1.1 General
Rivers are the channelised routes through which continental materials like weathered products and anthropogenic materials are transported to the land-ocean boundary. Removal of both suspended and dissolved materials takes place during the mixing of river water with sea water due to gradients in pH, salinity and other physico-chemical parameters like dissolved oxygen, Eh, turbidity and humic acids (Sholkovitz, 1976; Bourg, 1983, 1987; Dumker, 1986, 1989). About 92% of the river-borne sediments (13.5 billion tons/yr, Milliman and Meade, 1983) are trapped in estuaries and connected drainage basins like lagoons, tidal flats, marshes and adjacent continental shelves due to flocculation, agglutination and fecal pelletisation processes (Gibbs, 1981; Schubel and Kennedy, 1984; He Songlin, 1987). This is the prime reason for the accumulation of contaminants like heavy metals (Bruland et al., 1974; Goldberg et al., 1978; Crecelius and Bloom, 1988; Finney and Huh, 1989; Gearing et al., 1991; Buckley et al., 1995), radionuclides (Bhat et al., 1981), and organic contaminants like polychlorinated biphenyls, polychlorinated dibenz-p-dioxins, polycyclic dibenzofurans, polycyclic aromatic hydrocarbons (Pruell et al., 1990) in densely populated and industrialised coastal belts of the world. Therefore, the emphasis has shifted to monitoring and protecting the coastal sector from various types of contaminants that are transported by rivers and atmosphere.
The river-transported materials are derived from the physical degradation and chemical dissolution of continental rocks. Physical degradation is predominant in temperate regions, whereas chemical weathering is important in the tropics and subtropics (Martin and Meybeck, 1979). Intense chemical weathering in the tropics leads to the leaching of alkali and alkaline earth elements from soil and their addition to rivers as dissolved load. Trace and rare earth elements, Al and Fe are relatively immobile and particle reactive, and hence are transported as particulate load (Martin and Meybeck, 1979). As rivers carry a wide variety of continental materials including anthropogenic products in both dissolved and particulate phases, it is difficult to determine their fate during river-ocean mixing. Therefore, laboratory studies have been designed to understand the fate of dissolved materials during estuarine mixing which help in quantifying (i) the net transport of dissolved metals to the coastal ocean and (ii) the flocculation of dissolved trace metals at varying salinities; the latter provides data on the degree of removal of individual trace metals in the estuary (Sholkovitz, 1976, 1978; Li et al., 1984; Maest et al., 1984; Zhiquing et al., 1987).

The fate of particulate metals can also be studied by using radiotracers. Through this approach, Li et al. (1984) have shown that a significant proportion of dissolved Fe, Sn, Bi, Ce and Hg undergo coagulation whereas Co, Mn, Cs, Cd and Ba are desorbed from river-suspended matter during the mixing of Hudson and Mississippi river waters with sea water. Nearshore regions serve
as a sink or filter for continental detritus, but they are not a permanent sink for base metals. Due to the rapid accumulation of organic matter in these sediments, diagenetic processes result in the depletion of dissolved oxygen producing anoxic conditions under which redox sensitive metals are easily remobilised from the sedimentary column and added through the pore water to the overlying water (Duinker et al., 1974; Bewers and Yeats, 1978; Trefry and Presley, 1982, Martin and Whitfield, 1983; Brugmann, 1986, 1988). Remobilised metals may again undergo adsorption and precipitation and thus be incorporated into the particulate phase under oxic conditions (Sundby et al., 1981; Kersten, 1988). The direction of bottom currents influences the transport of remobilised elements either landward (Sundby et al., 1981) or seaward (Yeats et al., 1979; Sundby et al., 1981). In general, because of the seaward decrease of terrigenous influx and the existence of oxic conditions in the open ocean, base metals are enriched in open ocean sediments when compared to nearshore sediments (Sundby et al., 1981; Trefry and Presley, 1982; Martin and Whitfield, 1983).

As two thirds of the world population lives in and around coastal areas, it is imperative to monitor pollution in the aquatic system. Baseline data for the various organic and inorganic constituents in the environment (air, water and land) and their periodic monitoring are needed to evaluate the impact of industries on the environment. Baseline studies will not only help in evaluating the impact from upcoming industries on the environment but also in understanding natural processes operating
in the area.

India's vast coastline is densely populated and characterised by a number of industries like chemical and fertiliser plants, oil refineries, nuclear power plants, ports etc. Karnataka has a coastline of about 300 km bordered by the Western Ghats on the east and the Arabian Sea on the west. This coastline is punctuated by a number of natural as well as man-made features; man-made features include ports / harbours, fertiliser plant, etc. A number of industries have come up and a few others are in the process of being set up in the coastal zone like the Mangalore Chemicals and Fertilisers (Panambur), Mangalore Refineries and Petrochemicals Limited (Surathkal), Cogentrix thermal power plant (Padubidri), nuclear power plant (Kaiga), etc. Therefore, the coastal environment of Karnataka is under stress.

With this background, the present study was taken up to fill the gaps in our understanding of the weathering and erosion of geological materials in a tropical region, transport of selected elements and radionuclides through the agency of river and their behaviour in the estuarine and marine realms.

1.2 Previous work

Martin and Meybeck (1979) have studied the concentrations of 40 elements in the suspended particulates of 20 major rivers of the world located in different regions ranging from subarctic to equatorial and from mountains to plains. They concluded that river particulates in the tropics are enriched in Fe, Al and Ti
and depleted in Ca and Mg because of predominant chemical weathering. In temperate regions, there is relatively less enrichment of Al, Ti and Fe and relatively more enrichment of Ca and Mg in particulates mainly because of the mechanical weathering prevailing there. Thus, particulates of temperate regions reflect the catchment rock composition. Around the world, very few studies have been made in the polar and subpolar regions on the mode of transport of chemical constituents by rivers and their behaviour in the river-estuary-ocean systems. Dai and Martin (1995) have reported the levels of dissolved and particulate elements and their transport in two major Arctic river-estuarine systems in Russia and the adjacent Kara Sea. They have documented the role of colloids in controlling the dissolved elemental concentrations and their net input into the sea. Studies carried out by Callender and Granina (1997) on the transport of rock-forming elements to Lake Baikal in the Siberian region have indicated the physical transport of sediments as suspended load and bedload with minimal action of biogeochemical processes.

Several studies have been carried out on the riverine-estuarine-oceanic environments of temperate regions. Trefry et al. (1986) have studied the Mississippi river delta system and noted that 90% of the trace metal load carried by the river is associated with detrital particles derived from the bed-rock. Cameron et al. (1995) have noted the dominant influence of catchment geology on the major and trace element composition of water of Fraser river, Canada; however, pulp mills have contributed anthropogenic
organic carbon and NaCl which are found in high concentrations. Albarede and Semhi (1995) have also reported the dominance of bedrock geology on the river-bed sediment geochemistry of the Meurthe River in France. The diverse geology existing in the metamorphic rocks of Colorado, USA has been deciphered through the chemical composition of river-bed sediments (Cullers, 1994). Elemental ratios like La/Sc, Th/Sc, La/Co, Th/Co and Ba/Co have distinguished between sediments derived from the most silicic source rocks from those derived from the most basic rocks.

Tropical rivers have been extensively studied to determine the dissolved and particulate metal concentrations and their transport to the land-ocean boundary and behaviour in the river-estuary-ocean environments. Data are available for the Zaire (Moore and Burton, 1978; Sholkovitz et al., 1978; Martin et al., 1978a; Eisma and van Bennekom, 1978), the Amazon (Sholkovitz and Price, 1980; Stallard and Edmond, 1981, 1983) and southeast Asian rivers (Nolting et al., 1989).

Behaviour of dissolved trace metals in the estuary and the changes in their concentrations resulting from the complex physico-chemical reactions occurring there have been the focus of a number of studies (Sholkovitz, 1976, Boyle et al., 1982; Froelich et al, 1985; Byrd et al., 1990; Shiller and Boyle, 1991). An overview of the quantity and chemical composition of the dissolved and particulate materials carried by rivers, the fate of these materials in the estuarine mixing zone and the quantity and composition of the material that is ultimately exported from the estuarine zone to the the open ocean has been
given in Chester (1990). He has concluded that the major process that controls the dissolved elemental composition of sea water is a balance between the rates at which elements are added to the system and the rates at which they are removed by the throughput of particulate material, which delivers them to the sediment sink.

There are several studies made on the behaviour and concentrations of REEs in rivers, estuaries and nearshore regions to determine the abundance and fractionation of REEs in riverine environment and their transport to marine environment (Martin et al., 1976; Gordeev et al., 1985, Upstill-Goddard et al., 1986; Goldstein and Jacobsen, 1988a, 1988b; Sholkovitz, 1988, 1993; Elderfield et al., 1990; Albarede and Semhi, 1995; Ross et al., 1995). Their distribution in soil and in riverine, estuarine and oceanic environments not only provide information on areas of possible REE enrichment in the catchment but also their abundance and fractionation in different aquatic environments. As REEs are relatively immobile, they can be used as tracers for understanding sedimentation processes (Sholkovitz, 1988, 1993; Elderfield et al., 1990; Goldstein and Jacobsen, 1988a, 1988b). Their enrichment in riverine sediments may provide information for detailed exploration.

Studies made on the geochemistry of major and minor rivers of India are sparse. Significant studies made in India are noted here. Shankar and Manjunatha (1996) have reviewed the geochemical and isotopic studies of riverine, estuarine and
marine environments of western India. The review has highlighted the dominant influence of lithology, climate and areal extent of drainage basin on the chemical composition of suspended matter in the west-flowing rivers of India (Fig. 1.1). The role of west coast estuaries in drastically altering the composition of dissolved and particulate loads reaching the sea have been brought out. An interesting phenomenon along the west coast is the landward transport of shelf sediments. The varying redox conditions during late Pleistocene - early Holocene are reflected in the initiation of non-steady-state diagenesis in the eastern Arabian Sea sediments. Studies on continental margin sediment cores have indicated higher terrigenous influx, higher primary productivity and a stronger southwest monsoon during early Holocene when compared to late Pleistocene.

Geochemical studies of river-estuary systems of India have not received much attention. Only a few investigations have been carried out in this direction (Borole, 1980; Borole et al., 1982a; Baskaran et al., 1984; Karbassi, 1989, Manjunatha, 1990; Shankar and Manjunatha, 1994b).

Borole et al. (1977) have calculated metal/Al ratios for bulk suspended sediment samples as well as the <4μm particles of the Narbada estuary. They have recorded a decrease in metal/Al ratios for the <4μm size fraction when compared to bulk suspended particulate matter (SPM), indicating that variation of particulate metals is due to variation in particle size. Borole et al. (1982b) have opined that lesser sorption of trace metals could be due to very high SPM concentrations in the Narbada and
Fig. 1.1 (a) Major peninsular rivers of India (after Subramaman et al., 1987); (b) Major and medium rivers flowing into the Arabian Sea; (c) Minor rivers and continental margin sediments of the west coast of India (after Rao, 1979; Vijaykumar, 1988; Shankar and Manjunatha, 1996).
Tapti estuaries.

Most studies of major Indian rivers have been aimed at understanding the processes of weathering, denudation, hydrological and environmental characteristics, and dissolved and particulate fluxes to the oceans (Subramanian, 1979, 1987; Subramanian et al., 1987) and the influence of geology, climate and anthropogenic activity on riverine chemistry (Biksham and Subramanian, 1988; Ramesh et al., 1989).

Studies made on Narbada, Tapti and Godavari estuaries (Borole et al., 1977; Fig. 1.1) revealed no systematic trend in the behaviour of particulate metals with increasing chlorosity; the variations observed are due to the changes in grain size and mineralogy. According to Borole et al. (1977), the degree of desorption in Indian estuaries is much less when compared to the European rivers. Baskaran et al. (1984) noted the enrichment of Fe, Mn, Zn, Cr, Co, Ni and Cu in the magnetic fraction by a factor of 1.2 to 4 when compared to the clay and silt - sand fraction of SPM and bottom sediments in the Narbada and Tapti estuaries and the adjacent coastal Arabian Sea.

Physico-chemical parameters such as pH, salinity, dissolved oxygen, turbidity, etc. are important factors that control the distribution of metals between the dissolved and particulate phases in aquatic environments (Duinker et al., 1982, Bourg, 1983, 1987). Karbassi (1989) has studied the influence of these parameters on particulate metal behaviour in the riverine, estuarine and coastal environments around Mulki (Fig. 1.1).
Mulki-Pavanje river waters are acidic and have low concentrations of SPM which is characterised by high Al and Fe, but low Ca because of the influence of tropical climate. Manjunatha (1990) in a similar study of the Netravati - Gurpur river system near Mangalore (Fig. 1.1) has recorded that Netravati - Gurpur SPM concentrations are considerably lower than those for Narbada and Tapti rivers (Borole et al., 1982b), Mahanadi river (Ray et al., 1984) and Krishna and Godavari rivers (Subramanian, 1979). However, they are comparable to SPM concentrations of Mulki and Pavanje rivers (Karbassi, 1989). Netravati and Gurpur SPM are enriched in Al, Fe, Ni and Co but strongly depleted in Ca in comparison with temperate and major rivers of the world. This illustrates the influence of intense chemical weathering that takes place in tropical regions.

Netravati river water - Arabian Sea water mixing experiments have shown that flocculation is slow because of the low dissolved metal contents of the small, seasonal, Netravati river (Shankar and Manjunatha, 1994a). Dissolved Fe is removed during estuarine mixing predominantly in the salinity range of 2.88-18.08 ppt. Dissolved Cu and Ni are removed mainly in high and low salinities (>18.08 and <12.08 ppt) respectively. Similar mixing experiments carried out with Mulki river water and Arabian Sea water (Shankar and Karbassi, 1992) show that flocculation of base metals takes place in the salinity range 2.5 to 29 ppt. Flocculation is more pronounced beyond a salinity of 22 ppt.

Rare earth element studies in India encompassing riverine,
estuarine and marine environments are sparse. Manjunatha et al. (1996b) reported the REE behaviour in sediments along the Netravati/Gurpur river - Laccadive Trough (open ocean) transect to determine the influence of intense chemical weathering on the composition of river suspended particulate matter, landward transport of coastal sediments through the formation of estuarine front and different redox conditions prevailing on the continental shelf / slope and Laccadive Trough. They concluded that Netravati - Gurpur SPM is enriched with HREEs over LREEs when normalised to parent rock REE data indicating the greater mobility of LREEs during chemical weathering. High total REE, positive Ce and Eu anomalies and (La/Er)_N ratios in the suspended matter collected from the estuarine front indicate the onshore transport of LREE-rich materials from the marine environment.

1.3 Aims and objectives

It appears from the above review that there are no detailed geochemical and radiochemical investigations carried out around Kaiga. In fact, such studies of tropical rivers around the globe are also sparse. Investigations on tropical river-estuary systems are particularly important because major rivers of the world flow in the tropics. Hence the geochemical processes that operate, and the quantity and composition of particulate and dissolved loads delivered by rivers in the tropics and subtropics are of paramount significance in determining the river inputs to the oceans and for elemental budget calculations.

The concentrations of U-Th series radionuclides (U-238, U-234, Th-232, Th-230, Pb-210), alkali and alkaline earths (Na, K, Mg,
Ca, Rb, Sr, Ba), trace elements (Fe, Al, Mn, Pb, Zn, Cu, Co, Zr, Mo, Cd), REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er) and organic carbon have been measured seasonally in soils around Kaiga, in particulate and dissolved phases in Kali river, its estuary and the adjoining coastal environment. The data obtained have been used to calculate correlation coefficients and carry out factor analysis with the following objectives:

(i) To understand the natural geochemical processes that operate in the riverine, estuarine and marine environments of a tropical region. In addition, the fractionation of radionuclides and REEs in the river environment would reveal the type of source rocks and the weathering and erosion processes occurring in the catchment,

(ii) To determine the mode of transport of these elements and isotopes from soils to river, and their inputs and deposition in estuary and adjacent coastal regions,

(iii) To know the flocculation and removal of dissolved trace elements when river water mixes with sea water through laboratory mixing experiments,

(iv) To determine elemental fluxes to the coastal zone, and fractionation of elements during estuarine mixing and sedimentation in estuarine - coastal environments,

(v) To investigate anthropogenic contribution of heavy metals if any, in the study area, and

(vi) To obtain baseline data which are especially important in view of the Kaiga nuclear power plant becoming operational by the first half of 1999. The data obtained in this study
would also help assess, in future, the impact of nuclear power reactors on the natural processes operating in the area of study.

1.4 Area of study
The area of study is located in Uttara Kannada district of Karnataka with Karwar as its headquarters (Figs. 2.1 and 2.2). It consists of Supa, Yellapur, Karwar and Ankola taluks spanning an area of 4879 sq kms (Gazetteer of India, 1985).

The climate is characterised by high humidity all through the year with daily temperatures varying from a minimum of 22°C to a maximum of 31°C. The mean annual rainfall is 2804 mm. About 89% of the rainfall is received during the southwest monsoon. The climate is seasonal; the three seasons in the study area are pre-monsoon (March to May), monsoon (June to September) and post-monsoon (October to February; Gazetteer of India, 1985).

Kali is the major river that drains the area of study. Taking birth near a village called Diggī in Supa taluk in the Western Ghats, it runs for 184 kms before debouching into the Arabian Sea about three kms north of Karwar (Gazetteer of India, 1985). The annual discharge of water and sediment from the Kali river to the Arabian Sea are 6213 x 10^6 m^3 and 0.7 x 10^6 tonnes respectively (Subramanian et al., 1987). Water depth in the Kali estuary and river mouth ranges from 1.5 to 7m (Bhat and Neelakantan, 1985).

The inner shelf off Karwar extends to water depths of 50m (Subrahmanyam et al., 1989). The direction of surface current along the west coast of India changes seasonally. Between
November and January, it is northerly, but reverses direction during monsoon (Kidwai et al., 1981).

The texture, age and type of sediment carpeting the western continental shelf of India have been extensively studied (Nair and Pylee, 1968; Nair, 1971, 1974, 1975; Nair et al., 1978; Nair and Hashimi, 1980; Hashimi and Nair, 1986). The sediments of the western continental shelf in general, and the area of study in particular, are of two types based on their texture, carbonate content and radiocarbon dates (Nair and Hashimi, 1980; Hashimi and Nair, 1986; Fig. 1.1): (i) Modern sediments that are restricted to the inner shelf (<50 m) and composed of silt and clay with low carbonate content (<10%) and high organic matter. They have been delivered by the Western Ghat rivers since the reinforcement of SW monsoon during Holocene, and (ii) Relict carbonate sediments present in the outer shelf (>50 m) that are characterised by coarse texture (sands), high carbonate content (30-90%) and low organic matter. They indicate a warm climate and low terrestrial run-off at the time of their deposition. Radiocarbon dates of these carbonates (shells, calcareous algae, limestone, etc.) range from 9,000 to 12,000 yr. B.P., suggesting that they are of Late Pleistocene age (Hashimi and Nair, 1986).

1.5 Geology of the drainage basin

Majority of the rock types in Karnataka belong to the Archaean and Proterozoic eons. The oldest formations must have been the ancient supracrustals which occur as enclaves in the oldest dated rocks, i.e., a group of grey gneiss (Gneissic Complex). The
major tectonothermal events that took place between 3400 and 3000 Ma must have led to the widespread upheaval of the gneissic complex or the peninsular gneiss. Around the same time (~3000 Ma) igneous intrusions took place to form the auriferous schist belts of Kolar type (Radhakrishna and Vaidyanadhan, 1997).

The gneissic complex is overlain by the younger schist belts of Dharwar type. These schist belts are interspersed between the gneissic complex in linear basins to form distinct belts which are of Archaean age and belong to the age group of 2900 to 2600 Ma. The older Bababudan group is mainly igneous and hosts the main iron formations. The younger Chitradurga group consists of schistose rocks and sedimentaries composed of conglomerate, quartzite, limestone, greywacke and associated manganiferous and ferruginous chert (Radhakrishna and Vaidyanadhan, 1997).

The lithology of the study area consists largely of sediments of greywacke composition which are classified as the topmost formation within the Chitradurga group (Fig. 1.2). The study area is further classified as belonging to the Shimoga belt of the larger Shimoga basin. The lithologic succession, corresponding groups and ages are given in Table 1.1. Geochronological studies of the granite and granodiorite bodies occurring around Dandeli and Karwar have indicated an age around 2900 Ma (Vishwanath et al., 1988). The dolerite and amphibolite dykes trending mostly N-S and E-W may belong to different ages, younger than 2400 Ma. Laterite and alluvium have formed during the Tertiary and late Quaternary - Recent periods respectively.
Fig. 1.2 Geological map of the area around Kaiga (after Geological Survey of India, 1981).
Table 1.1: Lithostratigraphic succession in the study area (after Radhakrishna and Vaidyanadhan, 1997).

<table>
<thead>
<tr>
<th>Tertiary to Late Quaternary</th>
<th>Laterites and Alluvium</th>
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<tbody>
<tr>
<td>Proterozoic (1700 Ma)</td>
<td>Dolerites and Amphibolite dykes</td>
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-------- Great Eparchaean interval (2500 - 1600 Ma) --------

<table>
<thead>
<tr>
<th>Dharwar type schist belts (2900 - 2600 Ma)</th>
<th>Ultramafic - mafic complex</th>
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<tbody>
<tr>
<td></td>
<td>Greywacke - argillite</td>
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<td></td>
<td>Ferruginous chert</td>
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<td>Metabasalt</td>
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<td>Polymict conglomerate</td>
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<td>Mn and Fe formations</td>
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<td>Limestone and Dolomite</td>
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<td>Granite and Granodiorite</td>
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Major tectonothermal events (3400 - 3000 Ma)

Migmatitic, granodioritic to tonalitic gneiss