CHAPTER – 2

REVIEW OF LITERATURE

River processes form a major link in the geochemical cycle. Biogeochemical cycling refers to the biologically driven chemical transformations that underlie exchange of water and nutrients between the biosphere and atmosphere, biosphere and geosphere or biosphere and hydrosphere. The biogeochemical cycling of various elements along with the hydrological cycle (Figure 2.1a & b) plays a significant role in the functioning of the ecosystem (Ittekot, 2003). The World Rivers with 1.2 thousand cubic kilometers of water, account for only 0.0001% of total volume of water in the hydrosphere (Lvovich, 1973). It is estimated that river also carry annually 13.5 billion tonnes of sediments (Milliman and Meade, 1983) and 3.2 billion tonnes of dissolved solids (Meybeck, 2003). There are, of course, other agencies of material transport such as wind, precipitation, volcanic activities etc., but rivers with a total of 16.7 billion tonnes of various elements in dissolved and solid forms, account for nearly 90% of all global mass transport to the oceans (Garrels and Mackenzie, 1971).

2.1 WATER CHEMISTRY

The chemistry of natural waters has been studied for its variety of purposes in ecological, geochemical and hydrological research. Some of these are water quality; solute acquisition, sediment yields and transport; geochemical processes involved therein and geochemical cycling of elements in the environment. Surface water chemistry is a cumulative reflection of the common natural climatic features of a given region (the amount of atmospheric precipitates, temperature regime, and the type of vegetation) and certain conditions in its drainage system (rock composition, geomorphology, and the character of vegetation). Some of the major chemical processes in a water body are dissociation, hydrolysis, oxidation and reduction, while important physical processes are thawing and freezing, growth of roots, mineral expansion due to hydration, diurnal temperature change etc. (Blatt and Middleton, 1972; Krauskof, 1979).
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Figure 2.1a Movement of trace metals in the hydrological cycle (Salomons and Forstner 1984)

Figure 2.1b Major processes and interactions between the dissolved and solid metal species in the surface water (Salomons and Forstner 1984)
2.1.1 Major ion chemistry

Major ion chemistry of river water (e.g. \( \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+, \text{HCO}_3^-, \text{SO}_4^{2-}, \text{Cl}^- \) and Si) provides important insight into global biogeochemical cycles of ions in the continent-ocean-atmosphere system. A complete evaluation of river water quality encompasses all these parameters. It also reveals the nature of weathering and a variety of other natural and anthropogenic processes on a basin-wide scale. In addition, river waters are affected by active (water consumption) and passive (wastewater disposal) anthropogenic loading; and their chemical composition, including trace elements can serve as a good integral indicator of the effect of anthropogenic activity on the landscape.

Geochemical studies in surface waters have been important as an aid in solving general problems of pollution load in the environment. Dissolved and suspended matter of continental waters have been investigated to find the nature and composition of the matter transported by rivers to the ocean (Subramanian 1979), to estimate erosion rates and to determine geochemical balances as a whole (Table 2.1). The solid transport was generally considered as the major process of material supply to the ocean. The first well-documented review on river transport is made by Livingstone (1963) and it is mainly concerned with the major dissolved elements. Since then, a lot of important works have been attempted on the world’s biggest rivers; for example Amazon (Mortatti et al., 2003), Parana (Ballester et al., 2003), Mekong (Cenci and Martin, 2004, Minh et al., 1997), Chinese rivers: Xijiang (Xu et al., 2007), Wujiang and Yuanjiang (Han et al., 2004), and Brahmaputra (Hren et al., 2007). The studies, from Himalayan crystalline terrain (Blum et al., 1998, Jacobson et al., 2000), major rivers in Canada (Cameron et al., 1995; Yang et al., 1996), watersheds in tropical environments (Tardy et al., 1993; Viers et al., 2000, Dupre et al., 1996; Negrel and Lachassagne, 2000), rivers in northern latitudes (Gaillardet et al., 2003; Millot et al., 2003) and catchments in mountains of the western united states (Mast et al., 1990; Horton et al., 1999) have greatly added to our knowledge of river geochemistry.
Table 2.1: Hydrological Characteristics of River Basins in India

<table>
<thead>
<tr>
<th>River</th>
<th>Mean annual discharge ($10^8$ m$^3$/yr)</th>
<th>Drainage area ($10^5$Km$^2$)</th>
<th>Mean basin elevation (m)</th>
<th>TDS (ppm)</th>
<th>TSM (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ganges</td>
<td>493</td>
<td>970</td>
<td>3000</td>
<td>178</td>
<td>1631</td>
</tr>
<tr>
<td>Brahmaputra</td>
<td>510</td>
<td>690</td>
<td>5000</td>
<td>148</td>
<td>1170</td>
</tr>
<tr>
<td>Indus</td>
<td>207</td>
<td>1165</td>
<td>2500</td>
<td>124</td>
<td>450</td>
</tr>
<tr>
<td>Godavari</td>
<td>92</td>
<td>313</td>
<td>400</td>
<td>181</td>
<td>1845</td>
</tr>
<tr>
<td>Krishna</td>
<td>30</td>
<td>251</td>
<td>420</td>
<td>360</td>
<td>1158</td>
</tr>
<tr>
<td>Mahanadi</td>
<td>67</td>
<td>132</td>
<td>500</td>
<td>155</td>
<td>31</td>
</tr>
<tr>
<td>Narmada</td>
<td>41</td>
<td>90</td>
<td>760</td>
<td>322</td>
<td>130</td>
</tr>
<tr>
<td>Cauvery</td>
<td>21</td>
<td>87</td>
<td>630</td>
<td>172</td>
<td>30</td>
</tr>
<tr>
<td>Tapti</td>
<td>18</td>
<td>62</td>
<td>740</td>
<td>322</td>
<td>333</td>
</tr>
<tr>
<td>Chambal*</td>
<td>6.3</td>
<td>31</td>
<td>-</td>
<td>243</td>
<td>31</td>
</tr>
</tbody>
</table>

*Present study
TDS-Total dissolved solid
TSM-Total suspended matter
Source: (Subramanian, 1987)

**Major ion chemistry of Indian Rivers**

India has a number of large and small rivers, which drain into the ocean through estuaries and coastal waters. Thus the study of physical, biological and chemical aspects of rivers is essential. All major rivers of India originate from one of the three watersheds. (1) the Himalaya and Karakoram ranges, (2) Vindhya and Satpura ranges and (3) Western Ghats in Western India. On the basis of origin, the rivers of India can be divided into Himalayan and Peninsular Rivers. The main Himalayan river systems are the Ganges, the Indus and the Brahmaputra. The main Peninsular River systems include the Narmada, the Tapti, the Godavari, the Krishna, the Cauvery and the Mahanadi. In India, river chemistry has been studied to understand the process of weathering, denudation, hydrological and environmental characteristics of river basins (Das *et al.*, 2005; Singh *et al.*, 2005; Sarin *et al.* 1989; Subramanian 1979, 1983, 1987; Gupta and Subramanian, 1994), the influence of basin geology, climate and anthropogenic activity on riverine chemistry (Biksham and Subramanian 1988; Ramesh *et al.*, 1990) and the transport of materials from rivers to coastal oceans (Ramanathan *et al.*, 1994; Sarin and Krishnaswamy 1984; Sarin *et al.*, 1989; Subramanian 1983).
Himalayan Rivers

The Himalayan ecosystem is characterized by wide variety of lithology, topography, relief, climate, vegetation and tectonic activity. Neo-tectonic activity in this region causes landslides and earthquakes, which contribute enormous amount of sediments to the upstream courses of rivers. Although the mighty Himalayas cover only 4% of the land surface of the globe, they are responsible for approximately 25% of the total loads entering the world’s ocean (Raymo and Ruddiman, 1992). Of the total world sediment load, 70-80% is carried by Himalayan Rivers of south Asian region and those from large islands around the west pacific and Indian oceans. Within Asia, the rivers draining the Himalaya supply as much as 20% of the global sediment input (Subramanian et al., 1985; Ahmad et al., 1998). This neo-tectonic activity and landslides in Himalayan region attracts researcher’s to study more about changes in composition of Himalayan Rivers and their tributaries.

Recent measures of the dissolved chemical load and total sediment flux from a number of Himalayan rivers show that the Brahmaputra exhibits significantly higher rates of physical and chemical weathering than the other large Himalayan catchments (Sarin et al., 1984, 1989; Harris et al., 1998, Galy et al., 1999, 2001; Dalai et al., 2002; Singh et al., 2002, 2005). Spatially averaged chemical denudation rates in the Brahmaputra basin ≈105 tons km\(^{-2}\) yr\(^{-1}\); (Sarin et al., 1989) are 2-3 times greater than the next largest Himalayan River, the Ganges (Galy et al., 1999) and 5 times greater than the world average. These high rates of chemical weathering result in consumption of ≈ 6×10\(^5\) mol km\(^{-2}\)yr\(^{-1}\) CO\(_2\) due to the weathering of silicate minerals. Hren et al., (2007) have studied major ion chemistry, of the Yarlung-Brahmaputra River that lies in southern Tibetan plateau, the eastern Himalayan syntaxis which is one of the most tectonically active regions on the globe. They have also quantified chemical weathering, fluxes and CO\(_2\) consumption by silicate weathering (15.2×10\(^5\) mol km\(^{-2}\)yr\(^{-1}\)) which is twice the Brahmaputra average.

Ganges is another large river, which originates from Himalayas at Gangotri and drains into the Bay of Bengal. Many attempts have been made to understand the geology of the basin. On the global scale, the Ganga-Brahmaputra river system together ranks first in terms of sediment transport and fourth in terms of water discharge to the world.
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ocean (Milliman and Meade, 1983). The Ganga-Bhramaputra river system transports about 130 million tons of dissolved salts to the Bay of Bengal, which is nearly 3% of the global river flux to the oceans (Sarin et al., 1989).

It is well known that physical weathering is dominant in Asian rivers but it should also be noted that the solute yield (69 tonnes/km²/year) of the Indian subcontinent is twice that of global average (35 tonnes/km²/year) (Subramanian, 1983). The geochemical characteristics of Indus water is interpreted to be mostly influenced by the lithology of the basin and weathering of a combination of carbonate and silicate rocks of the provenance area. It was also deduced by Ahmed et al., (1998) that anthropogenic activities in this region do not appear to have much impact on water quality of the system. More recently, Karim et al., 2000) have carried out extensive studies on the headwaters of the Indus to determine the sources of cations to these rivers.

Studies on chemical and isotopic composition of rivers provide important information on the sources of major ions to them, chemical weathering rates of basins and fluxes of dissolved materials from continents to oceans. Knowledge of chemical weathering rates is essential for determination of CO₂ consumption rates and their impact on global climate. Researchers have proposed a hypothesis to explain the connection between Himalayan uplift and CO₂ consumption rate. In this tectonic-weathering-climate hypothesis, the uplift of Himalayas has been suggested as a major driver of Cenozoic cooling as it can promote rapid silicate weathering and thereby enhance CO₂ drawdown from the atmosphere (Dalai et al., 2002). Yamuna is again one of the main Himalayan river that originates near the Yamunotri glacier and also forms a main tributary to Ganges, meets later at Allahabad. Dalai et al., (2002) have extensively studied major ion composition, their seasonal variation, chemical weathering, its temperature dependence and CO₂ consumption rate of the river Yamuna and its major tributaries.

Peninsular Rivers

Various studies have been carried out in smaller river basins to assess their water quality and their physical and chemical weathering patterns, like Godavari (Bhiksham and Subramanian, 1988), Krishna (Ramesh and Subramanian, 1988; Ramesh et al.,
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1989), Cauvery (Ramanathan et al., 1994), Mahanadi (Chakrapani and Subramanian, 1990) and Gomti (Gupta and Subramanian, 1994) to offer better understanding of various chemical and physical processes in the river system.

Godavari is one of the largest basins among non-Himalayan rivers of India. The nature of solute transport and their behavior in the Godavari basin has been extensively studied by collecting samples of river water and rain water. The fluxes of various elements of the basin have been calculated (Biksham and Subramanian, 1988). Godavari basin annually transports $16.8 \times 10^6$ tons of solute load representing 6% of chemical load from the Indian sub-continent.

Gomti River, a tributary of Ganges is found to have small or no influence on chemical loads of Ganges, perhaps because of its low discharge to the river (1.57%). But the river water shows a marked influence of anthropogenic loadings for a considerable distance near Lucknow (Gupta and Subramanian, 1994). Source apportionment, R mode factor analysis and interpretation of a few geochemical factors controlling the chemical nature of water and sediments of the river have also been reported elsewhere (Gupta and Subramanian, 1998).

Singh et al., (2005) have extensively studied the seasonal variation in Damodar basin and observed minimum concentration of most of the ions in post-monsoon and maximum concentration in pre-monsoon seasons, reflecting the concentrating effects due to elevated temperature and increased evaporation during the low water level period of the pre-monsoon season.

The study of Krishna basin and Western Ghat Rivers of Deccan traps brings to light the sources contributing to major ions, enhanced chemical and silicate weathering rates of west flowing rivers and interdependence of silicate weathering rates on the CO$_2$ consumption rate (Das et al., 2005). Weathering rates of west flowing rivers are $\approx 4$ times higher ($\approx 15$ t km$^{-2}$y$^{-1}$) than the east flowing rivers. This difference is due to the correspondingly higher rainfall and run-off in the western region and thus, reemphasizes the dominant role of run-off in regulating weathering rates.
2.1.2 **Heavy metals in river water**

Industrialisation, urbanization, use of fertilizers and pesticides in agriculture have resulted in increased contamination of the environment. Heavy metal pollution is a serious and widespread environmental problem due to persistent and non-biodegradable properties of these contaminants (Tokalioglu *et al*., 2000; Yuan *et al*., 2004). Metallic pollution of the environment from anthropogenic sources constitutes major health hazards of the century. This has led to global concern over long term as well as immediately imperceptible effects of heavy metals. In the beginning, trace metal analysis in continental waters were carried out mainly in areas where local anomalies from ore mineralization were expected. Due to low solubility of trace metals, metal-hydroxides of transition elements are precipitated from river water, even if a small change in composition of solution occurs. This results in an insignificant amount of heavy metals in natural waters. During the recent past, the amount of heavy metals released to the aquatic environment as a result of human activities has surpassed the amount released by natural weathering (Villaescusa *et al*., 2000). Pollution from chemicals has become all pervasive and now there are no parts of globe that have been spared.

Metal pollution in the river Godavari in India, due to discharges of liquid wastes from a paper mill, has been studied for a period of two years. At the discharge point and 1 km from the point of discharge, iron, manganese, and zinc were recorded in high concentrations, whereas cadmium and chromium were observed in low concentrations. Remarkable difference in the metal concentration has been observed due to the input of waste from the paper mill. No metal was in detectable concentration in water before the river receives the effluents. A considerable drop in pH values and an appreciable increase in organic matter, hardness, and calcium levels were noticed after entry of wastes (Sudhakar *et al*. 1991).

The Yamuna River is one of the heavily polluted rivers in India. The pollutants flowing into the river are contributed from the wastes of cities situated along its bank. The river originates from the snowclad Himalayan Mountains, flowing through the plains of Haryana, Delhi, and Uttar Pradesh provinces; it meets the Ganges River at Allahabad. The Yamuna River passes through Delhi, the capital of India, where it
receives large volumes of domestic and industrial effluents. The quality of water further gets deteriorated at Mathura, a city at a distance of 135 km from Delhi as well as at Agra, the city of Taj Mahal. Both these cities indiscriminately pour their domestic and industrial wastes, either partially treated or altogether untreated, into the river. High concentration of some heavy metals like Fe, Cd, Cr, Cu, Pb, and Zn were found at some locations like Allahabad, Delhi, Agra and Mathura in water samples of Yamuna River. The data showed that there was considerable variation in the concentration of elements from one sampling station to the other which may be due to the variation in the quality of industrial and sewage wastes being added to the river (Ajmal et al., 1985).

One of the consequences of the escalation in industrial activity is growing accumulation of recalcitrant elements in natural ecosystems. River Gomti in Lucknow urban area is a significant tributary of river Ganga. The exponential growth of Lucknow on both sides of Gomti River has led to severe pollution. The quality of water and sediment in the river is seriously affected by pollutants, which enter through drains that brings domestic as well as industrial effluents to the river. These industrial and domestic waste waters, besides other pollutants also contain high concentration of heavy metals. Gaur et al., (2005) found markable seasonal difference in the concentration of heavy metals. They have invariably found high concentrations in rainy seasons probably due to run-off coming from contaminated areas.

2.2 SEDIMENT CHEMISTRY
Sediments are the product of physical and chemical weathering on the continents (Holland, 1978). They begin their life cycle between rocks after weathering processes, which is promoted by water currents via chemical changes and provides physical transport (Golterman, 1984). During transportation, primary rock material is converted to fine sediments and carried away to the estuary and then to ocean. River input of water and sediments to the ocean exhibits seasonal as well as spatial variability, which is contributed by geological, climatological, and anthropogenic factors. Seasonality associated with rising and falling stages of the river water re-suspends and stores large quantities of fine-grained sediments. Catastrophic events, e.g., tropical storms, may increase the quantity of sediment transported by small
rivers, by one to several order of magnitude in a short period of time (Milliman, 1991).

2.2.1 Physical and Chemical Characteristics of Sediments
The physical properties (i.e. grain size) of sediments can affect the concentration of trace metals in aquatic systems (Ip. et al., 2007). The distribution of grain size is controlled by the physical transportation of sediment including sediment aggregation and deposition, gravitational circulation, tidal pumping, and tidal trapping (Grabemann et al., 1997; Mitchell et al., 1998; Wai et al., 2004). Current velocity, salinity and suspended particulate matter in water column influence sediment aggregation and deposition. The grain size of sediments is a reflection of the hydrodynamic processes and the deposition conditions in the region. In general coarse-grained sediments are concentrated at the upstream region and as the water flows to the downstream, rivers carry the finer particles away and get deposited. Finer particles tend to accumulate in places where waves and currents are absent or weak.

Metals are not homogeneously distributed over various sediment grain size fractions; they are mainly associated with finer sediments (Villaescusa-Celaya et al., 2000). Many studies have reported the physical separation in a wide variety of grain size fractions to reduce this effect. The recommendations over a wide range of sizes including the fractions <2, <16, <20, <40, <63, <125, <200 and <500 μm (Jenne et al., 1980; Groot et al., 1982 and Horowtz and Erick, 1987) To overcome differences in composition due to differences in the grain fraction, a specific grain size has to be used. Many authors (de Groot et al., 1982; Soares 1999; Villaescussa et al., 2000 and Casas, 2003) have suggested the grain size <63 μm as it is the grain size that seems to have the highest metal concentration. Some of the reasons given for the use of this size include (1) metals tend to accumulate in particle of silt-clay size; (2) this fraction is transported entirely by suspension; (3) sieving does not affect the metal concentration; (4) it is possible to compare results among samples with different textural characteristics.

Most data have indicated enrichment in metal concentration with decreasing particle size (Horowtz, 1991; Soares et al., 1999; Baptista et al., 2000 and Southerland, 2003).
According to Horowitz (1991), this correlation results from combination of physical (e.g. surface area) and chemical (e.g. geochemical substrate) factors. However, the highest metal concentration is not always associated with finest particles (Whitney, 1975; Tessier and Campbell, 1988; Martincic \textit{et al.}, 1990; Vaithiyanathan \textit{et al.}, 1993 and Droppo and Jaskot, 1995).

\subsection*{2.2.2 Biogeochemical Cycle of Nutrients and Heavy Metals}

Sediments have been reported to play an important role in the assessment of metal contamination and nutrients in natural water (Jha \textit{et al.}, 1990; Goncalves \textit{et al.}, 1992, 1994; Huang \textit{et al.}, 1994; Borovec, 1996 and Wardas \textit{et al.}, 1996). They are usually considered as a sink for trace metals, but when environmental condition changes, they can act as sources as well (Gabler, 1997; Izquierdo \textit{et al.}, 1997; Patrick and Verloo, 1998; Wen and Allen, 1999; Bachmann \textit{et al.}, 2001; Zounis \textit{et al.}, 2001; Morillo \textit{et al.}, 2002 and Martinez-Villegas \textit{et al.}, 2004). Sediments also play a role of reservoir of nutrients, for both aquatic organisms and planktonic. There are several sources of nutrients and trace metals in the environment, both natural and man-made. They may be soil parent material (rocks), commercial fertilizers, liming materials, sewage sludge, animal wastes, coal combustion residues, metal smelting industries, auto-emissions and others (Datta, 1996). From all these sources, nutrients and heavy metals enter into the river channel primarily by surface run-off and atmospheric fall-out.

Sediments help in maintaining the water quality by removing contaminants from the water column. However, the subsequent release of both nutrients and contaminants from the sediments can keep concentration of contaminants in water elevated long after the external source has been removed. For example, in some cases high quantities of trace elements have been found to re-enter water column via sediment-water exchange (Croot and Hunter, 2000). Coung \textit{et al.}, (2006) have evaluated the potential mobility and the possible transfer of heavy metals from sediments to the surrounding environment.

Contaminated sediments now appear to be the main source of toxins in many bays, lakes and rivers. Because of their potential adverse impact, the long periods of time
associated with natural assimilation of many in-place contaminants, and the high cost of mitigation, sediments have become a focus of concern for many research and regulatory programs (Thomas, 1994).

Studies on nutrient and heavy metals in India
Direct measurements of nutrients C, N and P in suspended and dissolved loads are rather limited in Indian rivers (Subramanian et al., 1991; Ittekot et al., 1985). However, nature and flux of organic matter, carbon and phosphorus in Indian rivers have been studied by Gupta (1996), Ramesh et al., (1995), Subramanian et al., (1991,1984), Ittekot et al., (1986) and Vaithiyanathan et al. (1989). Datta et al. (1999) have studied spatial distribution and biogeochemical processing of the C, N and P in the Ganges-Brahmaputra-Meghna (GBM) river system. They found that variations in Total Phosphorus (TP) and Total Nitrogen (TN) in bulk and 63 µm fraction of the bed sediments are statistically insignificant, but Total Carbon (TC) content varies significantly among the three basins. Low values of C/N ratio indicates complete degradation of organic matter and/or enrichment of inorganic nitrogen in the sediments. Ramesh et al., (1995) estimated that the transport of dissolved and particulate organic carbon by the Himalayan rivers is about 7.6 and 9 million tons per year and concentration of particulate organic and inorganic phosphorus is 0.2 and 1.5 million tons per year respectively.

Heavy metals as Fe, Mn, Pb, Zn, Cu, Ni, Cr, Cd and Hg have been studied in various rivers in India viz., Ganga (Subramanian et al., 1988), Krishna (Ramesh and Subramanian, 1988), Godavari (Biksham and Subramanian, 1988) and Cauvery (Subramanian et al., 1989). Fe (3.4%) and Mn (1310 ppm) levels are lower in Cauvery sediment than other tropical rivers such as Krishna [Fe (4.2%) and Mn (732 ppm)] (Ramesh and Subramanian, 1988). Organic carbon has direct relation with heavy metal concentration as they adsorb metal and form organic metal complexes in river waters. In Godavary, Krishna and Cauvery most trace metals show enrichment by a factor of 1-5 times due to anthropogenic activities (Subramanian et al., 1989). In all the rivers, concentration of heavy metals shows the influence of residential and industrial settlements in the region.
Core sediments were analysed to study the behavior and accumulation of heavy metals in the recent past. It was found that suspended matter of Cauvery river was depleted in Al and Si, and rich in Ca, Mn, Cr, Ni, Cu, Zn and Sr as compared to the world's average. Surface sediments show a homogeneous composition of heavy metals along the river course but their concentration is lower in suspended matter. Sediment flux of the Bhramaputra is higher than that of Cauvery River. The large and synchronous fluctuations in the temporal distribution of heavy metal concentration and mass accumulation rate have been attributed to the cyclic climatic changes over the Indian sub-continent. Urbanization and industrial activities could be assumed to cause the enrichment of transition elements in the uppermost core layers. (Dekov et al., 1998)

2.2.3 Pollution Load

There are various indicators and factors used to assess the extent of sediment contamination as Enrichment Factor (EF), Geo-accumulation index (I-geo) and Pollution Load Index (PLI). EF is a good tool to differentiate between natural and anthropogenic sources of metals (Morillo et al., 2004; Selvaraj et al., 2004; Adamo et al., 2005; Vald'es et al., 2005). According to this technique metal concentrations were normalized to the textural characteristic of sediments. The widely used element to normalize the metals in sediments is Al since it represents the aluminosilicates, the predominant contents of coastal sediments. EF can be used to determine the degree of sedimentation as well (Lee et al., 1998; Huang and Lin, 2003; Woitke et al., 2003). I-geo is also associated with the qualitative scale of pollution intensity, samples may be classified as unpolluted (I-geo≤ 0), unpolluted to moderately polluted (0 ≤ I-geo ≤1), moderately polluted (1≤ I-geo ≤ 2), moderate to strongly polluted (2≤ I-geo≤ 3), strongly polluted (3≤ I-geo ≤4), strongly to extremely polluted (4 ≤ I-geo ≤5), and extremely polluted (I-geo ≥ 5) (Farkas et al. 2007).

To quantify the magnitude of pollution by different metals, the contamination factor (CF) and Pollution Load Index (PLI) may be calculated to find out the cumulative pollution effect at different stations by different metals (El-Sammak et al., 1999).
2.2.4 Sequential Chemical extraction for metals

Sediment assessment needs to be done in separate analytical tracks, chemical and ecotoxicological (used as biological tests to obtain independent information about acute or chronic toxicity) (Simeonov, 2007). As the partitioning pattern of traces is of critical importance to the potential toxicity and mobility of contaminant metals (Macklin et al., 1989), knowledge on metal speciation in the sediments may be of more importance for hazard assessment studies than the total concentrations of traces (Barona et al., 1999; Filgueiras et al., 2004).

However, direct determination of specific chemical forms is generally impractical due to the various binding phases of the metals and their structural properties. Sequential extraction or metal fractionation techniques, which define the metal activity by their analytical schemes, provide more relevant information (Gozalez et al., 2000; Knight, 1998; Allen et al., 1996; Tessier et al., 1979). Sequential extraction has also been reported as the best approach to understand geochemical association of elements as it gives a direct estimate of mobility and potential bioavailability in the aquatic system (Irabren et al., 1999; Krishnamurty et al., 1995; Legret, 1993 and Forstner et al., 1990). Fractionation studies are also useful to distinguish metals with a lithogenic origin from those of anthropogenic origin.

The literature contains numerous studies in which sequential analysis has been applied to both soils and sediments (Kiratli et al., 1996; Cambier, 1997; Maiz et al., 2000; and Yu et al., 2004). One of the first sequential extraction schemes proposed was a five-step procedure published by Tessier et al., (1979). The method provides an operational means to quantify the relationship between metal partitioning in different geochemical phases and metal concentration in sediment (Tessier et al., 1979; and Dollar et al., 2001 and Todorovic et al., 2001). Several authors have modified method for extraction by varying the soil extractant ratio (Rauret et al., 1988), the extractant concentration (Gomez-Ariza et al., 1991) and the extraction time (Maher, 1984). Other authors, namely Meguellati et al., (1983) and Qiang et al., (1994), have changed the extractant order to leach the metal bound to the organic phase before dissolving the carbonate and iron oxide phase. Leleyter and Probst (1999) developed a
seven-step analytical procedure, which estimates specifically water-soluble and separates the Fe-Mn oxide fraction into Mn-Oxide and Fe-oxide fractions.

Despite the pitfall and operational character of the sequential techniques pointed out by many researchers e.g. lack of selectivity and efficiency in each step of the procedure, (Tipping et al., 1985; Rapin et al., 1986; Martin et al., 1987; Nirel and Morel, 1990 and Wallman et al., 1993), they still remain as one of the most widely used approaches to distinguish between different geochemical association of many trace metals and to gain a better insight of geochemical processes occurring in sediments.

Zhang et al., (1988) in their fractionation studies conducted in the sediments of Yellow River, found the residual fraction to be the predominant phase among other phases especially, for Cr, Fe, Zn and Ni. They attribute this observation to the dominance of physical weathering, high erosion rate along the river valley and high sedimentation rate. Ellsokkrary and Muller (1990) assessed and fractionated the sediment of river Nile and analysed the metals Ni, Cd, Cr and Pb. They observed that the exchangeable and carbonate bound C was the most geochemically significant fraction in the highly polluted sediment while Fe-Mn oxide fraction were the most dominant fraction in the highly polluted sediment. Steinberg and Dastmalian (1993) reported an increase in labile fractions of Al, Fe and Pb in the sediment of Black Forest Lake Wildesee in German. Adamo et al., (1996) reported that most of the Cu (on average 75%) was associated with non-residual soil forms while Ni was mostly associated with inorganic residual forms of sulphide and oxide nature in soils from Sudbary mining and smelting region of Canada.

Studies on fractionation of metals in India
Studies on the fractionation of Fe, Mn, Ni, Cu, Cr, Zn, Pb and Co in the surface sediments of Ganges have been carried out by Purushothaman and Chakrapani (2006). They have also calculated geo-accumulation factor (GAI) and Metal Enrichment Factor (MEF) for all the metals. The GAI values range between 4 to 5 and MEF values exceed 20 for nearly all downstream locations. This indicates the addition of metals through urban and industrial effluents, as compared to the low metal concentrations with less GAI and MEF in the pristine river sediments from the rivers.
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in Himalayas. Yamuna, the largest tributary of Ganges river system originates from Himalayas and passes through varied geological terrain. Chakrapani and Subramanian (1996) studied that in Yamuna, metals are mostly associated with residual fractions in the sediments followed by organics, Fe-Mn oxides, exchangeable and carbonates. In another study of Mahanadi river basin, Chakrapani and Subramanian (1993) have shown that Fe, Zn, Cu and Pb in suspended and surface sediments are associated with residual fraction and Mn with the exchangeable fraction. Panda and Sahu (1999) have also reported high trace metal concentrations in the residual fraction of the sediments of Bahuda estuary. The metal fractionation studies have also been carried out in the rivers and estuarine sediments by Ramesh and Subramanian (1988); Biksham and Subramanian (1988); Das et al., (1995); Datta and Subramanian (1997).

Elevated concentrations of trace metals in sediments pose toxicological risks to biota and may impair water quality (Baird and Cann, 2005). Under oxidizing conditions, trace metals bind to Organic Matter (OM), clays, and Fe plus Mn-oxides (Turner et al., 2004). These phases are frequently intimately associated with one another (Perret et al., 2000; Taillefert et al., 2002), making it difficult to separate them by physical and chemical techniques. Decomposition of OM and reductive dissolution of Fe and Mn-oxides, which tend to be highest near the sediment water interface (Canavan et al., 2006; Douglas and Adeney, 2000), may lead to the release of trace metals to the pore waters. The pollution of terrestrial soil and sediments in water bodies by pesticides and metals and its effects on ecosystems is a matter of great concern (Landrum et al., 1984; Ure et al., 1995). The binding of environmental pollutants by natural substrates like organic acids is of primary importance in understanding the behavior and fate in aquatic ecosystems (Senesi and Miano, 1995; Kamiya and Kameyama, 1998).

2.3 ORGANIC MATTER

2.3.1 Classification of Organic matter

Classification of naturally occurring organic matter is difficult. However, they are normally classified into non-humic and humic substances. Non-humic substances include carbohydrates, proteins, peptides, amino acids, fats, waxes and low molecular weight organic acids. These substances have well defined physical and chemical
properties, such as definite melting point, refractive index, elemental composition, and IR spectral pattern. Therefore, these substances are identifiable. They are rather easily degraded by micro-organisms and have usually limited life spans in the environment.

On the other hand, humic substances do not exhibit uniformity in their physical and chemical properties, normally associated with well defined organic compounds. Humic substances, a series of relatively high-molecular-weight, brown to black coloured substances formed by secondary synthesis reactions. The term is used as a generic name to describe coloured material or its fractions obtained on the basis of solubility characteristics (www.ar.wroc.pl/ weber/kwasy2.html).

**Humic acids** - the fraction of humic substances that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values. They can be extracted from soil by various reagents, which is insoluble in dilute acid. Humic acids are the major extractable components of soil humic substances. They are dark brown to black in colour.

**Fulvic acids** - the fraction of humic substances that is soluble in water under all pH conditions. They remain in solution after removal of humic acid by acidification. Fulvic acids are light yellow to yellow-brown in color.

**Humin** - the fraction of humic substances that is not soluble in water at any pH value and in Alkali. Humins are black in colour (Figure 2.2)

Humic substances are formed by the organic breakdown of plant materials and the decay of dead organisms, this process of degradation and mineralisation to produce humic substances is termed humification. Humification has also been defined as being “the prolonged stabilization of organic substances against biodegradation”. Traditionally it was assumed that humic substances in river and lake waters were same as those in soils, and that the major source of humic substances was the adjacent soil, which was leached or eroded directly into streams during rainfall. Recent studies have however shown that humic substances are different in soil, sediments and water. Humic substances in streams have different characteristics to humic substances of the
soils or the ocean, and marine humic substances have definite aromatic character. Despite intensive research, the reactions involved in the formation of humic substances remain largely unknown.

<table>
<thead>
<tr>
<th>Chemical properties of humic substances. (Stevenson 1982)</th>
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**2.3.2 Composition and Structure of Humic Substances**

Humic substances arise from transformation (through humification) of biomolecules, or build-up from interactions between small organic compounds released during metabolic processing of natural macromolecules. Various structures have been proposed based on pyrolytic degradation products, NMR, and computer modeling techniques (Figure 2.3 a,b)

![Model structure of fulvic acid by Buffle](image)
The importance of the knowledge of HS in aquatic ecosystems consists of the great complexing ability of HAs and FAs, which is attributed to the different oxygen containing functional groups, such as carboxylic, phenolic and carbonyl groups. HS form both soluble and insoluble complexes with metal ions, FAs solubilise metal ions and affect their transport, while HAs act as a sink for multicharged cations. Therefore, metal-HS interactions affect the bioavailability of metal ions in the aquatic ecosystem. The order of decreasing ability of metal ions to chelating is as follows: $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$.

The functional groups present in humic compounds, responsible for their complex forming ability, their reactivity and solubility are carboxyls, alcohols, ketonic, quinoid compounds and phenols (Petronio et al., 1993). Hence it is of immense importance to characterize Humic Substances using different techniques.

### 2.3.3 Characterisation of Humic Substances

The most common techniques to obtain structural and compositional information on Humic Substances include Elemental Analysis, UV-Visible, Spectrofluorescence, IR, $^1$H NMR and $^{13}$C NMR spectrometry and degradation methods (Belzile et al., 1997).

**Elemental Composition**

Elemental composition, mainly hydrogen, carbon, oxygen and nitrogen contents of Humic Substances, can establish the nature and origin of these compounds. This data
is normally used in terms of atomic ratios (H/C, O/C and C/N), which give information on different types of Humic Substances, structural changes of humates in soils and sediments and structural formulae for humates. Various studies have been taken up for establishing elemental composition of Humic and Fulvic acids from different sources like marine and coastal sediments (Sensi, 1994), surface marine sediments from an estuary (Moreda-Pineiro et al., 2006), compost, soil and amended soils (Campitelli et al., 2006), core sediments of the Baltic Sea (Pempkowiak et al., 1998), fractionated peat samples (Li et al., 2004) etc.

According to Agnelli et al. (2000), the H/C ratio is a measure of aromaticity: highly aromatic macromolecules have H/C<1. The O/C ratios are the index for the abundance of oxygen containing functional groups while C/N ratio indicates biological activity (Kononova, 1966). They have found that the C/N ratio decreases from fine earth to rock fragments. The lower C/N ratios of rock fragments suggest a higher degree of N incorporation in the humic structure, indicative of consistent biological activity. Lowest H/C values were calculated for rock fragments washing which suggests high degree of aromatisation. Wilson et al., (1999) also found that N/C ratio increases with increase in molecular weights, suggesting that N-containing compounds are concentrated in the higher molecular fractions and are less degradable.

Structural, functional and chemical properties of marine and coastal sedimentary humic acids were studied by Sensi (1994) and he concluded that humic acids from sub-surface marine sediments are less aliphatic in nature, low in nitrogen content, rich in free radicals and highly conjugated fluorophores. A combination of organic free radical concentration, C/N ratio, H% and C/H ratio may be a simple and reliable source indicator for distinguishing marine-derived (algal sources) from terrestrially-derived (vascular plant sources) humic acids. Positive correlation between C/H and C/N ratios of humic acids support the presence of lignin-derived components in the coastal river sediment, which indicates high contribution from terrestrial sources.

In another similar study Moreda-Pineiro et al., (2006) characterized surface marine sediments from Ria de Arousa estuary for humic and fulvic acids. After applying unsupervised chemometric techniques such as principal cluster analysis and cluster analysis, it was inferred that organic matter in surface sediments collected at the right
mouth of the estuary is mainly derived from marine sources (indicating higher values of H/C), while organic matter in sediments from inner-left part of the estuary derived mainly from terrestrial organic matter.

Campitelli *et al.* (2006) have compared chemical and physico-chemical characteristics of humic acids extracted from three different sources i.e. compost, soil and amended soils and found H/C ratio to be higher for composted soils, indicating high degree of saturation.

Pempkowiak *et al.*, (1998) isolated humic and fulvic acids from the core sediments of the Baltic Sea. They found that humic substances extracted from the core sediments deposited some 200 years ago, exhibit properties clearly differing from those in freshly deposited sediments, which is further substantiated by results of elemental composition. They found that contents of Nitrogen and Hydrogen both decrease by depth, thereby increasing C/N and C/H ratios.

**Spectral Studies**

Recent advances in molecular spectroscopy have helped derive valuable information on structural aspects of humic substances isolated from diverse sources. UV-Visible, Fluorescence, IR, NMR and ESR spectra have been widely used for the said purpose.

UV-Visible spectra of humic acids are featureless. However, it had been a general observation that different humic acid fractions have distinguishable colour differences. Swift *et al.*, (1970) had reported that the optical extinction coefficients of lower molecular weight humic acid fractions are greater than their counterparts. A review by Schnitzer and Khan (1972) on the UV-Visible spectral studies of humic substances indicate that the light absorption of humic substances appears to enhance with an increase in: (i) the degree of condensation of the aromatic rings they contain, (ii) the ratio of carbon in aromatic nuclei to carbon in aliphatic or alicyclic side chains, (iii) the total carbon content, and (iv) the molecular weight.

Although the visible absorption spectra does not provide much insight into chemical structure of humic acid molecules, the ratio of optical densities of humic acid and fulvic acid solutions at 465 and 665 nm is often used for characterization of humic
substances. This ratio often referred to as \( E_4/E_6 \), is independent of concentration of humic materials, but varies for humic acid extracted from different sources (Kononova, 1966). The \( E_4/E_6 \) ratios are also termed as quotient values denoted by \( Q_{4/6} \). According to Kononova (1966), a low ratio is indicative of relatively high degree of condensation of aromatic humic substances (Agnelli et al., 2000 and Chen et al., 1977).

\( A_2/A_4 \) ratio, absorbances at 270 and 407 nm and \( E_4/E_6 \) ratio, absorbances at 465 and 665 nm were used to distinguish between terrestrial and marine origin of humic and fulvic acids in Ria de Arousa surface marine sediments (Moreda-Pineiro et al., 2006).

UV spectroscopy was used as a tool for monitoring humification and proposing an index of the maturity of compost. A new index was obtained by UV spectroscopy using the deconvolution of an unknown spectrum of compost with three reference spectra (Domeizel et al., 2004). This index was compared to maturity indices usually used, such as total extraction of humic substances (rate of extraction), IP (index of polymerization) or the humic and fulvic acid ratio. UV spectroscopy makes it possible to approach the global chemical structure of molecules as a whole, in particular their aromatic structure.

**Fourier Transform Infra red Spectroscopy (FTIR)**

IR Spectra of Humic Substances show bands at the following frequencies: 3400 cm\(^{-1}\) (hydrogen bonded OH), 2900 cm\(^{-1}\) (aliphatic C-H stretch), 1720 cm\(^{-1}\) C=O of COOH, C=O stretch of Ketonic C=O), 1630 cm\(^{-1}\) (aromatic C=C, hydrogen bonded C-O of carbonyl or quinone, COO-I), 1450 cm\(^{-1}\) (aliphatic C-H), 1400 cm\(^{-1}\) (COO-I, aliphatic C-H), 1200 cm\(^{-1}\) (C-O strech of OH- deformation of COOH) and 1050 cm\(^{-1}\) (Si-O of silicate impurities) (Senesi and Sipos, 1985, Shin et al., 1999). The bands are broad, most likely because of extensive overlapping of individual absorptions. Although IR spectra of humic materials tell little about the chemical structure of humic nuclei, they provide worthwhile information on the distribution of functional groups. The IR spectra reflects the preponderance of oxygen-containing functional groups, that is -COOH, -OH and >C=O in humic materials. (Aiken et al., 1985, Stevenson, 1994, Baglieri et al., 2006, Campitelli et al., 2006, Agnelli et al., 2000)
Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) spectroscopy has been widely used for the study of humic substances (Hatcher et al., 2001), and although specific compound identification is not possible with this technique, information can be provided on the distribution of various functional groups present. Peaks in the NMR spectrum can usually be assigned to specific functional groups in complex materials such as humic substances. Despite this, NMR techniques have been valuable in advancing the understanding of humic substances. For example, $^1$H and $^{13}$C NMR has been used to examine the aromaticity / aliphatic nature of HS, leading to the discovery that they are primarily aliphatic and not predominantly aromatic in nature, as once thought. (Malcolm, 1990). NMR studies have also found that humic acids are composed of partially degraded plant constituent components, (Wershaw et al., 1990), that fulvic acid is a separate chemical entity to humic acid and that perhaps phenolic carbons are minor rather than major components of HS.

Proton Nuclear Magnetic Resonance (1H-NMR)

$^1$H NMR spectroscopy has become a standard method in many chemistry labs. A wide range of structural questions can be answered by its application, since there are clear-cut relationships between the data content in $^1$H NMR spectra and the arrangement of protons in the molecules under investigation.

Proton NMR spectroscopy is used for estimating the relative abundance of various humic substance functional groups. Spectra of humic and fulvic acids dissolved in alkaline or neutral solution provide information that is useful for characterizing their aromatic and aliphatic components. $^1$H-NMR spectra of humic substances dissolved in CDCl$_3$, CCl$_4$, deuterated water (D$_2$O), deuterated dimethyl sulfoxide (DMSO-d$_6$), and aqueous solutions of NaOD showed resonance signals at $\delta = 1.0-1.7$ ppm (aliphatic protons ), $\delta = 1.7-2.5$ ppm (protons on carbons adjacent functional groups such as carbonyls, aromatic and double bonds), $\delta = 4.0-4.4$ ppm (probably indicating some lactone structure) and $\delta = 7.3-7.9$ (aromatic protons).(Oka et al., 1969, Stuerman and Payne, 1976). Some of the authors have divided these proton resonances into the following categories: 0.5-2 ppm (methyl and methylene protons), 2-5 ppm (methyl and methylene protons linked to heteroatoms) and 5-10 ppm (aromatic protons).
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(Garcia et al., 1994). Francioso et al., 2003 and Baglieri et al., 2006 have allocated the region of the spectrum 0.5-3 ppm to the H forms linked to aliphatic groups, the region 3-4.2 ppm to the H forms linked to carbohydrate structures and the region 6-8 ppm to the H forms linked to aromatic molecules. Signals of < 0.5 ppm are attributable to organic Si components such as the compounds (Si-R and Si-O-R) in accordance with (Kovac et al., 2002).

Carbon –13 Nuclear Magnetic Resonance (13C-NMR)

13C-NMR spectra has several advantages over conventional 1H-NMR. It provides direct information on the carbon skeleton of the organic substances in addition, the larger chemical shifts recorded by this technique allow signals to be resolved for individual carbon atoms with only slightly different intrinsic magnetic environment.

Researches have categorized 13C-NMR spectra into different regions depending on their aliphatic and aromatic characters as: 0-105 ppm (aliphatic C), 105-165 ppm (aromatic C) and 165-185 ppm (C in COOH groups) (Agnelli et al., 2000 and Schnitzer, 1991); while others have divided NMR spectra into five regions according to chemical shift as 0-45 ppm (alkyl C), 45-110 ppm (O-alkyl C), 110-160 ppm (aromatic C), 160-190 ppm (Carboxylic C), 190-220 ppm (Carbonyl C) (Li et al., 2004). Aromatic carbon content for bulk samples and various fractions (<1, 1-3, 3-5, 5-10, 10-30, 30-100, 100-300 kDa) vary from 27.0 to 39.8%. The 13C-NMR spectra also suggests that H- and C- substituted aryl carbons may account for more than 80% and that the O- substituted aryl carbon is less than 20% of the total aryl carbons (Li et al., 2004).

Studies conducted by Schnitzer (1986, 1991) to characterize soil humic and fulvic acids revealed that : (i) humic acid contains more of carbon, hydrogen, nitrogen and sulphur, and less of oxygen than does the fulvic acid; (ii) Phenolic –OH, -COOH, total acidity, alcoholic –OH and ketonic >C=O group contents of fulvic acid are appreciably higher than those of the humic acid (however, the latter contains more quinonoid >C=O groups per unit weight; (iii) about 90% of oxygen in humic acid can be accounted for by the oxygen carrying functional groups, but in the fulvic acid nearly all the oxygens are held in similar functional groups; and (iv) E4/E6 ratio is
considerably higher than that of humic acid implying that the fulvic acids have lower particle size and/or molecular weight distributions as compared to the humic acids.

**Pyrolytic Gas Chromatograph –Mass Spectrometry (Py-GC-MS)**

Thermal degradation techniques such as pyrolysis have been frequently applied to the study of humic substances. Pyrolysis involve thermal degradation of the material into smaller components that can be theoretically related back to the original sample, and structural information obtained. Advantage with this technique is that only small sample volume is required, and that extensive pre-treatment of the sample is not necessary. However, degradation of products only partially reflects the source material, and their degradation pathways are often unknown. Limitations in the analysis of polar functional groups due to unwanted thermal reactions (decarboxylation) can lead to loss of information about the structural composition of the original macromolecule.

Characterization of humic substances by Py-GC-MS analysis was performed by Li *et al.*, (2004). They observed some prominent peaks at 15, 19 and 36, which indicates lignin-derived aromatic structures. 18, 20, 23, 24 and 29 are the peaks for aliphatic substituted phenols. In addition to the lignin-derived compounds, pyrolysates of various 1-alkene/n-alkane doublets with carbon number ranging from 9-29 indicate their possible derivations from micro-organisms and plant cutins or suberins. Other important pyrolysates identified in this study include protein derived nitrogen containing compounds (peaks 1, 2, 5, 6, and 47), carbohydrate derived furaldehyde compounds (peaks 4 and 13), and chlorophyll derived compounds. Li *et al.*, (2006) have extracted Pahokee peat and characterized using two complementary techniques, namely conventional pyrolysis and methylation pyrolysis (TMAH) GC-MS with similar findings.

**Matrix Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS)**

Determination of the HA structure is a complex problem. Recently a number of various soft ionization mass spectrometric techniques like Electrospray Ionization (ESI) (Stenson *et al.*, 2002, 2003) or the matrix assisted laser desorption/ionization
time of flight mass spectrometry (MALDI-TOF-MS) and lately laser desorption/ionization time of flight mass spectrometry (LDI-TOF-MS) are being applied more and more to the characterization of humic substances. (Gajdosova et al., 2000, 2001, 2003; Kujawinskai et al., 2002; Pena-Mendez, 2005, 2007). Application of MALDI-TOF-MS or LDI-TOF-MS to characterize HA to give complex mass spectra is preferred over Py-GS-MS because soft ionization technique is less destructive (Havel et al., 2001). In the case of LDI-TOF-MS, there is a danger of segmentation which needs to be avoided, while MALDI-TOF-MS also has limited use, not only due to fragmentation of HA, but also because of the formation of aggregates or clusters. Formation of cluster in MALDI has been reported by Pacheco et al., (2003), therefore, for both techniques careful optimization of the parameters affecting measurement is necessary.

Pena-Mendez et al., (2005) have taken mass spectra of Humic Acid (HA) from different sampling sites (Antartica, Brazil, Czech Republic, Mexico and USA) and origin (Plant, soil, peat, and coal derived) were obtained by laser desorption/ionization time of flight mass spectrometry (LDI-TOF MS). They found that reproducible mass spectra of HA samples were obtained, the majority of peaks are observed in m/z region 100-1000 Da. Very similar structural groups (patterns) of the peaks are present in the m/z range 717-918 Da for HA samples of quite different origins, countries or continents. After applying principal components and cluster analysis, they demonstrated that the most of the Antarctica HA samples show distinguishable differences when compared with humic acids from other continents and of different origin. In another study conducted by Gajdosova et al., (2003), they have also found the similar peak pattern between m/z 800-950 for all humic acid samples.

Gel Electrophoresis
There is no end to the techniques used to characterize humic substances but gel electrophoresis is another tool to separate humic substances according to their molecular weight. There are different view points regarding the sizes and shapes of humic substances in the scientific community. One suggested that humic substances are macromolecular and assume random coil conformations in solution; a second proposed that humic substances are molecular associations of relatively small
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molecules held together by weak interaction forces; third considered that HS remain as micelle or “pseudomiceller” structures in solution.

Trubetskoj et al., (1997) have fractionated soil by size-exclusion chromatography (SEC) on sephadex G-75 using water, Tris-HCl or 7 M urea as eluents, or by ultrafiltration in the presence of 7 M urea or water. These fractionated HAs were classified as 100K (normal retention size > 100 000); 30K (100 000-30 000); 10K (30 000-10 000) and 5K (10 000-5). Several pools from each chromatography and all ultrafiltration retentates were assayed by polyacrylamide gel electrophoresis (PAGE). Results have shown that PAGE in the presence of denaturing agents can be successfully used for checking the purity of HA fractions obtained by both SEC and UF.

Understanding the nature of OM in river sediments is essential to have a multiple analytical approaches as discussed above.

2.3.4 Studies on Organic Substances in India

Shanmukhappa et al., (1987) have studied both forms of humic acid (dissolved and particulate) in water quantitatively from three unique biotopes of Porto Novo in Southeast coast of India, viz., the sea, the estuary and the mangrove, from June 1982 to July 1983. The relative and progressive humification index of the water bodies as noted by E4/E6 ratio, has also been described. Sources, abundance and seasonal variation of HAs in each biotope in particular and humification in general have been discussed.

Laura, (1973) contributed to the study of nitrogen and humus contents of saline, saline-sodic, sodic and nonsaline non-sodic (normal) soils of three soil series near Delhi. The soils represent Typic and Aquatic Calciorthids and are sandy loam to silty clay loam in texture throughout the profiles. In the surface layers (0–15 cm), their total organic carbon ranges from 0.17 to 0.50%, total nitrogen from 0.026 to 0.077%, C/N ratio from 5.3 to 7.3, extractable carbon from 19.4 to 32.7 (of the total carbon in the soil), and humic acid to fulvic acid ratios from 0.62 to 1.06. Below the surface layer, total organic carbon, total nitrogen and C/N ratios decrease with depth and the
alkalinity of the profile. Throughout the profile, the extractable carbon is higher and the humic acid/fulvic acid ratios are lower in saline and normal profiles than in saline-sodic and sodic profiles. Mineralised nitrogen ranges from 4.1 to 20.9% of the total nitrogen in the soil without any consistent relationship to salinity or alkalinity.

Humic substances (Humic and Fulvic acids), extracted from cultivated and natural forest soils of Sikkim was characterized by physical, chemical and spectral characteristics. Decrease in C, H contents and C/H, C/N ratios but increase in O content and O/H ratio both in humic acid and fulvic acid was observed as a result of cultivation. Cultivation increases acidity of HA, perhaps because of higher content of phenolic OH-group, decreases the molecular weights and contents of alcoholic OH and carbonyl- groups of both HA and FA. It is also observed that humic substances from high altitude, cooler and high rainfall areas have low molecular weight and less condensed aromatic structures possibly with high content of polysaccharides (Martin et al., 1998). Singh, (1996) have investigated and established a linear relationship between acid equivalents and the atomic O/C ratio of regenerated Humic acids.

Most of the studies pertaining to water and sediment chemistry have been focused on large river systems like Ganges, Yamuna, Brahmaputra and so on. But water quality, elements stored in sediments have not been assessed for important tributaries like Chambal, which flows through three big states (Madhya Pradesh, Rajasthan and Uttar Pradesh) of the country.

Thus, the present study has been conceptualized and carried out in view of above mention facts and figures

**OBJECTIVES**

The present investigation was undertaken with the aim of understanding the nature, mechanisms and processes of accumulation of elements and behavior of organic matter (Humic Substances) in the aquatic system (Water and Sediments) of the river Chambal. Various internal and external controls and their responses as reflected in the hydrological, lithological and chemical composition of the river Chambal have been studied.
In the present study, I have tried to develop an understanding about the water quality, sediment texture, heavy metal determination in water and sediments, their fractionation and the characterization of humic substances.

**Main objectives of the present study were:**

- To evaluate the aspects related to variation in physicochemical parameters, ionic composition together with weathering processes and possible sources and mechanisms controlling the water chemistry in the river Chambal.
- To perform sediment quality assessment and to study the changes in the immediate past.
- Quantify the chemical forms of various heavy metals in the river Chambal.
- To Characterise Humic Substances.
- To make an assessment of state of pollution in the river Chambal.

**JUSTIFICATION**

- With the increasing urbanization and industrialization, the land disposal of industrial wastes is becoming a serious problem. Heavy metals are of concern because of their increasing abundance in the environment and their relatively high toxicity even at low concentrations. Once released into the soil matrix, heavy metals can impact environmental quality and human health via ground water and surface water. The factors influencing the bioavailability of hazardous metals to the biota are important in ecotoxicity assessment. Humic acid is a natural organic compound produced by biological and geochemical processes that contain structures that can complex metals, sequester anthropogenic organic compounds, oxidize and reduce elements to and from toxic forms, photosensitize chemical reactions and enhance and retard the uptake of toxic compounds or microbial organisms. In view of the above, in the present study, we have focused on the assessment of pollution load and determination and characterization of humic substances of the river Chambal.
Except for some studies on the water quality aspects of the Chambal River [Central Water Commission (CWC), New Delhi], no attempt has been made to study controlling factors of surface water chemistry and practically no information is available on the heavy metal content of the Chambal River sediments. The present work aims at studying the nature of solute and suspended load, elemental chemistry and metal pollution assessment and characterization of main component of organic matter i.e. humic substances of the Chambal River sediments.

Large low land rivers often have their nutrient concentrations modified by industrial emissions, sewage and agricultural effluent, and they are also likely to have their flow regime regulated by dams. The uniqueness of their catchment’s area, individual climate and geology make it difficult to generalize the characteristics of the drainage basins. River Chambal being a low land river itself shows all these salient features.

- Dams: Gandhi Sagar dam, located on the Rajasthan-Madhya Pradesh border in Neemach district, Rana Pratap Sagar dam located at Chittorgarh district, Jawahar Sagar Dam and Kota Barrage in Kota district.

- Industries: Gwalior Rayon Silk Mills (GRASIM), one of the Assia’s biggest rayon manufacturing units located at Nagda in Ujjain, about 20 large scale industries in the industrial city Kota itself. Some of the major industries are Rajasthan Atomic Power Plant (Rawatbhata), Kota Thermal Power Station (KTPS), Shriram Fertilisers and chemicals Ltd., Shriram Rayon Ltd., Multi metals Ltd., Instrumentation Ltd., Samchor Glass Ltd. (Naya Nohra), Chambal Fertilisers and Chemicals Ltd. (Gadepan). Besides these industries many crushing and grit units along with small-scale units are adding to the pollution load on the river Chambal.
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- Agricultural land: The general land use pattern of the valley indicates that the net sown area is concentrated in the southwest part. From the southwest it extends in northeast and northwest directions in descending order.

- Forest Land: In Chambal there are two major forest belts, the northwestern belt comprising the Bundi-Ranthambore-Kakrauli line of hills and the Mukandwara hills. Small patches of forests are also found in the ravine lands of the valley particularly around Sheopur, Vijaypur and Baran.

➢ Chambal river is the only river among the tributaries and sub-tributaries of Ganges which passes through a dense forest to a considerable distance. Moreover, Chambal is a small river but represents all the features like Forested area, many Dams, agricultural practices taking place near its bank, residential and industrial settlements, which can attribute to some interesting results.