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Chapter

Influence of Organic Matter on the Transport of Mineral Colloids in the River-Sea Transition Zone

Elena V. Lasareva and Aksana M. Parfenova

Abstract

The River-Sea Transition Zone has a significant impact on marine ecosystems, especially at present, due to increased anthropogenic pressure on rivers. The colloidal form of river runoff has not been practically studied, unlike the dissolved and suspended one, but this form is particularly important for the transport of river substances. The mechanisms of substance transfer were studied using model systems (colloidal clay, $Fe(OH)_3$ sol), particle aggregation was estimated by changes in optical density, turbidity and particle size. The influence of the nature of dissolved organic matter (DOM) and salinity on colloid transport was studied. It was found that humic substances (HS) (recalcitrant DOM) stabilize mineral colloids with increasing salinity, while their interaction with chitosan (labile DOM) promotes flocculation and further precipitation in the mixing zone. In natural conditions, labile DOM can be released during viral lysis of bacteria or salt stress of biota. It was shown that clay particles modified with HS are flocculated more effectively than pure clays. HS can facilitate the transport of $Fe(OH)_3$ into the outer part of the mixing zone even in the presence of flocculants. The flocculation mechanism and modern views on this process are considered.

Keywords: river-sea transition zone, colloids, clay, iron(III) hydroxide, humic substances, chitosan, extracellular polymer substances

1. Introduction

The zone of mixing of river and sea waters is an area of significant biogeochemical activity, also referred to as the river-sea transition zone (RSTZ) or marginal filter (MF) [1]. River substances enter the ocean through this region, but the possibility and extent of their input depend on the form in which these substances are present in the water in the mixing zone: dissolved, colloidal or in the form of suspended particles. The suspended component of natural water is usually defined as that which remains on the filter with pore sizes 0.45 μm after filtration and the dissolved component is the one that passes through these filters. Typically, colloid particles have a size in the range of 1 nm – 1 μm and belong to both analytically determined forms. However, according to other classifications, colloids are defined as the fraction within 1 nm–450 nm

(medium-sized colloidal (200–450 nm) and fine (<200 nm) fractions [2] or from 0.2 to 1 µm isolated by ultrafiltration or field-flow fractionation techniques [3]. Due to the developed particle surface and, consequently, a large excess of surface energy, colloids tend to absorb components of river water (including pollutants) on their surface and affect their further movement into the marine environment. Despite the importance of the colloidal component it practically has not been studied, in contrast to the dissolved and suspended forms [4]. This is due to the colloid fraction being highly unstable and therefore its isolation presents certain difficulties. Especially this instability manifests itself when the salinity of the water increases.

MF can be simplified as a system consisting of three parts. In the inner part (gravitational), with a decrease in the flow rate of river water, sandy-aleuritic fractions of the suspension are deposited and coagulation of clay matter take place. At the middle part (physico-chemical) with increasing salinity to 5–12‰, the formation of aggregates begins due to flocculation of dissolved, colloidal and suspended particles. The newly formed floccules can absorb various ions, oxyhydrates and dissolved organic substances, turning them into a suspended form, as well as microalgae, bacteria and their residues [5–10]. In the outer part (biological), when the waters are significantly clarified and the concentration of biogenic elements has high values, the role of the biological component increases [11, 12]. Thus, an MF zone acts as a giant treatment plant to purify river water before it enters the sea, and the study of its mechanisms may find further application in water treatment or wastewater treatment processes.

Among the various factors determining the transport mechanisms of river substances, the role of dissolved organic matter (DOM) should be particularly noted [13–15]. Depending on the nature (recalcitrant or labile) and its concentration, DOM can act either as a flocculant that causes aggregation of mineral particles, or a stabilizer that adsorbs on the surface of particles, increases their aggregative stability and helps them move through the mixing zone [16–20]. Currently, there is an increasing interest in extracellular polymeric substances (EPS) released by marine biota that can act as flocculants, as well as in the study of the bio-flocculation process itself. Such interest was driven by the concept of green chemistry, preferring the use of non-toxic and biodegradable biopolymers as flocculants in water treatment, in particular, EPS released by marine bio-flocculant-producing bacterium [21–28]. Various bio-flocculation mechanisms are considered depending on the amount and nature of organic matter (OM), pH and ionic strength [7]. But in most of the approaches, the particles of suspension or colloids are considered in unmodified form and the nature of labile OM remains controversial.

Our approach is based on the hypothesis that recalcitrant OM (HS) of river runoff can act as stabilizers of fine mineral particles. Moreover, the HS play a dual role – they protect mineral particles in river water, and at the same time enhance bio-flocculation when meeting marine fresh OM in MF compared to unmodified particles. The key role of salinity change is not only in particle coagulation due to the compression of the double electrical layer, but also in changing biota from fluvial to marine one. We assume that a bio-flocculant in MF may be fresh OM released during bacterial viral lysis, and labile EPS compounds of marine biota under salt stress. In order to clarify the effect of individual factors on the aggregative stability of colloids, the study was carried out in artificial seawater using model systems (clay, $Fe(OH)_3$ sol). The aim of our work was to model the transport of some mineral colloid components of river runoff at increasing salinity, taking into account the effects of the nature of organic substances and to review the current state of this issue.

2. Materials and methods

Bentonite > 50% of which is represented by a fraction <1 μm (Jebel field, Turkmenistan) was used to simulate colloid clay particles.

Chitosan (Ch), natural polysaccharide, acetic form, Mw 83 kDa, deacetylation degree 85% (Bioprogress production, Shchelkovo, Russia) was used as a model flocculant (labile OM).

Humic acid (HA) potassium salt, separated from brown coal leonardite (Powerhumus, Humintech Ltd., Germany) were used as HS, modeling recalcitrant DOM.

NaCl solutions were models of water along salinity gradient in the RSTZ.

Preparation of iron hydroxide sol by Krekke method.

In a flask, 250 mL of distilled water is heated to a boil. Then, with constant stirring, 10 mL of 2% ferric chloride solution is added in small portions. The resulting sol is boiled for 2–3 min [29].

Preparation of colloidal bentonite. Colloidal bentonite (0.3 g/L) was prepared from a supernatant liquid after decantation of the settled for a week bentonite suspension (2 g/L).

Natural waters were sampled in the MF of Arctic rivers using the Rosetta Niskin bathometer, after hydro-physical parameters were determined.

Flocculation of colloid clay was carried out by the addition of Ch solution to 10 mL of clay dispersion to obtain the required concentrations.

The modification of the Fe(OH)$_3$ sol and clay colloids was made by adsorption of HA (10 mg/L) within three days. For that 0.5 mL of HA solution with concentration of 1 g/L was added to 50 mL of studied dispersions and left samples for adsorption for a week.

The size of Fe(OH)$_3$ particles was determined with a Zetatrac analyzer (Microtrac Inc., USA).

The optical density and turbidity of colloids as a measure of the aggregative stability before and after the addition of flocculant (Ch) and coagulant NaCl, were measured using the spectrophotometer Agilent (USA) at λ = 535 nm and Turbidimeter HANNA HI 98713 (Romania).

Dynamic light scattering was used to determine the particle size of colloids with Zetatrac (Microtrac Inc., USA).

3. Results and discussion

The idea of V.I. Vernadsky about boundary zones in the ocean as zones of significant biogeochemical activity is especially relevant in the mixing river-sea zone [30]. As a result of physico-chemical and biological processes, up to 93–95% of suspended and 20–40% of dissolved river matter (on average for the rivers of the world) remains in this zone [31]. However, there is not much information about the fate of the colloidal fraction.

3.1 Definition of colloidal fraction

Colloid particles transported by rivers are a mixture of mineral colloids such as metallic oxyhydroxides (mainly iron-, aluminum- and manganese oxyhydroxides), clays, carbonates and siliceous phases as well as natural and anthropogenic OM,

microbiota, biogenic remains and aggregates of them with the incorporation of adsorbed cations (e.g., Ca^{2+}, Mg^{2+}, Na^+, etc.). The characterization of the colloidal fraction in water is difficult, in particular, because of artifacts from sampling and concentration techniques. Currently, the following methods are used to isolate the colloidal fraction of natural waters: filtration, dialysis, centrifugation, voltammetry, gels (DET/DGT), field-flow fractionation and SPLITT. Ultrafiltration membranes have been developed to separate the colloidal pool into several fractions (ranging from thousands of Daltons (Da) to hundreds of thousands of Daltons) [32]. We proposed a method for separating the colloid fraction of natural waters which has been field-tested. It was based on the coagulation of colloid particles (previously separated from the suspended matter) by electrolytes ($Al_2(SO_4)_3$ and $FeCl_3$) with the addition of $Ca(OH)_2$, transforming colloids into the particulate fraction, which was then separated by filtration through GF/F glass-fiber filters with a pore size of 0.6 μm. The addition of $Ca(OH)_2$ promoted the formation of Fe^{3+} and Al^{3+} hydroxides and, in addition, the precipitation of HS in calcium humate form [4].

3.2 Coagulation of river colloidal matter

3.2.1 Coagulation mechanism

Particles in natural waters, including OM, are negatively charged (at pH 6.0–8.0) [33]. An increase in the ionic strength of the solution with increasing water salinity in a mixing zone leads to a decrease in the surface charge of suspended and colloidal particles as a result of compression of the double electric layer and, as a consequence, their destabilization and coagulation. Due to the high surface energy of such particles, their surface in the natural environment is usually covered with a layer of adsorbed organic molecules of soil genesis, which gives them a protective function and helps to overcome the RSTZ.

3.2.2 The effect of humic substances on the coagulation of colloids

HS are the predominant group of DOM in river water, reaching ≈ 90% C_{org} with the prevalence of high molecular fraction of HS [34]. It is known that HS greatly increase the stability of bentonite colloid due to the enhancement of electrostatic repulsion and steric hindrance effects [35, 36]. Adsorption of HS may result in the stabilization of colloid system even with increasing salt concentration.

In some cases, the joint action of two or more factors enhances colloid stabilization. So, it was found that the presence of P and HA gives a synergistic effect enhancing the transfer of TiO_2 nanoparticles in columns with sand more significantly compared to that with a single presence of P or HA [37]. On the other hand, high concentration of oppositely charged ions can reduce zeta potential of colloid particles due to their adsorption and lead to destabilization of colloids containing HS. The results presented in the work [6] showed that EPS, as algal OM, enhanced the flocculation of cohesive sediments, while HS, as terrestrial OM, enhanced stabilization, rather than flocculation. This is confirmed by the observation of greater stabilization of the suspensions in the mixing zone during the period of heavy precipitation, when there is an increased intake of HS from the catchment basin. The opposite effect of EPS and HS has also been shown in this work in model tests for the ability of DOM to flocculate kaolinite suspension, which was carried out with artificial water containing purified EPS and HS.

3.2.3 Coagulation of clay colloids

The adsorption of HA on clay particles depends on the environment parameters as well as structures of clay minerals: montmorillonite (as well as bentonite which was used in our study) is characterized by a three-layered crystalline lattice, while kaolinite is characterized by a double-layer crystalline lattice and does not swell like montmorillonite. It was found that at pH 8–9, the affinity of soil HA to montmorillonite is higher compared to kaolinite, but at natural pH, the order changes and HA is better adsorbed on kaolinite [38]. In this work, it was found that the ionic strength did not affect the adsorption of HA on clay minerals with a low zeta potential. This indicates that charge screening is not the main mechanism of HA adsorption for these minerals, such as the exchange of ligands. The increase in ionic strength, however, contributed to the adsorption of HA on clay minerals with high zeta potentials. The results showed that although HA does not penetrate into the intracrystalline channels of fibrous clays, but such a structure contributes to the adsorption of HA. The study of the sorption of various fractions of HA on these clays at pH 6 and the ionic strength of NaCl 0.01 mol dm^{-3} showed that kaolinite mainly sorbs aromatic types of carbon, while montmorillonite mainly sorbs aliphatic carbon at low coverage [39]. Our earlier experiment revealed the stabilizing role of HA for both minerals without NaCl addition (4).

A laboratory study described in [18] on the effect of OM on aggregation in estuaries using montmorillonite and HA showed that river particles with a low HA content may be prone to rapid flocculation and settling in the immediate vicinity of river mouths when mixed with coastal waters rich in fresh OM. While suspended river particles rich in HA can resist immediate flocculation and be transported further away from the river mouth.

Studying the behavior of biomineral suspended particles in coastal zones with high turbidity (TMZ) and low turbidity on the shelf (OSZ), it was determined that, although the suspended particles of both zones had the same mineralogical composition, their behavior in these zones with respect to the action of bio-flocculants was different [40]. Suspended particulate matter (SPM) in TMZ formed precipitation-enriched, dense and settling biomineral aggregates, while SPM in the OSZ composed biomass-enriched, less dense, and less settleable marine snow. It can be assumed that coagulation of river material is more active in the coastal zone, while flocculation has a greater effect when particles are removed to a more marine part. Notable shifts in the molecular weight of OM from freshwater to the marine environment were noted in the work [15] in which was shown that the relatively large OM molecules in freshwater samples are transformed and/or removed effectively in the early stages of estuarine mixing.

3.2.4 Coagulation of iron(III) hydroxide sol

Fe is released during the chemical weathering of Fe-bearing minerals in the soil. During weathering under oxic conditions in the absence of organic ligands, Fe (II) is quickly oxidized to Fe (III), which in turn precipitates as oxides. Typically, the first-formed oxide mineral is amorphous, highly reactive ferrihydrite [41]. Iron oxides and hydroxides bind through various sorption reactions with the HS of the soil, forming nano-, micro- and macro aggregates that provide their protection and stabilization [42, 43]. Studying the fate of colloids along mixing zones in the Arctic, it was found that Fe exhibited a strong non-conservative coagulation/removal behavior at the

beginning of the mixing zone at low salinity (<5‰), at the same time, the smallest fraction of colloid organic carbon (1 kDa-0.22 microns) remained almost constant in the entire salinity zone [44]. It can be assumed that the flocculation of iron due to newly formed organic matter is added to the coagulation of iron at the very beginning of the mixing zones.

To reveal the influence of OM on the stability of iron hydroxide sol at increasing salinity, we conducted a model experiment which showed that its aggregative stability with the addition of HS was constant up to 18‰ NaCl, after which absorbance and the particle size increased sharply from 0.510 to 2.20 and from 10 to 500 nm, respectively (**Figure 1**). The addition of HA does not lead to the destabilization of sol, although it was possible to expect such sol behavior due to the differently charged
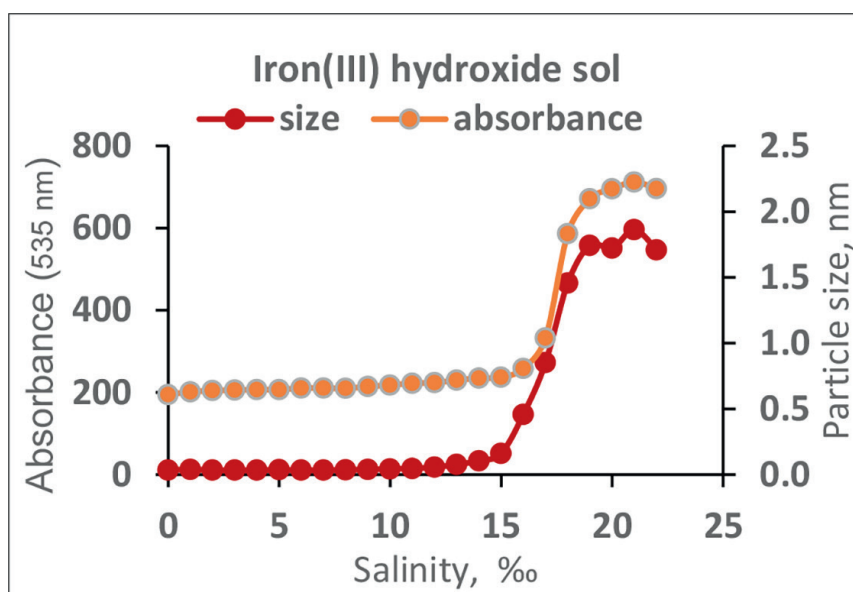

Figure 1.
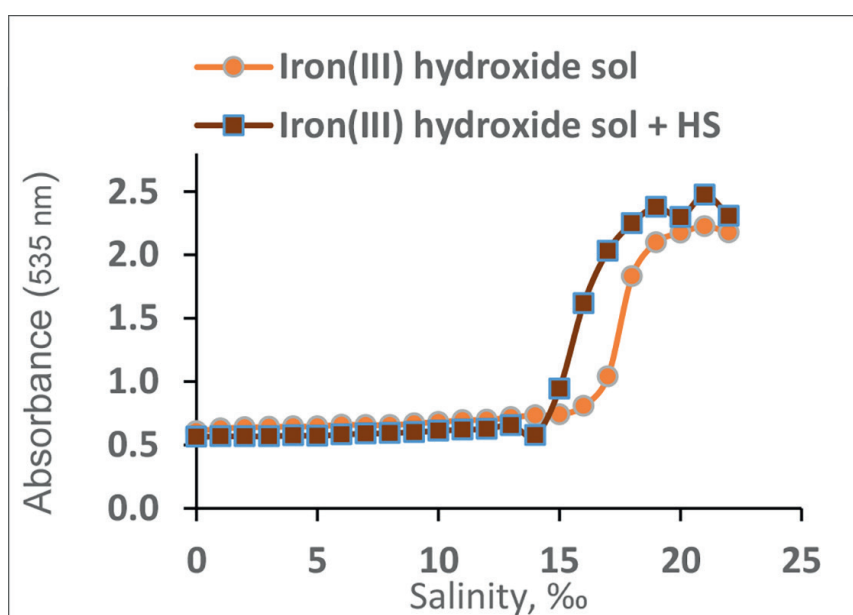*Effect of salinity on the absorbance and particle size of $Fe(OH)_3$ sol.*

Figure 2.
Effect of salinity on the absorbance of modified with HS $Fe(OH)_3$ sol.

surfaces of sol and HA particles (**Figure 2**). The size of iron hydroxide sol particles was measured for all studied systems, and correspondence with the data on the optical density of sol was determined.

The stabilizing function of HS on a suspension of Fe(III)-montmorillonite at different pH values is shown in [45]. Comparison of steric and electrostatic effects as stabilization mechanisms showed that the steric effect is more pronounced at low pH and high ionic strength. To better understand the effect of HA on the colloidal stability of nano zero-valent iron, three types of stabilizers (polyacrylic acid (PAA), Tween-20 and starch) were used in [46]. Adsorption of HA on the surface of nano Fe particles modified with PAA enhanced the effect of electrostatic repulsion, increasing the stability of the particles. However, for nanoparticles modified by Tween-20 or starch, aggregation of particles with HA was observed. In this experiment, the effect of two organic substances on the aggregative stability of iron nanoparticles caused the different aggregation behavior and showed not only the importance of the nature of OM on the stability of particles but also the sequence of its action The study of the interaction of HA, iron oxide and bacteria in the soil showed that the interaction between iron oxides and bacteria reduces the sorption of HA [47].

3.3 Flocculation of river colloidal matter

Flocculation is the process of binding suspended particles or colloids into flocks. In the mixing zone, it occurs together with the process of coagulation. Although the flocculation potential of river water is affected by various physical (flow velocity and turbulence, temperature), chemical (pH, O_2, salinity, ions and pollutants) and biological factors (stages of aquatic biota), the key factors are the nature and concentration of the flocculants.

3.3.1 Flocculation of iron(III) hydroxide sol

To evaluate the effect of flocculation on the aggregative stability of mineral colloidal systems (clay and $Fe(OH)_3$ sol) we conducted a model study in which
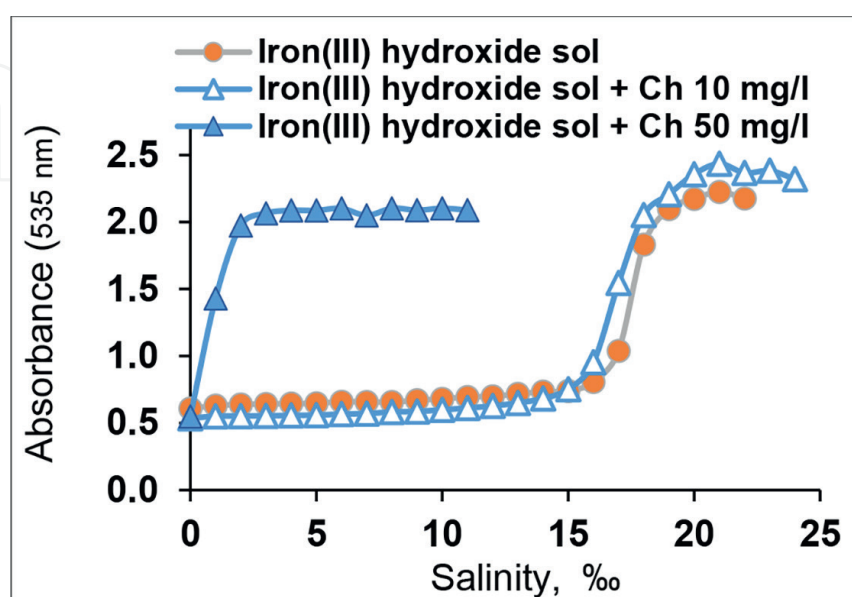

Figure 3.
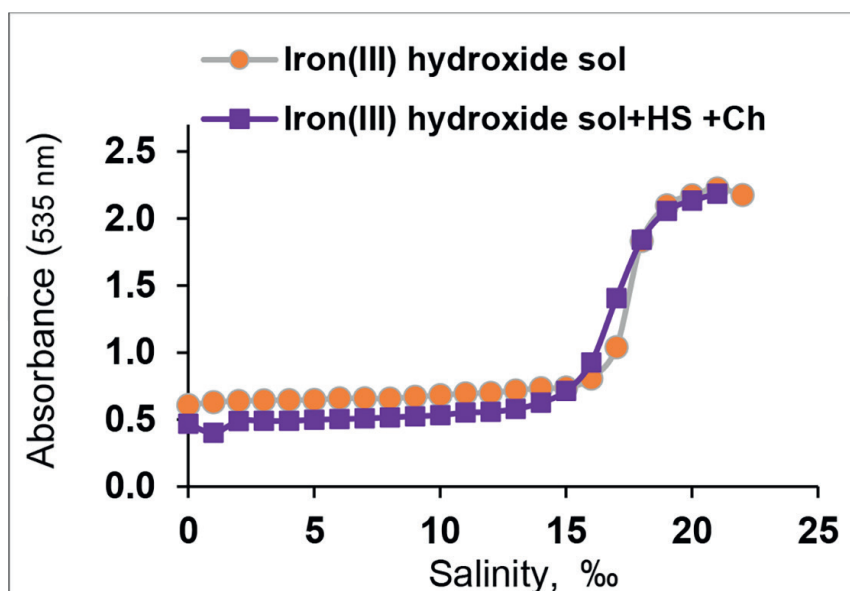*Effect of salinity on the absorbance of $Fe(OH)_3$ sol with the addition of chitosan.*

Figure 4.
Effect of salinity on the absorbance of Fe(OH)$_3$ sol modified with HS with the addition of chitosan.

chitosan (Ch) was used as a flocculant. Ch is widely used in the purification of drinking water and industrial wastewater [48, 49]. It was determined that the addition of Ch (50 mg/L) to Fe(OH)$_3$ sol leads to the formation of iron hydrosol flocks (an increase in optical density in **Figure 3**) at a salinity of 2‰, while a lower concentration of Ch (10 mg/l) did not affect the behavior of iron hydrosol. However, the behavior of the sol changes dramatically if a solution of Ch (50 mg/L) is added to Fe(OH)$_3$ sol modified with HS (**Figure 4**). In this case, the sol retains its stability up to 18‰ NaCl. HA probably creates a protective layer on iron hydrosol particles, which reduces the flocculation activity of Ch and facilitate the transport of colloidal iron to the outer part of the mixing zone even in the presence of flocculants (fresh DOM). The deposition of total Fe at 5‰, as was mentioned in [44] is probably due to the insufficient protective layer of the river iron particles, as well as the structure of HS coming from frozen soils and having rather fresh OM. This is consistent with our previous studies, in which the addition of freshwater bacteria to unmodified Fe(OH)$_3$ sol caused an increase in its particle size in the region of 5‰ from 20 nm to 500 nm due to flocculation [4].

3.3.2 Flocculation of clay colloids

Our previous tests on flocculation with clay (montmorillonite and kaolinite) showed different behavior of colloids compared with Fe(OH)$_3$ sol. The effect of Ch on modified HA clay particles led not to their stabilization but to better flocculation of colloid clay [4]. It was shown also that the increase in the hydrophobic properties of Ch results in more efficient flocculation of modified clay particles.

The turbidity of unmodified and modified bentonite colloid as a measure of flocculation over time is presented in **Figures 5** and **6**.

As follows from **Figure 6**, the flocculation of modified particles is more efficient (the gradient of the turbidity drop is greater) compared with unmodified bentonite. The results shown in **Figure 7** were obtained by repeatedly adding Ch to a colloidal solution three days later.
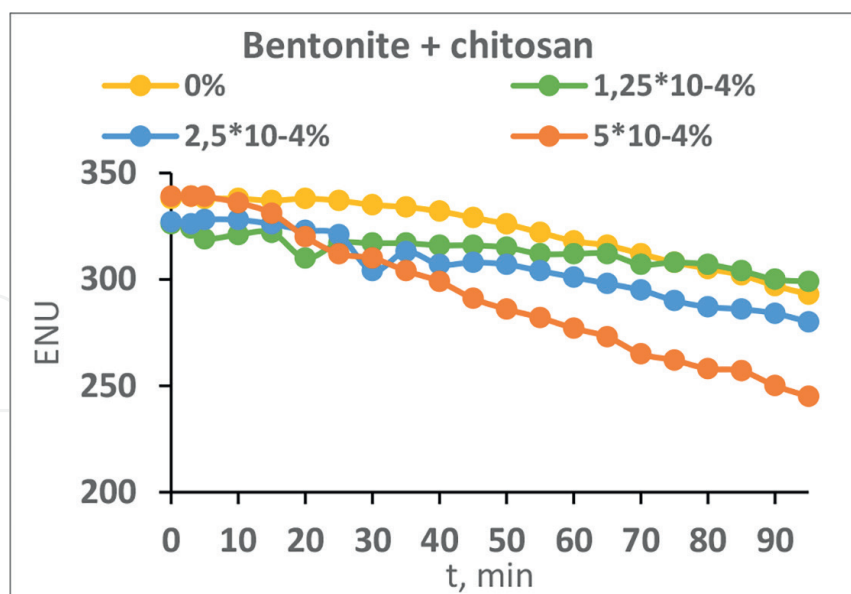
Figure 5.
Turbidity of bentonite colloid with the addition of various concentrations of chitosan as a function of time.
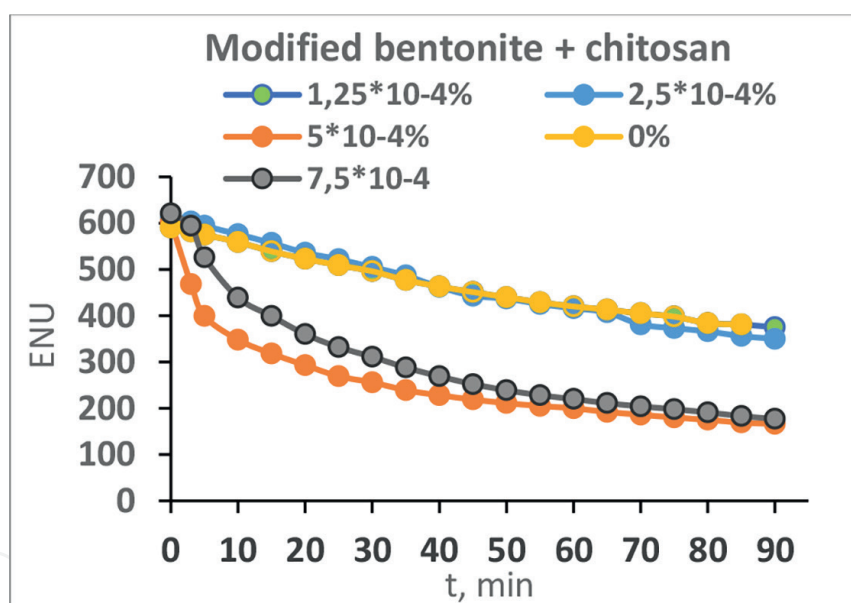

Figure 6.
Turbidity of bentonite colloid, modified with HS with the addition of various concentrations of chitosan as a function of time.

The sharp drop in turbidity after the addition of Ch 1 10–3 mg/L may indicate an increase in flocculation due to the interaction of the molecules of the newly introduced Ch with the surface-layer substances created by its early addition. The addition of NaCl leads to an even greater clarification of the solution (at Ch concentrations of 5.0×10^{-4}% and $7.5 \, 10^{-4}$%.). Whereas Ch concentrations of 1.25×10^{-4}% and 2.5×10^{-4}% do not lead to flocculation of stabilized bentonite particles (**Figure 8**).

3.3.3 The composition of flocculants

Biologically mediated flocculation is currently attracting a lot of attention not only because of the study of processes in the mixing zone but also because of the search for
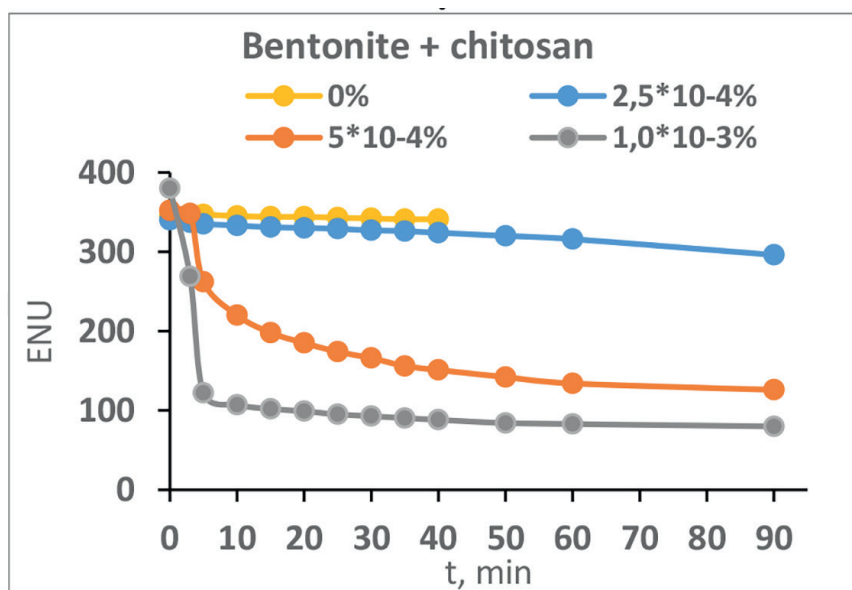
Figure 7.
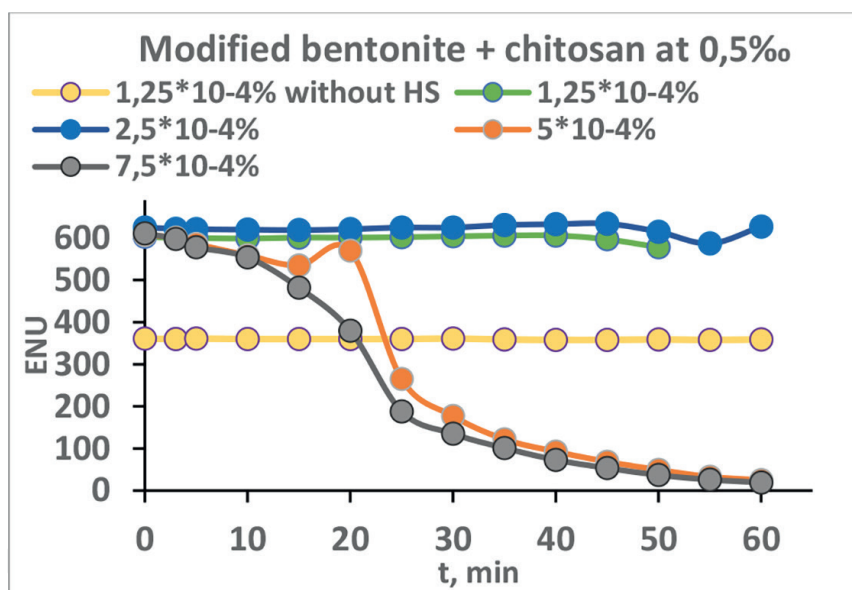*Turbidity of bentonite colloid with repeat chitosan addition as a function of time.*

Figure 8.
Turbidity of modified with HA bentonite with chitosan addition at 0.5‰ NaCl.

environmentally safe bio-flocculants for water purification, removal of toxic organic compounds and soil remediation [7, 19, 50, 51]. EPS and/or transparent extracellular polymers (TEPs) are defined as biopolymers of microbial origin which in microbial aggregate systems are frequently responsible for binding cells and other particulate materials together (cohesion) [52]. EPS, being formed as a result of cell lysis, can be present both inside and outside microbial aggregates; usually, they consist of a mixture of macromolecules, including proteins, polysaccharides, human-like substances, nucleic acids, lipids that hold microbial cells in a three-dimensional matrix [53, 54].

As it was shown in [55], when studying EPS cyanobacterial extracellular polymeric substance, that about two-thirds of total OM within bulk EPS matrix were distributed in the HMW fraction, leaving one-third in the LMW fraction. The hydroxyl group is the most commonly mentioned functional group that promotes

bio-coagulation, followed by the amine and carboxyl groups, as well as the proteins [56]. Experimental results showed the maximum flocculation activity of a natural bio-flocculant resource of *Ruditapes philippinarum* conglutination mud to kaolin clay (91.8% in seawater) that contained of 97.8% (w/w) polysaccharides and 2.2% (w/w) protein [57]. A high glucose content (47 mol. %) was noted in the DOM secreted by bacteria, while DOM, remaining after bacterial degradation, contained more galactose (33 mol. %), followed by glucose (22 mol. %) and other neutral sugars (7–11 mol. %) [58]. The chemical analysis of the purified product extracted from marine bio-flocculant the Actinomycete *Nocardiopsis aegyptia* sp. nov. revealed, that it contained mainly polysaccharides (85%) and proteins (7%) [27]. The predominantly polysaccharide composition was indicated for a bio-flocculant obtained from marine bacterium *Bacillus* sp. [59].

3.3.4 Flocculation mechanisms

Flocculation mechanisms in which biopolymers act as flocculants, such as adsorption, bridging, charge neutralization, net trapping and sweeping, as well as some other special mechanisms are summarized in [24, 49]. To clarify the role of natural OM in the aggregation of surface water particles, progressive filtration of river water samples through membranes with decreasing pore sizes (microfiltration, ultrafiltration and two degrees of nanofiltration) was used [60]. While microfiltration had a negligible effect on the spectrum of organic substances present, ultrafiltration allowed the separation of biopolymers (MW > 100 kDa), which significantly affected the size of the flakes. The authors suggest that OM with a lower Mw (<10 kDa) can create a protective layer on aluminum hydroxide particles (which was used for the coagulation test), and the modified particles are bound together by biopolymers due to a bridging mechanism. According to our view, it can be assumed that the primary adsorption layer on the surface of mineral particles in river water is formed by soil HS, which due to their amphiphilicity can be adsorbed on both hydrophobic and hydrophilic surfaces, forming a protective layer, so we modeled our system by mineral particles modified with HA (anionic polymer).

When considering a polymer mixture as flocculants, it is important to note the sequence of their addition, since pre-adsorbed polymer can have two effects: providing adsorption sites for the second polymer or blocking them, when the polycation due to the surface charge comes close to the surface of the clay particle [61]. In this case, a polyanion can have more extended adsorbed conformation. The study of the influence of cationic and anionic polyelectrolytes and their binary mixtures on the electrokinetic potential and the degree of bentonite aggregation showed that the ability to aggregate (through the formation of polymer bridges) is mainly determined by the adsorption of anionic polymer [62].

A similar result was mentioned in [63], in which a broad flocculation window was obtained due to a combination of highly charged polycation (Ch) and small amounts of high-molecular polyanion (HA), where the floccules with clay were larger compared with mono-flocculation. The results presented in [64] on the effect of various MW fractions of EPS (HW, MW and LW) obtained from wastewater on the flocculation of kaolinite and montmorillonite also confirm the effectiveness of a mixture of organic flocculants. It was determined that both the mixed EPS and the HMW-EPS demonstrate comparable flocculation characteristics in single-clay systems. However, the mixed fraction turned out to be more effective than the HMW-EPS fraction for two-component clay flocculation due to the adsorption mechanism, in which the extended anionic

polymer tails of mixed EPS in solution thereby enhancing particle flocculation. The efficiency of a mixture of alginate-protamine solutions was high in flocculating kaolin and quartz particles, while neither alginate nor protamine has flocculating ability [65].

Many works devoted to flocculation in the coastal zone mention that increased flocculation is associated with the plankton bloom. To assess the influence of algae, it is proposed to introduce some indicators, such as CC/SSC ratio (the chlorophyll-a concentration to suspended sediment concentration) that increases in summer when algae-rich macro-flocs are abundant and reduced in winter when amount and size of flocks are very reduced [12]. Flocculation capability of river water was also characterized by POC/SPM ratio (where POC is particulate organic carbon). The POC/SPM value increases during the algal bloom period when stickier, particle-binding polymeric substances are formed [6]. In our study, we have proposed COC/PM and COC/CM criteria (where COC is colloid organic carbon, PM is particulate matter and CM is colloid matter) the values of which increase sharply in the flocculation zone. In combination with microbiological data, these indicators allow us to identify flocculation zones [17].

Greater effectiveness of the bio-flocculant in the presence of Ca^{2+} and Al^{3+} cations was noted in [59, 66–68]. According to the Divalent Cation Bridging Theory (DCBT), the presence of divalent cations induces bio-flocculation through bridging of negatively charged sites on EPS with cations [69]. The presence of Ca^{2+} and Mg^{2+} in seawater suggests the inclusion of these ions in the flocculation mechanism in the river-sea zone enhancing it.

The concept of biomolecular corona that formed by spontaneous adsorption of biomolecules to the highly reactive surface of nanoparticles when they enter in contact with the components of biological or environmental system was introduced to explain of colloidal stability of nanoparticles in the aquatic environment [70]. The release of EPS can also be observed during salinity stress (as cell protection), during viral lysis of microorganisms and during the death of biota species intolerant to changes in salinity [71–73]. The idea that the precipitation of river suspension in estuaries and coastal waters is significantly influenced by EPS released by microalgae is found in a number of works [13, 19, 51]. The importance of the fresh part of the TEP fraction, which contributes to the formation of larger and rapidly settling biomineral flakes in spring and summer is emphasized in [20]. However, flocculation in MF can be observed to a lesser extent in other seasons due to the reaction of biota to the change of salinity. In our opinion, the interaction of this fresh OM with mineral particles coated with recalcitrant OM (HS) leads to effective flocculation due to the synergistic effect of cationic and anionic polyelectrolytes on particle aggregation. Studies of phytoplankton in the Ob River delta have shown that the amount of DOM entering the aquatic environment as a result of viral lysis of bacteria is sufficient to trigger the flocculation process [74].

3.3.5 Field study of flocculation

Using the method described above (isolation of the colloids by electrolytic coagulation) colloidal fraction of natural waters were obtained in RSTZ of Arctic rivers (Northern Dvina, Lena and Ob) [17]. Colloids have been shown to be a key form of transport of riverine matter to the sea, two orders of magnitude higher than particulate matter. The content of the colloid component varies from 98.7 to 62.0, 96.1 to 46.4 and from 153 to 21 mg/l in the surface layer of these rivers, respectively. The waters of the Northern Dvina River are characterized by a higher content of colloidal fraction (five times higher compared to the Ob River), which is due to the nature of the water, fed from wetlands with low physical weathering The concentration of

COC decreases from the inner to the outer part of the MF with increasing salinity from 11.08 to 1.28, from 4.26 to 1.22 and from 4.65 to 1.9o mgC/L, respectively. However, at higher salinity levels, all three rivers show an increase in the colloidal fraction hundreds of times over the suspended fraction. This suggests that the main form of transfer of river material to the marine environment is the colloid fraction; the suspended fraction and the newly formed suspension remain in the MF. The low content of organic carbon in the colloidal fraction in the outer part of the MF (about 1.0–1.5%) indicates that the main form of transfer is mineral colloids.

4. Conclusions

The River-Sea Transition Zone is a natural filter system that influences the riverine colloid input to the marine environment. In this zone, due to the physico-chemical and biological processes, the substances of the river flow are transformed and most parts of the river particulate and partially dissolved matter are removed. Data on the colloidal fraction in the mixing zone are very limited due to the difficulty of isolating this fraction. It should be emphasized, however, that it is the colloidal fraction, due to its developed particle surface (reaching up to 1000 m^2/g), that has a significant effect on the behavior of other forms of riverine matter. Previously, using the method we proposed, the colloidal fraction of the water of some Arctic rivers was isolated, and it was shown that colloids significantly exceed the proportion of particulate fraction in the outer part of the MF. Among the factors influencing the transfer, one of the main ones is the content and nature of the OM. In model experiments carried out with clay colloids and iron(III) hydroxide, we have shown that, depending on the nature and concentration of OM it can lead to the stabilization or flocculation of mineral colloids. Highly transformed HS, adsorbed on clays and on iron hydroxide, stabilizes colloidal systems. However, when such coated particles meet with freshly released OM (EPS or TEP), their flocculation occurs. If Fe(III) hydroxide particles are insufficiently protected by the adsorption layer, this deposition may occur in the inner part of the missing zone at initial salinity. Otherwise, they may migrate to the outer part of the mixing zone and further towards the sea. In the case of clay colloids, the HS protective layer contributes to more efficient flocculation due to the synergistic action of polycationite (flocculant) and polyanionite (HS). The principles of natural flocculation mechanisms are already being used in the technological processes such as water and wastewater treatment, soil remediation and others ones associated with the aggregation of colloidal systems. An interdisciplinary approach to the study of the transformation of riverine colloids, and especially the study of biological processes in the mixing zone, will clarify many features of the behavior of this complex system.

Author details

Elena V. Lasareva* and Aksana M. Parfenova
Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia

*Address all correspondence to: elasareva@yandex.ru

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