

Laboratory experiments on river-estuary geonanomaterials

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Estuaries represent the mixing or transition zone between fresh water (rivers) and saline water (sea) and form very complex systems, which play an important role in the biogeochemical cycles of elements. In order to understand the processes that occur in this environment, laboratory experiments were carried out by mixing river water and seawater, and the resultant floccules or aggregates were studied. It was observed that colloidal flocculation took place, followed by re-stabilization of colloids until a steady state was obtained. This behaviour was reflected by the electrical conductivity (or dissolved components). The scanning electron microscope photomicrographs show the presence of flocculated clumps and particles less than 0.1 μm in size. The electron probe micro-analyser analysis of the mixed water floccules show them to be enriched in Fe_2O_3 and MnO as compared to the river suspensions. The present study although preliminary, shows that flocculation is a significant process in the marginal marine environment and flocculation occurs within a few hours of mixing. Over long time scales, the mixing phenomenon may act as a significant process for removal of dissolved metals onto the flocculated particles.

Keywords: Flocculation, geonanomaterials, ionic strength, mixing zone.

BECAUSE seawater has much greater salinity than river water, most of the major dissolved elements have greater concentrations in seawater compared to river water. Metals such as Fe, Al, Mn (and trace metals such as Zn, Cu, Co, etc.) as well as nutrients such as P, N, Si, and dissolved organic matter (DOM) generally have a greater concentration in river water than ocean water¹. As seawater composition is fairly constant, the dissolved material that gets carried by the rivers to the sea must be subjected to removal processes²⁻⁶. One such site where these processes might be active are the estuaries, where river water enters into the sea. Colloids consist of small particles within the size range of 1 nm to 1 μm characterized by high surface area to volume ratio. Due to their small size and large surface area to volume ratio, in colloidal suspensions gravitational effect is negligible and surface phenomena predominate. Because of their ubiquitous existence and distinctive behaviour as a function of size, nanophase minerals may act as carriers of toxic

metals and radionuclides in the earth's near surface environment.

River water samples for the laboratory experiment were collected from the Bhagirathi River at Gangotri in Uttarakhand (lat. 30°59.64'N; long. 78°56.48'N). Twenty-five samples were collected during January 2009. The water samples were collected at an interval of 15–30 min in 1 litre polypropylene bottles, during the entire course of the day and pooled together to get a representative sample. For the laboratory experiment, seawater samples were collected from the Arabian Sea at Mumbai (lat. 19°7'48.46"; long. 72°48'46.20") during January 2009. The sample bottles were rinsed on site with the water to be sampled, equilibrated and the bottles were filled up to the brim to ensure that no air was trapped in the bottle. Electrical conductivity (EC) was measured in the field using a HACH HQ portable meter, after calibrating with KCl solution. In the laboratory, 5 l each of unfiltered seawater and unfiltered river water were taken (200 ml from each Bhagirathi river water sample) and the samples were mixed thoroughly and agitated. pH and conductivity were measured daily for two months. After two months, the mixed water was filtered using a 0.45 μm cellulose nitrate filter paper and a manually operated filtering apparatus and then all the filter papers were studied using a scanning electron microscope (SEM) and electron probe micro-analyser (EPMA) to observe any change that occurred in the floccules. Samples were coated with carbon to make them conducting for SEM and the photomicrographs were scanned to determine size range and distribution. For EPMA analysis, the sample was first mounted into plastic holders using araldite, followed by grinding, polishing and subsequently coated with carbon prior to EPMA analysis. As our interest was to understand the Fe and Mn contents, the EPMA midpoint data ($n = 8$ each) alone is presented here.

After mixing river water with seawater, EC was found to be nearly constant at ~26 mS/cm for the first 12 days after mixing, after which there was a sudden change (Figure 1). It reached a minimum of 17.73 mS/cm after which there was a rise in EC and ultimately stabilization was attained. EC of a solution depends on the availability of ions to conduct electricity. It is directly proportional to the total dissolved solids (TDS). As TDS is removed from solution, EC decreases as well. As a result, after 12 days of mixing, coagulation reaches its maximum, after which restabilization of the colloids takes place. This was probably caused by the reversal of colloidal surface charges. Restabilization is indicated by the rise in EC and the levelling off of the curve. During restabilization, the adsorbed ions are released into the water until a steady state is obtained. This release of ions to the solution causes EC to rise and then attain a constant value. Humic and fulvic acids are bound to colloidal iron surfaces by ligand exchange. With increasing concentrations, they are found to be more effective in causing charge reversals on

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colloidal iron surface compared to ions like Cl^- , Na^+ , SO_4^{2-} , Na^+ and Ca^{2+} , which are held by electrostatic forces. This accounts for restabilization of colloids⁷.

During the first 12 days after mixing, destabilization of colloids probably removes cations from the solution as they act as counterions to stabilize a negative colloidal surface charge. The removal of cations increases the relative abundance of H^+ ions in the solution. This causes a gradual drop in pH. During restabilization of the colloids, cations adsorbed on the surface are released into solution, decreasing the relative abundance of H^+ ions in the solution. This causes a gradual increase in pH. The reasons for the initial destabilization observed may be due to (i) compression of the electrical double layer, (ii) polymer destabilization by bridging or (iii) haloing mechanisms of nanoparticles. The restabilization that follows has been attributed by some authors to the process of charge reversal; however this process is not fully understood.

When two particles approach each other, the Gouy layer (i.e. the diffuse layer that forms a part of the electrical double layer) (Figure 2) of each particle repels the other and the particles remain in stable suspension⁸. When there is an increase in the ionic strength of the solution, the Gouy layers get compressed and the particles come closer together. The van der Waals forces of attraction overcomes the repulsive forces and the suspension becomes unstable causing flocculation. Uncharged large colloidal particles may be stabilized by highly charged nanoparticles in the system that form a halo around each colloidal particle. The repulsion between the halos of each colloidal sphere can stabilize the system. Vesaratchanon *et al.*⁹ have shown that nanoparticle concentrations

can affect the stability of these colloidal particles. At a low nanoparticle concentration, the effective volume of nanoparticles is small, the number of nanoparticles on the surface of colloidal microspheres is low, and no stabilization occurs. At a moderate nanoparticle concentration, the charged nanoparticles self-organize themselves around the microspheres, resulting in a structural stabilization barrier which prevents the flocculation of the microspheres. Upon increasing nanoparticle volume fraction, the electrolyte strength increases, the double layer shrinks, and the system stability is reversed. At very high nanoparticle concentrations (and therefore, a very high electrolyte concentration), the nanoparticles behave like hard spheres, the structural stabilization barrier diminishes and the microspheres flocculate.

SEM photomicrographs show the various size ranges in river water, seawater and mixed water (Figure 3). River water suspended matter has particles in a large range of sizes. In the mixed water sediments, organic matter seems to play an important role in adsorption. Minerals are adsorbed on the organic matter. Coagulated clumps can

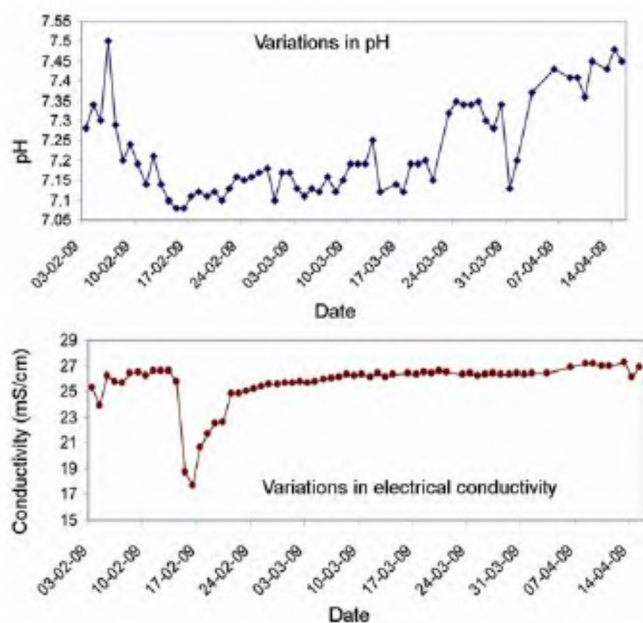


Figure 1. Variations in pH and electrical conductivity in laboratory mixed water.

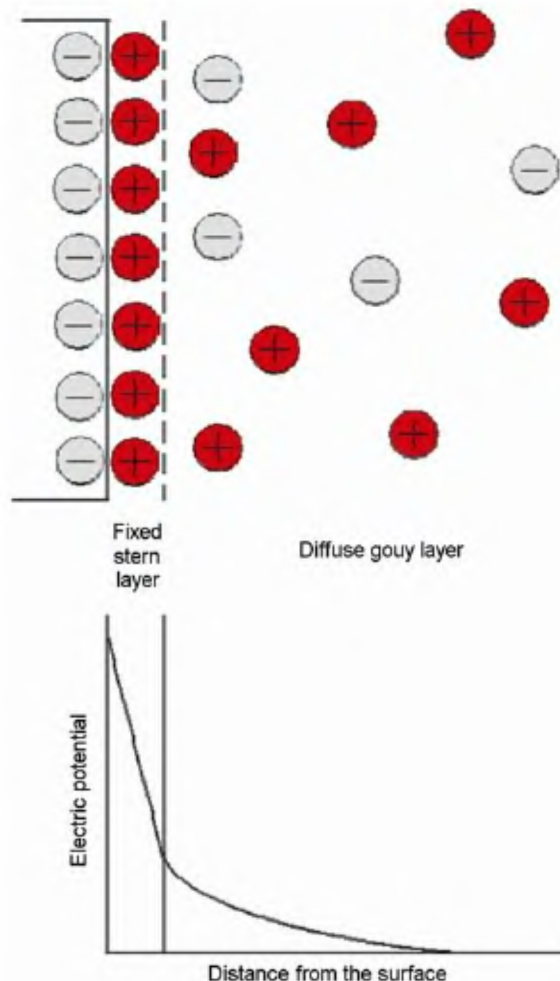


Figure 2. Schematic representation of the electrical double layer (from Drever⁸).

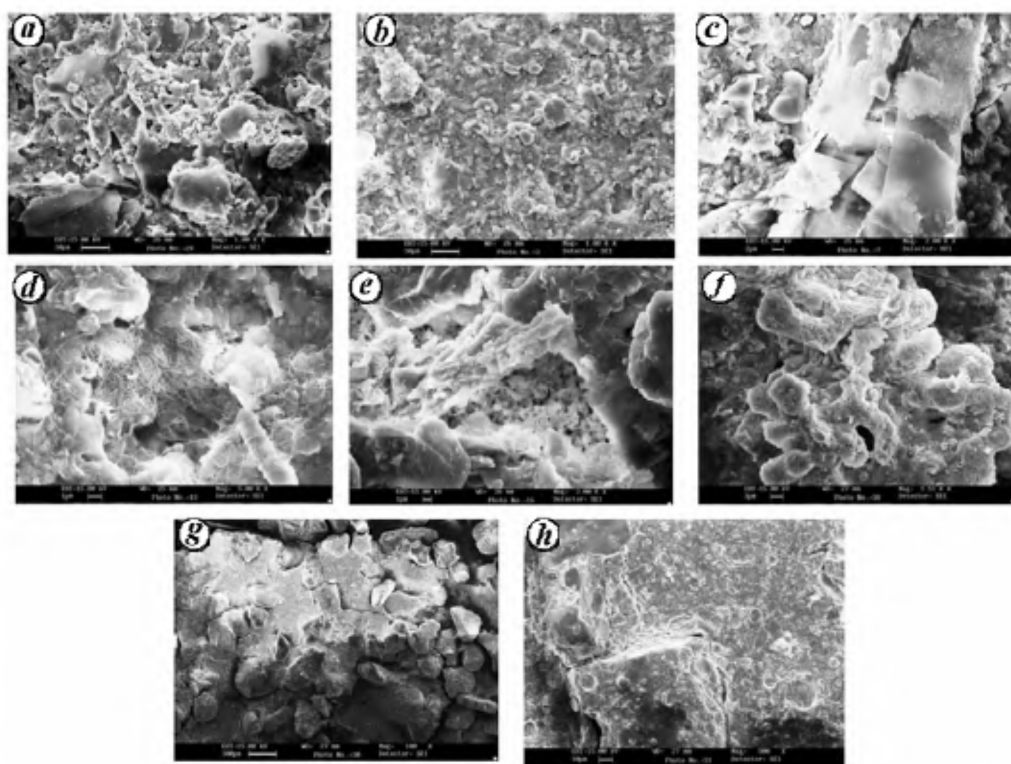


Figure 3. SEM photomicrographs of field and lab samples. *a*, Filtered suspended sediments in Bhagirathi river water show a range of particle sizes. *b*, Suspended materials filtered from laboratory mixed water. Coagulated clumps appear to have formed on the left top corner of the image. *c*, Suspended matter filtered from laboratory mixed water. The organic matter (porous) appears to have minerals adsorbed on the surface. *d*, Fibrous materials present in the mixed water sediments. These are nanorods as two dimensions fall within the nanoscale range. *e*, Mixed water sediments with particle sizes less than 1 µm at least in one dimension. *f*, Seawater sediments contain a cluster of particles that are individually less than 1 µm in size. *g*, Silica grains present in the sediment filtered from seawater. *h*, Magnification of the grains in seawater sediments shows that minerals are adsorbed on their surfaces.

Table 1. EPMA midpoint data ($n = 8$) of Fe_2O_3 and MnO

Sample	MnO (%)	Fe_2O_3 (%)
River suspensions	0.18	13.21
Mixed water suspensions	0.62	16.7
Seawater suspensions	0.14	19.24

also be identified. A few mineral grains were found to be less than 1 µm at least in one dimension in the mixed water sediments. The sediments retained after filtering seawater mainly consist of quartz grains. On magnification of the grain surface, finer mineral particles appear to be present. Fe and Mn contents as determined by EPMA in the river water suspensions, mixed water suspensions and seawater suspensions are presented in Table 1. It is observed that, mixed water suspensions show considerable Fe and Mn compared to river water suspensions. Interestingly, the mixed water suspensions act as efficient sinks for Mn from both river and seawater mixing processes. The mixing of freshwater with low-ionic strength and saline water with high-ionic strength results in flocculation as shown by the various SEM photomicrographs. The silica, Al-Fe hydroxide phases and organic matter may act as sinks for dissolved heavy metals.

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