated in the upper part of the sedimentation tube.

The results of these experiments were compared with sedimentation observations obtained for the "whole" lake (see below).

Transmission electron microscopy observations

During sedimentation experiments, a very large number of TEM photographs have been recorded of the iron globules and the associations between themselves and with other lake materials. This allowed to make a semiquantitative estimation of the most frequent types of associations and morphologies. Typical pictures are reported in Fig. 5(a)–(h). The colloidal iron oxyhydroxide globules were identified on the basis of their size, shape, and EDS spectral characteristics as were other major particle types (Leppard, 1992). The influence of many different types of particles on the agglomeration of iron oxyhydroxides is clearly demonstrated in these pictures which show associations of iron oxyhydroxide globules with spores [Fig. 5(a)], organic debris [Fig. 5(b)], bacteria [Fig. 5(c)], the refractory organic remains of filamentous bacteria [Fig. 5(d)], diatom frustules [Fig. 5(e)], clays [Fig. 5(f)], mineralized organic fibres [Fig. 5(g)] and a fibrillar diffuse organic mesh [Fig. 5(h)]. Many other situations have been observed. The important features coming out from the whole of these observations are the following:

(i) Iron globules appear to adsorb on or aggregate with most other aquatic colloids:

biogenic or non-biogenic silica, clay fragments, organic debris material of all kinds, bacteria, and calcium-rich grains (possibly calcium carbonate). In some cases, association of the globules with organic material is not obvious because the latter is very little electron dense and needs special TEM conditions to be visualized. Figure 5(d) for instance does not allow one to see any support for the aggregate, but, considering the special and well defined shape of the aggregate, a "ghost" organic structure is likely to be present (possibly a cell wall). For the same reason, adsorption of globules on organic fibrils or loose organic spongy material is often difficult to visualize, and many globules may appear as being independent from each other, while in reality they are associated with organic matrices, when the right TEM conditions are used (e.g. the use of electron opaque stains or unusually small apertures).

(ii) The materials to which the globules seem to be the most frequently and strongly associated are diatom frustules [Fig. 5(e)], clays [Fig. 5(f)], spores [Fig. 5(a)], fibrils [Fig. 5(g)] and loose spongy organic matrices [Fig. 5(h)] which look like the aggregates of organic fibrils (Leppard, 1992) or of pedogenic fulvic compounds described elsewhere (Leppard *et al.*, 1986). In the very large majority of cases, these aggregates of globules with other material have a size in the range of 0.5 to not more than a few microns. Aggregation with calcium (carbonate) was found to be very uncommon.

(iii) Most iron globules have a size close to 100 nm [Fig. 5(a)–(g)]. When smaller globules are seen, they are often associated to fibrils or loose organic matrices [Fig. 5(h)]. Globules not associated to organic matrices and smaller than 50 nm are rare.

(iv) Associations of iron globules with clays deserve special mention. There can be a

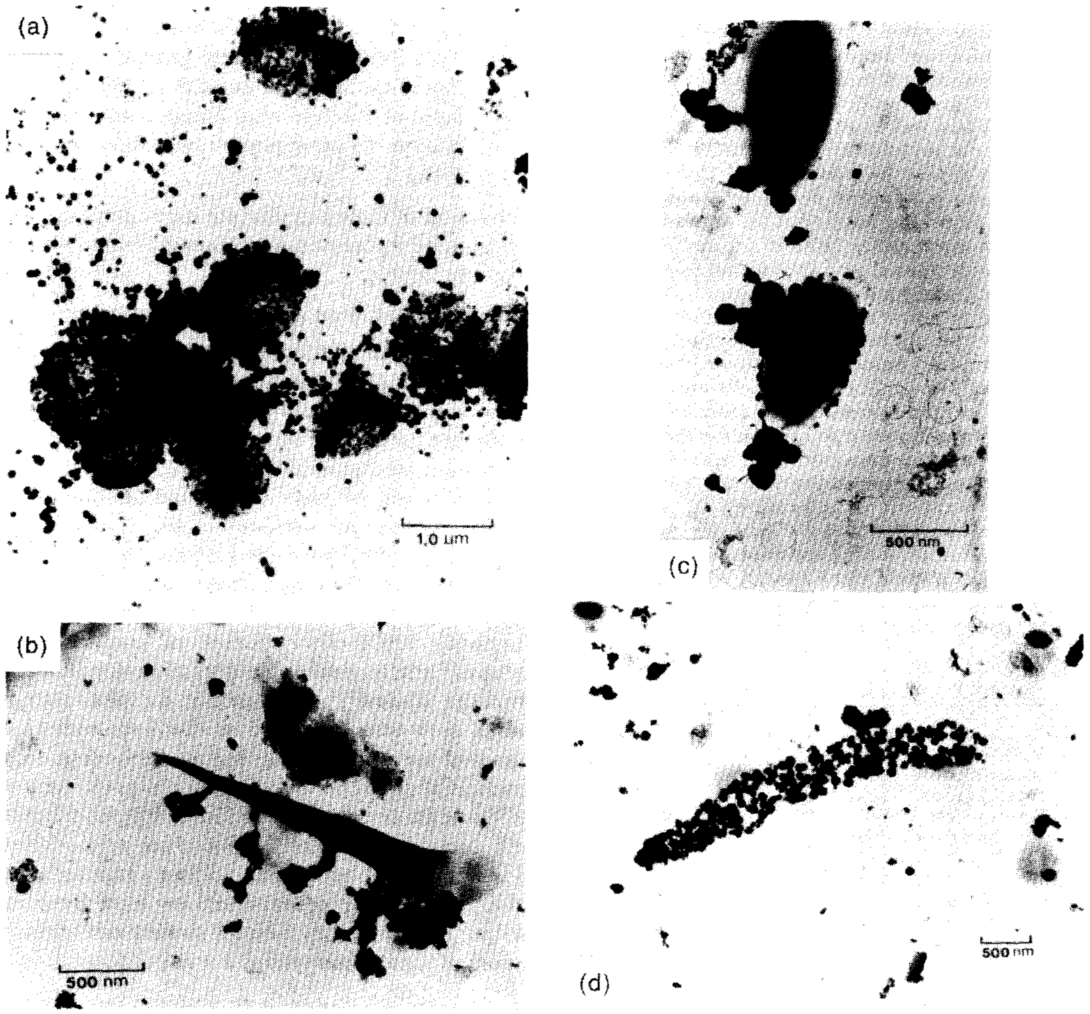

Fig. 5. (a–d) *Caption on facing page.*

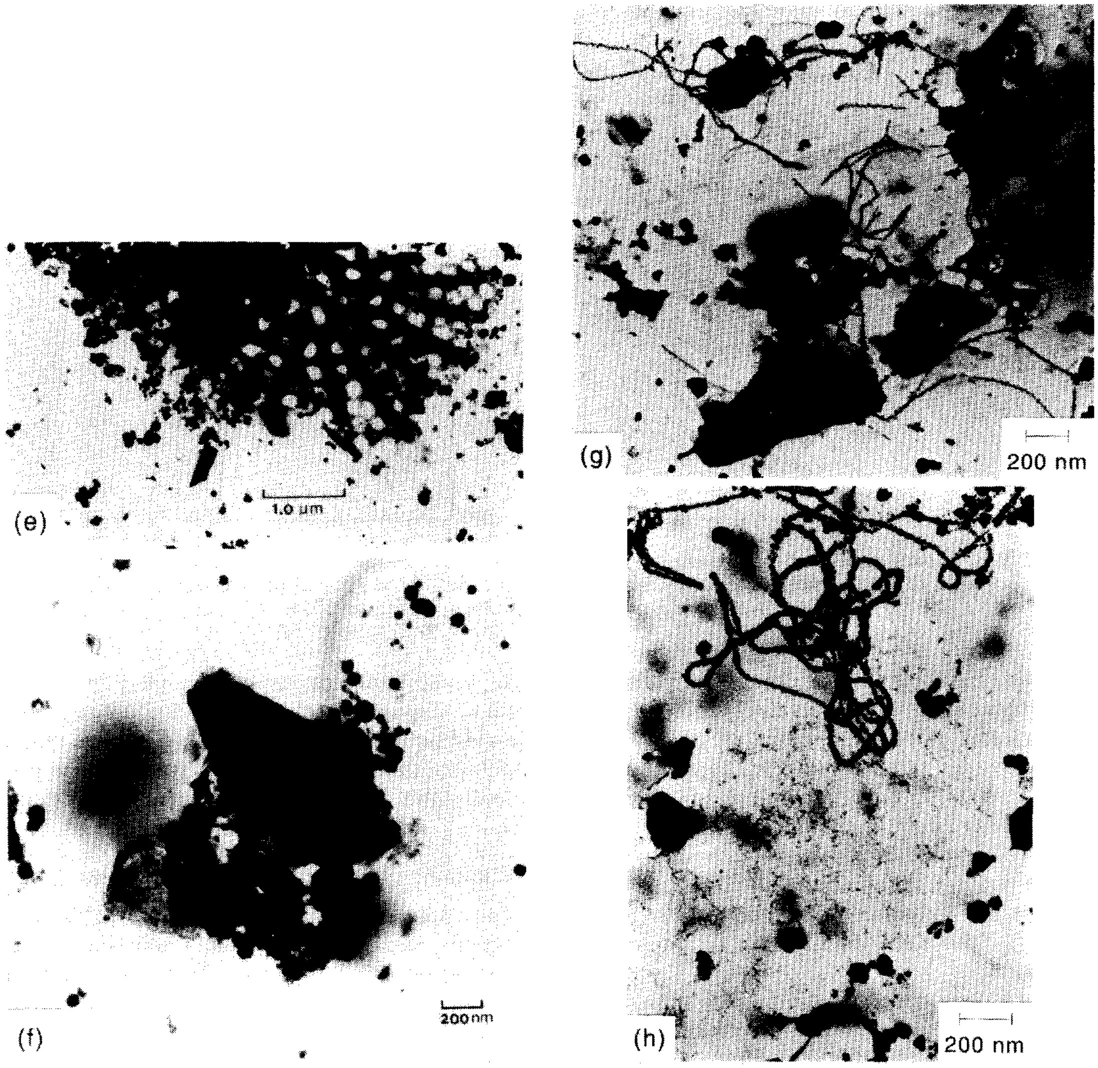

Fig. 5. Typical colloidal iron hydroxophosphate globules associated with the surfaces of larger particles to form heterogeneous aggregates. (a) Large number of globules associated with biological materials, tentatively identified as spores. Note that individual iron colloid-spore associations appear to be aggregating with each other thanks to the iron globules serving as gluing material. (b) Globules associated with biological material, tentatively identified as a fragment of the exoskeleton of a planktonic organism. (c) Globules associated with the outer surface of bacteria. (d) Globule aggregate in the shape of a small filamentous microbe. It is possible that this aggregate was formed by adhesion to the surface of a microbe which then decomposed or became detached. The remains of mucilage fibrils, often found on microbe surfaces, can be detected between individual globules of the aggregate. (e) Globules adhering to a portion of a broken silica frustule, the mineral cell wall of a diatom alga. (f) Globules associated with a colloidal clay particle. (g) Heterogeneous aggregates associated by mineralized bridging fibrils. (h) Globules and other colloids associated with a highly porous fibrillar matrix.

direct association with clay particle, an indirect association by means of polymer bridges which create heteroaggregates [Fig. 5(g)] and a direct association of iron and clays by means of an iron coating. It is possible that some iron coatings are merely eroded globules on a clay surface.

Sedimentation in the sedimentation tube

Typical profiles of particulate iron concentration *versus* time obtained for type 2 and type 3 experiments (i.e. without and with circulation of large particles) are shown in Fig. 6(a) and (b), respectively. The variation in iron concentration with depth at a given time is of the same order of magnitude as the precision of the sampling and analytical measurement (see Methods). Therefore, the concentration of iron particles as a function of depth was found to be constant within experimental error.

The results obtained for the evolution of mean particulate concentration in the sedimentation tube by the three types of experiments are shown in

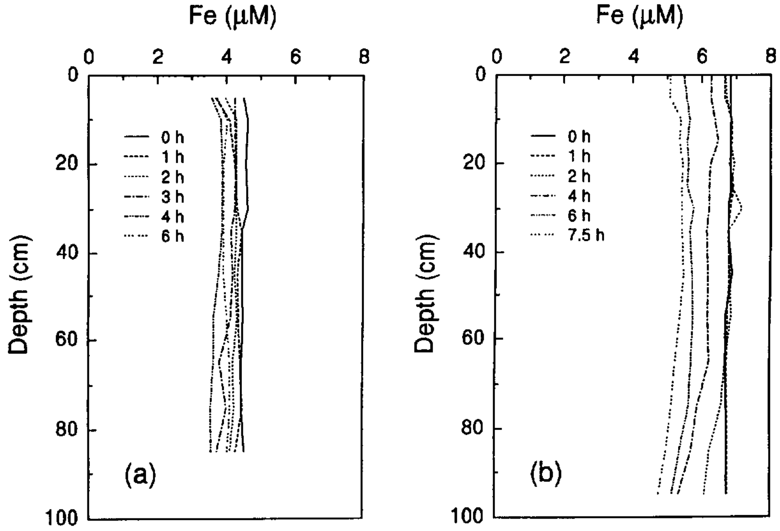

Fig. 6. Typical profiles of total particulate iron inside the sedimentation tube. (a) Experience without circulation of large particles (type 2 experiment). Date: 27 June 1990. (b) Experience with circulation of large particles (type 3 experiment). Date: 22 August 1990.

Fig. 7 and in Table 2. The characteristic features of the plots in Fig. 7 are that the concentration of iron decreases slowly with time, obeying in most cases first-order rate law (exceptions are samples collected on 24–25 July 1990 which are discussed later). These observations cannot be explained in terms of simple sedimentation process because of the fact that the profiles remain vertical while the concentration decreases with time. The salient features will be discussed more in the subsequent sections.

Constant iron concentration profiles were found for the three types of experiments indicating that: (i) the synthetic and natural iron oxyhydroxides behave alike; and (ii) the continuous sedimentation of large particles through the tube does not significantly affect the sedimentation of iron particles (compare type 2 and 3 experiments), i.e. the coagulation of small iron globules with the fast sedimenting particles is negligible.

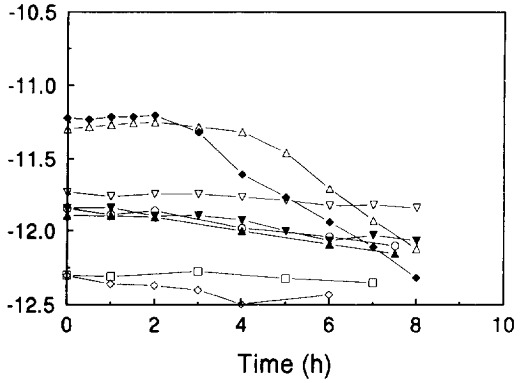

Fig. 7. Evolution with time of the mean concentration of total particulate iron for different type of experiments. Correspondence of symbols with samples are as follows: ◇—◇ 27 June 1990; ◆—◆ 24 July 1990; △—△ 25 July 1990; ▲—▲ 22 August 1990; ○—○ 4 September 1990; □—□ 18 September 1990; ▽—▽ 7 September 1992; ▼—▼ 9 September 1992. See Table 2 for complementary information.

Sedimentation in the whole lakewater column

The results obtained from sedimentation tube experiments were compared with a "whole lake" experiment performed in November 1986. That year the thermal stratification was maintained until the beginning of November, i.e. the lake was oxygenated up to −12 m depth and was anoxic below this depth, the anoxic water containing high concentrations of Fe(II) and S(−II). A sudden drop in the air temperature resulted in very fast lake turnover (a few days) and Fe(II) was oxidised to Fe(III) particles and homogenised in the whole lake during this period of time. Although only two iron profiles could be recorded before complete sedimentation of the particles (Fig. 8), the following interesting features could be observed: (i) vertical profiles are observed, (ii) the slope of the first-order rate plot (-0.002 h^{-1}) is of the

Table 2. Sedimentation of iron oxyhydroxides under different experimental conditions

Experiment type[a]	Date	k' (h^{-1})[b]
1	7 Sep 1992	-0.013 ± 0.002[c]
1	9 Sep 1992	-0.031 ± 0.004
2	27 Jun 1990	-0.025 ± 0.009
2	25 Jul 1990[d]	-0.208 ± 0.009
2	18 Sep 1990	-0.006 ± 0.001
3	24 Jul 1990[d]	-0.188 ± 0.007
3	22 Aug 1990	-0.037 ± 0.004
3	4 Sep 1990	-0.034 ± 0.004

[a] See text for description of the different experiment types.
[b] Sedimentation first-order rate constant.
[c] Standard error (95%). [d] Only non-horizontal segments considered.

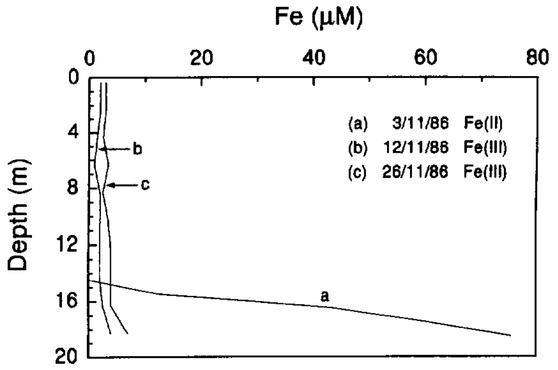

Fig. 8. Change in the concentration profiles of particulate iron formed by oxidation of the Fe(II) present in the anoxic part of the lake, after its abrupt turnover. Date: November 1986.

same order of magnitude as the one obtained by sedimentation tube experiments on 18 September 1990.

Coagulation/sedimentation simulations

In order to get an insight on the nature of the main factors influencing the behaviour of lacustrine submicron colloids, three types of simulation studies were made:

(i) Time evolution of particle size distribution as a function of the initial particle size distribution and of the value of the coagulation efficiency, α.

(ii) Time evolution of submicron colloid concentration profiles in the sedimentation tube as a function of the initial size distribution, without settling of larger particles.

(iii) Time evolution of submicron colloid concentration profiles in the sedimentation tube in the presence of a continuous settling of larger particles.

The results most relevant for this paper are summarised in Figs 9–11. Complementary results are published elsewhere (Filella and Buffle, 1993; Filella *et al.*, 1993; Newman *et al.*, 1994).

The particle size distributions of four one day old suspensions (initial particle size distributions: monodisperse 1 nm, monodisperse 10 nm, monodisperse 100 nm particles, or uniform volume distribution of particles of sizes ranging from 1 to 300 nm), under the conditions given in Table 1 are shown in Fig. 9. Results are presented as discrete plots of particle volume, $dV/d(\log d_p)$, vs $\log d_p$ (d_p = particle diameter). Although the resulting size distribution depends on the values of the physico-chemical parameters chosen, the following important features are always observed: colloids smaller than 100 nm coagulate very quickly into aggregates of *ca* 100 to a few hundreds of nm. These aggregates do not settle down and their size does not change appreciably within days.

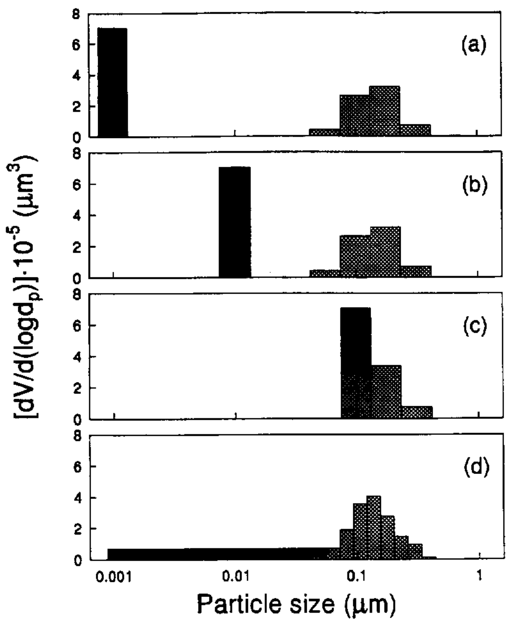

Fig. 9. Simulation results. Evolution after one day of four initial particle size distributions: (a) monodisperse 1 nm particles, (b) monodisperse 10 nm particles, (c) monodisperse 100 nm particles, (d) continuous with $\beta = 4$ and size ranging from 1 to 300 nm. Note: the size distribution function, $n(d_p)$, of populations of coagulating particles has been found to exhibit a power-law: $n(d_p) = Ad_p^{-\beta}$ where the β exponent is a constant in many environmental samples. Initial distributions appear in black and final distributions as grey areas. Values of other parameters as in Table 1 ($G = 0.5$).

The position of the peak at *ca* 100 nm changes little with total particle concentration, with the nature of the initial size distribution and with time (Filella and Buffle, 1993; Newman *et al.*, 1994). Figure 10 shows that the peak position depends little on the coagulation efficiency, α, at least for values between 0.001 and 0.1, which are typical for lake conditions. All these results are in accordance with the TEM

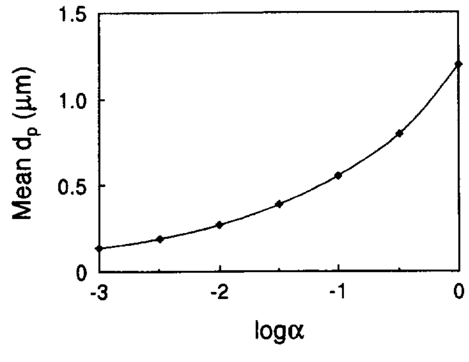

Fig. 10. Effect of coagulation efficiency, α, on the evolution of an initially continuous particle size distribution with $\beta = 4$ and size ranging from 1 to 300 at 10 days. Results shown as evolution of weighted mean size at 10 days, with α. Values of other parameters as in Table 1 ($G = 0.5$).

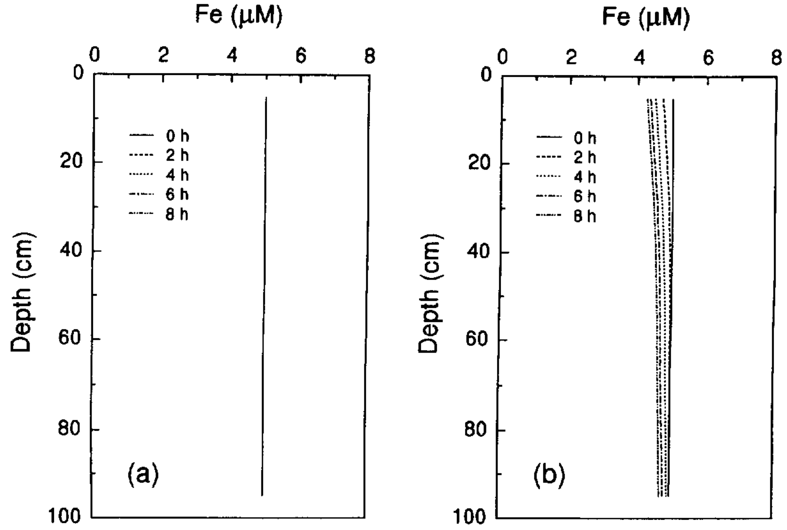

Fig. 11. Simulated profiles of Fe concentration in the sedimentation tube. (a) Initial particle size distribution: either monodisperse 140 nm or continuous with $\beta = 4$ and size ranging from 1 to 300 nm. The same result is obtained in both cases. (b) Initial particle size distribution: continuous with $\beta = 4$ and size ranging from 10 nm to 10 μm. Values of other parameters as in Table 1 ($G = 0.0$).

observations reported for our lacustrine iron globules (Leppard *et al.*, 1988; Buffle *et al.*, 1989):

(i) Their size is mostly in the range 50–300 nm (typically with a value of 140 nm for the samples studied in this work).

(ii) They are composed of aggregates of very small entities (1–2 nm). The small entities may also exist as free units (see Discussion), but the above simulation results suggest that coagulation of such units into globules of 100–300 nm should be very fast.

The simulated concentration profiles in the sedimentation tube obtained at different times as well as three different initial particle size distributions viz (i) a monodisperse suspension of 140 nm particles, (ii) a uniform volume distribution of particles in the range 1–300 nm, (iii) a uniform volume distribution of particles in the range 10 nm–100 μm, are shown in Fig. 11. As can be seen, identical results are obtained for (i) and (ii). The important features of the simulated plots in Fig. 11 are as follows:

(i) Particles of 140 nm or 1–300 nm ($\beta = 4$) do not settle down within 8 h [Fig. 11(a)]. After 8 h, 0.04 and 0.03% of the initial particle mass concentration (and 10.9 and 99.997% of the initial particle number concentration) disappear in the case of 140 nm and 1–300 nm ($\beta = 4$) particles, respectively. These values have been calculated using the parameters in Table 1.

(ii) Sedimentation of particles in the range 10 nm to 100 μm [Fig. 11(b)] is apparently faster (<2 h) in comparison to the time span of sedimentation experiments, and is manifested by a shift of the concentration profile which is more marked at the top of the tube. A close look at calculation results however shows that this shift only corresponds to the sedimentation of particles larger than a few μm, the concentration of the submicron particles remaining unchanged.

Profiles similar to those shown in Fig. 11(a) were obtained for the iron-containing particles when simultaneous settling of larger particles was considered. Since particles smaller than 500 nm never form aggregates of size ⩾500 nm within a day (see above), the simulation program can easily discriminate between the concentration of submicron particles and the aggregates between themselves on the one hand, and that of the continuously settling large particles (>2 μm) including the submicron particles aggregated on them, on the other. Calculations have been performed for various combinations of (i) submicron colloids representative of the iron-containing particles [either monodisperse suspensions of 140 nm or polydisperse suspensions of 1–300 nm ($\beta = 4$)] with (ii) large particles (monodisperse suspensions ranging from 10 to 100 μm). Since the flux of the various particles in Lake Bret is not known, different concentrations of influent large particles that give fluxes of particles in the range 4 to 40 $g \cdot m^{-2} \cdot day^{-1}$ (assuming a particle density of 3 $g \cdot cm^{-3}$) were tested. At any rate, the model used did not predict any influence of the continuous settling of particles larger than a few μm on the sedimentation of the submicron colloids under the conditions used, in agreement with experimental results.

DISCUSSION

The important information that can be obtained from the results of this work is discussed below.

(1) The fate of submicron colloids is strongly influenced by organic material released during primary production period

Previous studies on the iron oxyhydroxide globule size distribution in Lake Bret (Leppard *et al.*, 1988; Perret, 1989) have shown that the majority of iron globules are of diameters less than 300 nm and their size distribution obeys Pareto's law (Lerman, 1979) yielding a slope of 2.6 (Buffle *et al.*, 1989). TEM observations in the present study show the iron globules to be of diameter 140 nm. A comparison of the experimental data (Figs 6–8 and Table 2) with the simulated results based on classical coagulation theory of hydrophobic colloids combined with Stokes' law (Figs 9–11) and taking into account the above mentioned size range of the iron globules reveals the following:

> *Simple sedimentation of iron globules.* Simulations [Figs. 9 and 11(a)] suggest that, under the experimental time scales used, particles of such small size can neither sediment to significant extent as individual entities nor even coagulate between themselves (self-coagulation) into aggregates large enough to sediment at a significant rate.
>
> *Coagulation/sedimentation with larger settling particles.* Both simulations and experiments [Fig. 6(b)] suggest that aggregation of iron globules with large ($\geqslant 10\,\mu$m), quickly sedimenting particles is not an important process for the removal of the globules from the water column.
>
> *Interaction of iron globules with other colloidal material.* The natural lakewater contains many inorganic and organic colloids, mostly smaller than a few microns and with which the iron globules aggregate (Fig. 5). If the sedimentation of these aggregates was the limiting step for the elimination of iron colloids, iron concentration at the top of the tube should decrease [Fig. 11(b)]. Experimental observation, however, reveals that iron concentration is independent of depth, but that it decreases slowly with time at all depths in the tube.

This behaviour implies that a step slower than sedimentation causes the formation of aggregates large enough to be "instantaneously" (i.e. in the hour interval between sampling times) eliminated by sedimentation at the bottom of the tube. Moreover, this slow step should be fast enough to allow observable decrease in iron concentration in the lake within 6–10 h, i.e. time scale of the experiment. Regarding this, the simulation results show that self-coagulation of particles $\simeq 100$ nm is a much too slow process. Based on TEM observations, the following reaction scheme can, however, be proposed to explain the sedimentation results in the lake.

TEM pictures show that there is a very high probability for iron containing particles to coagulate with (or adsorb on) "medium sized, compact" colloids. These colloids may be of all types, but they are primarily organic debris or fine clay leaflets [Fig. 5(a)–(f)]. As the size of these colloids is not large (0.5–4 μm) and their density is low (density of hydrated clay leaflets may be as low as $1.5\,\mathrm{g \cdot cm^{-3}}$ (Jerlov, 1976)), their sedimentation is also very slow. TEM observations however show that lakewater also has a high content of large sized "loose" organic matrices, such as filaments, fibres, gel or mesh [Fig. 5(g)–(h)], which can bind with each other or entrap the medium-sized colloids (along with the associated globules), forming large aggregates. Although this entrapment or bridging process is probably an additional slow step, the resulting aggregates may readily grow into sizes large enough to sediment quickly. Many TEM pictures [e.g. Fig. 5(a)] in fact suggest that iron globules can themselves act as a "glue" to help aggregating larger colloids.

According to this scheme, elimination of lake-born iron globules should occur by (i) adsorption onto small inorganic colloids and (ii) bridging of these colloids by large organic matrices. It might be expected, as a first approximation, that the rate of elimination of iron globules by such a mechanism, be first-order with respect to the number concentration of the globules. Also, since the number concentration of globules is proportional to the concentration of iron, the following first-order rate law (Fig. 7):

$$\mathrm{d[Fe]}/\mathrm{d}t = k' \cdot \mathrm{[Fe]} \qquad (2)$$

is expected, provided k' remains constant within the experiment.

According to this interpretation, k' should remain constant if the concentration of inorganic colloids $\leqslant$ *ca* 10 μm and the large organic "bridging" matrices do not change during the experiment. This is likely to be so for most of the cases within the time scales of the experiment ($\leqslant 8$ h). However, the value of k' would be expected to vary from one experiment to another, particularly with respect to lake productivity. Two observations seem to support the proposed interpretation:

(i) Experimental values of k' (Table 2, Fig. 12) are much higher in July, i.e. a period when the temperature is high, and lake productivity is maximum corresponding to large release of organic matter with marked consumption of oxygen in even relatively shallow water layers (>5 m) (Fig. 2). In addition, the elimination rate of iron is minimum in synthetic Bret water (i.e. in absence of organic matter), in the period

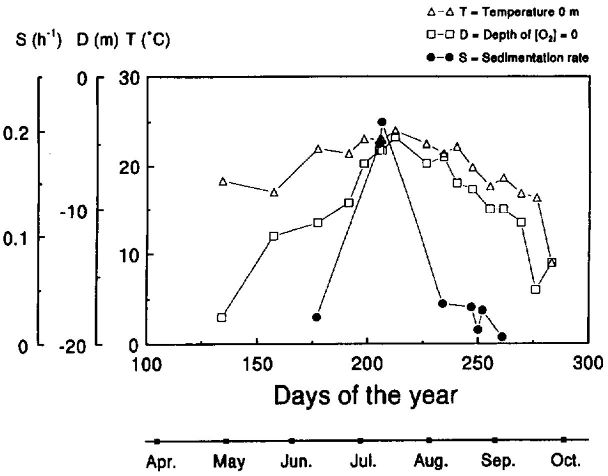

Fig. 12. Relationship between k' and the lake productivity. Although productivity has not been directly measured, temperature and the limiting depth below which oxygen concentration is $\simeq 0$ are indirect indicators of the maximum productivity period.

when primary productivity is lower (June and September), and at the turnover period (November, Fig. 8 and 12), i.e. when most of lacustrine organic matter has been eliminated (in October) by sedimentation/ microbial oxidation and/or by the outflow of the lake.

(ii) A non first-order elimination rate is observed in two cases (24 and 25 July 1990) where productivity is maximum. This might be due to the growth of organisms and release of organic material in the sedimentation tube *during* the sedimentation experiment. Indeed, an initial induction period followed by fast kinetics is a common feature of organism growth.

These latter observations suggest that even under normal conditions (first-order rate law) the elimination rate of iron particles might be controlled (or partly controlled) by microbial life.

(2) Role of pedogenic and aquogenic organic matter on coagulation/sedimentation of submicron particles

In the literature, dissolved organic matter is reported to stabilize inorganic colloids. This has been observed, for instance, with synthetic haematite (Tipping and Higgins, 1982), natural clays (Gibbs, 1983) and lacustrine particles (Ali *et al.*, 1984; Weilenmann *et al.*, 1989). However, the main focus in these studies has been on the stability of particles $\geqslant 1\ \mu$m, i.e. particles that sediment by themselves, and which, in addition, are larger than or of similar size than most of the organic components of natural waters. Consequently, the role of organic matter is assumed to be that of forming an organic coating on particles. Therefore, it is stated that the organic coating on particles may alter the coagulation efficiency value, α, but the coagulation process is assumed to remain the same (i.e. based on classical interactions of compact hydrophobic colloids). Moreover, these investigations have been carried out with pedogenic humics or using DOC as a global parameter, without discriminating between aquagenic and pedogenic forms of organic matter. Since pedogenic NOM predominate in most lakes, the specific role of aquagenic compounds cannot be tested. In Lake Bret, it has been shown (Zumstein and Buffle, 1989) that most of sedimenting colloidal organic matter is of aquagenic origin, which is supported by TEM pictures which shows fibrillar type material associated with inorganic colloids. Thus, the present results suggest that the influence of aquagenic organic matter is markedly different from that of pedogenic humics reported in the literature. Whereas the latter may form an organic coating on colloids, thus decreasing their sticking coefficient and increasing their stability, the large aquagenic fibrillar organic macromolecules may form bridges between colloids and destabilize them. In this case, DOC is not a relevant parameter for determining the role of colloid matter in colloid stability.

(3) Comparison between coagulation/sedimentation within the sedimentation tube and within the water column

The sedimentation fluxes of iron particles estimated from the values in Table 2 have been compared with the formation fluxes of iron oxyhydroxide estimated from the diffusion of Fe(II) at the oxic-anoxic interface of sediments and its subsequent oxidation in Fe(III). The value of the former are systematically larger than the latter during the summer-autumn period, sometimes *ca* 10–20 times larger. This observation is interesting, as it suggests the occurrence of processes which are important in the open water column, but not observed in the closed sedimentation tube. Although from the present results no definite conclusion can be drawn about these, they are briefly discussed below. The main causes of the discrepancy may be the following:

(i) The net sedimentation rate in the lake is the resultant of the sedimentation rate measured in the sedimentation tube, and of a counter flux due to the upward eddy diffusion resulting from concentration gradient shown in Fig. 2(b). The contribution of the second factor has been quantitatively estimated but it is not sufficiently high to account for the observed difference.

(ii) Iron particles deposited at intermediate depth on sides of the lake basin may be resuspended by local turbulences and spread over the whole lake by horizontal eddy diffusion.

(iii) Sedimentation in the whole water column may be slowed down by disaggregation due to microbial degradation of organic matrices (Sundh, 1992).

(iv) Above all, any particular k' value given in Table 2 should not be considered to be valid for the coagulation/sedimentation of all iron particles but only to those sedimenting during the first 6–8 h. Typically they represent 10–30% of the total. Because iron particles and their aggregates with other colloidal material cover a broad spectrum (from 1 nm to 1 μm) and occur in many types of shapes and chemical associations, it is highly probable that their coagulation/sedimentation rates cannot be represented by one single k' value. Since values given in Table 2 correspond to a "short" coagulation/sedimentation time span, they should be considered to be the highest possible values. Simulation results reported here indeed suggest that the measured k' values correspond to the fastest coagulating particles, and that k' values for the iron particles that coagulates very slowly, *ca* 10–20 times slower, i.e. days to weeks, representing a major fraction of total iron particles, cannot be measured by our technique.

It is presently difficult to discriminate between the relative importance of points (i) to (iv) stated above. It must be borne in mind that the analytical method used for measuring the concentration of iron particles in the sedimentation tube is not uniquely selective to lake-born iron oxyhydroxide, but perhaps it also measures a small fraction of iron incorporated in clays (see Methods). Hence, the values of coagulation/sedimentation rates measured during non productive periods might be affected by the sedimentation of soil derived iron-containing clay particles and consequently they cannot be rigorously compared to the formation flux of globules by oxidation of Fe(II) within the lake. In fact, sediment trap results reported previously showed that there is also a strong correlation between the sedimentation fluxes of clays and of lake-born organic material (Zali, 1983; Zumstein and Buffle, 1989), suggesting that sedimentation of clays is also influenced by their coagulation with organic matter.

The foregoing remarks however do not affect the main conclusion drawn from the findings of this study, i.e. the predominant role of floculation by larger organic filaments and matrices in the sedimentation of submicron colloids. Point (iv), however, provides an important supplementary information regarding the choices of sampling procedures for suspended particles to study the fluxes of sedimenting compounds. In particular, techniques of collecting particles within short periods, allow only to collect the largest fast settling particles and do not necessarily allow the measurement of the most relevant fluxes required for understanding of the process of interest. For instance, in the present case, an 8 h period of sedimentation might be too short to allow studies on the cycling of iron in the lake. In general, techniques allowing the measurement of a wide spectrum of coagulation/sedimentation rates are preferable.

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