

Provenance of minerals in the Assi river sediments, Varanasi, Uttar Pradesh, India

Ranjan Pratap Singh¹, Anis², Vertika Shukla², D. K Soni³, Anita¹, Aneet Kumar Yadav¹, Narendra Kumar^{1*}

¹Department of Environmental Science, Babasaheb Bhimrao Ambedkar University, Lucknow-226025

²Department of Geology, Babasaheb Bhimrao Ambedkar University, Lucknow-226025

³Central Pollution Control Board (CPCB), Lucknow-226010

*Email: narendrakumar_lko@yahoo.co.in

ABSTRACT

Grain size analysis and mineralogical characterization are important sedimentological tools to interpret the depositional environment, source, hydrodynamic conditions, and mode of transport of river sediments. Clays derived from chemical weathering are an important group of minerals found in various sedimentary environments such as rivers, estuaries, and ocean. In the present study, mineralogy of Assi river sediments was investigated with the help of Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Scanning Electron Microscopy (SEM). Results revealed that the sediments are dominated by sand and mud. Further, the sediments were found to be abundant in quartz with subordinate amount of feldspars, kaolinite, illite, chlorite, and montmorillonite. Abundance of these minerals suggests that the Himalayan and Vindhyan sedimentary rocks are the primary source for the Assi river sediments.

Keywords: Assi river sediments, Provenance, Mineralogical characterization, Grain size

INTRODUCTION

Rivers play a vital role in distributing sediments. Irrigation, potable water, inexpensive transportation, and energy are all provided by river systems, which also provide livelihoods for a significant number of people across the world. In India, there are 12 major, 46 medium, 14 small and desert river basins make up about 45000 km long river system (Balagurunathan and Shanmugasundaram, 2015). Rivers are very important for the deposition of fertile soil on the plains, formation of deltas, home and industrial water supply, hydroelectric power generation, and inland fishing. Sediments are mainly the product of weathering and denudation of pre-existing rocks.

Understanding river systems in the context of various forcing mechanisms such as climatic condition, tectonics, eustacy and their linkages is crucial for fluvial geoscientists (Singh et al, 2007; Blum and Törnqvist, 2000). Erosional, transportation, and depositional processes of clastic sediments are essentially controlled by crustal deformation and climatic conditions. These clastic sediments are transported to the ocean through rivers from the continents and offering insights into Earth's geological history by recording the effects of climatic conditions, tectonics and sea level changes. A river derives its sediments from various sources distributed throughout its drainage basin and transports them in a wide range of grain size.

Grain size analysis of river sediments is an important tool for understanding the intrinsic properties and dynamic forces that operated during deposition. Moreover, grain size analysis also gives

direction to investigate the depositional environment and energy flux of diverse agents that transported the sediments (Moiola and Weiser, 1968). Remarkable work has been carried out on grain size analysis for deducing source of sediment, transport mechanism, sedimentary processes and depositional environment (Folk and Ward, 1957; Friedman, 1961, 1967; Sahu, 1983; Ghosh and Chatterjee, 1994; Hartmann, 2007; Srivastava and Mankar, 2008; Tripathi and Hota, 2013; Kanhaiya and Singh, 2014; Kanhaiya et al., 2017; Ghaznavi et al., 2019).

The mineralogical analysis of sediments reflects the transportation history and sorting processes and provides valuable information for understanding provenance, tectonic setting and weathering signatures, paleoclimate and paleogeography (Verma and Armstrong-Altrin, 2013; Zou et al., 2016; Ramasamy et al., 2017; Armstrong-Altrin et al., 2015, 2022a, b). The framework grains of sediments commonly indicate the lithological characteristics of the source rocks and depositional environment (Dickinson, 1985; Garzanti et al., 2009). The original composition of clastic sediments may be affected by transportation history, sorting, redox condition as well as lithification, diagenesis, and metamorphism (Johnsson, 1993; Tawfik et al., 2018; Sopic et al., 2023).

The River Ganga is one of the most important dynamic components of the Indian subcontinent and appears among the world's major rivers. Major sediment sources of the River Ganga viz. Himalaya orogenic belt, the Indo-Gangetic plain and the northern Indian craton regions are

topographically and geologically distinct in nature (Singh et al., 2007). Various tributaries of River Ganga also play an important role in controlling total sediment load of the main river. Assi river is one of the tributaries of Ganga joining in the Holy city of Varanasi. Previous studies on Assi river are focussed on land use classification and watershed analysis (Srivastava et al., 2017), palaeo and present channel (Mishra et al., 2020), delineation of palaeo-course using remote sensing data (Mishra and Raju, 2022) and ground water quality assessment (Chaurasia et al., 2018; Singh et al., 2022). However, provenance study of Assi river sediments is still lacking. Therefore, this study was conducted along the course of Assi river, a tributary of River Ganga to characterize the nature and source of sediments based on the grain size characteristics and mineralogy.

GEOLOGICAL SETTING

The study area lies in the Varanasi district of Uttar Pradesh between the Latitude 25.28° N and Longitude 82.96° E. Sediment samples were collected from the Assi river from different locations (Fig. 1). Generally, sediments derived from Himalayan region are grey in colour comprising fine-grained silty sand with abundant mica. However, sediments derived from the craton are fine to coarse-grained sand with abundant potassium feldspars (Shukla and Raju, 2008). At Varanasi, the Ganga river carries a mixed sediment load derived from the Himalayan and peninsular regions including Vindhyan sedimentary rocks. The sediment fill of the Ganga basin is asymmetric decreasing in thickness from north to south. In the piedmont zone the alluvial fill is 3–8 km thick decreasing to about 0.5–1.0 km in the central part (Sastri et al., 1971; Shukla and Raju, 2008).

Varanasi City and its environs are located at an average height of about 76 m above the MSL (mean sea level) (Gupta and Mishra, 2022). The Varanasi City spreading over 100 km² area is part of the Indo-Gangetic Plain underlain by Quaternary alluvial sediments of Pleistocene to Holocene (Raju, 2012). The earliest phase of the geological history of the Indo-Gangetic Plain commenced with the formation of fore-deep concurrent with uplift of the Himalayan mountain system (Raju et al., 2011). In the Varanasi area, unconsolidated sediments form a sequence of clay, silt and sand of different grades. The presence of kankar carbonates is at times intercalated with clays and sands forming potential aquifers at various depths. Throughout the Central Ganga Plain the top few meters shows a distinctive fining upward succession terminating with clay-rich sediments (Shukla and Raju, 2008). OSL (Optically Stimulated Luminescence) dating techniques has been performed on an about 20 m thick fine-grained sedimentary sequence exposed on the eastern bank of River Ganga near Ramnagar dated between 59 ±

6 ka at the base to 7 ± 1 ka near the top (Raju et al., 2011). The sand, silt, and clays were originated from the alluvial deposits, and the precipitation of calcium carbonate from the groundwaters results in the formation of kankar (Raju et al., 2011). The Quaternary alluvial deposits are divided into older and recent alluviums (Shukla and Raju 2008; Raju et al., 2011).

Varanasi is the world's oldest city, situated between the Varuna river in the north and Assi river in the south (Fig. 1). The Assi river in Varanasi, Uttar Pradesh, India, is a small, local, ephemeral floodplain tributary of the River Ganga, with a length of about 8 km and catchment area of about 22 km² (Mishra et al., 2020). The Assi river originates from the Karmdeswar Mahadev Kund in Kandwa village of Varanasi and Chitaipur, Karaundi, Newada, Sundarpur, Shukulpura, Naria, and Nagwa joins the Ganges (Das and Tamminga, 2012). The Ganges River flows in the eastern part of Varanasi; the Assi river joins the southern end while the Varuna River forms the northern boundary (Mishra and Raju, 2022). These rivers receive vast quantities of untreated sewage, agriculture runoff with fertilizers and pesticides from the catchment areas, which leads to degradation of water quality (Singh et al., 2022).

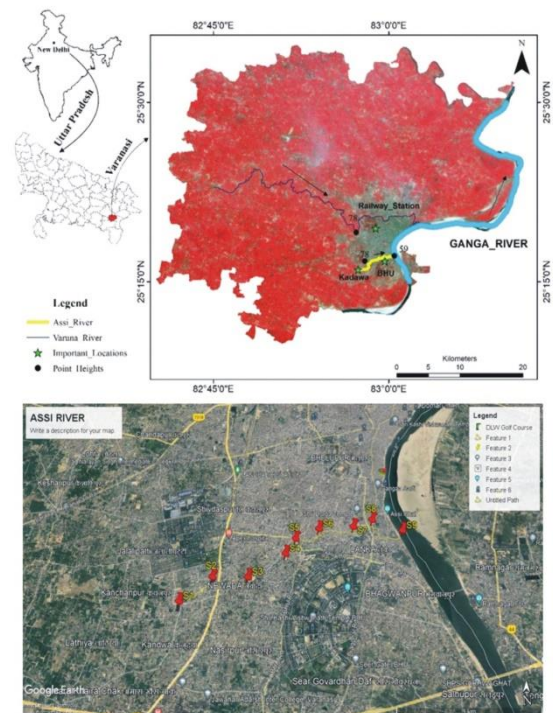


Fig. 1: Map showing sampling locations in the Assi River, Varanasi district, India

ANALYTICAL METHODS

A total of nine representative sediment samples were collected from different locations of Assi river. Sampling sites were carefully chosen to

avoid contamination and about 2 kg of sediment sample was collected with the help of a spatula and scraper. The collected samples were kept in the pre-cleaned zip-locked polyethylene bags for laboratory analysis. For the grain size analysis, standardized laboratory techniques were used following the methodology of Folk's (1980) scheme. Grain size of the bulk sediment samples was analysed using laser diffraction particle size analyser (CILAS 1190).

XRD (X-ray Diffraction) is a powerful technique for characterizing crystalline and polycrystalline materials. It gives information about structures, phases, texture, and other structural features, such as average grain size, crystallinity, strain, and crystal defects. X-ray diffraction (XRD) analysis is used to understand the source of sediments through identification of mineralogical composition of sediments to explain the causes and mechanisms of sedimentation (Kumar et al, 2018). The sediment samples were subjected to X-ray Diffraction for quantitative analysis of bulk mineralogy.

The IR technique is most powerful when used in conjunction with XRD (X-Ray diffraction) and other techniques. In earlier work, quantitative determination of quartz by infrared spectroscopy in soil, sediments, dust, other silicates and powdered coal was reported by Hlavay et al. (1978). Madejova (2003) applied infrared spectroscopy to identify various types of clay minerals from different angles. River sediments were analyzed for its vibration spectra with the aid of Fourier Transform Infrared Spectroscopy (FTIR, Nocolet 6700; Thermo-Scientific). Samples were mixed with KBr and pellets were prepared under a hydraulic press. Pellets were analyzed for vibration spectra of clay mineral by FTIR in the range 400–4000 cm^{-1} .

EDS analysis provides information about elemental composition of the particular particles in the sediments and allows determination of the relative mineral abundance (Rajkumar et al., 2012). The sediment samples were analyzed with the help of Scanning Electron Microscopy (SEM) attached to the Electron Diffraction Spectra (EDS) (JSM 6490 JEOL). The SEM was fitted with a Moran Scientific EDS analyzer that was employed to confirm mineral identification.

RESULTS AND DISCUSSION

Grain size Analysis

Grain size analysis is a reliable procedure to characterize the sediment and provide information on its depositional environment and transport mechanism (Folk and Ward, 1957). To identify the grain size distribution of the sediment samples (gravel, sand, and mud), sieving technique was used. The grain weight of the collected samples was calculated by Folk's (1980) method, using the measured grain weight and cumulative percentages of the grain weights obtained. The percentage values

of gravel, sand, and mud were plotted on a ternary diagram for classification of sediments. A ternary diagram is a three-component system where each side corresponds to an individual binary system. However, in three dimensions the diagram is more complex with surfaces emerging rather than lines as in the binary system (Flemming, 2000). The ternary diagram representing the gravel, mud and sand fractions suggest that the sediments are primarily muddy sand in texture (Fig. 2). In this plot the average percentages of gravel, sand and mud was found to be 0.0%, 76.7%, 32.3% respectively. Proportion of sand was higher than mud and gravels indicating that the nature of river was turbulent.

Many studies have attempted to distinguish between the sediments of modern depositional environments using the grain size distribution. Friedman (1961) proposed that river, beach and dune sands could be differentiated by movement parameters which reflect differences in the mode and energy of sediment transport. Glaister and Nelson (1974) and Sagoe and Visser (1977) suggested that environment of deposition can be interpreted on the basis of the shapes of grain size cumulative curves. The energy conditions and sediment supply within river systems can be considerably differ from one river to another river and even within different parts of the same river system. Thus, in some cases, the grain size characteristics of sediments may show higher variability within different parts of the same environmental conditions (Boggs, 2014). The particle size in a particular deposit reflects weathering and erosion, which generate particles of various sizes, and the nature of subsequent transport processes. Finally, since the size and sorting of sediment grains may reflect sedimentation mechanisms and depositional conditions, grain size data are assumed to be useful for interpreting the depositional environments of ancient sediments or sedimentary rocks (Boggs, 2014). The grain size data show high contribution of medium sand followed by fine sand and very fine sand. The silt fraction is composed of very coarse silt with a low percentage of coarse, medium and fine silts. The grain size data shows both sand and silt content in variable proportions, which suggesting varying energy conditions.

XRD Analysis

The XRD patterns and results reflected the presence of quartz, kaolinite, illite, chlorite, K-feldspar, plagioclase and the main reflections of the

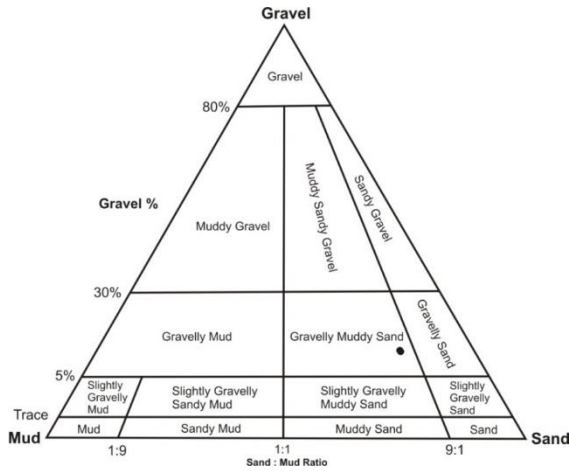


Fig. 2: Ternary plot for sediment classification based on Folk's scheme

major minerals such as quartz (78.38; 2θ), (120.87; 2θ), kaolinite (10.78; 2θ), (13.67; 2θ), illite (10.78;

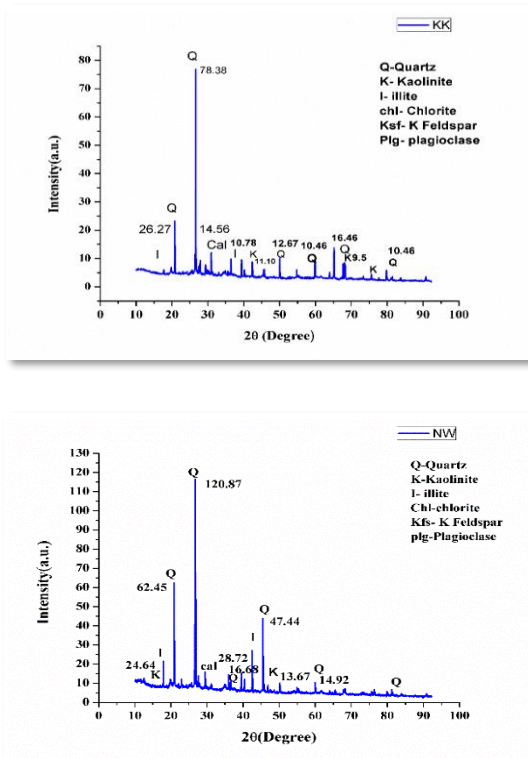


Fig. 3: X-ray Diffraction (XRD) spectra for the Assi river sediments

2θ), (28.72; 2θ) were found, probably derived from igneous and sedimentary rocks (Fig. 3) (Maity and Maiti, 2016; Khan et al., 2020). Presence of different clay mineral indicates a significant change in the physico-chemical conditions operating within the system. Weathering of k-feldspar under acidic condition produces mainly the kaolinite group without any exchangeable cations, whereas illite and chlorite are derived by alteration of mica, K-

feldspars, biotite, etc. under alkaline conditions (Kotoky et al., 2006).

Kaolinite formation is favoured under tropical to subtropical humid climate (Chamley, 1989; Hallam et al., 1991). In addition, detrital origin of kaolinite may also develop by diagenetic processes due to the circulation of acidic solutions (Ghandour et al., 2003). Presence of illite and kaolinite suggests prominent chemical weathering of feldspar and muscovite. Under acidic conditions, weathering or hydrothermal alteration of aluminosilicate minerals facilitate leaching of Ca, Mg, Na and Fe ions (Sheldon and Tabor, 2009).

FTIR analysis

The band position or location of the peaks from the conspicuous FTIR absorption peaks are used in qualitative analysis to detect the primary and minor constituent minerals present in the samples. The FTIR spectra of the samples were recorded. The observed wave numbers are analyzed, and the

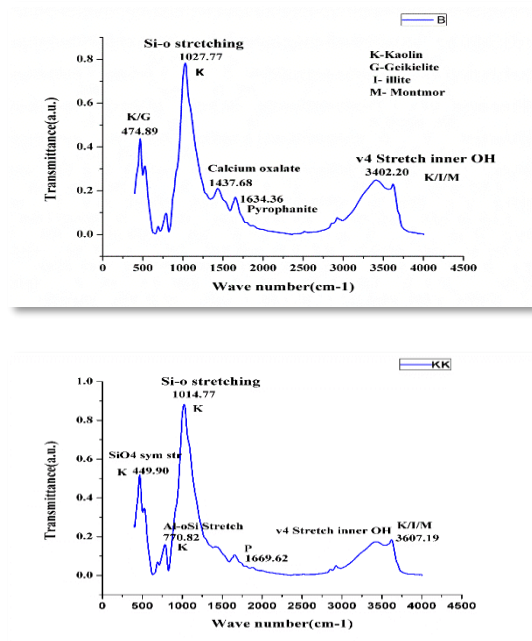


Fig. 4: FTIR spectra for the sediment samples showing the presence of various minerals

minerals are assigned using available literatures (Ramasamy et al., 2006). FTIR spectra revealed the presence of kaolinite, illite, montmorillonite, and Geikielite in different sediment samples (Fig. 4).

Quartz is a non-clay mineral that is found in abundance in all the samples. The strongest bonds in the silicate structure are the Si-O bonds, which may be seen in the infrared spectra of such minerals. The presence of quartz in the sediment samples can be explained by Si-O asymmetrical bending vibrations around 464 cm⁻¹, Si-O symmetrical bending vibrations around 694 cm⁻¹, Si-O symmetrical stretching vibrations at around 778 and 796 cm⁻¹, while the 1082 and 1162 cm⁻¹ absorption

region arises from Si-O asymmetrical stretching vibrations due to low Al for Si substitution. The infrared determination of quartz in sediments has been characterized by Chester and Green (1968). Kaolinite, illite and montmorillonite are most important clay minerals. The presence of absorption band at or around 3690, 3620, 1030 and 1015 cm^{-1} indicates kaolinite (Ramasamy et al., 2006). The intensity of the bands varies from sample to sample, which shows the quantity. If four peaks are observed in the minerals between 3697 and 3620 cm^{-1} they are said to be ordered state (Russell, 1987; Ramasamy et al., 2005). Kotoy et al. (2006), have highlighted the use of Fourier Transform Infrared Spectra to establish mineral association of kaolinite with traces of illite and chlorite. Calcite is one of the most common carbonate mineral in sediments. From the existence of a peak in the range 1420-1438 cm^{-1} it is easily recognized that the calcite is present in the studied samples.

SEM-EDS analysis

The size, shape, composition, crystallography, and other physico-chemical aspects of a specimen are studied in the SEM (Ural, 2021). SEM allows for a high-resolution image to be created by analyzing the material to be inspected with an electron beam generated in a vacuum environment and thinned with electromagnetic lenses in the same environment (Armstrong-Altrin, 2020). Sediment samples were subjected to SEM-EDS analysis in order to determine the presence of characteristic micro-morphology of the clay minerals and their relationship to non-clay minerals

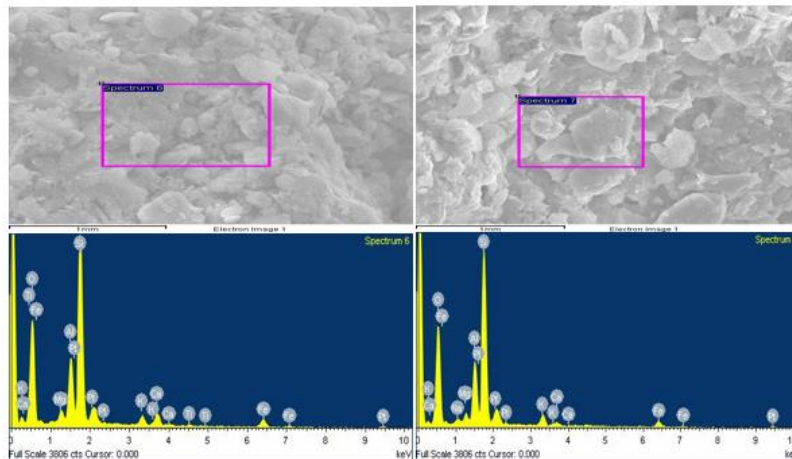


Fig. 5: Scanning Electron Microscopy (SEM-EDS) spectra and results of studied sediment samples at selected points

(Bassin, 1975). During the EDX measurement different areas were focus and the corresponding peaks are shown. The studied samples are composed mainly of Si, Al, Fe, Mg, K, Ca, and P etc. (Fig. 5). Percentage of elements present in the sediment samples is given in Table 1.

Table 1: Average percentage of elements present in the studied sediment samples		
Element	Weight%	Atomic%
O K	53.75	70.61
Na K	0.97	0.89
Mg K	1.32	1.14
Al K	7.90	6.15
Si K	24.19	18.10
K	2.11	1.14
Ca K	0.48	0.25
Fe K	2.70	1.01
Pt M	6.57	0.71
Total	100.00	100.00

Results indicate that mineralogical characterization of sediments is an important tool to understand source of sediments, hydrodynamic conditions, mode of transportation and deposition. The drainage pattern of Varanasi environs is primarily controlled by Assi and Varuna rivers (Shukla and Raju, 2008). At Varanasi, the River Ganga carries mixed load sediments derived both from Himalaya and peninsular craton including Vindhyan rocks (Shukla and Raju, 2008). The sand is fine-to-medium grained and grey coloured with significant mica content. Sand is mainly point bars deposits flanked by narrow flood plains confined to river valley. Presence of kaolinite indicates acidic environment and sediments derived from weathering of granite and Ca-poor igneous and metamorphic rocks (Kotoky et al., 2006). Kaolinite forms in both reducing and oxidizing environmental conditions (Kotoky et al., 2006). Montmorillonite is the alteration product of basic rocks, where alteration of stable minerals formed in alkaline conditions due to availability of Ca and Mg, whereas illite is a stable alteration product of acidic rocks due to high weathering conditions in humid climate and confined to shale (Ramasamy et al., 2004). Chlorite is possibly derived from aggradations of less oxidized sheet minerals and degradation of pre-existing ferromagnesian bearing minerals (Rajkumar et al., 2012).

CONCLUSIONS

Grain size analysis, chemical and mineralogical compositions are the three basic parameters to infer sediment provenance. A precise approximation of the parametric distributions of particle size is needed for the modelling of sediment transport, particularly to predict erosion and depositional conditions. The mineralogical characterization of sediments reflects the geological history of transport and sorting processes. Moreover, the scientific studies of the

identification of minerals in sediments lead to useful information about possible origin of minerals. In the present work, grain size, XRD, SEM and FTIR techniques were applied for the mineralogical components of the Assi river sediments. The Himalayan rivers carries the micaceous greywacke sand towards peninsular craton probably under increased water budget conditions. They were interacting with NE flowing southern rivers carrying pink arkosic sand from craton side near Varanasi. This led to mixing and superposition of sediments derived from two different sources across the zone of present-day water of Ganga. The interpreted source rocks for the Assi river sediments are Himalayan derived grey micaceous sands, were being carried by the southward flowing rivers beyond the present-day water divide of Ganga and mixed with pink arkosic sand brought by the northward flowing peninsular rivers.

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