Distribution of Clay Minerals and Textural studies of Surface Sediments Along the Chapora Estuary

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DECLARATION BY STUDENT

I hereby declare that the data presented in this Dissertation report entitled "Distribution of Clay Minerals and Textural studies of Surface Sediments Along the Chapora Estuary" is based on the results of investigations carried out by me in the Discipline of Marine Sciences at the School of Earth, Ocean and Atmospheric Sciences, Goa University under the Supervision of Ms. Manjusha Madkaikar and the same has not been submitted elsewhere for the award of a degree or diploma by me. Further, I understand that Goa University or its authorities will not be responsible for the correctness of observations / experimental or other findings given in the dissertation.

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COMPLETION CERTIFICATE

This is to certify that the dissertation report "Distribution of Clay Minerals and Textural studies of Surface Sediments Along the Chapora Estuary" is a bonafide work carried out by **Ms. Priyanka Rajendra Nagvekar** under my supervision in partial fulfilment of the requirements for the award of the degree of **Master of Science** in the Discipline of Marine Sciences at the School of Earth, Ocean and Atmospheric Sciences, Goa University.

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PREFACE

The study of surface sediments along the Chapora Estuary holds significant importance in understanding the dynamic interplay between geological processes, hydrodynamics, and environmental changes in coastal ecosystems. Estuaries serve as vital interfaces where freshwater from rivers meets the saline water of the sea, creating unique habitats that support diverse flora and fauna.

Textural and clay mineral studies of surface sediments in this estuarine environment provide invaluable insights into sedimentary processes, depositional environments, and sources of sedimentary materials. Textural analysis involves the characterization of sediment particle size distribution, which is crucial for understanding sediment transport mechanisms, sedimentation rates, and sedimentary facies variations within the estuarine system. Concurrently, clay mineral studies shed light on the composition and origin of clay minerals present in the sediment, offering clues about weathering processes, provenance, and sedimentary digenesis.

Elucidating the sedimentary characteristics and processes operating within this estuarine environment, this study aims to contribute to our broader understanding of coastal sedimentary systems and their response to natural and anthropogenic influences. This motivated me to study on the topic "Distribution of Clay Minerals and Textural studies of Surface Sediments Along the Chapora Estuary".

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LIST OF ABBREVIATIONS

Entity	Abbreviation
Armstrong	Ȧ
Chlorite	Ch
Ferrous ammonium sulphate	$(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$
Illite	I
Iron	Fe
Kaolinite	K
Magnesium	Mg
Micrometres	µm
Millilitre	Ml
Millimetres	Mm
Orthophosphoric acid	(H_3PO_4)
Phi	Ø
Potassium dichromate	$(K_2Cr_2O_7)$
Sulphuric acid	(H_2SO_4)
Smectite	S
Sodium fluoride	NaF
Total Organic Carbon	TOC
Square Kilometre	Sq. Km
Suspended Particulate Matter	SPM
X-ray Diffraction	XRD

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ABSTRACT

The Chapora Estuary, situated in North Goa, represents a dynamic coastal ecosystem characterized by the interaction of freshwater and marine influences. This study investigates the textural and clay mineral characteristics of surface sediments along the Chapora Estuary to elucidate sedimentary processes and environmental conditions within this estuarine system. Textural analysis reveals a predominance of fine-grained sediments, with varying particle size distributions along the estuarine gradient. Sediment deposition within the Estuary is influenced by hydrodynamic factors, including river discharge, tidal currents, and wave action, leading to spatial heterogeneity in sedimentary facies. Clay mineral studies indicate the presence of diverse clay mineral assemblages, including illite, kaolinite, and smectite. The distribution and composition of clay minerals reflect the complex interplay of weathering processes, sediment sources, and depositional environments within the estuarine system. Integrating textural and clay mineral data provides insights into sediment provenance, transport pathways, and depositional dynamics along the Chapora Estuary. These findings contribute to a comprehensive understanding of coastal sedimentary systems and inform strategies for sustainable estuarine management and conservation in the context of ongoing environmental changes and human activities.

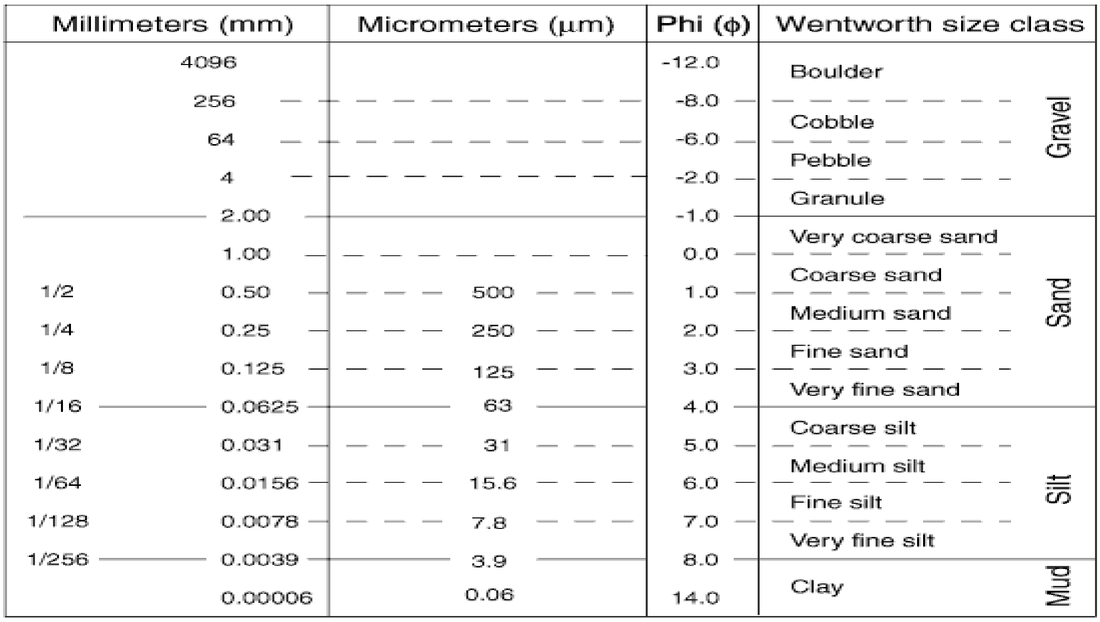
KEYWORDS: Clay Mineral, Estuary, Grain Size, XRD

CHAPTER 1: INTRODUCTION

1.1BACKGROUND

An Estuary is described as "An Inlet of Sea, reaching into a river valley as far as the upper limit of tidal rise," according to geomorphology **(Fairbridge, 1980).** The yearly discharge of river water into the ocean is roughly 37,400 cubic kilometres, constituting a mere 2.7 x 10^-3 percent of the total volume of seawater in the global ocean. This flow of river water transports around 15 x 10^15 grams of particulate matter and 4 x 10^15 grams of dissolved salts annually **(Martin and Whitfield, 1983).** The prominent part of the fluvial materials transported by the rivers is deposited in estuarine and coastal areas ~90%; **(Martin and Whitfield, 1983)**. The interference of marine-freshwater creates a complex and dynamic environment **(Morris et al. 1995)** with constant changes in physico-chemical parameters like temperature, salinity and pH. The runoff into the Estuary may be from diverse sources that may impact the quality of water. The water transported from catchment areas may carry sediments/particulate matter containing metals that may eventually settle in the sediments **(Regnier and Wollast, 1993).** These metals associated with particulate and sediments may be ingested by organisms living in the estuarine system (Campbell et al., 1988; Miller et al., 1992) or lead to metal bioaccumulation in organisms **(Young and Harvey, 1991).** Further presence of metals in the estuaries with their environmental persistence and biogeochemical behaviour may impact the water and sediment quality and their implication ultimately is felt on the health of humans and ecosystem **(Gao et al. 2015).** Estuaries may act as a source and/or sink of sediments of the sea/river having different grain size and mineralogy. Zones with higher Suspended Particulate Matter (SPM) are developed in the water column compared to elsewhere along the Estuary. Such zones are called Estuarine Turbidity Maxima (ETM) **(Postma, 1967; Dyer, 1995).** Estuarine Turbidity Maxima are formed and affected by tidal movements, salinity gradient, estuarine circulation, re-suspension of bottom sediments or a combination of one or more of these events **(Schubel, 1968; Festa and Hansen, 1978; Allen et al. 1980; Eisma, 1986; Uncles and Stephens, 1993; Brenon and Le Hir, 1999).**

In marine environments, particle transport is influenced by various factors such as currents, waves, and sediment characteristics. The two main types of particle transport in marine environments are bed load and suspended load. Bed load refers to the movement of sediment particles along the seabed or riverbed. This type of transport occurs when the force of the water (currents or waves) is sufficient to move particles along the bottom. Bed load transport typically involves larger and heavier particles such as sand and gravel. The movement of bed load particles is characterized by rolling, sliding, or saltating (bouncing) along the bed, often in the direction of the flow. Suspended load involves the transport of sediment particles within the water column. These particles remain suspended in the water due to the upward force exerted by turbulence or the buoyancy of fine particles. Suspended load can consist of a wide range of particle sizes, from clay and silt to sand and even coarser materials under certain conditions. The movement of suspended load is influenced by factors such as water turbulence, currents, and wave action. Suspended load transport is particularly important in areas with moderate to low flow velocities, where sediment remains suspended rather than settling on the bed **(Baskaran & Santschi, 1993)** Grain size is the diameter of singular sediment grains, or the lithified particles in clastic rocks. This is different from crystallite size, which is the size of an individual crystal within a single particle or grain. Grain size analysis is used to measure the size of various particles that make up a specific unconsolidated sedimentary deposit, sedimentary rock, archaeological locus, or soil unit. The analysis of analytical findings may be impacted significantly due to the pronounced influence of the distribution of grain sizes on the composition of suspended matter and sediment (**De Groot, 1964, 1973; Loring, 1988; Windom et al. 1989).** Historically, sediments were categorized into three primary groups: mud, sand, and gravel. Within the gravel category, clay and silt were distinguished, mainly based on mineralogical disparities rather than hydrodynamic attributes. Since the early 1900s, these size classifications have been standardized using diverse grading systems, constrained by range boundaries or particle size constraints. Particle size is typically assessed by nominal diameter, commonly denoted in millimetres (mm), micrometres (μm), or phi (Ø) units. The scale was initially developed by Udden in 1898 and later refined and broadened by Wentworth in 1922. Wentworth, or Udden-Wentworth scale (Figure 1.1), categorizes size ranges into textural groups with precise terminology, ranging from boulders (> 200 mm) to clay (< 0.004 mm).



Millimeters (mm)		Micrometers (μm)	Phi (ϕ)	Wentworth size class	
	4096		-12.0	Boulder	Gravel
	256		-8.0	Cobble	
	64		-6.0	Pebble	
	4		-2.0	Granule	
	2.00		-1.0	Very coarse sand	Sand
	1.00		0.0	Coarse sand	
1/2	0.50	500	1.0	Medium sand	
1/4	0.25	250	2.0	Fine sand	
1/8	0.125	125	3.0	Very fine sand	
1/16	0.0625	63	4.0	Coarse silt	Silt
1/32	0.031	31	5.0	Medium silt	
1/64	0.0156	15.6	6.0	Fine silt	
1/128	0.0078	7.8	7.0	Very fine silt	
1/256	0.0039	3.9	8.0	Clay	Mud
	0.00006	0.06	14.0		

Figure1.1 Wentworth (1922), grain size scale

(HTTPS://WWW.PLANETARY.ORG/SPACE-IMAGES/WENTWORTH-1922-GRAIN-SIZE)

Indian Ocean on the south, Arabian Sea on the southwest, Bay of Bengal on the southeast, and Himalayan Mountains in the north defines the country’s boundaries **(NG, K. C. 2021)**. There are many different types of landscapes in India **(Bhat, L.S. 2009)**, including cold glaciated mountains, arid deserts, vast plains, hot, humid plateaus, and wide seashores and tropical islands. India’s topography can be broken down into six general types: Himalayan Mountains, Northern Plains, Peninsular Plateau, Deserts, Coastal Plains, and Islands. Geologically speaking, the oldest and most stable peninsular India is what is left of the Indian Plate. It reaches the central Indian Satpura and Vindhya ranges in the north. These parallel chains extend from Gujarat’s coast along the Arabian Sea in the west to Jharkhand’s coal-rich Chota Nagpur Plateau in the east. The Deccan Plateau is bordered on the west and east by the Western and Eastern Ghats, and it is home to some of the oldest rock formations in the nation that date back more than a billion years **(Duff, 1993).** Different regions of India have rocks of different geologic ages. The principal rock types (Figure 1.2) can be categorized from oldest to youngest **(Grout, 1990; Medlicott & William, 2011).**

Weathering of continental rocks produces sediments of different sizes. They are predominantly transported to oceans via rivers. Along the inner shelf and continental slope of India's western coast, abundant detrital fine-grained sediments are found. These sediments primarily comprise clay minerals originating from the weathering of inland rocks, primarily transported by rivers **(Kessarkar et al. 2003).** A naturally occurring substance called "clay" is mainly made up of fine-grained minerals. The term "clay" is used to describe a family of minerals with a similar chemical composition and crystal structure properties as well as materials with particle sizes less than 2 micrometres (25,400 micrometres = 1 inch) **(Velde, 1995).** Clay minerals are formed by alteration of primary minerals like mica and feldspar. These processes occur over vast geological timescales, shaped by India's tectonic history, climatic variability, and geomorphological dynamics. The formation of clay minerals involves intricate chemical reactions and physical processes, typically occurring in aqueous environments under specific temperature and pressure conditions. The depositional environment further influences clay mineral composition and characteristics, ranging from marine sediments along India's extensive coastline to fluvial deposits in river basins and lacustrine settings within interior regions.

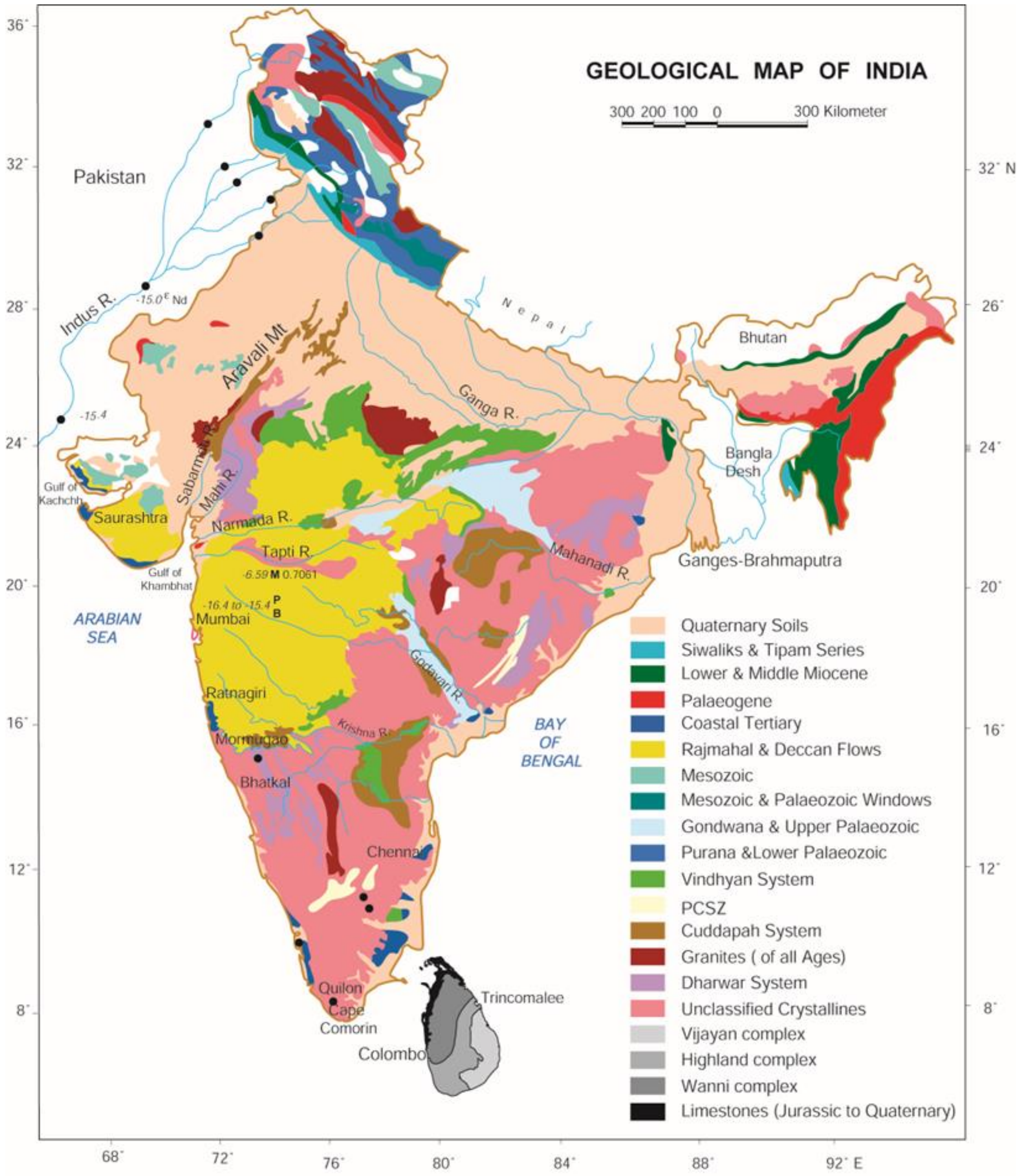


Figure 1.2 Generalised geological map of India **(Mir et al. 2023)**

Clay minerals primarily consist of silica, alumina, magnesia, or both, along with water. Iron can replace magnesium and aluminium in varying amounts, and significant levels of potassium, sodium, and calcium are commonly present as well. Research indicates that the chemical and structural composition of clay minerals closely resembles that of primary minerals, which are predominantly found in igneous or metamorphic rocks within the Earth's crust. Transformations may occur in ambient conditions. While some of the less resistant fundamental minerals (pyroxenes, amphiboles) are prone to weathering-induced disintegration and the formation of secondary minerals, some of the most resistant primary minerals (quartz, micas, and feldspar) may persist in soils. Either the primary mineral structure is modified (incongruent reaction) or the dissolved components of the original mineral precipitate or recrystallize into a more stable structure (neoformation), resulting in the formation of the ensuing secondary minerals (congruent reaction). Since these secondary minerals have a platy or flaky structure with irregular edges, as suggested by their name (Greek: phylon, leaf), they are most likely classified as phyllosilicates. An extended SiO4 tetrahedra sheet is one of their most significant basic structural units. The most intriguing class of minerals that have garnered significant global interest and funding for research and development are clay minerals. In 1930, the nature of clay can be defined with advanced development in X-Ray diffraction technology used to investigate the molecular nature of clay particles. Some clay minerals may be expressed using ideal chemical formulas as the following: $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$ (kaolinite), $4SiO_2 \cdot Al_2O_3 \cdot H_2O$ (pyrophyllite), $4SiO_2 \cdot 3MgO \cdot H_2O$ (talc), and $3SiO_2 \cdot Al_2O_3 \cdot 5FeO \cdot 4H_2O$ (chamosite).The primary criterion in defining the types of clay minerals in a formula is the SiO2 ratio. Nine groups of minerals can be distinguished based on differences in their atomic structure and chemical composition:

(1) kaolin-serpentine (kaolinite, halloysite, lizardite, chrysotile); (2) pyrophyllite-talc; (3) mica (illite, glauconite, celadonite); (4) vermiculite; (5) smectite (montmorillonite, nontronite, saponite); (6) chlorite (sudoite, clinochlore, chamosite); (7) sepiolite-palygorskite; (8) interstratified clay minerals (e.g., rectorite, corrensite, tosudite); and (9) allophane-imogolite.

Clay minerals, also known as phyllosilicates, are alumina silicates characterized by their sheet-like grain morphology. Their structure comprises tetrahedral and octahedral coordinated cation sheets bound to oxygen (Figure 1.2). This multi-level structure involves tetrahedral atoms connected to octahedral sheets. Ionic substitution and interlayer bonds give rise to various mineral groups. The four primary clay mineral groups include kaolinite, smectite, illite, and chlorite. The composition of the sheets and the connections between layers differ among these groups.

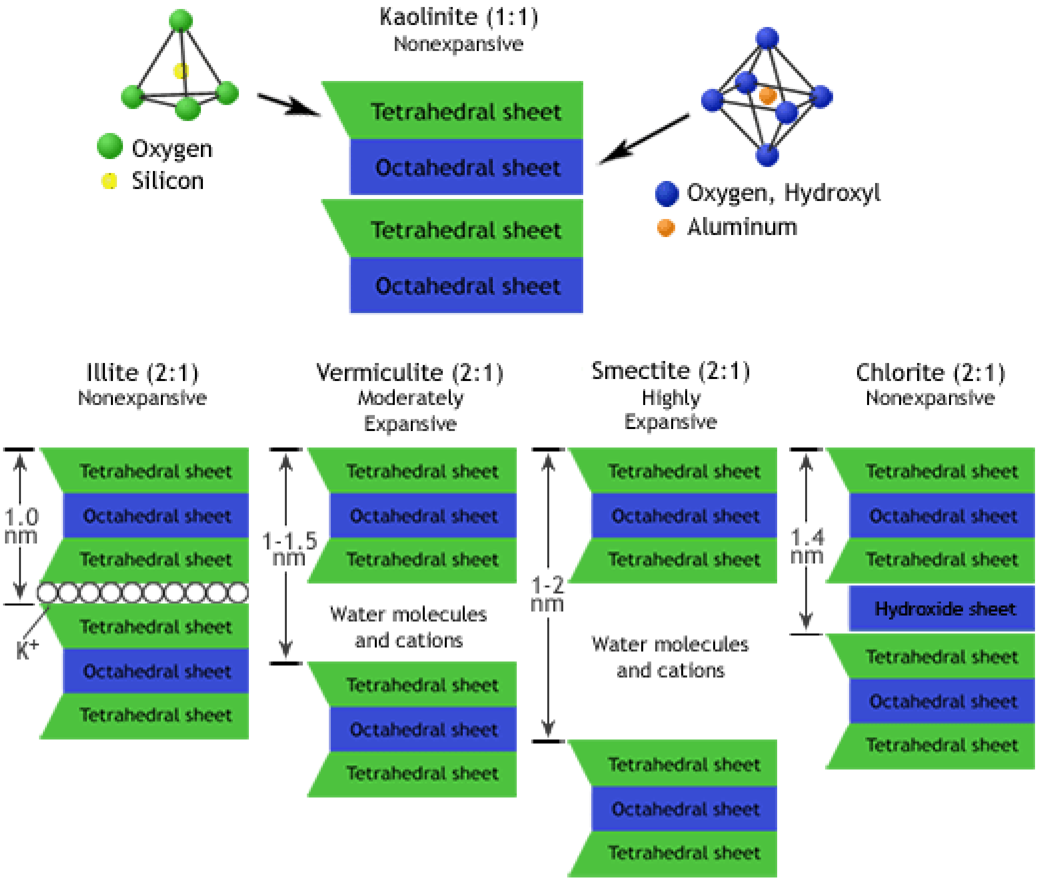


Figure 1.3 Overall structures of 1:1 and 2:1 Clays:

Kaolinite Group:

Kaolinite is a 1:1 clay mineral (figure1.4) with chemical formula $Si_4Al_4O_{10}(OH)_8$ China clay, or kaolin, is the term used to describe rocks that are found to be rich in kaolinite. All members of the kaolinite group form primarily during hydrothermal alteration or weathering of feldspar under acid conditions; but kaolinite and halloysite are probably the only members formed in soil **(Deer et al. 1973; Swindale, 1975).** Rare varieties of kaolinite that are amorphous in nature yet chemically comparable to kaolinite are dickite and nacrite. It is discovered that kaolinite has triclinic symmetry and is electrostatically neutral. In the paired layers, hydrogen bonds are present between the oxygen atoms and the hydroxyl ions.

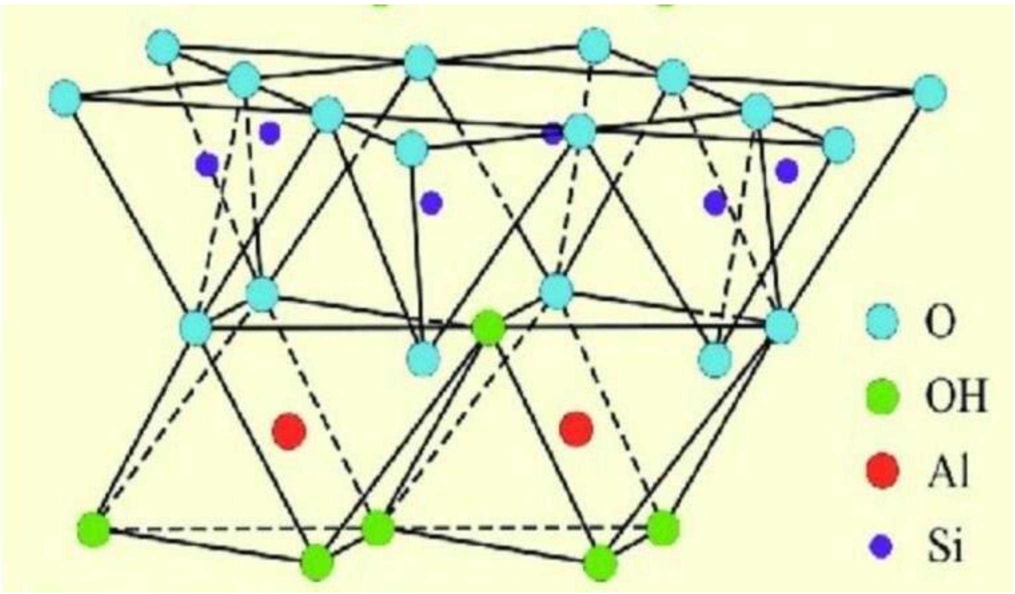


Figure 1.4 Structure of Kaolinite Mineral **(Grim, 1962)**

Due to weak hydrogen bonding and frequent random movements between layers, kaolinite minerals exhibit less crystallinity compared to triclinic kaolinite. In a perfect kaolinite structure, there is no charge. Kaolinite's enduring structures, upheld by hydrogen bonding, lead to slight shrinkage between layers and restrict its capacity to swell significantly when wet. Kaolinite possesses a low cation exchange capacity (< 1 centimole/kg), low surface area, and does not swell in water. Its low surface area and minimal isomorphous substitution contribute to a reduced ability to absorb ions. Large kaolinite crystals have low specific surface area, moderately low permeability, low cation exchange capacity, and consequently, limited partitioning ability due to strong hydrogen bonds and Van der Waals forces. It is resilient to chemical assault. Because of its modest net negative charge on kaolinite particles and low surface area (surface-to-volume ratio), it is the least plastic and electrochemically active clay mineral. It is also impacted by pH.

Smectite Group:

Smectites predominantly exhibit either a trioctahedral 2:1 structure (like talc) or a dioctahedral 2:1 structure (similar to pyrophyllite), differing from these neutral structures due to isomorphous substitution in either the octahedral or tetrahedral layer (Figure 1.5). The Smectite group of clay minerals comprises two further subgroups: Saponites (trioctahedral) and Montmorillonite (dioctahedral), with Bentonite being a significant additional member. Bentonite clay, sometimes termed sedimentary clay, possesses a unique capacity to retain water. The most notable members of this group include Montmorillonite, Beidellite, Nontronite, and Saponite. Smectite, also known as montmorillonite, consists of flake-like crystals with an expanding lattice, representing a 2:1 type clay mineral. Each layer comprises an octahedral sheet sandwiched between two tetrahedral (silica) sheets.

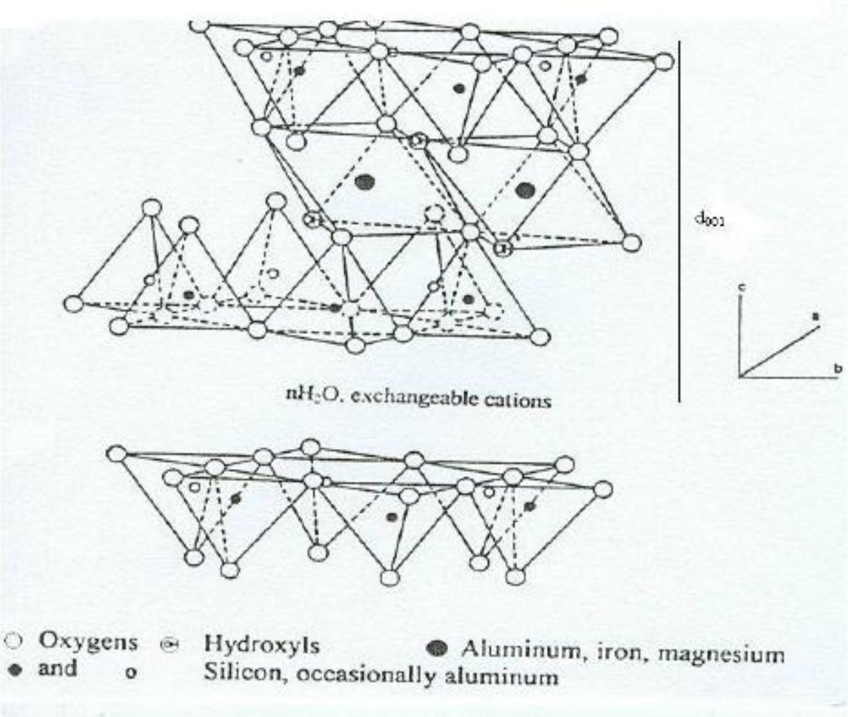


Figure1.5 Structure of Smectite Mineral **(Rhouta et al. 2006)**

Between the oxygen atoms in the top tetrahedral sheet of one unit and the bottom tetrahedral sheet of another, there is a little attraction. Water and exchangeable cations occupy the variable space that is created between the layers as a result. As a result, water and exchangeable cations can readily enter the interlayer gap, causing layers to expand to a potential diameter of 9.6 Å to 20 Å. Van der Waals forces, which hold the layers together, are weak, making it easy for water or other polar liquids to adsorb on the layers and separate them. High activity and a high swelling potential are the outcomes of the interlayer spacing. Smectite are used in industry as filers, carriers, absorbents, and a component in drilling fluids **(Grim, 1962).**

Illite Group:

Illite are two silica tetrahedral sheets (silica-gibbsite-silica) sandwiched between octahedral sheets, all held together by fixed or exchangeable cations, form a three-layer (2:1) structure (figure 1.6). This particular kind of clay mineral is a member of the class of phyllosilicate minerals that do not swell or expand. It is frequently present in worn rocks and soils as well as sedimentary rocks like shale. Illite has a silvery look and a smooth feel due to its composition of small, flat particles or plates that are smaller than two microns. Its chemical makeup is primarily alumina, silica, and water, with trace amounts of additional elements including potassium, magnesium, and iron. In general, this makes it similar to other clay minerals. Illite is used in many different applications, such as soil conditioning in agriculture, as filler in paper and paint, and as an addition to drilling mud in oil and gas exploration. Using the peak intensity ratio at 5A can provide an approximation of the 'octahedral character'. This method relies on analysing the intensity of five peaks to estimate the composition of octahedral illite in clay minerals. The rapid technique has been demonstrated to be a reliable estimator of the octahedral composition of illite

(Hunziker et al. 1986). Additionally, it can be valuable for identifying clay mineral origins and the transportation dynamics of clay minerals in marine sediments **(Moriarty, 1987). Esquevin (1969)** states that alkali-rich (muscovite) illites have high values (> 0.40). The ratio falls when the octahedral aluminium is replaced with magnesium and iron. Biotitic (mg and Fe-rich) illites are limited to levels < 0.15 **(Esquevin, 1969).**

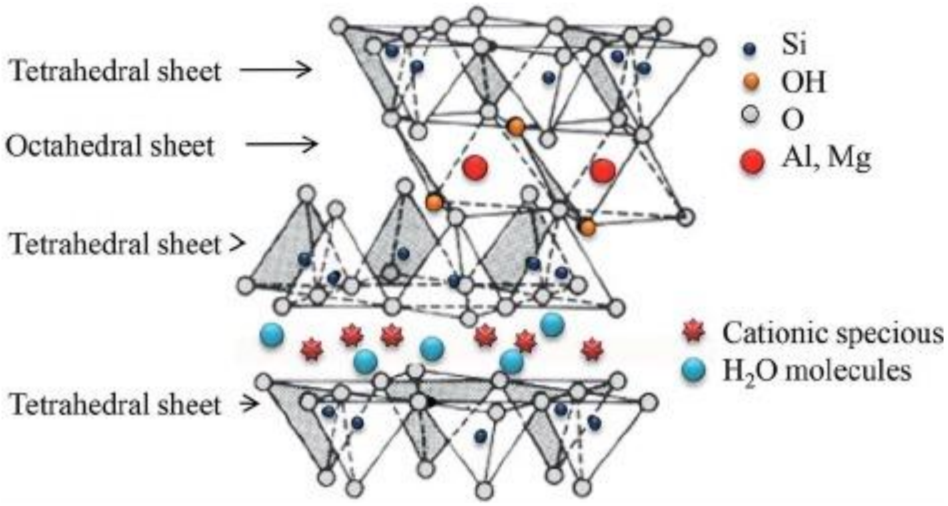


Figure 1.6 Structure of Illite Mineral (https://www.researchgate.net/figure/Smectite-structure-of-a-2-1-clay-mineral-showing-two-tetrahedral-sheets-sandwiched_fig2_274095227)

The chemical formula is $(K, H_3O)\ (Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2.(H_2O)]$. They are insoluble in water and organic solvents. pH is typically neutral to slightly acidic. Unlike other clay minerals like smectite, illite does not exhibit substantial swelling qualities. Illite is stable up to around 600°C, at which point it starts to decompose. The arrangement of the tetrahedral and octahedral sheets in illite's crystal structure is fundamentally different from that of other clay minerals, such as montmorillonite and kaolinite, because of these variations, illite has unique qualities and is used extensively in both geological and industrial contexts.

Chlorite Group:

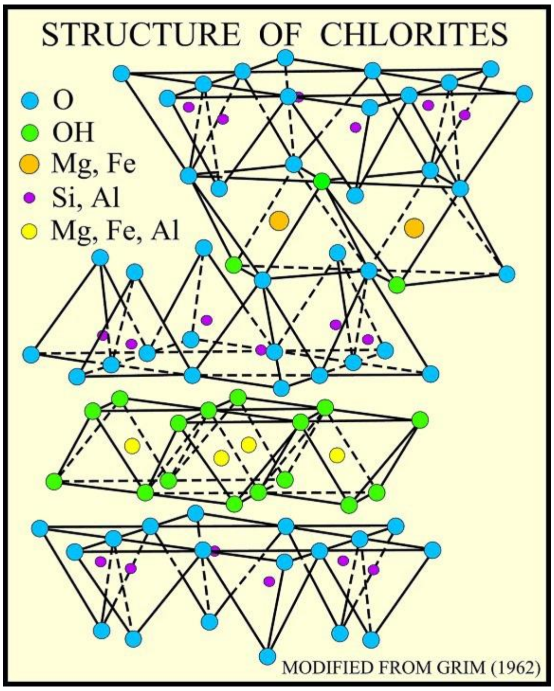


Figure 1.7 structure of chlorite mineral (Grim, 1962)

A class of common sheet silicate minerals that form in the early phases of metamorphism are called chlorites (Figure 1.7) The majority of chlorite minerals have an oily to soapy feel, are green in hue, and seem foliated with flawless cleavage. They are found in igneous, metamorphic and sedimentary rocks. Rocks that have undergone deep burial, plate tectonics, hydrothermal activity, or contact metamorphism include chlorite minerals. Chlorite is frequently found in large quantities in the rocks greenschist, phyllite, chlorite schist, and greenstone. The usual chemical composition of chlorite minerals is $(X, Y)_{4-6}(Si, Al)_4O_{10}(OH, O)_8$. Heating, solvation with ethylene glycol or ion saturation all deplete peak locations. Nevertheless, peak intensities are changed by heat treatments exceeding 500 C **(Barnhisel and Bertsch, 1989; Moore and Reynolds, 1997).**

1.2 AIM AND OBJECTIVES

Aim: Distribution of Clay Minerals and Textural studies of Surface Sediments Along Chapora Estuary.

Objectives:

- ☐ To determine the textural parameters of the sediments.
- ☐ To study the regional distribution of clay minerals and to find provenance of sediment along the Chapora Estuary.

1.3 SCOPE

Geological Processes: Soils, weathering products, and sedimentary rocks all contain clay minerals. Geological processes including sedimentation, diagenesis, and metamorphism can be better understood by taking into account these minerals' creation processes, transformations, and interactions with other minerals.

Soil science: The formation, fertility, and cycling of nutrients in soil are significantly influenced by clay minerals. Understanding soil characteristics, such as cation exchange capability, water retention, and soil structure, which are crucial for agricultural productivity and land management, is aided by research in clay mineralogy.

Environmental Geochemistry: The fate and movement of pollutants in the environment are influenced by clay minerals. Understanding their surface chemistry, adsorption capabilities, and ways in which they interact with pollutants is crucial for waste management, environmental remediation, and risk assessment.

Energy Resources: The production and exploration of hydrocarbons, as well as unconventional energy sources like tight oil and shale gas, are impacted by clay minerals. Drilling operations, hydraulic fracturing, and reservoir characterisation all depend on an understanding of their distribution, mechanical characteristics, and interactions with fluids.

Archaeology and Cultural Heritage: Clay minerals are vital ingredients in ceramics and pottery, and they can reveal information about prehistoric societies, trade routes, and technological advancements. This information is relevant to archaeology and cultural heritage. Researching the clay mineralogy of archaeological artifacts helps with provenance investigations, dating methods, and conservation tactics.

Water Resources Management: Aquifer characteristics and groundwater quality are impacted by clay minerals. The behaviour of clays as aquitards or aquicludes, their function in groundwater flow and storage, and the effects of clay mineralogy on resource management and water treatment are all better understood via research in this field.

Applications in Industry: Clay minerals are used in a wide range of industries, such as environmental engineering, construction materials, medicines, and cosmetics. Researching their characteristics, methods of modification, and uses in several industries promotes innovation and sustainable growth.

Planetary Science: The presence of clay minerals on other solar system planets and moons can reveal information about their geological past and possible habitability.

Remote sensing, sample analysis, and comparative planetology are all used in planetary clay mineralogy research to further our knowledge of planetary evolution and the hunt for extraterrestrial life.

Materials Science: Basic concepts in surface reactivity, crystal chemistry, and nanotechnology can be understood by utilizing clay minerals as model systems. They present prospects for interdisciplinary study and technological improvement when their structure-property correlations are studied and novel applications in materials science, catalysis, and nanomaterials production are explored.

CHAPTER 2: LITERATURE REVIEW

- **Nasnolkar et al. (1996)** studied the monsoon and post-monsoon seasons surface sediment gathered from four locations inside the Mandovi Estuary. The Mandovi Estuary displayed a variety of textural types of sediments, including sandy sediment at station M1 and a mixture of silt, clay, and sand in diverse combinations at other sites. Sand sediment is indicative of an energy zone with strong turbulence when it is present at stations. M1–M3 during the monsoon and at sts. M1 and M2 during the post monsoon.
- **Rao et al. (2015)** reported investigations on sediment samples that were taken in August along Estuary transect points. A total of thirteen surface sediment samples were collected specifically for clay mineral analysis, comprising fourteen samples from the Mandovi Estuary and seventeen from the Zuari Estuary. During the monsoon and pre-monsoon, the Mandovi Estuary's sediments were clayey silts at some stations and sandy at the mid-station. The sediments in the Zuari Estuary were clayey silts at the mid-station, sandy silts in the bay, and sandy silts in the upper Estuary. Both during monsoon and pre-monsoon, the concentration of kaolinite and illite was higher at river end sites and decreased seaward with an increase in sedimentation in these estuaries. In the sediment of both estuaries, there was more smectite, but more in Zuari than in Mandovi.
- **Jeshma et al. (2017)** reported a field work along the Puravadaiyanar and Vettar Estuary to study the various aspects of benthic foraminifera in the Puravadaiyanar Estuary, a total of 47 species and variations of foraminifera, representing 27 genera, 19 families, 13 superfamilies, and 5 suborders of Foraminiferidea, had been discovered. Likewise, the Vettar Estuary contained 26 benthic foraminiferal species and variants, classified into 13 genera, 10

families, 8 superfamilies, and 3 suborders of Foraminiferidea. Surface samples from the Puravadaiyanar Estuary were composed of silty sand, sandy silt, and sand, while those from the Vettar Estuary comprised silty sand, sandy silt, and natural sand. The overall distribution of foraminifera was observed to be greater in the lower and intermediate estuaries of the Puravadaiyanar and Vettar estuaries.

- The author reported that surface sediments were collected from the 15 stations at the coastline of Saurashtra during monsoon and pre-monsoon. Using a trowel, the top 0–1 cm of silt was collected at each station and placed in a 10 cm x 10 cm x 1 cm grid. A total of 35 species of foraminifera belonging to 17 genera, 12 families and 2 suborders were identified. Nummulites venosus and Amphistegina radiata, two shallower, bigger benthic foraminifera, were observed in a characteristic manner. The TFN is higher in pre-monsoon. **Dipankar Buragohain and Anupam Ghosh (2021).**
- **Ma et al. (2010)** reported analysis of 70 surface sediment samples for Grain size and X-ray diffraction (XRD) (collected from the upper 5 cm) from the eastern Beibu Gulf, located in the northern part of the South China Sea. All the samples were taken from grab samplers. In most of the study area, the surface sediments consist mainly of clayey silt or silt and in some small areas of silty sand to sand.
- **Peng et al. (2022)** reported the study site lying within the eastern Sichuan Basin, bounded by Huayingshan to the north, Dianjiang to the west, Nanchuan to the south, and Shizhu to the east. The primary benthic foraminifera present consist of uniserial nodosariids, carbonate microgranular foraminifera exhibiting glomospire coiling such as Glomospira and Glomospirella, as well

as Globivalvalinoidea. Additional benthic foraminifera taxa include Palaeotextularioidea and Fusulinida.

- **S. Saravanan & N. Chandrasekar (2010)** reported the study along the southern coast of Tamil Nadu, India. Soil samples were obtained using a manual auger from areas designated as low-tide, high-tide, and berm, reaching a depth of 25cm. The sampling stations were spaced approximately 10 kilometres apart. The sediments within the study area predominantly consist of medium to fine grains, exhibiting medium to poor sorting and a negative skewness.
- **Rajganapathi et al. (2012)** reported in the month of April, preceding the monsoon season, samples were collected using a hand auger from three distinct zones: the low tide line, high tide line, and berm. Sampling was executed to a depth of 25 cm, with an approximate spacing of 1 km between each sampling station. In total, 84 samples were acquired from 28 stations for a comprehensive sedimentological assessment. Textural analysis indicated that medium to fine-grained sediments were prevalent in samples obtained from both the high tide line and berm. Conversely, samples from the low tide line demonstrated a prevalence of medium to coarse-grained sediments, attributed to the higher energy conditions prevailing in that particular area.
- **Al-Ameri, S. A. & Kadhim, L. S. (2023)** reported a total of 13 samples collected from Ijana formation. The mudstone was composed of a variable mixture of clay and silt percentages. The primary clay minerals found in the mudstone include chlorite, kaolinite, illite, and smectite. The clay mineral composition of the Injana mudstone suggested an arid to semi-arid climate.

- **Jackson, (1957)** studied the properties of the parent material minerals, time, climate, topography, and biological influences can each independently impact the clay mineral composition of soils. The predominant minerals found in clays derived from minimally weathered parent materials include illite, quartz, feldspars, ferro-magnesian minerals, carbonates, and gypsum.
- **Minhat et al. (2021)** reported in this research that 24 surface samples were gathered from the northern area of the Strait of Malacca with the aim of comprehending the distribution patterns of foraminifera communities in shallow tropical waters. A grand total of 49 benthic foraminifera species were distinguished in the analysis.
- **Müller & Stein, (2000)** studied on three sediment cores retrieved from the Laptev Sea continental margin underwent X-ray diffraction analysis to examine the clay mineral composition, aiming to investigate the sediment influx since the late Weichsel Ian period. In the designated research area, the surface sediment's clay-mineral composition displayed discernible regional disparities. On the contrary, elevated levels of smectite content (reaching up to 30 %) in Holocene sediments stem from heightened sediment influx originating from the Khatanga River and the Kara Sea, facilitated by the Vilkitsky Strait and the St. Anna Trough, into the western Laptev Sea.
- **Manassero et al. (2008)** reported a study in mud-sandy bottom sediments of the Paraná Basin in Argentina where three distinct clay mineral compositions had been identified. The lower Paraná River Basin's tributaries exhibited a prevalent Illitic-Smectitic clay mineral association, originating from erosion and transportation processes from the Pampean Plains. This study outlines three primary clay mineral associations (Illite-Chlorite, Smectite-I/S, and

Kaolinite) observed in stream sediments from the Paraná River and its tributaries across a broad region of Argentina.

- **Magno et al. (2012)** reported a total of 137 sediment samples gathered from three distinct Italian National Relevance Sites (Bagnoli, Baia, and Augusta), each experiencing varying degrees and types of pollution. These samples underwent analysis for both grain size distribution and benthic foraminifera content. The distribution of pollution-tolerant species, previously identified, was influenced by sediment type, with a preference observed for silty and/or clayey sediments.
- **Romano et al. (2013)** studied about a cruise conducted in 2005, a sum of 37 surface samples was obtained utilizing a Van Veen grab. The sediment's texture characteristics indicated a predominance of fine-grained sediments, with comparable proportions of silt and clay (median values of 37.1% and 38.5%, respectively). In the examined samples, a total of 197 species were identified, consisting of 105 species with a hyaline test, 78 species with a porcelaneous test, and 14 species with an agglutinated test.
- **K. R. Rao. (1974)** reported 14 Sediment samples from both the Mandovi and Zuari estuaries were thoroughly examined to analyse the presence and distribution of benthic Foraminifera. The Zuari Estuary stands out for its relatively greater abundance of total Foraminifera, encompassing both living and deceased individuals, as well as its remarkable species diversity. In the upper reaches of both the Mandovi and Zuari rivers, the percentage ratio of live Foraminifera to the total population was higher. This indicated a comparatively swifter rate of sedimentation in those particular areas.

- **Anbuselvan & D. (2018)** reported a total of 23 surface sediment samples gathered from various water depths within the shelf part of Bay of Bengal. These samples underwent thorough analysis for both foraminifera presence and sediment characteristics. In total, 147 species classified under 59 genera and spanning 6 orders were identified. However, among these, only 22 species were found to be abundant. The distribution patterns of benthic foraminifera across this shelf region are primarily influenced by both sediment characteristics and the underwater topography (bathymetry).
- **Nigam et al. (2002)** reported total of 10 sediment samples collected in 1990 from the Mandovi Estuary, Goa. The findings of the study indicate a significant decrease in total foraminiferal numbers over an 18-year period. The study suggested that the decline in fauna is likely attributed to the ongoing rise in suspended load within the environment.
- **Austin & Evans. (2000)** reported research at the Ocean Drilling Program. Hence, examined sedimentological and faunal records from the transitional period marking the beginning of widespread glaciation in the northern hemisphere.
- **Coccioni et al. (2009)** reported about researchers that examined benthic foraminiferal communities in surface samples obtained from the Venice Lagoon in Italy. The primary objective was to explore the correlation between these delicate microorganisms and pollution from trace elements. Benthic foraminifera serve as valuable, efficient, and cost-effective bio-indicators for assessing the environmental health of the Venice Lagoon.

CHAPTER 3: MATERIALS AND METHODOLOGY

3.1 STUDY AREA

The Chapora River, located in northern Goa, India, serves as the demarcation line between the Pernem and Bardez talukas in North Goa. Its course runs westward, ultimately meeting the Arabian Sea at Chapora. It lies approximately 10 kilometres northwest of Mapusa, one of the main cities in North Goa. Chapora River Originates in Maharashtra’s Ramghat. The total catchment area of Chapora River basin is 530 sq. Km. The river traverses through Goa before reaching its endpoint. Estuaries are typically characterized by brackish water, which is a mix of freshwater from rivers and saltwater from the sea. The Chapora Estuary exhibits this unique blend of waters. The Estuary supports a rich and diverse ecosystem. It serves as a habitat for various species of fish, crustaceans, and birds. Mangrove forests often fringe the edges of estuaries like Chapora, providing important breeding grounds and shelter for marine life. Adjacent to Chapora, there exists a jetty primarily utilized for trawler fishing activities. Geologically, the Chapora Estuary's basin area comprises metamorphosed rocks, including quartz-chlorite-biotite schist and laterites **(Dessai, 2011).**

3.1.1 Physiography of Chapora Estuary

The Chapora Estuary is situated along the coast of the Arabian Sea in the northern part of Goa. It lies near the town of Chapora and is bordered by coastal plains and hills. The Estuary is formed where the Chapora River meets the Arabian Sea. At the mouth of the Estuary, there may be sandbars or spits formed by the deposition of sediments carried by the river. These sediments often contribute to the formation of a deltaic plain, which can vary in size and shape depending on factors such as river flow and tidal influences. Within the Estuary, there are numerous channels and creeks that meander through the landscape. These waterways facilitate the flow of both freshwater from the river and saltwater from the sea, creating a dynamic and interconnected system. The estuarine environment often includes tidal flats and mudflats, which are areas of exposed sediment that are inundated by the tide. These flats provide important habitat for various organisms, including migratory birds, crabs, and small fish. Mangrove forests and salt marshes are common vegetation types found in estuarine environments like the Chapora Estuary. These coastal wetlands play crucial roles in stabilizing shorelines, filtering pollutants, and providing habitat for diverse flora and fauna.

3.1.2 Hydrology

The hydrology of the Chapora Estuary is influenced by various factors, including rainfall, river discharge, tidal dynamics, and groundwater flow. The primary freshwater input into the Chapora Estuary comes from the Chapora River. The amount of water discharged by the river into the Estuary can vary significantly depending on seasonal rainfall patterns, land use changes in the watershed, and anthropogenic factors such as dam construction or water extraction for irrigation. The Chapora Estuary experiences tidal fluctuations due to its connection to the Arabian Sea. Tides play a significant role in regulating water levels and circulation patterns within the Estuary. The mixing of freshwater from the Chapora River and seawater from the Arabian Sea creates a gradient of salinity within the Estuary. Salinity levels vary spatially and temporally, with higher salinity near the mouth of the Estuary and lower salinity inland, closer to the river source. Groundwater discharge and recharge also contribute to the hydrology of the Chapora Estuary. Groundwater flow from adjacent coastal aquifers can introduce nutrients and pollutants into the estuarine system, affecting water quality and ecosystem dynamics.

3.2 PREPARATION OF BASE MAP, STUDY AREA MAP AND BEACH PROFILE MAP

The study area was selected after the available literature survey and survey of India toposheet number 48E/10 and a Google Earth image was used for preparing the base map (figure 3.1). The study area map (Figure 3.2) showing the sampling locations were prepared using QGIS version 3.8.2. The location pins were identified using the Google Earth Pro software. A total of 6 locations pins were marked along the Chapora Estuary, sequentially labelled from Location 1 to Location 6, tracing the course from its mouth to its source further inland.

The coordinates of the location markers were recorded in Table1. The Chapora Estuary is an important ecosystem where freshwater and marine ecosystems interact dynamically. This surface sediment sampling expedition, which took place in June 2023, had the goal of evaluating the sediment surface in order to investigate the Textural and Clay Mineral Studies of Surface Sediments along Chapora Estuary.

Table 3.1 Co-ordinates of sampling locations of the study area

Location	Latitude	Longitude
Sample 1	15°36'24"N	73°44'44"E
Sample 2	15°36'58"N	73°45'19"E
Sample 3	15°38'52"N	73°49'22"E
Sample 4	15°38'54"N	73°50'07"E
Sample 5	15°42'00"N	73°55'59"E
Sample 6	15°41'59"N	73°55'40"E

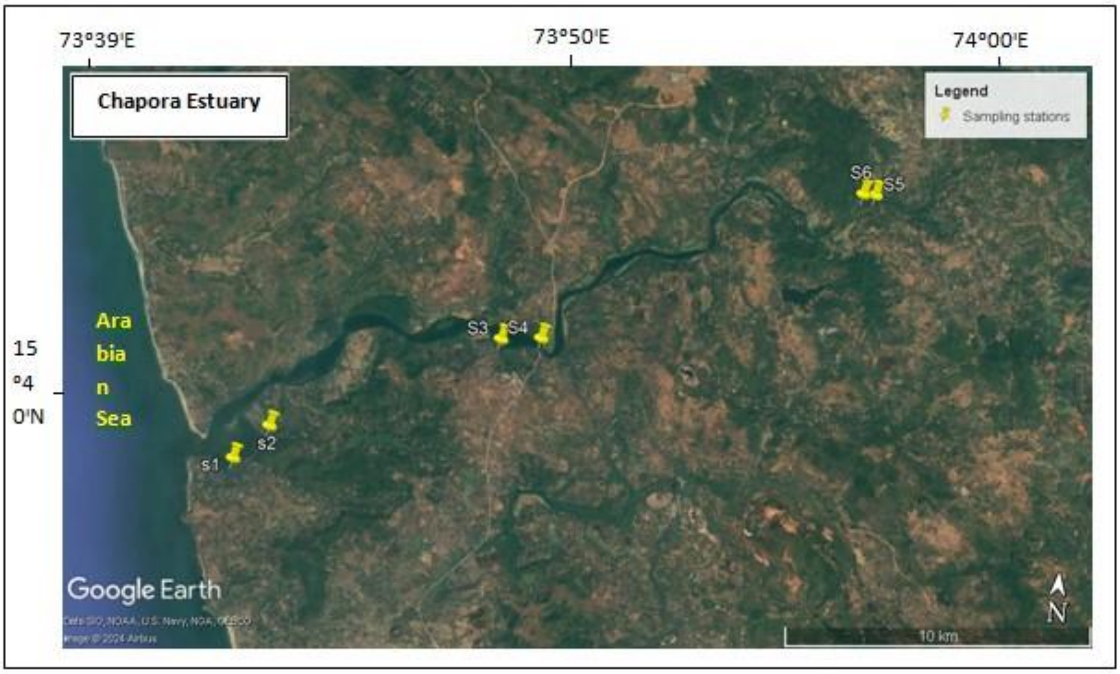


Figure 3.1 Sampling Locations of Chapora Estuary.

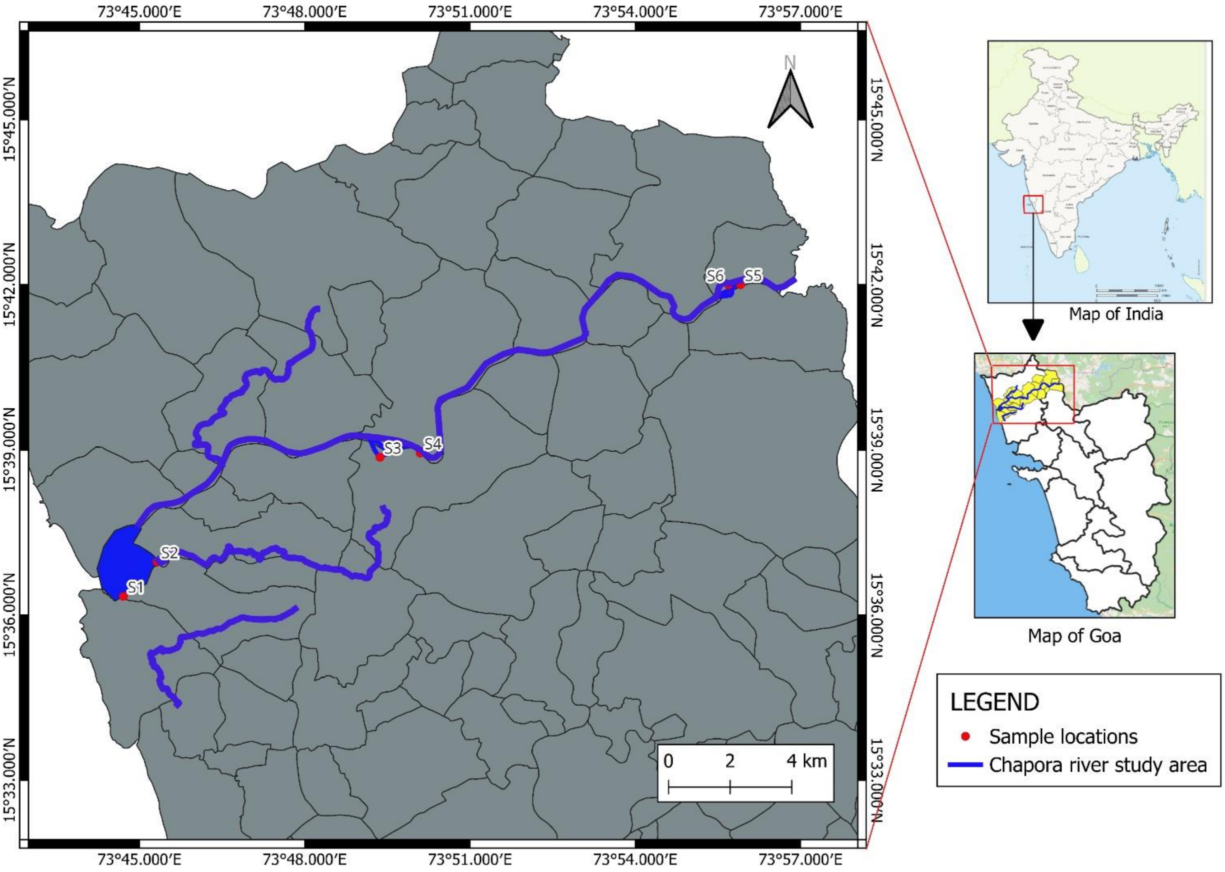


Figure 3.2 Study area map

3.3 FIELD WORK

Sediment samples collected on 15th and16th June 2023 along the transect stations of Estuary were investigated (Figure 3.3). For study of clay minerals and benthic foraminifera total of 6 samples were collected from 6 locations starting from vagator to Colvale till Ibrahmpur (i.e. from mouth to head of the Estuary). From every station 2 samples were collected. The samples were collected during the low tides using plastic scoop. The samples were placed in zip-lock bag and then stored ice box. Later the sample was shifted to laboratory and placed in refrigerator till further analysis.

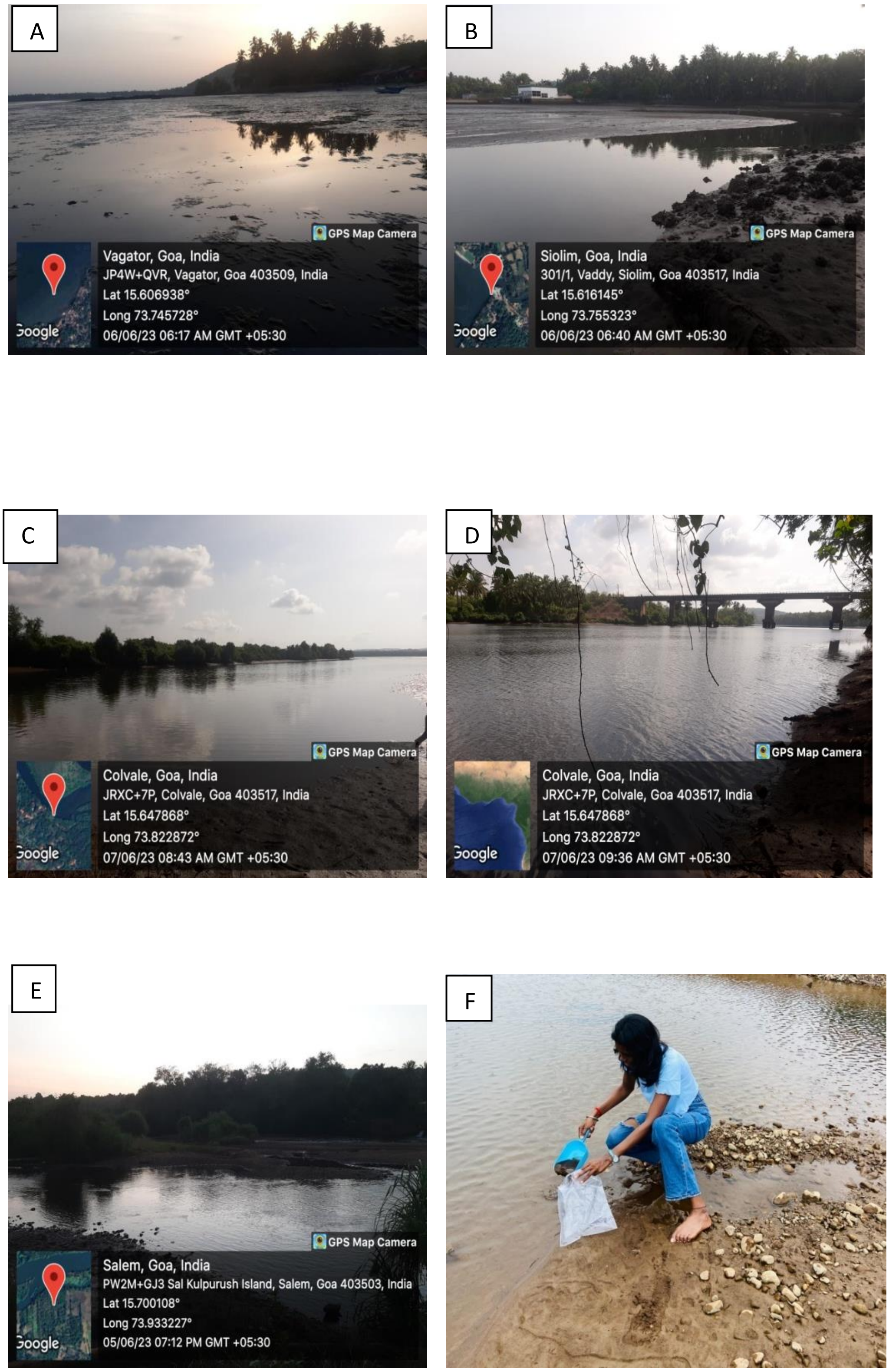


Figure 3.3 A, B, C, D, E and F shows sampling locations 1, 2, 3, 4, 5 and 6 respectively along the Chapora Estuary

3.4 LABORATORY ANALYSIS

Upon reaching to the laboratory samples were oven dried at 60˚C. Part of dried sediment was used for the analysis of sediment components (sand, silt, clay) and Clay mineralogy. Portion of the dried sample was finely powdered using a gate mortar and pestle. The powdered sediment samples were used for the estimation of Total organic carbon (TOC).

3.4.1 Sediment component analysis (sand: silt: clay)

To determine sand: silt: clay ratio, pipette analysis was used following the method given by Folk (1968). The analysis is based on Stoke’s settling velocity principle. Distilled water was added to 1000ml glass beaker containing 10g of oven dried sediment sample stirred with the help of glass rod. After allowing the sediment to settle for overnight, the water from beaker is decanted using a decanting pipe without disturbing the sediment in the beaker. This step is repeated for 4-5 times in order to remove the salinity of the sediment. The salinity is checked using a salinometer. Upon the removal of salinity, 10ml of 10% sodium hexametaphosphate is added to the sediment sample to dissociate clay particles and was kept overnight. On the next day, 5 ml of 30% hydrogen peroxide solution is added to oxidize organic matter completely and is kept undisturbed for a day. The treated samples are then sieved through a 63µm (230 mesh size) sieve and the filter is collected in a 1000ml measuring cylinder. The beaker as well as the material collected over the sieve is washed thoroughly until the solution became clear. The solution from the cylinder is made up to 1000ml mark using the distilled water and homogenized for about 2 minutes with the help of stirrer. The stirring time is noted down and the solution is allowed to settle. The sand particles remaining on the sieve are transferred into a 100ml pre-weighed beaker and are oven dried at 60˚C. After 1 hour 30 minutes 25ml of the clay solution was pipette at 10cm depth, and transferred into a 100ml pre-weighed beaker and then it is oven dried at 60˚C.Later after 6 hour 30 minutes the remaining sample from 10cm is decanted in 500ml beaker using decanting pipe and the sample is kept for settling in the room temperature for X-ray diffraction (XRD).

Table 3.2 Pipette Analysis Table

Size Ø	Depth at which pipette is to be inserted (cm)	Time at which water is to be pipette out Hours: Minutes: Seconds				
		28˚C	29˚C	30˚C	31˚C	32˚C
4	20	00:00:48	00:00:46	00:00:46	00:00:44	00:00:44
5	10	00:01:36	00:01:32	00:01:32	00:01:29	00:01:28
6	10	00:06:25	00:06:15	00:06:06	00:06:57	00:05:52
7	10	00:25:40	00:25:02	00:24:25	00:24:49	00:23:27
8	10	01:42:45	01:40:13	01:37:42	01:37:15	01:33:51
9	10	06:30:00	06:40:40	06:32:50	06:32:10	06:11:30
10	10	27:06:00	26:30:00	--	--	--

The dried sample is weighed to calculate the percentage of sand, silt and clay using the formula:

% Sand= weight of sand/ Total weight of sediments) ×100

X= (weight of clay × 1000/25)-1

% Clay= (X/Total weight of sediment) ×100

% Silt= 100- (% of sand + % of clay).

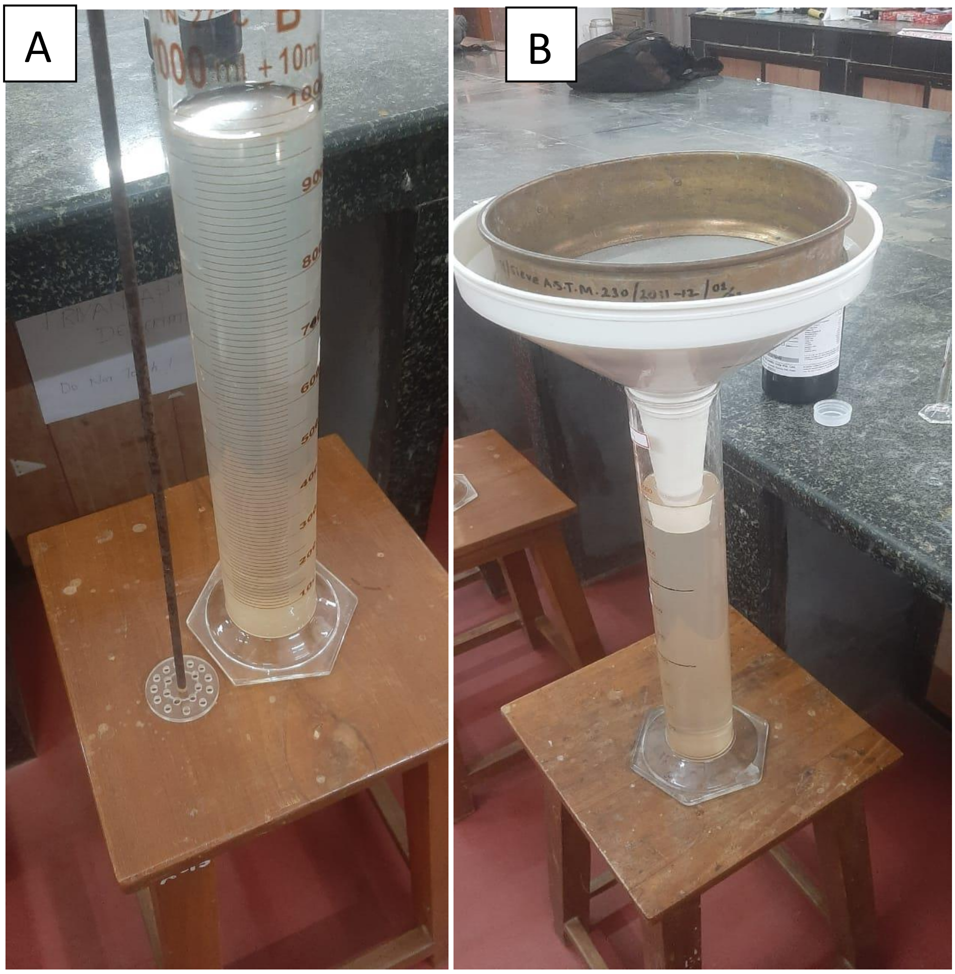


Figure 3.4 A and B shows pipette analysis method of sediment component (sand: silt: clay).

3.4.2 Clay mineral analysis

X-ray diffraction is used to ascertain a material's crystal structure. This is an experimental technique where a sample of the substance under test is exposed to an X-ray beam. In crystals, the atoms are arranged in a given order, which causes the beam to diffract at specific angles and intensities.

The following procedure is followed:

Clay mineral analysis of dried sub sampled was carried out. It involves same procedure as followed for pipette analysis up to studying the sample in a 1000ml cylinder. However, the pipetting time for the clay mineral analysis was calculated for 9ϕ. After 6 hours 30 minutes, 25ml of sample is pipette out from 10 cm depth. Add 10ml acetic acid to remove calcareous material and 10ml hydrogen peroxide to remove organic carbon. The content from the beaker was then allowed to settle for overnight. Later, the supernatant was Decanted using decanting pipe and distilled water was added to the beaker and content was allowed to settle overnight. This procedure was repeated 4-5 times to free clay from access reagents. Pipette out 1ml of slurry and spread uniformly over a pre numbered clean glass slide. These slides were air dried completely to obtain uniformly distributed thin layer of clay. Later, the prepared slides were glycolated using ethylene glycol at 100˚C for 1 hour 30 minutes. These slides were then scanned from 3˚ to 15˚ 2ɵ for 15 minutes on the X-ray diffractometer. Further, slide was scanned again in the range of 24˚ to 26˚ 2ɵ at 0.5˚ 2ɵ/min in order to distinguish between kaolinite and Chlorite peak. The percentage of clay mineral was calculated by weighting the integrated peak area of basal reflection in the glycolated X-ray diffractograms by following the semi-quantitative method given by **Biscaye (1965).**

The percentage of clay minerals is calculated using the following formula:

Smectite $(S_o) = S_o \times 1$

Illite $(I_o) = (I_o) \times 4$

Kaolinite + Chlorite $(K + Ch)_o = (K + Ch)_o \times 2$

$S + I + K = 100\%$

$S\% = (S_0 \times 1 / S + I + (K + Ch)) \times 100$

$I\% = ((I_o) \times 4 / S + I + (K + Ch)) \times 100$

$(K+Ch)\ \% = (K + Ch)_o \times 2 / S + I + (K + Ch)) \times 100$

$K\% = ((K_o / (K_o + Ch_o / (K+Ch)\ \%) \times 100) \times 100$

$$Ch\% = ((Ch_o / (K_o + Ch_o / (K+Ch)\ \%) \times 100) \times 100$$

The rapid technique has been demonstrated to be a reliable estimator of the octahedral composition of illite **(Hunziker et al. 1986).** Additionally, it can be valuable for identifying clay mineral origins and the transportation dynamics of clay minerals in marine sediments **(Moriarty, 1987). Esquevin (1969)** states that alkali-rich (muscovite) illites have hi values (> 0.40). The ratio falls when the octahedral aluminium is replaced with magnesium and iron. Biotitic (mg and Fe-rich) illites are limited to levels < 0.15 **(Esquevin, 1969).**

Formula to calculate Illite chemistry is:

$$I_o = 5\dot{A} / 10\dot{A}$$

3.4.3 Total Organic Carbon Estimation

TOC in sediment sample was estimated by using Walkley-Black method **(Gaudette et al. 1974).** It utilizes exothermic heating and oxidation with potassium dichromate ($K_2Cr_2O_7$) and concentrated sulphuric acid (H_2SO_4). The powdered sediment sub-sample of 0.5g is taken in a 500ml conical flask. The sediment is treated with 10ml of 1N standard potassium dichromate solution, and 20ml of sulphuric acid and silver sulphate mixture. The conical flask is gently swirled for 1 minute and allowed to stand for 30 minutes. After 30 minutes, 200 ml of Milli-Q water is added. To this, 10ml of 85% orthophosphoric acid (H_3PO_4) and 0.2g of sodium fluoride (NaF) are added, and solution is gently mixed. Later, few drops of diphenylamine indicator are added. The solution is titrated against 0.5N ferrous ammonium sulphate $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ till an end point (one drop end point) is obtained showing brilliant green. The oxidation of chloride ions is prevented by addition of silver sulphate. The standardization blank is performed using the same procedure as above without the sediment sample.

The percentage of TOC is calculated using the following formula:

% of TOC= 10(1-T/S) × F

Where,

S= Standardization blank titration, ml of ferrous solution

T= Sample titration, ml of ferrous solution

F= (1.0 N) × 12/4000 × 100/sample weight= 0.6, when the sample weight is exactly 0.5g, Where, 12/4000=m. eq. wt. Carbon.

CHAPTER 4: ANALYSIS AND CONCLUSION

4.1 SEDIMENT COMPONENT

Study area constitutes 6 representative samples along Chapora Estuary from mouth to head.

Grain size refers to the diameter or size of individual particles in a sediment or soil sample. It's commonly categorized into sand, silt, and clay based on their sizes. The percentage of sand varies from 16.95% to 63.25%, percentage of silt varies from 9.1% to 45.05% and percentage of clay varies from 5.4% to 65%. The percentages of sand, silt and clay for each sample are represented graphically in figure 4.1. Sample 1 has 63.25% of sand, 29.95% of silt and 6.8% of clay. Sample 2 consists 57.85% of sand, 36.75% of silt and 5.4% of clay. Sample 3 has 16.95% of sand, 45.05% of silt and 38% of clay present. Sample 4 has 33% of sand, 45% of silt and 22% of clay. Sample 5 has 39.9% of sand, 9.1% of silt and 51% of clay. Sample 6 has 31.75% of sand, 3.25% of silt and 65% of clay (Table 4.1). Sediment sample from mouth region of the Estuary i.e. sample 1 and sample 2 has higher percentage of sand followed by samples from head region i.e. sample 5 and sample 6 followed by samples from middle region i.e. sample 3 and sample 4. However, silt percentage is highest in sample 3 and sample 4 of middle region followed by sample from mouth regions followed by sample from head region. While clay percentage shows decreasing trend from head region to mouth region (Figure4.1). To understand the textural characteristics of sediments and hydrodynamic conditions of depositional environment a ternary diagram (Figure 4.2) proposed by **Flemming (2002)** and **Pejrup (1988)** is used respectively.

Figure 4.1 A, B, C, D, E, and F shows graphical representation of Sand, Silt and Clay percentages in sample 1, 2, 3, 4, 5, and 6 respectively.

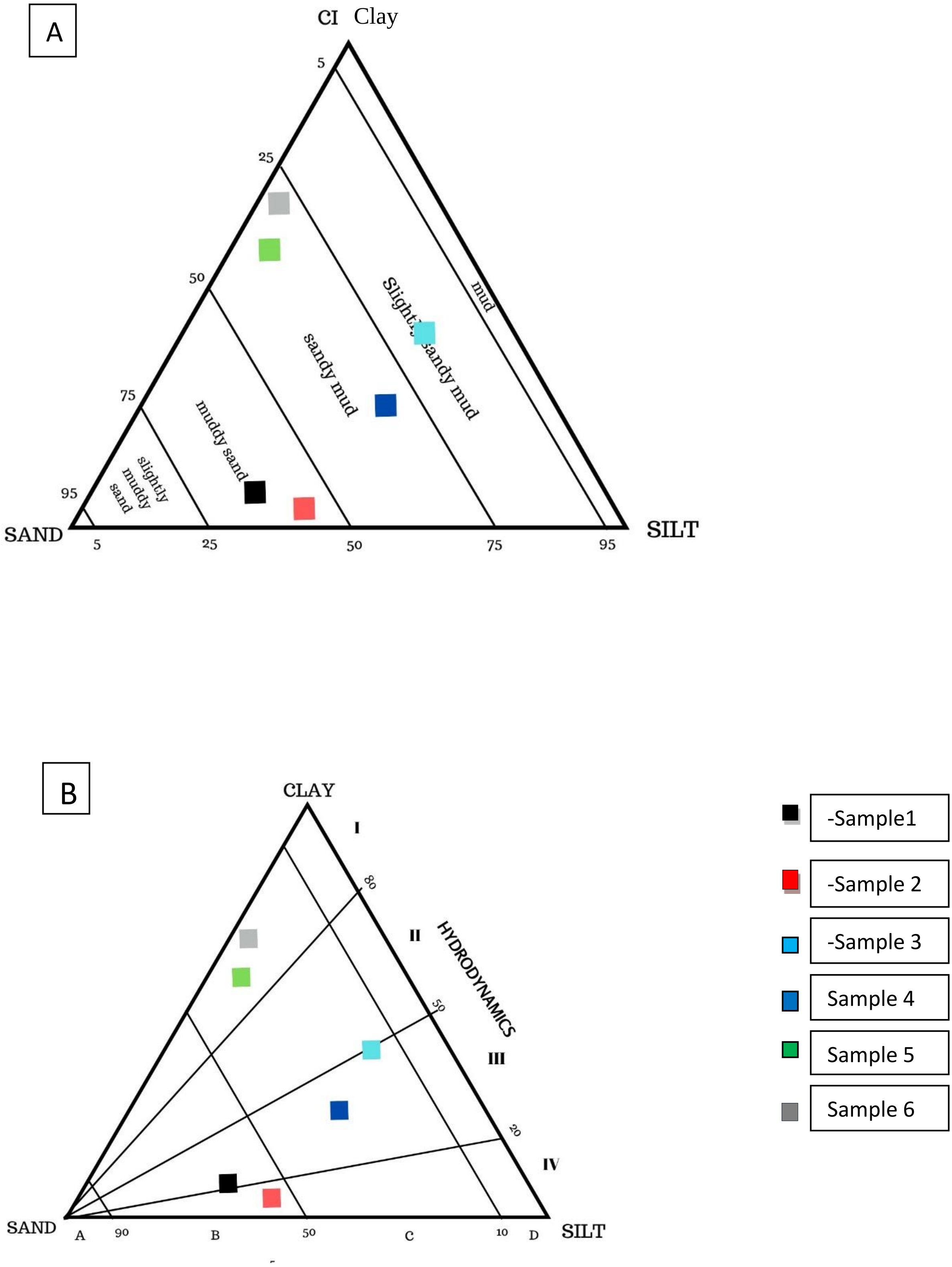


Figure 4.2 Ternary diagrams for the textural classification of sediments on the basis of sand/mud ratios. Diagram A: after **Flemming (2002)**; B: after **Pejrup (1988).**

The data plotted in ternary diagram **Flemming (2002)** witnesses highly variable grain size character that is sample 1 and sample 2 shows muddy sand texture, sample 3, sample 5 and sample 6 has sandy mud textural characteristic and sample 4 has slightly sandy mud. This highly variable grain size character reflects change in hydrodynamic condition of depositional environment which is inferred by plotting the data in ternary diagram **Pejrup (1988).** Sample 1 and sample 2 falls in B-IV and B-II respectively which shows violent hydrodynamic condition, While Sample 3 and sample 4 falls in C-III which indicates slightly violent hydrodynamic condition however, sample 5 and sample 6 falls in C-I which represents a calm and quiet hydrodynamic condition.

4.2 TOTAL ORGANIC CARBON (TOC)

Total Organic Carbon (TOC) is the measure of the total amount of carbon in organic compounds in pure water and aqueous systems. TOC is a valued, analytical technique that is applied by organizations and labs to determine how suitable a solution is for their processes. The percentage of TOC for all samples is given in Table 4.1. The organic carbon content varies from minimum of 0.942% in location 1 where silt and clay content are also low, to a maximum of 2.706% at location 3 where sediment sample is dominated by silt and clay content.

Table 4.1 Percentage of Sand, Silt, Clay and Total Organic Matter (TOC)

SAMPLE NUMBERS	SAND (%)	SILT (%)	CLAY (%)	TOC (%)
Sample 1 (Mouth)	63.25%	29.95%	6.8%	0.942%
Sample 2 (Mouth)	57.85%	36.75%	5.4%	1.47%
Sample 3 (Mid)	16.95%	45.05%	38%	2.706%
Sample 4 (Mid)	33%	45%	22%	2.13%
Sample 5 (Head)	39.9%	9.1%	51%	1.032%
Sample 6 (Head)	31.75%	3.25%	65%	1.494%

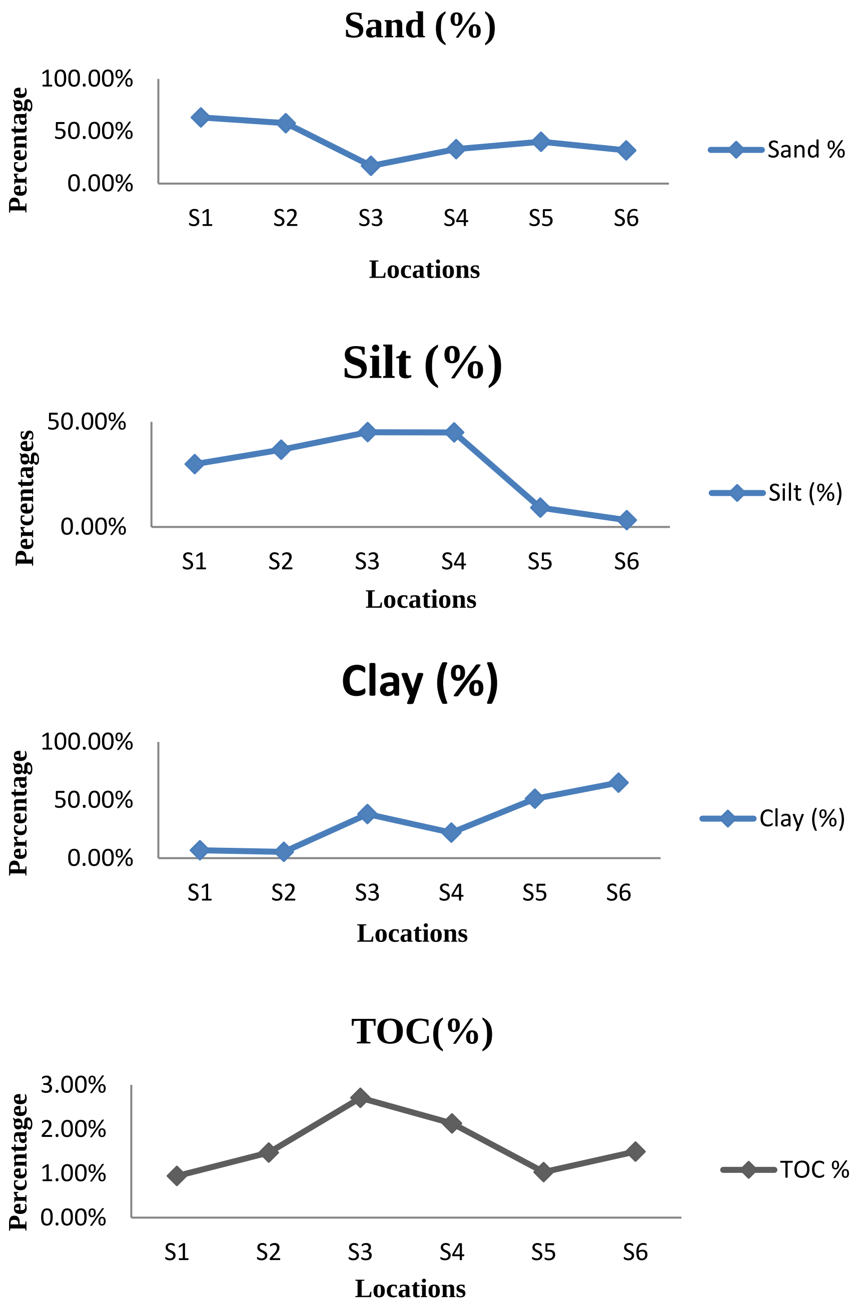


Figure 4.3 Graph representing Sand, Silt, Clay and TOC percentage in Chapora Estuary

The mid-region samples exhibit higher content of organic matter compared to samples from the mouth and head locations (Figure 4.3). There is variation within each location, suggesting differences in organic matter content even within the same area.

4.3 CLAY MINERALOGY

The XRD analysis was carried out for all six sediment samples and identified clay minerals are Illite, Smectite, Kaolinite and Chlorite (Table 4.2). The abundance of clay mineral is in the order of Kaolinite> Illite> Smectite. The percentage of smectite ranges from 5.4% to 8.4% followed by illite percentage ranging from 7.27% to 17.7% and kaolinite percentage from 64% to 100% respectively (Figure 4.4). The distribution pattern of smectite shows decrease in trend from mouth to head region. It is present in decreasing trend from sample 1 to 3 and is found absent in later sediment samples. Similarly, illite follows same distribution pattern as that of smectite. Whereas, the distribution pattern of kaolinite is largely opposite to that of smectite and illite trend. Kaolinite decreases from sample 6 to sample 1 i.e. from head to mouth region. However, chlorite is found only at one location i.e. sample 5 (Figure 4.5).

Tabl3 4.2 Percentage of clay minerals in Chapora Estuary

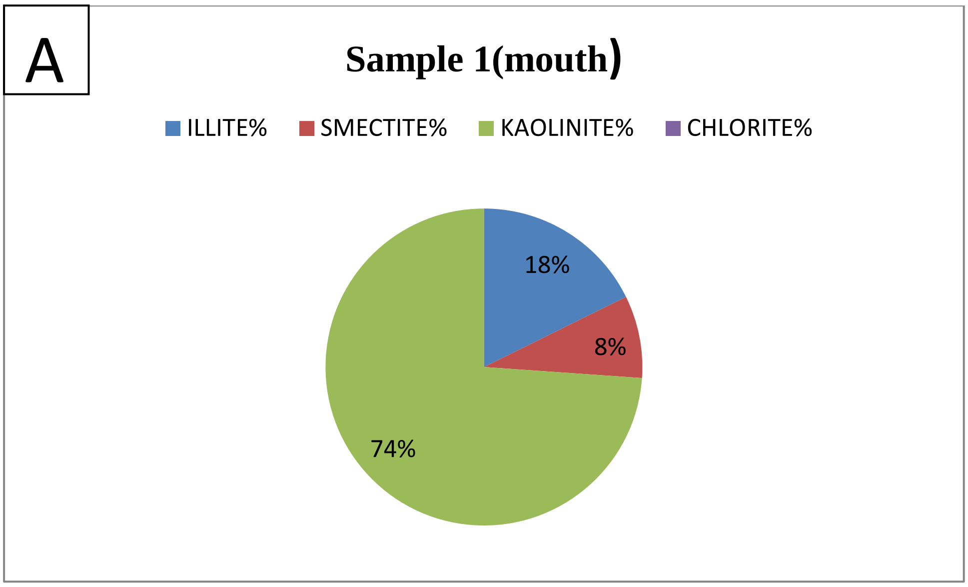
SAMPLE NUMBER.	ILLITE%	SMECTITE%	(K+Ch) %	KAOLINITE%	CHLORITE%
Sample 1	17.7%	8.4%	73.86%	73.86%	0
Sample 2	14.76%	6.27%	78.96%	78.96%	0
Sample 3	7.27%	5.45%.	87.28%	87.28%	0
Sample 4	0	0	100%	100%	0
Sample 5	0	0	100%	64%	36%
Sample 6	0	0	100%	100%	0

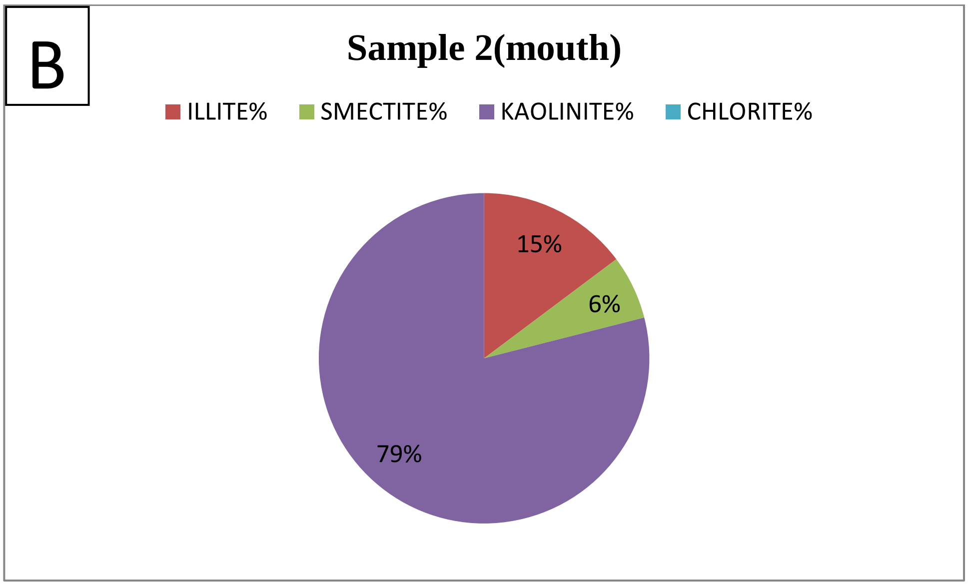
4.4 CLAY MINERAL CHEMISTRY

Further, Illite chemistry was found out to be Fe and Mg rich in nature (Table 4.3).

Table 4.3 Illite chemistry of the sediment

SAMPLE NUMBER	ILLITE CHEMISTRY
Sample 1	0.4
Sample 2	0.3


A
Sample 1(mouth)
ILLITE%
SMECTITE%
KAOLINITE%
CHLORITE%
18%
8%
74%


B
Sample 2(mouth)
ILLITE%
SMECTITE%
KAOLINITE%
CHLORITE%
15%
6%
79%

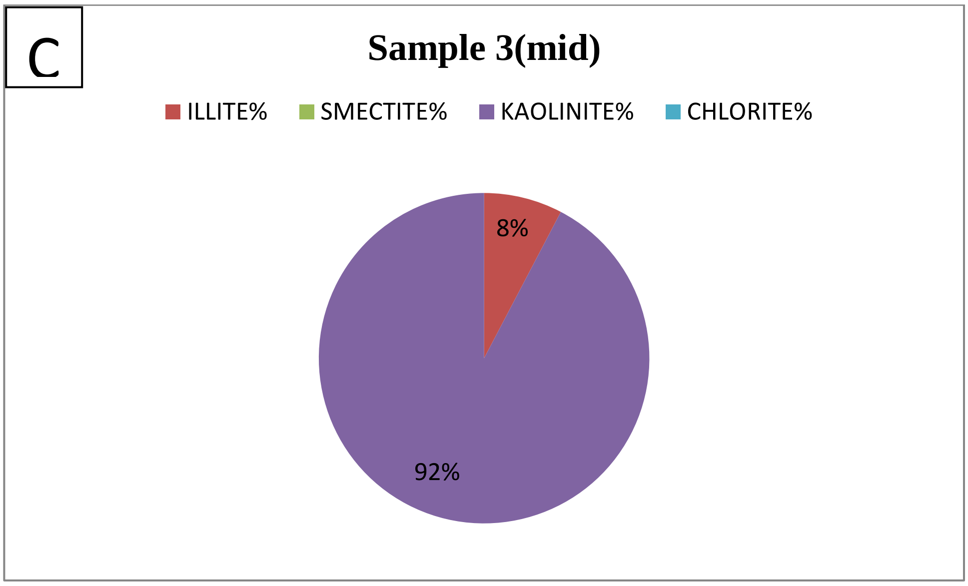
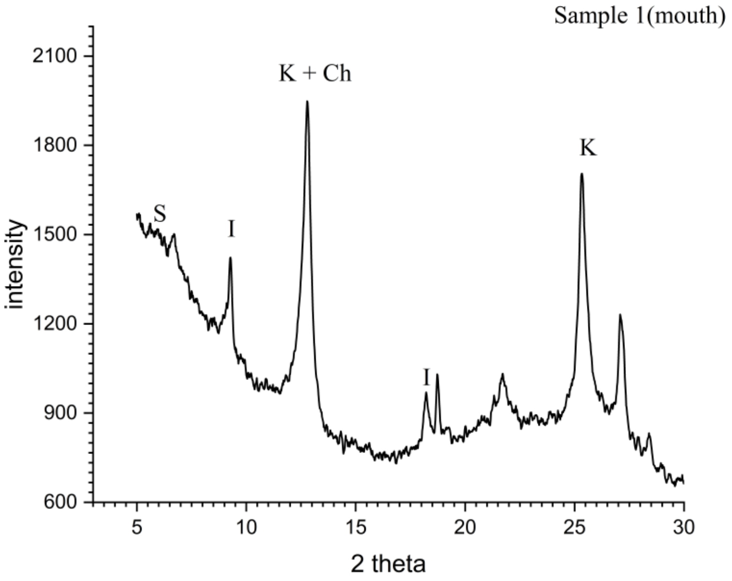
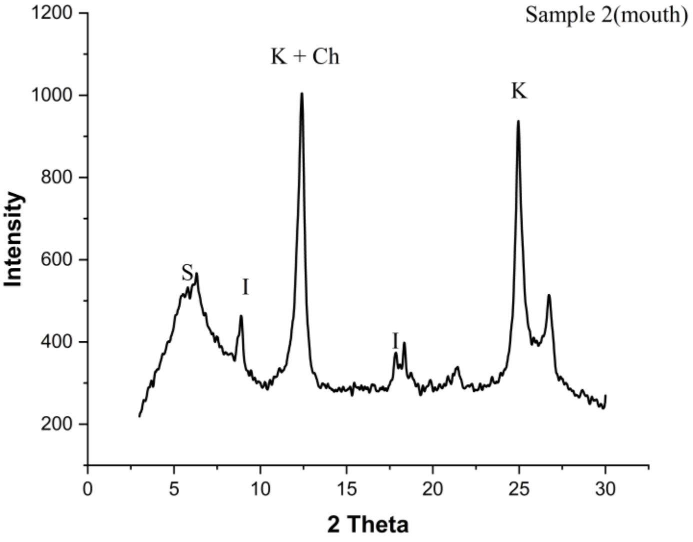

C
Sample 3(mid)
ILLITE%
SMECTITE%
KAOLINITE%
CHLORITE%
8%
92%

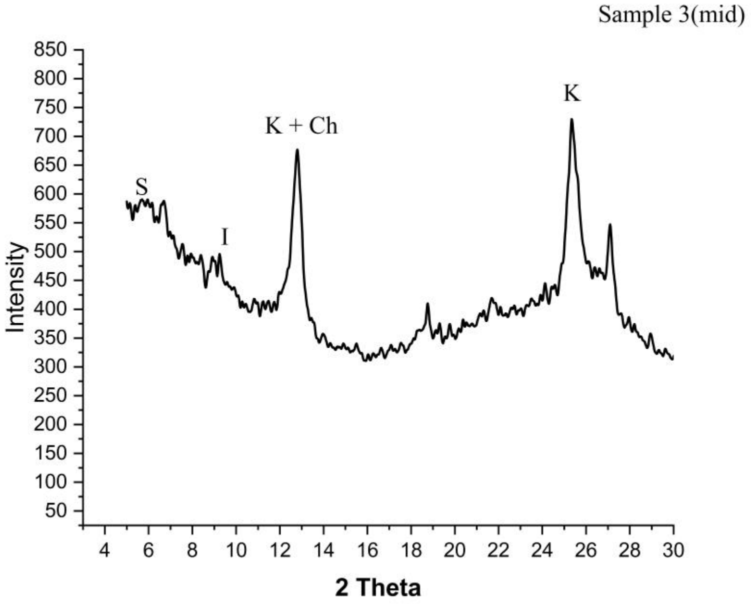
Figure 4.4 A, B, C, D, E and F showing percentage of clay minerals in sample 1, 2, 3, 4, 5, and 6 respectively.



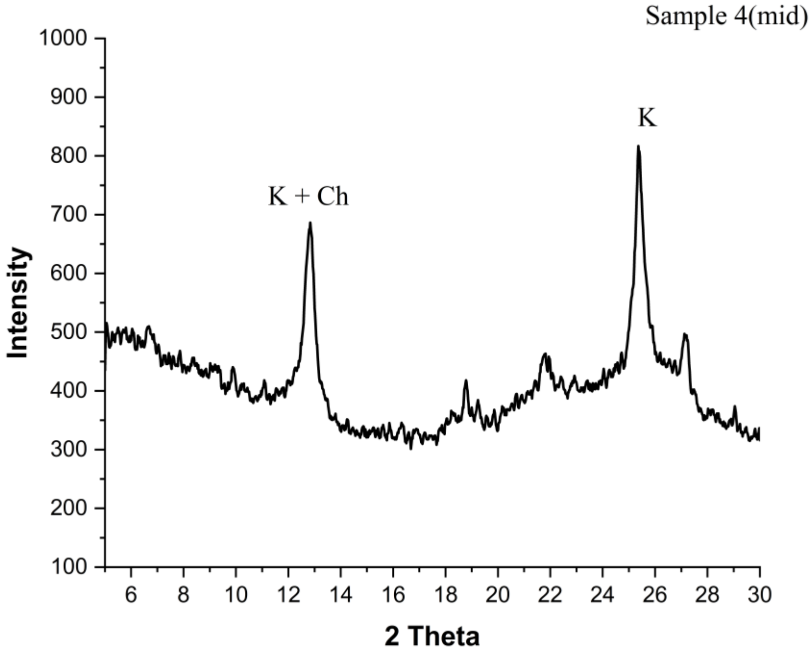
A: Location 1



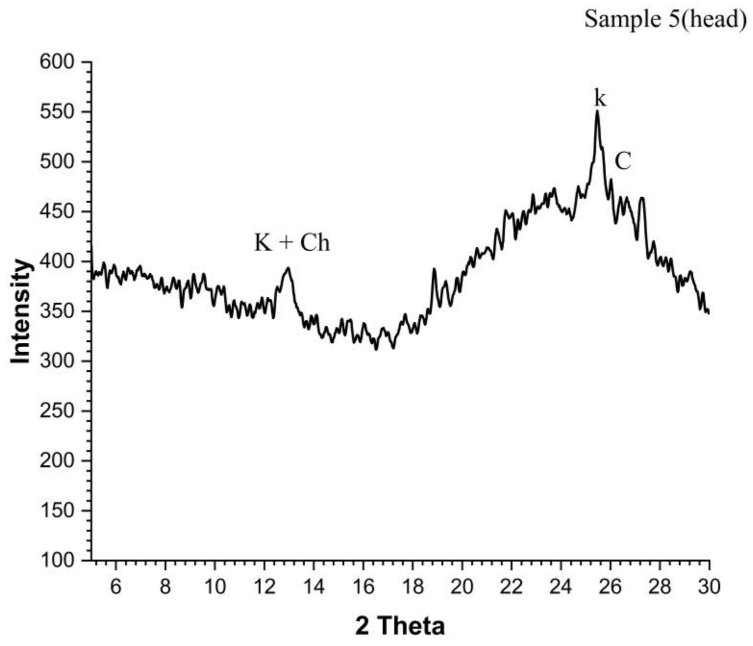
B: Location 2



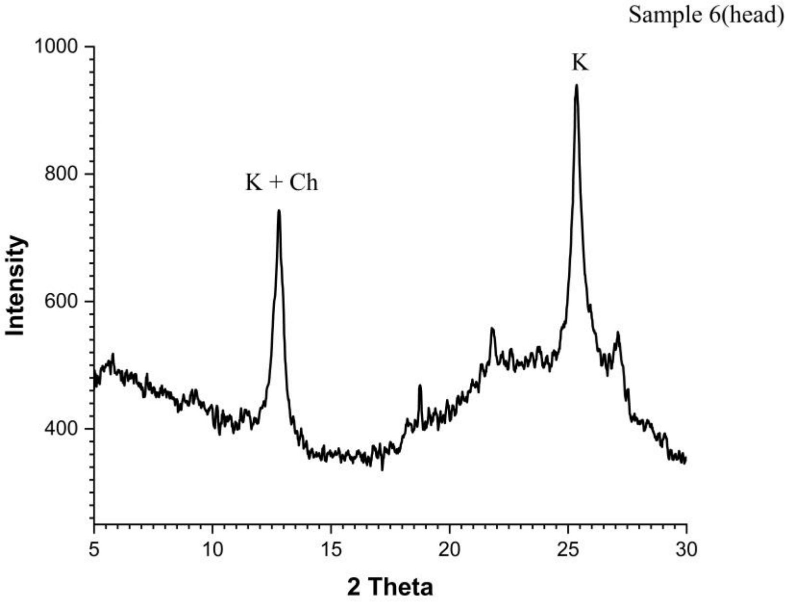
C: Location 3



D: Location 4



E: Location 5



F: Location 6

Figure 4.5 A, B, C, D, E and F showing XRD graphs of sample 1, 2, 3, 4, 5, and 6 respectively.

Discussion

The observed variations in sediment composition across the sampling locations within the Estuary provide valuable insights into the mineralogy textural compositions of sediments and hydrodynamics of environmental conditions within the Chapora Estuary.

The sediment component and grain size variations along the Estuary indicate change in energy gradient which reflects change in the process of sediment transport. Increase in sand fraction in the sediment of mouth region corresponds to high energy condition. Whereas increase in mud fraction in the sediment corresponds to low energy conditions which is true for middle Estuary region and head region. The dominance of sand and silt particles at the location could be attributed to the higher energy regime associated with tidal currents and wave action near the Estuary mouth **(Nasnolkar et al. 1996).** These processes facilitate the transportation and deposition of coarser sediment particles, resulting in the observed composition. The differences in clay and sand content between Sample 3 and Sample 4, despite similar silt percentages, are likely due to a combination of geological, hydrological, ecological, and anthropogenic factors that influence soil formation and composition **(Sm, 2018).** The head region is restricted by hence, the qualities outlined account for the presence of the smallest sediment particles located at the upstream end of the Estuary, where water circulation is at its weakest **(Romano et al. 2013).**

Total organic content is highest in sample 3 and sample 4 (middle Estuary) seems to be due to mud size particle. The grain size of sediments influences the distribution and concentration of TOC. Finer sediments, such as silts and clays, typically have higher surface areas and higher organic carbon contents due to their greater adsorption capacity. Coarser sediments, such as sands, generally have lower TOC content because they have less surface area available for organic matter adsorption. Clay minerals have a high affinity for organic matter. In estuarine environments like Chapora, clay minerals can adsorb organic matter, leading to higher TOC content in sediments. Organic matter can be derived from terrestrial sources (such as plant debris) or from aquatic sources (such as phytoplankton). The presence of clay minerals can influence the preservation and accumulation of organic matter in sediment.

It is observed that kaolinite is predominately present along the Estuary. The peak indicating the presence of kaolinite could be seen as primarily representing kaolinite rather than chlorite, as kaolinite is more expected to be dominant under the typical conditions of the study area (**Bukhari & Nayak, 1996**). The abundance of kaolinite in the Chapora Estuary reflects the ongoing chemical weathering of source rocks, specifically granites and granitic gneisses, in the region. The breakdown of feldspar minerals in these rocks due to water and acidic reactions leads to the formation of kaolinite **(Nasnodkar & Nayak, 2019).** Higher amount of Kaolinite and its decreasing trend from head to mouth region clearly reflects its derivation from catchment area and hinterland area which consists mainly of pre-Cambrian crystalline rock. Illite typically originated from the weathering of potassium-rich minerals, especially potassium feldspar **(Bejugam & Nayak, 2017).** Presence of Illite in location 1, 2 and 3 indicates that it has derived from marine origin. Smectite often originates from the weathering of volcanic ash and tuff **(Kessarkar et al. 2012).** Decreasing trend of smectite from sample 1, 2, 3 and complete absence of smectite indicates reflects its marine origin. Chlorite is a mineral commonly found in rocks, particularly in metamorphic rocks like schist and slate. The geology of the area surrounding the Chapora Estuary and catchment area could contain rocks rich in chlorite minerals. Presence of Chlorite only in sample 4 could be of weathering of metamorphic rocks like schist and slate rocks due to natural processes could release chlorite particles into the water, contributing to its presence.

CONCLUSION

The sediment composition within the Chapora Estuary varies across its spatial extents influenced by several factors including its proximity to the Estuary mouth, local hydrodynamics, the origin of sediments, and the specific conditions of where sediments settle.

The distribution of Total Organic Carbon (TOC) varies along the estuarine gradient. The mid-region samples of the Chapora Estuary display higher levels of organic matter compared to those from the mouth and head locations. Additionally, there are variations within each location, indicating differences in organic matter content even within the same area. The Total Organic Carbon (TOC) percentages offer valuable insights into the organic richness or decomposition levels present in the soil or sediment samples collected from these diverse locations.

Analysis of clay mineralogy using XRD graphs reveals the presence of smectite, illite, kaolinite, and chlorite, with kaolinite being the dominant mineral.

The presence of smectite and illite at the mouth of the Chapora Estuary is likely the result of a complex interplay of geological, hydrological, and sedimentological processes acting within the estuarine system and its surrounding watershed. It also indicates that it has come from marine origin.

The abundance of these clay minerals, particularly kaolinite is likely influenced by dominance of potassium-bearing minerals and kaolinite-rich sediments in the Chapora Estuary. This could be influenced by the weathering of local bedrock or input from surrounding catchment areas.

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