The similar landward convexities in the 5 m depth contour at Gangapatnam (Figure 5 b) and Chinnamailavanilanka (Figure 5 c) are perhaps responsible for tsunami amplification and funnelling through the narrow zones to push the sediment up onto the coastal land akin to what was observed earlier from the Tamil Nadu coast[9] where the seaward concavity (i.e. the landward convexity) in the 200 m depth contour was considered responsible for amplification of the tsunami to as much as 7 m leading to widespread inundation and loss of life. While more or less similar canyon-like features may be present along other coastal parts, it may be a combination of factors such as the nature of coastal and offshore topography, besides the angular direction of the coast with respect to the direction of tsunami approach that could determine the degree of tsunami amplification.

The present study based on the identification of the maximum tsunami-affected locations along the AP coast and the juxtaposition of the satellite images vis-á-vis, the DEMs of the underwater topography off the respective locations has indicated the possible role of coastal bathymetry in tsunami impact on the coastal lands. Therefore, detailed mapping of the nearshore bathymetry would also be an important input to the tsunami warning system being set up in India for accurate assessment of the vulnerability of different coastal segments to tsunamis.

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Characterization of colloids in the late Quaternary sediment sequences of Mahi River basin, Gujarat, India

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Mobile colloidal particles are known to be ubiquitous in Quaternary fluvial sediments and subsurface environments which facilitate the transport of contaminants to the aquifer. Despite this harmful effect, very few efforts have been made to study the properties and transport of colloids in Quaternary sediments. In order to understand the properties of these colloids, samples were collected from the exposed late Quaternary sediment sequences dating back to 125 ka from the Mahi River basin. The isolated colloids from these sequences were characterized for their size distribution, electrical conductivity and concentration. The polydispersed colloidal particles occur in varying amounts at different depth intervals. The low electrical conductivity of colloids in the Rayka section could be related to the low concentration of colloids.

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THE presence of colloids in subsurface environments and their influence on the transport of contaminants in the natural aquifer system have drawn the attention of researchers worldwide[1]. Particles in the 10 nm–10 µm size range are construed as colloids and this size range indicates a long settling time in water from days to months. These colloidal particles possess a large surface area that enables them to adsorb contaminants leading to their transport in natural aquatic systems[2–6]. Quaternary fluvial sediments are considered to be the potential source of clay colloids in natural environments[7]. Thus characterization of natural colloids present in sediments and natural waters is important to understand their transport behaviour in subsurface porous media. Natural water archives such as rivers, estuaries and sea are complex systems of electrolytes, dissolved and particulate organic matter and inorganic colloids consisting of quartz, clays, oxides and oxyhydroxides of iron and aluminum[8]. Detailed studies on characterizing the mineralogy of sediment and aquifer colloids and their size distribution are generally not available, despite evidences suggesting the implications of size on contaminant adsorption and transport in the subsurface environment. Although a few studies are available on the characterization of natural aquatic colloids[9–11], the general aim of such characterization has been to understand the role of colloids as carriers of contaminants in natural environments such as river, lake, ocean, sediment, groundwater, etc. Seaman et al.[12] have studied the bulk mineralogy of colloids mobilized from sediments and reported the differences in their mineralogy.

A number of studies have shown that colloidal particles are released from the sediments as a result of changes in solution chemistry[13–17]. There are several conditions by which colloids are released from the sediments. Dispersion of sediment aggregates results in the release of colloidal particles which migrate in the downward direction[18]. It has been estimated[19] that during the rainy season, concentration of these mobile colloidal particles ranges from less than 1 mg/l to a few hundred mg/l. It has been reported[3] that the concentration of colloids released from the sediment-packed column exceeds a few hundred milligrams per litre[3]. This communication attempts to characterize the colloids isolated from the sediments of Mahi River basin to determine their size distribution and dispersal at varying depths and to understand the changes in electrical conductivity with respect to their concentration. It also attempts to understand mobilization of colloids in the unconsolidated sediments.

The Mahi River originates from the Mahi Kanta Hills in the Vindhyachal range of Madhya Pradesh. Crossing through a vast alluvial stretch in Gujarat it debouches into the Gulf of Cambay (Figure 1). In the alluvial plain, the river is bounded by cliffs rising about 30–40 m exposing Quaternary sediment sequences. Semiarid climate prevails in the Mahi River basin, which receives rain during the SW monsoon[20].

Sediment samples were collected from the Jaspur (22°18′31 N, 73°02′69 E) and Rayka sections (21°29′52 N, 73°9′54 E) of the Mahi River at 0.25 m interval for colloid separation (Figure 1). The lithological variations in the sediment sequences as reported by Juyal et al.[21,22] are shown in Figure 2. Prior to experiments, the sediment samples were thoroughly mixed to generate the homogeneous sample, air-dried and sieved in BSS: 8 mesh screen to separate the coarse particles. The organic carbon content was determined by wet oxidation method[23] and cation exchange capacity by column technique[24].

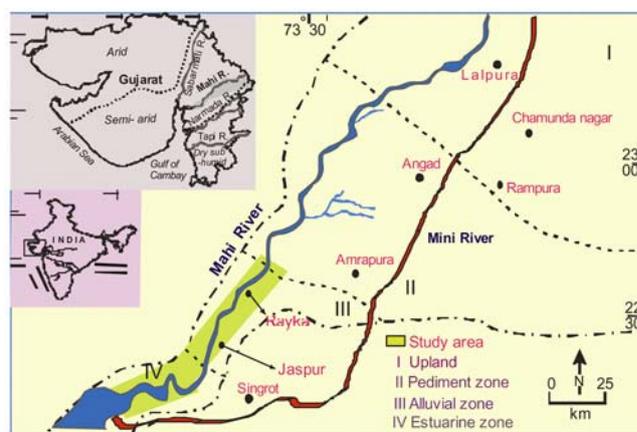The ground and river water samples were collected from five different locations along the Mini River, a

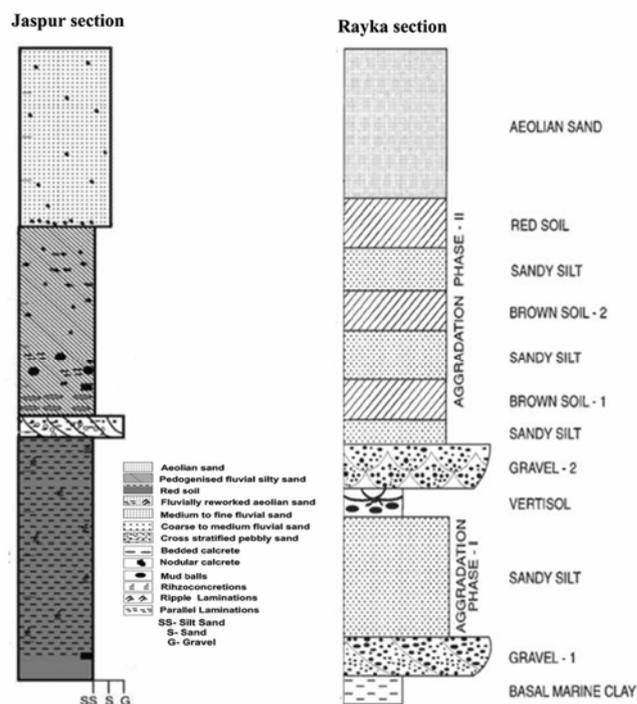**Figure 1.** Location map of sampling sites in Mahi River basin.

Figure 2. Lithology of the sequence at Jaspur and Rayka sections (after Juyal et al.[21,22]).

tributary of Mahi River (Figure 1). The locations from where the groundwater samples were collected are Chamunda nagar (14 m), Rampura (9 m), Angad (16 m), Lalpura (12 m) and Amrapura (10 m) (Figure 1). The groundwater level (m) is given in brackets. The river water samples were collected from five locations, namely Chamunda nagar (two samples), Angad, Amrapura and Sindhrot (one each).

Colloidal particles were separated by mixing 100 g of sediment sample with 500 ml distilled water in a beaker. The mixture was stirred overnight using a mechanical stirrer. To ensure a better separation and retention of colloids, centrifugation was carried out for 15 min at 750 rpm to settle the solids, although 3.5 min of centrifugation at 750 rpm is known to be sufficient to separate the native colloid particles from the sediments[25].

The relative centrifugal force (RCF) was calculated by using the formula given below[26] and is an indication of the efficiency of separation, i.e. separation of the non-colloidal particulates.

$$\text{RCF} = \frac{G}{g} = \frac{4\pi^2 (\text{rpm})^2 r}{3600 \times 981},$$

where $\pi = 3.14$, rotations per minute (rpm) = 750 and radius (r) = 4 cm. The RCF value was 25.12 and sufficiently high to separate out all suspended matter except the colloidal dimensions.

The supernatant colloidal solution was collected and divided into two parts. One part of this solution was concentrated by flocculation with 1 M $CaCl_2$ solution, to yield a solid deposit that was separated and dried. Another part was preserved for size analysis of colloids without adding electrolyte solution.

The mineralogy of colloids was characterized by X-ray diffraction analysis (Panalytical, X'per PRO, CuK, 2.2 KW Max). Size of the colloidal particles was measured by static light scattering technique (Mini Dawn Tristar, Wyatt technology) equipped with Ga–As semiconductor laser with an operating wavelength of 690 nm.

The electrical conductivity (EC) of the colloidal suspensions was measured on a conductivity meter (Elico CM 180) at room temperature ($30 \pm 2°C$). The instrument was calibrated with 0.01 M KCl before making measurements. Colloidal concentration in the suspension was determined by drying the solution at 100°C following the method of Kjaergaard et al.[27]. The collected water samples were filtered using Whatmann 40 filter paper and centrifuged at 750 rpm for 15 min. The supernatant samples were used for the size distribution analysis.

EC and concentration of colloidal suspension of the sediments of Jaspur section are shown in Figure 3 a. It can be seen that the EC of the colloidal suspension of the sample collected at the depth of 13 m is high at 3.2 mS/cm. This is followed by 2.7 and 2.5 mS/cm for samples

collected at 12.75 and 12.5 m respectively. The concentration of colloids is also relatively high for the sample at 13 m, which turns out to be 2,400 mg/l. However, EC falls between 2 and 2.5 mS/cm for the samples above 12.5 m, except that at 5 m depth, whose value is 2.7 mS/cm. The colloidal suspension of the top samples showed relatively lower EC and concentration than the bottom sediments.

The EC and concentration values of colloidal suspensions of Rayka section are shown in Figure 3 b. The EC values of all the samples lay between 2 and 3 mS/cm, except samples at 3.5 and 8.5 m depth, which showed EC of 0.43 and 0.41 mS/cm respectively. Such typical behaviour of very low EC observed in red soil and sandy silt of Rayka section is consistent with the low concentration of colloids, which turns out to be 400 mg/l. The low concentration of colloids in the suspension of samples at 3.5 and 8.5 m depth was confirmed with ICP–AES analysis and the amount of indicator elements of colloids such as Si, Al, Mg and Ca is shown in Table 1. The presence of lower amount of Si, Al, Mg and Ca in samples at 3.5 and 8.5 m depth, confirms the observed low concentration of colloids and EC and for the samples having higher colloidal concentration and EC, the elemental content was higher.
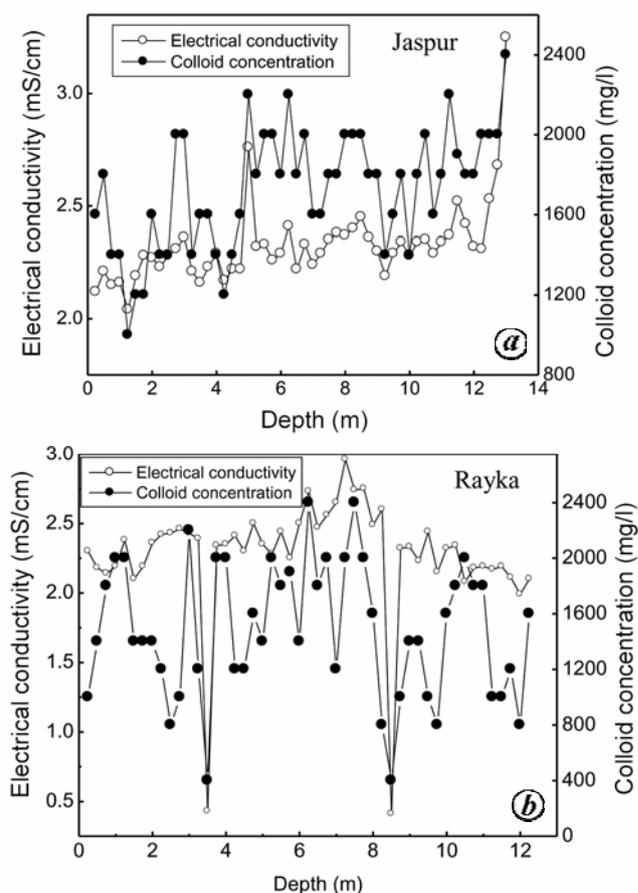

Figure 3. Electrical conductivity and concentration of colloidal suspensions of (*a*) Jaspur and (*b*) Rayka sediments.

Table 1. ICP–AES analysis of colloidal suspension

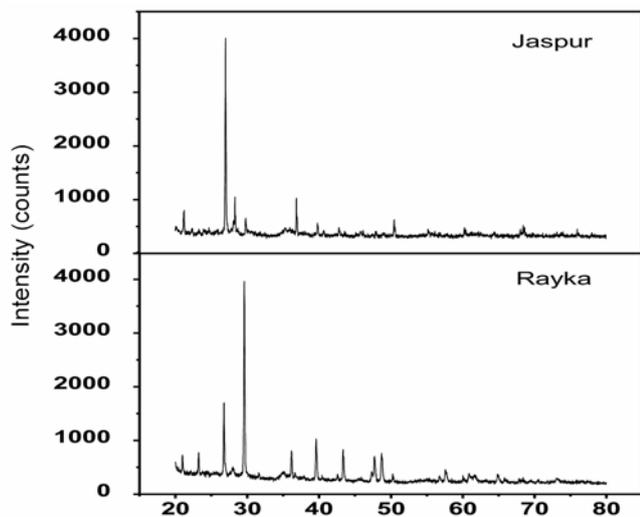| Sample depth (m)	Electrical conductivity (mS/cm)	Al (ppm)	Ca (ppm)	Mg (ppm)	Si (ppm)
3.25	2.39	0.0385	21.13	23.39	12.22
3.50	0.43	0.0341	16.35	5.406	5.112
3.75	2.34	0.0293	21.43	24.39	11.98
8.25	2.60	0.0234	13.00	8.066	9.754
8.50	0.41	0.0234	19.49	3.684	3.921
8.75	2.32	0.0222	28.63	15.80	10.46

Figure 4. X-ray diffraction analysis of colloids of Jaspur and Rayka sediments.

A variety of minerals in sediments exist as colloidal particles. The X-ray diffraction pattern of colloids of Jaspur and Rayka sections is shown in Figure 4. The heterogeneity in mineralogical composition of colloids was observed with minerals identified being quartz, calcite and kaolinite from 2θ values of 27, 30 and 28 respectively[7,28].

The size distribution of colloids is given in Figure 5. Majority of the colloids isolated from the samples of Jaspur section are highly poly-dispersive with respect to their size, i.e. each sample or suspension has particles of varying size. In the Rayka section, size distribution is much less compared to the Jaspur section. Samples collected at depths of 4.25 and 5.25 m in Jaspur and Rayka sections respectively, do not show a range in size distribution, i.e. particles of almost the same size are found in suspensions as shown in Figure 5. The size distribution of colloids in river water and groundwater is shown in Figure 6. Except for the groundwater sample collected at Lalpura, which shows monodispersive character, all others show large variation in size distribution of colloids, indicating the complex nature of colloids in aquatic environments. Whereas the size distribution of particles in river water at Chamunda nagar is higher, the sample from Sindhrot has particles of smaller size.
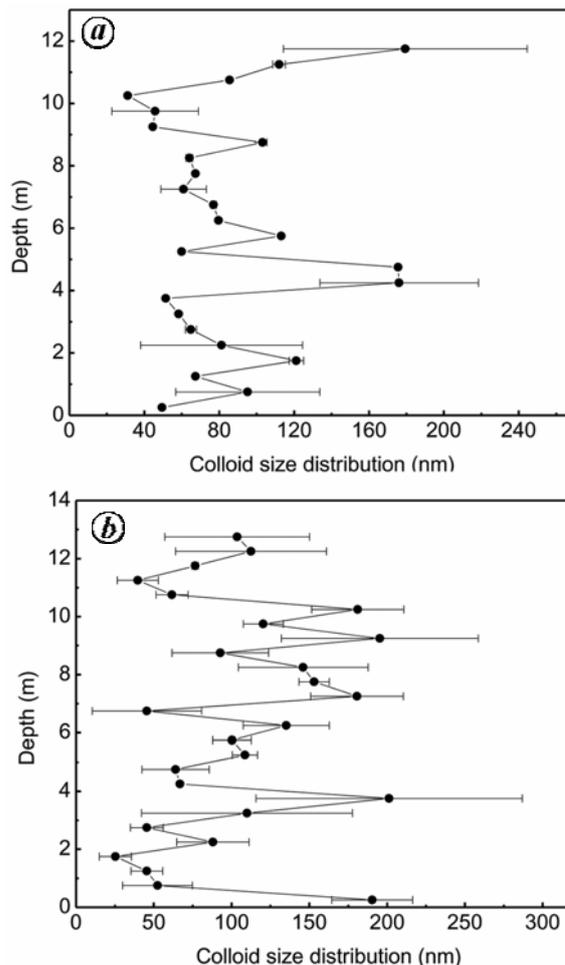

Figure 5. Size distribution of colloids: (*a*) Rayka and (*b*) Jaspur.

Six sediment samples (depth: 3.25–3.75 m and 8.25–8.75 m) from the Rayka section, which differed considerably in EC and colloidal concentration, were used for colloid release experiments and their physical properties are given in Table 2. The average packed height of the sediment column was 15 cm. The colloid mobilization experiments consisted of leaching with distilled water using a dropping funnel at the top of the column with the constant flow rate of 0.3 ml/min. The effluent was collected at the bottom of the column at regular intervals for measuring colloidal concentration. This was done by

drying the collected solution at 100°C according to the procedure of Kjaergaard et al.[27].

The breakthrough curves of colloids mobilized from the sediments are given in Figure 7 a. For all the experiments, the colloid concentration in the effluent exhibited a peak at the beginning and then decreased to low concentration. We explain this phenomenon as due to the detachment of colloids by shear stress along macropore walls at the onset of flow. For the sample at 3.25 m, significant amount of colloids was found in the effluent at 5 PV after which concentration reached a maxima of about 9600 mg/l at around 0.7 PV followed by gradual decrease to low concentration. The decrease in concentration after 0.7 PV is due to the depletion of mobile colloids in the column.

In the case of the sample at 3.5 m, the maximum colloidal concentration of about 5200 mg/l was observed at about 0.4 PV, which then started decreasing to a low level. A sudden jump in concentration was observed after 0.2 PV indicating the mobility of colloids in the sediment column. Though the observed release trend of colloids was the same, the concentration obtained for the sample at 3.25 m was higher than the sample at 3.5 m. The low concentration of mobilized colloids at 3.5 m substantiates the results of elemental analysis of colloidal suspensions. The colloid concentration peaked at 0.6 PV for the sample collected at 3.75 m. The maximum peak concentration was almost two times higher for samples at 3.25 and 3.75 m than the sample at 3.5 m.

The mass of the colloids was calculated at 5 min intervals for the flow rate of 0.3 ml/min of distilled water. The cumulative mass of the colloids was calculated using the mass of the colloids (Figure 7 b). The experiments were also carried out for a few selected samples (depth: 8.25, 8.5 and 8.75 m) of the Rayka section. The breakthrough curves clearly indicate the release and mobility of colloids from sediments with flowing water. Although the experiments are performed in a similar manner with the constant flow rate, the maxima of colloidal concentration are obtained at different PVs. The column experiments clearly imply the presence of small amounts of colloids in the sediments at 3.5 and 8.5 m depth, which contributed to their low concentration in the effluent.

The present study indicates that besides the charged ions, presence of charged colloidal particles in large numbers in the suspensions of the Jaspur section sediments contributes to EC significantly. Variation in the EC of colloids of the Jaspur sediments could be due to the amount of colloids present at various depth intervals and thus the amount of colloids has been quantified in terms of concentration. High EC was observed in a few samples with high concentration. Thus, it is evident that the EC is proportional to the concentration of colloids in suspension. Based on the results obtained from the determination of concentration of colloids isolated from sediments

Table 2. Characterization of the sediments

Properties	3.25 m	3.5 m	3.75 m	8.25 m	8.5 m	8.75 m
Organic carbon (g kg^{-1})	1.8	2.2	2.2	2.8	1.5	2.2
CEC (mmol kg^{-1})	20	20	14	30	17	15
Bulk density (kg l^{-1})	1.5	1.6	1.6	1.8	1.9	1.7
Pore volume (cm^3)	50	45	48	48	50	45
Porosity	0.26	0.23	0.25	0.25	0.26	0.23

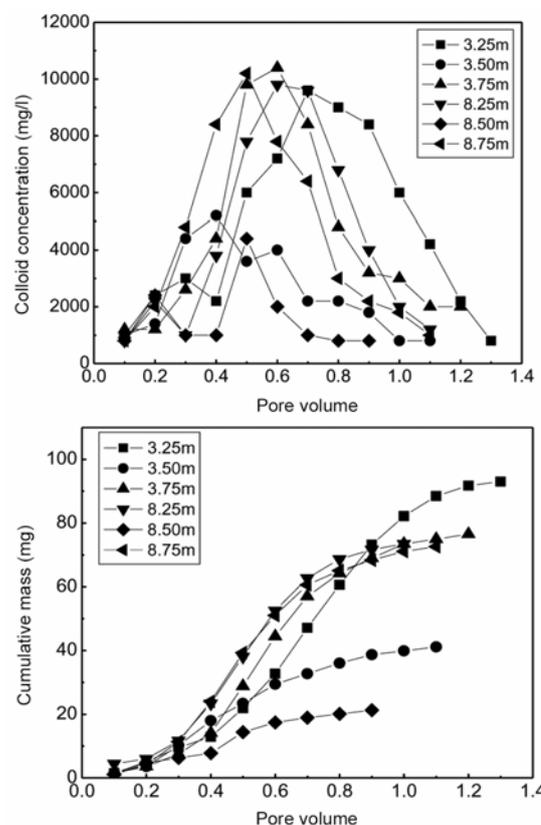**Figure 6.** Size of colloids in water samples.

Figure 7. Breakthrough curves of colloid mobilization experiments from Rayka sediments.

of Jaspur and Rayka sections, it can be seen that the sediment is a significant source of colloids.

The reason for the low EC and less concentration of colloids in the topsoil of Jaspur section is probably due to higher aggregate stability of soil because of higher organic matter content. These results are in agreement with similar observations by Jacobsen et al.[5].

In the case of the Rayka section, a perfect match between EC and concentration was observed for a few samples. The low EC and concentration obtained for two samples at depths of 3.5 and 8.5 m, could be due to the presence of low amount of colloids at those depths. The degree of geochemical alteration of minerals at the particular depth interval may have contributed to the low concentration of colloids. Such low EC associated with sedimentary materials varies with particle size and mineral species. A correlation between low EC and sand content has been reported[29], wherein the presence of high sand content has been reported to be the major contributing factor for the observed low EC and it increases with increase in clay content. Though our results are not particle size-dependent, presence of lower amount of colloids alone at a particular depth interval in the Rayka section contributes to the low EC.

A combination of light scattering and X-ray diffraction techniques has been used to obtain reliable information about particle size distribution of colloids and mineral composition. The calcite content is relatively less in the colloids of the Jaspur section. The type of minerals identified in colloids isolated from sediments is found to be similar irrespective of their sampling site. Quartz is found to be the dominant mineral in all the colloidal samples.

The experiments performed with light scattering technique reveal the existence of particles of colloidal size range in sediments and their wide size distribution. A variety of minerals exist as discrete colloids in sediments, which are of different sizes and shapes. Majority are authegenic, as observed by McCarthy and Zachara[1]. Detrital particles generated during the weathering processes decompose further to particles of small size and shape.

The size distribution of colloids present in water samples has been determined using scanning electron microscopy[30], transmission electron microscopy[30,31], photo correlation spectroscopy[32] and field flow fractionation[33]. A wide size distribution of colloidal particles has been reported, ranging from as small as 4 to 4000 nm. The size distribution of colloids present in Mini River water, is in the size range 4–163 nm and the size distribution of colloids present in the groundwater sample of Nandesari, falls between 28 and 148 nm. These results corroborate well with our observations of polydispersivity, though the instrumental technique used for determining the size distribution is not similar.

Though the observed colloid size distribution in our samples is less, the results prove the presence of colloids at a nanometre level, which have high stability and non-

settling nature. Thus, the possibility of their mobility in natural aquatic systems and groundwater is high. As the adsorption of contaminants is closely related to size and surface area of the colloids, small amounts of colloids can play an important role in the transport of contaminants in natural environments.

The particles mobilized from soil during rainwater run-off ultimately reach the aquatic systems. Thus the particles cannot be expected to be of similar size as they tend to lose their stability based on the chemical and physical conditions prevailing in the aquatic systems. For instance, high salinity promotes aggregation of suspended particles, leading to destabilization and subsequent deposition. The size of colloids in sediment and water samples also cannot be compared as the charge and aggregation behaviour of colloids may change based on the pH of aquatic systems. The number and size of the particles depend on the pH of the solution in which they exists. These types of particles exhibit a real colloidal behaviour as they can be transported over long distances depending upon the prevailing hydrological conditions. It has been observed that the natural organic matter (NOM) coating on the surface of colloids, leads to the development of negative surface charge and inter-particle repulsion among colloids upon dissociation of NOM, leading to their mobility in natural environments[34].

In all the colloid mobilization experiments, the colloid concentration in the effluent increased initially and then attained a low concentration level. The amount of available colloidal particles in the sediment-packed column is limited and the decrease in concentration is due to the finite supply of mobilized colloids from the sediments. The increase in colloidal concentration with time is expected as the influent water soaks the sediments for a longer time and so the dispersion of binding agents such as silica, iron oxide and carbonate that bind colloids to larger mineral grains would be more. When the sediment is subjected to continuous wetting with water, that changes the moisture content of the sediment, the dispersibility of colloids would be more. The colloidal concentration in the effluent would become higher as the soil wetness increases.

The cumulative mass of colloids is the total mass of colloids released from sediments during flow of water. It can be seen from Figure 7 b that the cumulative mass curve of colloids exhibits a nonlinear pattern. It has been previously reported that the cumulative mass of colloidal particles is flow rate-dependent; it shows linearity at low flow rate, while at high flow rate it shows nonlinearity[5]. Our observations indicate nonlinearity similar to that at high flow rate, though our flow rate was not as high. Diffusion-limited colloid mobilization was explained to be the cause of linearity of cumulative mass at low flow rate. In contrast, the nonlinear trend in our experiments may be due to the non-equilibrium processes and physico-chemical characteristics of the soil on colloid mobilization. One of the reasons for the non-equilibrium process could

also be due to the size variation of the colloidal particles leading to different adsorption capacity of the colloids.

The study has led to the following conclusions. (1) The size distribution of colloids in sediments and aquifers varies greatly and shows a polydispersal pattern. (2) No correlation exists between size of the colloids in sediments and water samples and it has been observed that they have a tendency to lose stability based on the prevailing chemical and physical conditions in the aquatic system. (3) The EC and concentration of colloids of bottom sediments were higher and a correlation between them was found. (4) The column experiments suggest the possibility of considerable mobilization of colloids from sediments during the rainy season and the mass of colloids was lower for samples with low EC.

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