CHAPTER 1

INTRODUCTION

1.1 COASTAL ECOSYSTEMS

Coastal ecosystems, found along continental margins, are regions of significant biological productivity and high accessibility. Despite their relatively small area, accounting for just 7% of the World Ocean's surface, coastal zones play an important part in the global Carbon (C) cycle and in buffering human impacts on marine systems. They are thought to support 10 - 15% of the World Ocean's net annual productivity and may be responsible for > 40% of the annual C sequestration (Muller-Karger et al 2005). The coastal zone represents 90% of the world’s fish catch (Pauly and Christensen 1995) and its overall economic value is 43% of the value of the world’s ecosystem services and natural capital (Costanza et al 1997). Coastal zone is the area of the greatest human impact on the marine environment since ~61% (22 of the 32 largest cities in the world) of the world population lives along the coastline (Alongi 1998). This study is based on the biogeochemical dynamics of one of the globally significant coastal regions, the Bengal Basin, where two ecosystems, namely estuarine and mangroves coexist.

1.2 ESTUARIES

Estuary is an integral part of the coastal environment. It is the outfall region of the river, making the transitional zone between the fluvial and marine environs. Estuaries provide two major ecosystem services, water
filtration and habitat protection (Daily et al 1997). These dynamic ecosystems effectively trap nutrients and provide a direct source of natural resources to human beings and are used for commercial, industrial and recreational purposes. They act as a resource for commercially important estuarine species of fishes and shellfish and also provide shelter and food resources for economically important shelf species that spend some of their juvenile stages in estuarine marshes (Bianchi 2007).

### 1.2.1 Major Global Estuaries

Approximately, 87% of Earth’s land surface is connected to the ocean by rivers (Ludwig and Probst 1998). Modern-day estuaries were formed over the past 5000 - 6000 years during the stable interglacial period. Only 12% of the world’s 177 longest rivers run freely from the source to the sea and form major or minor estuaries (Wang et al 2007). The Ganges River claimed as one of the largest rivers (2,510 km length) in the world, stands in the third position (after the Amazon and the Congo) for draining water to Bay of Bengal from land through the Hooghly estuary, is the present study interest.

### 1.2.2 Estuaries of India

India has a long coastline of 7,517 km and estuaries comprising about 2.7 x 10^4 km^2. 26% of India’s population lives within 100 kms from the coast (Kumar et al 2006). 14 major, 44 medium and 162 minor rivers with a total catchment area of 3.12 x 10^6 km^2, the combined length of 45,000 kms flowing through Indian subcontinent and discharging 1645 km^2 of freshwater every year to the seas around the country (Estuaries of India 2002). The important major rivers are Ganges, Mahanadi, Godavari, Krishna and Cauvery on the east coast and Narmada and Tapti on the west coast. The
Ganges estuary (Hooghly - Matla estuary) is considered as the largest estuary in India.

1.2.3 Estuarine Processes

Estuaries represent a biogeochemically active zone, since it receives massive inputs of terrestrial organic matter and nutrient and exchanges large amounts of matter and energy with the open ocean (Bouillon et al 2007a). In tropical estuaries, where water temperature is more or less stable, the number of plants and animals are less affected. Tides are necessary for healthy estuaries as they flush the systems and provide nutrients to keep the food webs functional. However, tides create constantly changing conditions of exposure to air and inundation to water. Water circulation is important because it transports animals and plants, mixes nutrients, oxygen and sediments, and removes wastes. Estuarine circulation, river and groundwater discharge, tidal flooding, re-suspension events, and exchange flow with adjacent areas (Leonard and Luther 1995); all constitute important physical variables that exert some level of control on estuarine biogeochemical cycles.

A general schematic representation of an estuary, as defined by Pritchard (1967), and further modified by Dalrymple et al (1992) to include more physical and geomorphological processes, is shown in Figure 1.1. This diagram shows a wide range of salinities (0.1 - 32), wave processes that dominate at the mouth of the estuary, tidal processes that occur in the middle region and river or fluvial processes at the head of the estuary. The relative importance of physical forcing from each of these regions can vary seasonally (e.g., coastal wave energy versus river discharges), and ultimately determines the mixing dynamics of both water and sediments in estuaries (Bianchi 2007).
1.2.4 Causes of Estuarine Degradation

Estuaries are fragile ecosystems that are very susceptible to disturbances. Despite their utmost importance to humans, estuarine systems are amongst the most modified and threatened ecosystems in the world, suffering from anthropogenic impacts that interfere with both the riverine and marine influences necessary for natural ecological functioning (Blaber et al 2000). About, 60% of the largest cities of the world located on estuaries and by the year of 2025, an estimated 75% of world’s population is expected to live in the coastal zone, with many of the remaining 25% living near major rivers (Bianchi 2007). These impacts of demographic pressure have clearly had detrimental effects on the overall biogeochemical cycling in estuaries.

Nutrient enrichment and its associated problems (e.g. Eutrophication, Algal bloom, etc.) are perhaps the most widespread problem
in estuaries around the world (Howarth et al 2002). Because of rapid economical growth and development, estuaries are among the most imperiled ecosystems. Higher volumes of urban non-point source runoff, discharge of the substantial amount of untreated / semi treated industrial effluents into the estuary along with sewage from domestics jeopardize the ecosystem. Consequently, the impact to the human race through bio-magnification is an expected trend. Estuaries are also suffering degradation because of sedimentation from soil erosion from deforestation, overgrazing and other poor farming practices. Likewise, other problems on estuaries are over fishing, drainage, filling of wetlands, release of pollutants, including heavy metals, polychlorinated biphenyls (PCBs), radionuclides and hydrocarbons from sewage inputs. Man-made dams and even reservoirs minimize the freshwater flow into the estuary and dredging of canals destroys benthic community and changes the nature and flow of water.

1.2.5 Impact of Climate Change on Estuaries

It is known that disturbance in natural processes limits the estuarine health and viability (Goldberg 1995), making them all the more vulnerable to the consequences of climate change. Some of the greatest potential impacts of climate change on estuaries may result from changes in physical mixing characteristics caused by changes in freshwater runoff (Scavia et al 2002). A globally intensified hydrological cycle and regional changes in runoff, all comprehensively indicates changes in coastal water quality. Freshwater inflows into estuaries influence water residence time, nutrient delivery, vertical stratification, salinity and control of phytoplankton growth rates. Increased freshwater inflows decrease the water residence time and increase vertical stratification, and vice versa (Moore et al 1997). The effects of altered residence times can have significant effects on phytoplankton populations, which have the potential to increase fourfold per day. Changes in the timing of freshwater delivery to estuaries could lead to a decoupling of the juvenile
phases of many estuarine and marine fishery species from the available nursery habitat. Increased water temperature also affects important microbial processes such as nitrogen fixation and denitrification in estuaries (Lomas et al 2002). Apart from that, extreme weather events such as cyclones and flooding are likely to be the future threat to estuarine systems (Nicholls et al 2007).

1.3 MANGROVES

The word “Mangroves” is used to refer to the plants and also to the forest community. To avoid the confusion, MacNae (1968) proposed, “Mangal” as a term to refer to the habitat or the forest community and “Mangroves” to the plant species. Mangrove forests consist of a consortium of tree and shrub species that inhabit at the confluence of land and sea, primarily found along sheltered tropical and subtropical coastal regions within 30º of the equator and form complex food webs and unique ecosystem dynamics (Alongi 2002; Upadhyay et al 2002). Mangroves exist under very hostile and inhospitable conditions (higher salinity, tidal extremes, wind velocity, high temperature and muddy anaerobic soil conditions) (Kathiresan and Ramesh 1991). Their complex architecture, combined with their location on the edge of land and sea, makes mangrove forests strategic greenbelts that have especially protective function also (Kathiresan and Bingham 2001).

1.3.1 Global Distribution of Mangroves

A combination of factors comes into play over space and time to shape the intertidal distribution of mangroves (Bunt 1996). Gradients in salinity, soil type and chemistry, nutrient content, physiological tolerances, predation, and competition have all been cited as important factors controlling the zonation of mangroves (Saenger and Snedakar 1993; Hensel 2002).
Mangroves are found in 112 countries and territories. Globally, mangroves dominate over $1.5 \times 10^7$ ha of large river deltas, estuaries and barrier islands. Total global mangrove coverage is 18 million hectares and is just about 0.45% of world’s forests and woodland (Spalding 1997). About, 41.4% world’s mangrove forest lies in South and Southeast Asia.

Mangroves occur in two distinct bio-geographical regions: the Indo-West Pacific (IWP), which includes Asia, Australia, Oceania, and the eastern coast of Africa; and the Atlantic-East Pacific region (AEP), which covers the America and the western coast of Africa. The IWP region contains more than three times as many genera, and roughly five times as many mangrove tree species, as the AEP region does (Spalding 1997).

1.3.2 Mangroves of India

Mangroves are found in the islands, major deltas, estuaries and backwaters of the east and west coast of India. Indian mangroves are distributed in about 6,768 km$^2$ (Table 1.1) which constituted about 7% of the world mangroves (Krishnamurthy 1987) and 8% of the Indian coastline (Untawale 1987).

Of the Country’s total area under the mangrove vegetation, 70% is recorded on the east coast and 12% on the west coast. The bay islands (Andaman and Nicobar) account for 18% of the country’s total mangrove area (Kathiresan 1995). The Sundarbans is the largest mangrove forest in the world, located in India and Bangladesh. The mangroves have a vast existence on the east coast of India due to the nutrient-rich alluvial soil formed by the rivers - Ganges, Brahmaputra, Mahanadi, Godavari, Krishna and Cauvery and perennial supply of freshwater along the deltaic coast. However, mangroves
of the west coast are of peculiarly bedrock valley type, scattered, comparatively smaller than the east coast (Geetha 2002).

Table 1.1  Area of the mangroves wetlands of India (Source: Forest Survey of India 2007)

<table>
<thead>
<tr>
<th>State</th>
<th>Mangrove ecosystem</th>
<th>Total area of the system (km²)</th>
<th>Actual forest cover (km²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Coast</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>West Bengal</td>
<td>Sundarbans</td>
<td>4260</td>
<td>2125</td>
</tr>
<tr>
<td>Orissa</td>
<td>Mahanadi (Bhitarkanika)</td>
<td>670</td>
<td>215</td>
</tr>
<tr>
<td>Andhra Pradesh</td>
<td>Godavari (Coringa)</td>
<td>332</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>Krishna</td>
<td>250</td>
<td>156</td>
</tr>
<tr>
<td>Tamilnadu</td>
<td>Pichavaram</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Muthupet</td>
<td>130</td>
<td>12</td>
</tr>
<tr>
<td>West Coast</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gujarat</td>
<td>Gulf of Kutch</td>
<td>582</td>
<td>854</td>
</tr>
<tr>
<td></td>
<td>Gulf of Khambat</td>
<td>531</td>
<td>177</td>
</tr>
<tr>
<td>Other mangroves</td>
<td>-</td>
<td>-</td>
<td>116</td>
</tr>
<tr>
<td>Andaman &amp; Nicobar Islands</td>
<td>Andaman islands</td>
<td>-</td>
<td>929</td>
</tr>
<tr>
<td></td>
<td>Nicobar islands</td>
<td>-</td>
<td>37</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>6768</td>
<td>4871</td>
</tr>
</tbody>
</table>

1.3.3  Significance of Mangroves

1.3.3.1  Ecological significance of mangroves

Mangrove ecosystems are important, "transformative interfaces" between land and sea. Mangroves form an important ecological asset and economic resource of the coastal environment. Mangroves are the most productive ecosystems, which can efficiently fertilize the sea, potentially protect the coastal zone and vitally serve as the breeding and feeding grounds of fishes (Mangroves of India 2002). They are the second largest source of primary production next to rainforests (Singh et al 2005a). The important biogeochemical services of mangroves include the entrapment of sediments and pollutants, filtering of nutrients, re-mineralization of organic and
inorganic matter, and export of organic matter to the coastal waters (Alongi et al 1992). Mangroves efficiently absorb excess nitrates and phosphates and prevent the coastal waters from contamination. In so doing, they play a vital role in protecting other coastal ecosystems from siltation and eutrophication (Upadhyay et al 2002). Mangroves possess mechanisms to deal with intense sunlight rays and solar UV-B radiation. Mangroves also act as carbon dioxide sinks by removing and storing carbon dioxide from the atmosphere, which is a major contributor to global warming (Chauhan et al 2008).

### 1.3.3.2 Eco-service of mangroves

Mangroves have wider ecological and economic importance and provide numerous services to humans (Dahdouh-Guebas 2006). People derive many harvestable benefits from mangrove forests. The mangrove wood with high content of tannin is used as timber for its durability. Due to high calorific values, mangrove twigs are used for making charcoal and firewood. Apart from that mangrove wood is used for making furniture, mats, baskets, thatching (Nypa leaves) and construction, a source for paper, dyes, chemicals and incense. The foliage of mangrove species (specially *Avicennia*) is used to feed livestock, and several mangrove plants extracts are used for traditional medicine. Shells of mangrove molluscs are used to manufacture lime. Mangroves attract honey bees and facilitate apiculture activities in some areas. The mangroves provide wild seeds for aquaculture industries. Globally, the world’s mangrove forest resources are worth an estimated US$180,900,000,000, based on the valuation of Costanza et al (1998).

### 1.3.3.3 Role of mangroves against natural calamities

Mangroves prevent coastal erosion, and act as a barrier against typhoons, cyclones, hurricanes, and tsunamis, help to minimize damage done to property and life (Mazda et al 1997). Mangrove tree species that inhabit
lower tidal zones can block or buffer wave action with their stems, which can measure 30 m high and several meters in circumference (Dahdouh-Guebas 2006). The trees both shield the land from wind and trap sediment in their roots, maintaining a shallow slope on the seabed that absorbs the energy of tidal surges and tsunamis (Pearce 1999).

1.3.4 Causes of Mangrove Degradation

Despite Mangrove’s natural resilience, approximately 30 - 50% of the world’s mangrove forest extent has been declined over the past half century due to human interference (Alongi 2002). It is estimated that mangroves may functionally disappear in as little as 100 years (Duke et al 2007). Rapid sea-level-rise of twenty-first century has been cited as a primary threat to mangroves (Gilman et al 2008). Several specific issues, which deserve immediate attention in mangrove forests of India, are 1) prawn farming practices, 2) cattle grazing, 3) tree felling, 4) reduced freshwater supply, 5) hyper-salinity, 6) heavy sedimentation, 7) natural calamities, 8) pest problems, 9) unsustainable fishing practices, and 10) lack of people’s participation (Kathiresan 1999). Donato and his colleagues (2011) estimated that, mangrove deforestation generates emissions of 0.02 - 0.12 Pg C y⁻¹, as much as around 10% of emissions from deforestation globally. Owing to these threats, India has lost about 40% of its mangrove cover within this century (Krishnamurthy et al 1987; Kathiresan 2000). Of this, Indian east coast has lost about 28%; west coast about 44%; and Andaman & Nicobar Islands about 32% (Jagtap et al 1993; Naskar 2004). Degradation of mangroves is a serious environmental and economic concern; thus immediate efforts are required to protect these critical habitats.
1.3.5 Effect of Climate Change on Mangroves

Anticipated effects of climate change could be positive or negative on mangroves, and it is highly uncertain on the site specific exact impact. Sea-level-rise and the associated impacts of climate change, like changes in weather patterns (temperature, winds, precipitation, etc.), coastal erosion, changes in the frequency of extreme events, including potential increases in the intensity of tropical cyclones / hurricanes may have effect on mangroves (Church and White 2006). As temperatures rise, mangroves may start to colonize higher latitudinal areas. A warmer climate may result in an increase in frequency and strength of tropical storms. Thus, the previously sheltered areas suitable for mangrove growth may become exposed. Conversely, any reduction in temperature could shrink mangrove range. Any changes in temperature, salinity, storm frequency or precipitation will have effects on flora and fauna composition within mangrove forests. Another climate change factor that may directly affect mangrove growth is increased atmospheric carbon dioxide concentration, which may increase mangrove growth by stimulating photosynthesis or improving water use efficiency. Even though, the consequences of this growth enhancement for the ecosystem are unknown.

1.4 NUTRIENT DYNAMICS IN COASTAL ECOSYSTEMS

Over the last three to four decades nutrient input in many coastal watersheds has been increased dramatically through anthropogenic activities (Seitzinger et al 2002; Green et al 2004), resulting in changes in structure and function of near-shore coastal ecosystems (Cloern 2001; Biswas et al 2009). The C: Si: N: P molar composition of diatoms is proposed to be 106:16:16:1 (Redfield et al 1963) and these values represent the ratios in which the nutrients containing these elements are incorporated during the growth of phytoplankton and are released during their decomposition. The source of nutrients (C, N, P, Si) in river water, as well as their fate during their travel
from land based sources to the sea, differs largely according to meteorological conditions, hydrological regime, and human management of the watershed and its drainage network (Billen et al 1991; Billen and Garnier 2007). Since 1980s, there is a growing concern to understand the impacts of increased nutrient addition (full magnitude and seasonality of inputs) to the coastal areas vis a vis its relationship with climate change, land use and urbanization in the watershed areas.

1.4.1 Nutrient Cycling in Mangrove Ecosystem

The acquisition of nutrients and the maintenance of a balanced nutrient budget in mangrove ecosystems, rely on a variety of processes and nutrient sources. These include the direct uptake of nutrients by mangrove leaves and roots from the water column, nitrogen fixation, internal recycling, and the trapping of organic matter and minerals. A complex range of interacting abiotic and biotic factors, control the availability of nutrients to mangrove ecosystems (Rivera-Monroy et al 1995; Alongi 1998). Decomposition of mangrove vegetative material majorly contributes in nutrient cycling of the system. The degradation processes vary seasonally, with more intense during monsoon in the presence of less salinity and more availability of dissolved oxygen (Reef et al 2010). Thom (1982) proposed that the combination of geophysical energies (rainfall, river discharge, tidal amplitude, turbidity, and wave power) with the geomorphology of the coastal zone is important to establishing the ecological characteristics of mangroves. Tidal driven currents are important for understanding material cycling in the mangrove ecosystems. Tidal creeks enhance the exchange of materials between coastal areas and mangrove swamps (Akamatsu et al 2009). Several studies have suggested that high productivity of mangroves is achieved where nutrients limit growth through efficient couplings among benthic nutrient pools, microbes, and mangrove trees, acting as mechanisms to maximize utilization and conservation of scarce nutrients (Alongi et al 1998).
1.4.1.1 Role of leaf litter in mangroves

Mangrove areas have one of the highest levels of productivity (2 to 50 Mg C ha$^{-1} \text{y}^{-1}$) as they receive nutrients from both sea and land (Alongi 2009). In mangroves, primary productivity is often estimated by measuring litter fall from mangrove trees, especially in view of its contribution to the estuarine system at forest sites (Hossain et al 2007). 60% of leaf material in tropical estuaries originates from mangroves. Dead plant material enters the soil in two ways - it falls on the surface as litter, and it is contributed below the surface from roots. Leaf litter production from mangrove forests is the source of input of organic matter into inshore ecosystems on many tropical coasts and is an important source of nutrients due to mineralization (Lee 1999; Imgraben and Dittmann 2008). Up to half of this leaf litter is exported via creeks to the adjacent coastal waters. As a result, mangrove surrounding waters act as a net source of Carbon dioxide (CO$_2$) (Borges et al 2005). Rate of litter decomposition is influenced by tidal position (Feller et al 1999), salinity (Day et al 1996), pollution (Silva et al 1998), mangrove tree species, weather and season (Saenger and Snedaker 1993). Humid condition, high temperature, low salinity (sub-tidal regions) along with aerobic conditions facilitates the litter decomposition process (Hoq et al 2002; Dorothy et al 2003). In systems where decomposition is minimal, tidal export of leaf litter may provide nutrients to nearby coastal waters (Alongi 1998). Submersion in water results in the rapid leaching of nutrients from mangrove leaves, which can then be broken down by heterogeneous microbial action, macro fauna such as crabs, or the physical impact of tides (Thongtham and Kristensen 2005; Imgraben and Dittmann 2008). Decomposition of litter and mineralization of nutrients strongly influence soil nutrient availability and ultimately ecosystem's primary productivity.
1.4.1.2 Role of microbial processes in mangroves

There is an unseen but fascinating universe of microbes living within the soil. They are the foundation of all of Earth's ecosystems, being responsible for the degradation and recycling of nutrients such as carbon, nitrogen and phosphorus, especially in soil of detritus-based marine ecosystems like mangroves (Steinke 2000, Mumby et al 2004; Rajendran and Kathiresan 2007). A great diversity (perhaps as many as 1000 species in a cubic centimeter) of microbes live in different intertidal zones and estuarine soil over time based on grain size, organic C and N content (Alongi 1994). The microbial activity results in mineralization of detritus and a decrease in C/N ratio (Blum et al 1988). These microbes are very sensitive to the organic carbon (OC) content of the soil as well as the temperature and water content, respiring faster at higher carbon concentrations, higher temperatures and in moisture conditions, and efficiently recycle nutrients.

1.4.2 Estuarine Nutrient Dynamics

Ecosystem responses depend on several critical physico-chemical characteristics and processes. The transport, transformation, retention, and export of nutrients in estuarine ecosystems are strongly influenced by estuary size (surface area), depth, volume, flushing rate, water residence time, tidal exchange, vertical mixing, and stratification. Riverine input influences estuarine hydrography by creating salinity gradients and stratification, and assures large transport of silt, organic material and inorganic nutrients to the estuaries (Figure 1.2). The open marine areas impose large-scale physical and chemical forcing on the estuarine ecosystem, due to tide and wind generated water exchange (Berner and Berner 1996; Flindt et al 1999).
Figure 1.2 Major estuarine processes related to estuarine Eutrophication. DOM and POM refers to dissolved and particulate organic matter, respectively (Source: Pinckney et al 2001)

During the last six decades, global riverine C, N and P inputs (inorganic nutrient flux) into the ocean have trebled due to regional climate, geology and human activities whereas the input of dissolved silicate stemming from natural sources was significantly reduced (Turner et al 2005; Lohrenz et al 2008). Changed ratios of the essential nutrients Si, N and P entail changes of the plankton community and the biogeochemical cycles (Smith et al 2003; Jennerjahn et al 2004). These enhanced inputs of C, N, and P are due to increasing population density in the areas of major river drainage basins and close oceanic coastlines, socio-economic development and changes in land-use practices, enhanced discharges of industrial, agricultural, municipal waste into continental margin waters via river, groundwater discharges and atmospheric transport (Meybeck and Vörösmarty 2005). Engineering projects (damming of the rivers) have an opposite effect by altering the hydrological regime of most of the world’s major rivers. The current state of knowledge indicates that the impact of dams on estuarine
ecosystems is profound, complex, varied, multiple and mostly negative (Adams 2000). By storing or diverting water, dams alter the natural distribution and timing of stream flows. This in turn changes sediment and nutrient regimes and alters water temperature and chemistry, with consequent ecological and economic impacts.

1.5 GLOBAL CARBON CYCLE

Carbon (C) is a fundamental element of life and thus is a key component of all organic compounds. Understanding how the global C cycle works is essential for monitoring and predicting future scenarios, and their impacts on the planetary climate system. It is also important to understand the C cycle as CO$_2$ concentration controls pH of oceans, maintains life, and carbonate chemistry. Although the total global reservoir of C is massive (more than $10^{19}$ kg), only a very small fraction of this C is actively involved in the fluxes of the C cycle.

The global C cycle refers to the exchanges of carbon within and between four major reservoirs: the atmosphere, the oceans, land, and fossil fuels. The exchanges may occur in seconds (for example, the fixation of atmospheric CO$_2$ into sugar through photosynthesis) or over a millennia [for example, the accumulation of fossil carbon (coal, oil, gas) through deposition and diagenesis of organic matter]. The cycling of C throughout the spheres of the earth on different time scales can be referred to as short and long term cycles (Berner 2004). The carbon cycle is inextricably linked to other chemical cycles, including those of nitrogen, phosphorus, and sulfur, as well as to the global hydrological cycle. The contemporary global carbon cycle is shown in a simplified form in Figure 1.3.
1.5.1 Short Term Carbon Cycle

The word “short-term” indicates the characteristic times for transferring C between reservoirs, which may range from days to tens of thousands of years. Because the earth is more than four billion years old, this is short on a geological time scale (Royer et al 2004). The short term C cycle centers on the interactions between the atmosphere and the biosphere and includes processes like photosynthesis, plant and animal respiration, and the movement of CO$_2$ across the air - sea interface. It has terrestrial (land) and marine (ocean) components. The short term C cycle is concerned with the fixing of C as OC and removing of CO$_2$ from the atmosphere via photosynthesis by green plants on the continents or phytoplankton in the
ocean. Terrestrial plants remove about 120 Pg of C annually (Figure 1.3) which is about 14% of the atmosphere’s total C (Hopkinson and Smith 2005). In terrestrial biosphere, C is transferred to soils by the dropping of leaves, root growth, and respiration, the death of plants, and the development of soil biota. Mature terrestrial forests are now thought to be C neutral (Hurtt et al 2002, Churkina et al 2007). Oceans are recognized as the most important sink for C, and it restores 50 times greater C than the atmosphere (Houghton 2007). The marine biosphere operates like a 'biological pump'. The oceanic C sink operates on annual time scales and thus can be included in the short term C cycle. During respiration and upon death of plants, plankton and animals ultimately produce CO$_2$. CO$_2$ is exchanged between the oceans and atmosphere, and dissolved organic matter is carried in solution by rivers from soils to the sea. However, in the ocean, some of the organic detritus of dead marine plants and animals, settles to the ocean floor and respired by marine biota and releases CO$_2$ to the atmosphere.

1.5.2 Long Term Carbon Cycle

Over millions of year’s carbon transfers to and from rocks can result in changes in atmospheric CO$_2$, hence called long-term C cycle. This is because there is so much more carbon in rocks than there is in the oceans, atmosphere, biosphere, and soils combined. Figure 1.4 mentioned below shows some of the major processes and reservoirs that are important in the long-term behavior of the C cycle. Gradual changes in plate tectonics lead to gradual, long-term changes in the rate of volcanic/metamorphic emissions of CO$_2$ and uplift related to mountain-building lead to changes in the global weathering rate, or changes in sea-level affect carbonate deposition, and/or the nutrient supply to the oceans and thus the strength of the "biologic pump." Carbonate sedimentation extracts C from the oceans and ties it up in the form of Limestones. Pelagic limestones deposited in the deep ocean can be
subducted and melted. Limestones deposited on continental crust are recycled much more slowly— if they are exposed and weathered, their remains may end up as oceanic carbonates. Limestones if get caught up in a continental collision, they can be metamorphosed and liberating their CO$_2$.

**Figure 1.4** Long-Term Carbon Cycle (Source: www.geosc.psu.edu)

### 1.5.3 Estuarine Carbon Cycle

Rivers and estuaries receive a steady input of natural and anthropogenic constituents from land. Recent observations have shown that river-estuary systems release a significant amount of CO$_2$ into the atmosphere in addition to the commonly recognized fluvial export of inorganic/organic matter (Borges et al 2006; Hofmann et al 2008). The emission of excess CO$_2$ from estuarine systems may be sustained by several processes; both biotic and abiotic (Figure 1.5).
Figure 1.5  Estuarine C dynamics in aerobic environments. The boxes are reservoirs, and the arrows are fluxes (Source: Bianchi 2007)

Distribution of C between air and sea is dependent on the seawater chemistry, so 98.5% of the C in the ocean-atmosphere systems is in the sea. Nearly this entire C exists as inorganic carbon reservoir. The carbonate reservoir can be divided into two primary sub-reservoirs: (1) dissolved inorganic carbon (DIC) in the ocean (H$_2$CO$_3$, HCO$_3^-$, and CO$_3^{2-}$), and (2) solid carbonate minerals [CaCO$_3$, CaMg(CO$_3$)$_2$, and FeCO$_3$] (Sarmiento 1993; Holmén 2000). Less than 1% of the DIC is present in the form of dissolved CO$_2$ (pCO$_2$). Much of the DIC in rivers is derived from the dissolution of
carbonate rock (80%) with the remainder (20%) coming from weathering of aluminosilicates. Over 97% of the runoff has been classified as the \( \text{Ca(HCO}_3\text{)}_2 \) type, making \( \text{HCO}_3^- \), \( \text{Ca}^{2+} \), \( \text{SO}_4^{2-} \), and \( \text{SiO}_2 \) the dominant dissolved constituents in global surface river waters (Mehrbach et al 1973; Bianchi 2007). Rivers have generally been considered as net heterotrophic, resulted in greater consumption of \( \text{HCO}_3^- \) by river phytoplankton (Bianchi et al 2004). High decomposition rates in estuarine systems may result in the export of DIC that rivals that of riverine export to coastal waters (Wang and Cai 2004). Estuarine and freshwater systems are close to equilibrium with atmospheric \( \text{CO}_2 \) and influenced by temperature and salinity (Wetzel 2001).

Abiotic source of \( \text{CO}_2 \) in rivers and estuaries is photochemical mineralization of dissolved organic carbon (DOC). This process happens either by direct photo-oxidation of DOC to \( \text{CO}_2 \) by solar UV - radiation (Granéli et al 1996) or by cleavage of DOC molecules into low molecular weight compounds available for bacterial metabolism (Bertilsson and Tranvik 1998). Allochthonous DOC is preferentially photomineralized, while autochthonous DOC is preferentially mineralized by heterotrophic microbes (Obernosterer and Benner 2004). Finally, \( \text{CO}_2 \) in estuarine water also be the result of respiration by heterotrophic organisms. \( \text{CO}_2 \) loss from estuaries is supported largely by microbial decomposition of OC produced in coastal wetlands (Cai 2011).

Annually, world-rivers transport large quantities of C to coastal seas (0.9 Gt C of which 40% is organic and 60% inorganic) (Meybeck 1993; Etcheber et al 2007). Particulate organic carbon (POC) in estuarine systems is derived from a multitude of sources. The autochthonous POC includes phytoplankton, submerged vegetation, benthic diatoms and cyanobacteria, and periphyton living on stems of emergent plants, whereas the allochthonous sources of POC consist of marginal marsh and swamp vegetation; marine- or
river-borne phytoplankton and detritus; and beach, shoreline, and wind-blown material (Schlesinger 1997). Increased CO$_2$ in the atmosphere, increased inorganic nutrient flux, and decreased sedimentary OC supply to the coastal ocean (due to damming) likely will lead to further uptake of atmospheric CO$_2$ in the coastal zone.

### 1.5.4 Carbon Dynamics in Mangrove Ecosystem

Mangroves are thought to export to the coastal zone a significant amount of the C they fix, either as organic or inorganic carbon (Gedan et al 2009). According to Bouillon et al (2008) global mangrove Net Primary Productivity (NPP) is approximately 0.22 Pg C y$^{-1}$, which is slightly less than half of the total production. A large part of this NPP is respired within the mangrove systems, and some is exported to estuarine and near-shore waters. Donato et al 2011 reported that mangrove forests surrounding the Indian and Pacific oceans are among the most carbon-rich forests in the tropics. The total amount of C stored in mangrove sediments ranges from 4 to 20 Pg C. Mangroves’ highly efficient particle-trapping mechanism (Furukawa et al 1997), lead to the sequestration of C. These coastal C sinks are thought to bury C at rates up to 50 times higher than those in tropical rainforests (Laffoley and Grimsditch 2009). Degradation of mangrove forest leads to decrease in carbon sequestration. As forests are removed, the OC built up over decades to millennia is subject to increase re-mineralization and erosion, and therefore, to release of CO$_2$ in-situ or to the atmosphere.

### 1.6 GREENHOUSE GASES (GHGs)

The Global C cycle has the potential to influence the climate system primarily through affecting the atmospheric concentrations of the radiatively active greenhouse gases (GHGs). GHGs affect climate by altering
incoming solar radiation and out-going infrared (thermal) radiation that are part of Earth’s energy balance. These gases are at historically unprecedented levels in today’s atmosphere (Spahni et al 2005). Temperature of the climatic system depends on change in the atmospheric abundance or properties of GHGs. Since the beginning of industrial revolution (about 1750), the overall effect of human activities on climate has been a warming influence (IPCC 2007). The important long-lived greenhouse gases (LLGHGs) that are directly influenced by human activities are carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), halogenated compounds (mainly CFCs) and Ozone (O$_3$) (Table 1.2). These gases are chemically stable and persist in the atmosphere over time scales of a decade to centuries or longer, with a long-term influence on climate. As these gases are long lived, they become well mixed throughout the atmosphere much faster than they are removed.

**Table 1.2** Global concentrations (Pre-industrial and Current), Lifetimes, radiative efficiencies and global warming potentials (GWP) relative to CO$_2$ of GHGs

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pre-1750 concentration</th>
<th>Current tropospheric concentration (2010)</th>
<th>GWP (100-yr time horizon)</th>
<th>Atmospheric life time (years)</th>
<th>Major Anthropogenic Sources</th>
<th>Radiative Forcing (W m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$  (ppmv)</td>
<td>280</td>
<td>387.2</td>
<td>1</td>
<td>50-200</td>
<td>Fossil-Fuel Combustion, Deforestation, Cement industry</td>
<td>1.66</td>
</tr>
<tr>
<td>CH$_4$  (ppbv)</td>
<td>730</td>
<td>1,774</td>
<td>25</td>
<td>12</td>
<td>Rice Fields, Cattle, Landfills, Fossil -Fuel Production</td>
<td>0.48</td>
</tr>
<tr>
<td>N$_2$O  (ppbv)</td>
<td>270</td>
<td>319</td>
<td>298</td>
<td>114</td>
<td>N Fertilizers, Deforestation, Biomass Burning</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Short-lived gases [e.g., sulphur-dioxide (SO$_2$) and carbon monoxide (CO)] are chemically reactive and generally removed by natural oxidation processes in the atmosphere, by removal at the surface or by washout in precipitation; their concentrations are hence highly variable.

1.6.1 Carbon Dioxide (CO$_2$)

CO$_2$ is an important biogeochemical parameter that provides insights into biological production, calcification and potential hydrogen (pH) changes (Dai et al 2009). CO$_2$ is the largest contributor to the anthropogenically enhanced greenhouse effect and is likely to remain so in the future.

1.6.1.1 Sources

Emission of CO$_2$ is the main contributor to anthropogenic climate change. The primary source of anthropogenic CO$_2$ is the emission from burning fossil fuels, which account for about 55% of global anthropogenic CO$_2$ emissions (Bickle 2009). The amount of CO$_2$ released depends on the type of fossil fuel used. Cement production, is responsible for an estimated 20% of the increase in atmospheric CO$_2$ concentrations since pre-industrial times (IPCC 2007). Changes in land use (biomass burning, crop production) and land conversion (like conversion of grasslands to croplands) are also considered a significant source of CO$_2$ and currently account for 8 - 20% of global anthropogenic CO$_2$ emissions, second only to fossil fuel combustion (IPCC 2007; van der Werf et al 2009).

CO$_2$ is produced naturally by animal and plant respiration. In ocean-atmosphere exchange, the oceans absorb and release CO$_2$ at the sea surface. Estuarine waters are significant sources of CO$_2$ to the atmosphere, with partial
pressure of CO$_2$ (pCO$_2$) varying from 400 - 10,000 μatm (Cai 2011). Animal and plant decay process and forest fire also releases CO$_2$. Volcanic eruptions which release C from rocks deep in the Earth’s crust are the negligible natural source.

1.6.1.2 Sink

On average only 45% of each year’s emissions remain in the atmosphere (IPCC 2001). The remaining 55% is absorbed by land and ocean sinks. According to Carbon Budget 2010, natural land and ocean, CO$_2$ sinks removed 56% of all CO$_2$ emitted from human activities during the 1958 - 2010. Oceans and terrestrial plants are considered to be major sinks for atmospheric CO$_2$ (Cox et al 2000). The oceanic sink accounts for ~48% of the total fossil-fuel and cement-manufacturing emissions (Sabine et al 2004). However, CO$_2$ sinks have not kept pace with rapidly increasing emissions, as the fraction of emissions remaining in the atmosphere has increased over the past 50 years. Through increasing global temperatures, via human induced global warming, rising sea temperatures have significant effects on the oceanic CO$_2$ sink. Increasing CO$_2$ concentrations in the atmosphere may slightly reduce oceanic pH and so lead to a small increase in CO$_2$ uptake. However, as water temperatures increase the solubility of CO$_2$ is reduced, and the likelihood of water stratification is increased - both leading to an overall reduction in oceanic CO$_2$ uptake.

1.6.1.3 Global CO$_2$ Concentration

Atmospheric CO$_2$ continued to increase; reached a globally averaged concentration of 387.2 ppm at the end of 2009 (Friedlingstein et al 2010). According to Carbon Budget (2010), the annual growth rate of atmospheric CO$_2$ was 2.36 ± 0.09 ppm in 2010, one of the largest growth
rates in the past decade. The average for the decade 2000-2009 was
1.9 ± 0.1 ppm per annum, 1.5 ± 0.1 ppm for the decade 1990 - 1999, and
1.6 ± 0.1 for the decade 1980 - 1989 (Carbon Budget 2010). Recent CO₂
emissions from deforestation and other land-use changes (LUCs) have
dropped compared with the 1990s, primarily because of reduced rates of
deforestation in the tropics (Global Forest Resources Assessment 2010). In
2010 atmospheric CO₂ concentration reached to 389.6 ppm, 39% above the
concentration at the start of the Industrial Revolution (about 278 ppm in 1750)
(Peters et al 2011). The present concentration is the highest during at least the
last 800,000 years. The IPCC (2007) has predicted that if anthropogenic
emissions of CO₂ continue at present day levels, the atmospheric
concentration of CO₂ would increase to 415 - 480 ppmv by 2050, rising to
460 - 560 ppmv by 2100.

1.6.2 Methane (CH₄)

Methane (CH₄) is one of the atmospheric infrared active GHGs that
is both highly dynamic in atmospheric photochemistry and of significance in
radiative forcing (Solomon et al 2007). The radiative efficiency of CH₄ is 1
order of magnitude larger than that of CO₂ (3.7 × 10⁻⁴ versus 1.548 × 10⁻⁵
Wm⁻² ppb⁻¹) (Ramaswamy et al 2001). This is why the contribution of CH₄ to
atmospheric radiative forcing is currently ranked second after CO₂ (IPCC
2007). Following water vapor and CO₂, CH₄ is the most abundant GHG in the
troposphere.

1.6.2.1 Sources

CH₄ emissions are very diverse, covering a wide range of natural
(wetlands, termites, oceans, marine hydrates, geological sources, wild
animals, and wildfires) and anthropogenic (energy production from coal and
natural gas, mining, landfills and waste treatment, ruminants, rice cultivation, and biomass burning) sources (Denman et al. 2007). The total flux of CH$_4$ into the atmosphere from all sources is currently 566 Tg CH$_4$ y$^{-1}$, which is more than double the pre-industrial value (Solomon et al. 2007) and of which 60 - 70% is of anthropogenic origin. Natural sources of CH$_4$ are estimated to produce 37% of the total CH$_4$ flux into the atmosphere every year. The largest source of natural CH$_4$ emissions is natural wetlands, which contribute 170 Tg CH$_4$ y$^{-1}$ (U.S. EPA 2010). CH$_4$ sources to the atmosphere generated by human activities exceed CH$_4$ sources from natural systems.

1.6.2.2 Sink

CH$_4$ is important to both tropospheric and stratospheric chemistry, significantly affecting levels of ozone, water vapor, the hydroxyl radical, and numerous other compounds. The photochemical oxidation of CH$_4$ by hydroxyl free radical (OH•) in the troposphere leads to the formation of formaldehyde (CH$_2$O), carbon monoxide (CO), and ozone (O$_3$), in the presence of sufficiently high levels of nitrogen oxides (NO$_x$) (Wuebbles and Hayhoe 2002). Along with CO, methane helps to control the amount of hydroxyl free radical (OH•) in the troposphere. This is the largest sink for atmospheric CH$_4$ (90%). Other smaller sinks include reaction with free chlorine (Platt et al. 2004; Allan et al. 2005); destruction in the stratosphere and soil sinks (Born et al. 1990). In the stratosphere, CH$_4$ reacts with OH• and produces water vapor and ozone, and plays a key role in the conversion of reactive chlorine to less reactive HCl. Both tropospheric O$_3$ and stratospheric water vapor are also GHGs thereby further increasing RF. The final oxidation product of CH$_4$ is CO$_2$. 
1.6.2.3 Global CH$_4$ Concentration

CH$_4$ emission generated by human activities has exceeded natural emissions over the last 25 years. Atmospheric concentration of CH$_4$ in dry air mole fractions (nmol mol$^{-1}$, abbreviated ppb) has increased from 380 ppb in the Last Glacial Maximum (LGM) (Monnin et al 2001) to 715 ppb in 1750 (Etheridge et al 1998) and 1787 ppb in 2008 (Dlugokencky et al 2009). The present day global atmospheric mean methane concentration contributing an RF of +0.48 [± 0.05] W m$^{-2}$. Dlugokencky et al 2001 reported that the global methane increase averaged 3.9 ppb per annum during the three-year period 1995 - 1997, but it was 12.7 ppb in 1998. Abrupt changes in the CH$_4$ growth rate during 1991, 1992, and 1998 in CH$_4$ concentration assumed to be related with chemical sink (Dlugokencky et al 2003), wetland emission rates (Walter et al 2001), and emissions from biomass burning (Langenfelds et al 2002).

1.7 AIR-SEA GAS EXCHANGE (ASGE)

Air-sea gas exchange (ASGE) plays a vital role in climate and has been the focus of continuing research. Several important atmospheric gases are present in coastal waters in excess levels. The exchange of gas between the air and the sea is, in theory, governed by the rate of molecular and turbulent diffusion, the distance the diffusion has to cover, and through bubble ebullition (particularly for CH$_4$, but sometimes for other trace gases also) (Upstill-Goddard 2006). ASGE has its own importance in biogeochemical cycling of climate, weather, and health-related gaseous compounds (Wanninkhof et al 2009). ASGE for specific gas determines its concentration in the atmosphere and water and in turn change climate radiative forcing, ecosystem health. With that interest, intense research has been done over the past two decades on ASGE and its environmental controls (Donelan et al 2002).
The concentrations of trace gases in the air and the sea are relatively constant since these two media undergo rapid and turbulent mixing. The exception to this is a thin layer of water, just 20 - 40 μ thick, which, because of the surface tension of the water, is unable to mix well (Jähne and Haußecker 1998). This stagnant film is the barrier across which the diffusion has to occur. Apart from the process of bubble ebullition, air-water gas exchange is driven by molecular and turbulent diffusion (Zappa et al 2003). For gases that are very soluble or react with water, the atmospheric sub-layer provides the greatest resistance to gas exchange, whereas for sparingly soluble gases transport through the aqueous sub-layer is the rate limiting step. Most gases of biogeochemical interest (e.g. CO₂, O₂, CH₄, N₂O, DMS, COS, CS₂, CO) fall into the latter category and so for these the air-side boundary can be ignored for all practical purposes (Upstill-Goddard 2006).

Though trace gas flux data are sporadic from tropical ecosystems (Nirmal Rajkumar et al 2008), this provides a need for detailed estimation of gas flux data from tropics. Present study supplies some essential CO₂ and CH₄ ASGE data from globally significant mangroves and estuary on the northeast coast of India.

1.7.1 Flux Measurements

The rate of gas exchange between air and water is an essential quantity in a number of contexts, from mass balances to the calculation of whole-system metabolism (Cole et al 2010). Direct measurements of the air-sea fluxes are too few to contribute directly to the calculation of large-scale flux fields. Rather they are important for developing, calibrating, and verifying the parameterization formula used to estimate the fluxes from the basic variables. Thus, the accuracy of the direct flux determinations represents
an accuracy limit for the indirect estimates. Instantaneous air-sea fluxes can be measured directly with floating chambers (FCs) (Frankignoulle 1988). Partial pressure of CO$_2$ (pCO$_2$) contained in the air can be measured with an infrared gas analyzer connected to the FC by an air pump (Frankignoulle and Disteche 1984). The decreasing or increasing partial pressure of trace gas of the headspace over time indicates influx from the atmosphere and efflux from the water column respectively. This technique is simple, inexpensive, and highly portable. However, FC-derived fluxes are problematic as well because this method suppresses the direct wind effect (such as surface turbulence) on ASGE during brief time intervals (Frankignoulle 1988) but takes into account sea turbulence due to the sea state and exchange due to bubbling. Some researchers have reported large discrepancies between fluxes measured using floating chamber and other techniques (Kremer et al 2003) whereas another group supported this direct method (Repo et al 2007; Soumis et al 2008).

The actual physics of gas exchange is complex (MacIntyre et al 1995). Nevertheless, the indirect method of measuring diffusive transfer of gases (like, CO$_2$) to or from aquatic surfaces can be adequately described using the equation:

$$F = k \alpha \Delta pCO_2$$  \hspace{1cm} (1.1)

In this, the flux (F) of CO$_2$ in mmol m$^{-2}$ d$^{-1}$ across the air - water interfaces. Here k is the piston velocity (e.g., cm h$^{-1}$) which can be conceptualized as the depth of the water column equilibrating with the atmosphere per unit time, $\alpha$ is the solubility coefficient of the gas (mol m$^{-3}$ atm$^{-1}$), $\Delta pCO_2$ is the difference of CO$_2$ partial pressure between water and air (atm). The solubility of gas (like CO$_2$) follows a known relationship with Sea Surface Temperature (SST) and salinity and climatological values of $\Delta pCO_2$. 

Since both the atmospheric and aqueous CO$_2$, partial pressure can be easily measured in the field (Cole and Prairie 2009), the main challenge is estimating the gas transfer velocity $k$ (Vachon et al 2010) accurately. In order to make easier comparisons, the term $k_{600}$ is used, which is the $k$ for CO$_2$ at 20°C in freshwater, that is, $k$ using a Schmidt number (Sc) of 600 (Raymond and Cole 2001). The variation of $k$ values among gases and temperatures are related via the Schmidt number for each gas (the ratio of kinematic viscosity of water and the gas diffusion coefficient) (Cole et al 2010).

1.7.2 Measuring $k_{600}$

The transfer velocity ($k_{600}$) which controls the movement of gas particles across the air-water interface is therefore, a critical variable in the global C cycle research. One of the major sources of uncertainty in the calculation of air-sea fluxes on a global scale is the parameterization of the gas transfer velocity ($k_{600}$). $k_{600}$ is a function of wind speed and tidally induced turbulence within the water (Kremer et al 2003). In the estuarine system $k_{600}$ will then be a function of depth, mean tidal velocity and wind speed (Borges et al 2004b). Direct measurement of $k_{600}$ has been done through mass balance techniques that use O$_2$ (Devol et al 1987) and $^{222}$Rn (Elsinger and Moore 1983), it was ambiguous until the advent of the dual deliberate tracer methods ($^3$He and SF$_6$) that clear patterns of gas transfer with wind over the ocean were observed (Clark et al 1994, 1996; Carini et al 1996).

Several authors have proposed equations that best describe the conditions of the system studied. First popular gas exchange - wind speed parameterization was derived from the conceptual model of wind-wave tunnel and theoretical considerations of natural environment (lake) by Liss and Merlivat (1986). They assumed three linear segments of gas transfer with
wind: (i) the smooth regime, (ii) a regime with an undulating surface, and (iii) a regime with breaking waves (Wanninkhof et al 2009).

\[ k_{600} = 0.17 \, U_{10} \, (U_{10} < 3.6 \, \text{m s}^{-1}), \, (i) \]
\[ k_{600} = 2.85 \, U_{10} - 9.65 \, (3.6 < U_{10} < 13 \, \text{m s}^{-1}), \, (ii) \]
\[ k_{600} = 5.9 \, U_{10} - 49.3 \, (U_{10} > 13 \, \text{m s}^{-1}), \, (iii) \]

\( k_{600} \) is expressed in cm h\(^{-1}\) and \( U_{10} \) is expressed in m s\(^{-1}\).

Wanninkhof (1992) used the global bomb \(^{14}\)C and suggested that \( k \) scaled with \( U_{10}^2 \)

\[ k = 0.32(U_{10})^2 \, (Sc/600)^{0.5} \]

According to Clark et al 1995: \( k = 2 + 0.24U_{10}^2 \)
According to Borges and his colleagues 2004b: \( k = 1.0 + 1.719 \, w^{0.5} \, h^{-0.5} + 2.58 \, U_{10} \)

Where \( k \) is gas piston velocity in cm hr\(^{-1}\), \( w \) is water current (cm s\(^{-1}\)), \( h \) is the depth (m), \( U_{10} \) is the wind speed at 10 m height and \( Sc \) is calculated from the relationships described in Clark et al (1995).

1.7.3 Factors Influencing Flux

The many different mechanisms and properties that control the air-sea fluxes of trace gases can have large spatial and temporal variability, particularly in the coastal environment. Rates of air-sea gas transfer across the coupled boundary layers are controlled by several physical and biogeochemical controls (Upstill-Goddard 2006). Upscaling involves relating gas transfer to the environmental factors that influence the ASGE (Figure 1.6). Most commonly, upscaling is achieved by relating gas transfer to wind speed (Wanninkhof 1992), surface films (Zappa et al 2001, 2004; Tsai and Liu 2003), bubble entrainment (Zhang et al 2006; McNeil and
d’Asaro 2007), rainfall (Ho et al 2004; Takagaki and Komori 2007), boundary-layer stability (Erickson 1993) and presence of organic matter or hydrocarbons at the air-sea interface (Frankignoule 1988).

In Figure 1.6, on the left are environmental forcing factors (kinetic forcing) that control the \( k \), and the variables that influence the forcing.

![Simplified schematic of factors that affect air-sea CO\(_2\) fluxes](image)

**Figure 1.6**  *Simplified schematic of factors that affect air-sea CO\(_2\) fluxes (Source: Wanninkhof et al 2009) (\( u_* \) = water side friction velocity)*

On the right are the factors that affect the air-sea pCO\(_2\) difference (thermodynamic forcing), also called thermodynamic driving potential. Friction velocity is a better environmental variable to estimate gas transfer than wind because it is intrinsically related to turbulence at the water surface (Wanninkhof et al 2009). The solubility coefficient \( \alpha \) of a gas is influenced by temperature and salinity (Wiesenburg and Guinasso 1979; Weiss and Price 1980) and also by its Sc (Wanninkhof 1992; Clark et al 1995). Temperature
impacts on the air-water gradient of the gas (ΔC) and salinity affects $k$. Solubility decreases by 50% over a temperature range of 0 - 25°C at any specified salinity and about 20% over a salinity range of 0 - 35 at any specified temperature. $Sc$ is influenced by temperature as there is a threefold decrease in $Sc$ between temperatures 0 - 20°C and changes only a few percent over the salinity range of 0 - 35 (Neetha 2008). Irrespective of the mechanism of gas transfer, it is clear that wave field will strongly affect the exchange. Therefore, fetch, the distance the winds blow over the ocean, is believed to have a first-order effect on the transfer (Fairall et al 2006). Bubble effects are often considered additive to transfer across the air-water interface, especially for CH$_4$ (Shalini et al 2006; Wanninkhof et al 2009). Studies suggest that the enhancement by bubbles can be scaled roughly to the cube of the wind with strong solubility dependence (Asher et al 2002). According to Woolf (1997), bubbles contribute 30% of the global gas transfer velocity of CO$_2$. Surfactants inhibit the exchange primarily through inhibition of surface turbulence (Frew 1997). Rain has an increased effect on the gas transfer velocity (Ho et al 1997, 2004; Takagaki and Komori 2007). Controlled studies show that higher rainfall rate and larger drop size maximize the potential contribution to gas exchange. Komori et al (2007) have estimated that the effect of rain on CO$_2$ exchange on the global scale is less than 5%.

1.7.4 Trace Gas Emissions from Coastal Ecosystems

Coastal ecosystems are considered to be the important sources of climatically active trace gases to the atmosphere, impacting regional or even global tropospheric budgets (Bange 1994; Frankignoullle et al 1998; Upstill-Goddard et al 2000, Borges et al 2003; Upstill-Goddard 2006).
1.7.4.1 Carbon dioxide (CO$_2$) in coastal ecosystems

Several studies showed that near-shore ecosystems such as estuaries, mangrove waters, salt marsh waters and coral reefs are assumed to be a net source of CO$_2$ (Cai and Dai 2004; Borges et al 2005; Cai et al 2006) because they receive massive inputs of organic matter, which is decomposed in the coastal ocean and releases CO$_2$ (Borges 2005). However, besides the organic matter, there are also nutrients coming from the land, enhancing the primary production and thus causing an uptake of CO$_2$, which possibly could result in a net CO$_2$ influx at the coastal ocean. In general, estuaries are CO$_2$-supersaturated as a result of the respiration of the riverine OC input (Chen 2004). The overall source of CO$_2$ from near-shore ecosystems has been evaluated to $\sim$0.50 Pg C y$^{-1}$, mainly related to the emission of CO$_2$ to the atmosphere from estuaries ($\sim$0.36 Pg C y$^{-1}$) (Chen and Borges 2009). Borges et al (2003a) reported oversaturation of CO$_2$ in different mangrove forest surrounding waters, suggesting that this surface water be a significant source of CO$_2$ to the atmosphere, though the entire ecosystems (sediment, water and vegetation) are probably sinks. The direction and magnitude of air-water CO$_2$ exchanges strongly depend on the type of ecosystem at the coast (Borges et al 2005), the ocean currents dominating at a respective coast (Liu et al 2000) and the geographical latitude (Liu et al 2000; Borges et al 2005). Isotopic signatures from sediments suggest that most of the terrestrial POC is degraded in estuaries (Hedges et al 1997) in accordance with the strong net heterotrophic nature of the system (Gattuso et al 1998; Hopkinson and Smith 2005).

Most of the terrestrial DOC is removed before reaching the deep ocean (Borges et al 2005). Of the total amount of removed DOC only the fraction removed by degradation contributes to the CO$_2$ emissions, but there is a certain amount removed by flocculation and adsorption. A significant
fraction of the CO$_2$ emission from estuaries might as well be sustained by mixing in OC and DIC from the open ocean (Borges et al 2005).

1.7.4.2 Methane (CH$_4$) in Coastal Ecosystems

Wetlands are the dominant natural source of CH$_4$ over the globe and emit between 100 and 231 Tg CH$_4$ y$^{-1}$ globally (Denman et al 2007) and expected to remain largely unchanged in the future (U.S. EPA 2010). Bange et al 1994 reported that up to 75% of total oceanic CH$_4$ emissions are from estuarine and coastal areas, which contribute around 2% of global atmospheric CH$_4$ emission.

Mangroves and estuarine waters are rich in nutrients and tend to have higher rates of primary productivity (Morris and Bradley 1999), which in turn leads to more organic material falling to depth, depleting oxygen levels and creating favorable conditions for methane-producing bacteria (Chanton and Whiting 1995; Heyer and Berger 2000). A large portion of CH$_4$ emissions can be linked to the biological process of anaerobic decomposition, in which bacteria break organic matter (that occur both in the water column and in sediments) down in the absence of oxygen (Liikanen et al 2009). Methanogens are specialized group of microbes (bacteria) that break down OC molecules to produce CH$_4$ through the process of methanogenesis. Some of this CH$_4$ can be partly or completely oxidized by another group of bacteria, called methanotrophs with the presence of O$_2$. While the remainder CH$_4$ can bypass the oxidizing zone by bubble ebullition (Chanton and Whiting 1995) or by vegetation-mediated (through the roots of many species of wetland plants) and ultimately enter the atmosphere (Krithika et al 2008). Highest rate of CH$_4$ oxidation occurs at the interface of anoxic and oxic zones, where both CH$_4$ and O$_2$ are present in high amount (Hanson and Hanson 1996). Anaerobic oxidation of CH$_4$ is also possible if enough
SO$_4^{2-}$ is present in the system (Boetius et al 2000; Valentine 2002). Whalen (2005) recently summarized wetland biogeochemical controls on CH$_4$ emissions and grouped these into process-level and ecosystem-level factors. The rate of CH$_4$ production is dependent on several process-level factors such as soil temperature, the amount and quality of substrate available from vegetation primary production and organic matter decomposition (Christensen et al 2003), and soil pH (Garcia et al 2000).

1.8 CARBON IN FUTURE

Statistical analyses of historical data suggest that population growth and urbanization have been the major drivers of energy use and GHG emission's growth over the past several decades (Dietz and Rosa 1997; Cole and Neumayer 2004; O’Neill et al 2010). To prevent runaway global warming, which would become very likely if global average temperatures exceed 2°C above pre-industrial levels, the world community must cut GHG emissions by at least 60% by 2050 (Diesendorf 2007).

Forests currently store about 40% of the entire C held in terrestrial ecosystems. An estimated 50% of the C in the atmosphere that becomes bound or ‘sequestered’ in natural systems, is cycled into the seas and oceans (Nellemann et al 2009). “Blue carbon” is the C stored by coastal and marine ecosystems. Some 93% of the earth’s CO$_2$ (40Tt) is stored in the oceans. In addition, oceans cycle about 90 Gt of CO$_2$ y$^{-1}$ (González et al 2008), and remove over 30% of the C released to the atmosphere. Conserving key coastal and marine ecosystems, like conserving forests, is an immediately available and cost-effective tool for removing GHGs already in the atmosphere (Trumper et al 2009). Another approach of reduction in GHG emissions are possible by accelerating energy efficiency measures, boosting the deployment
of cleaner energy generation and by using renewable such as solar, wind and geothermal.

1.9 SEDIMENT ACCUMULATION IN COASTAL ECOSYSTEMS

Sedimentation (as well as erosion) also is a basic phenomenon of nature dealing with loose sediments within the transporting cycle from source to sink locations. Sedimentation of coastal environment is often associated with human interference in the physical system, such as land-use changes (Walling 2006), construction of artificial structures or the dredging of sediment from the bed to increase the flow depth or width. Sedimentation affects the navigation, shoreline erosion and stability, migration of shoals, fate of nutrients and contaminants such as heavy metals and pesticides, turbidity, primary productivity (Wolanski 1995).

1.9.1 Role of Mangroves in Sedimentation

The mangrove forests play a significant role in trapping sediment from tidal creeks and coastal oceans, and they are presumed to be an important sink of suspended sediment (Wolanski 1995; Furukawa et al 1997). Mangrove trees possess highly developed and complex root structures that slow down the flow of water during tidal inundation and induce sedimentation of suspended soil particles from the overlying water column (Kathiresan 2003). The efficiency of sediment trapping also varies with sediment grain size, as fine-grained sediments accumulate faster than coarse grained sediments (Mazda et al 1995). Mangrove species with widely spread pneumatophores (eg. *Avicennia* spp.) and compact networking of stilt roots (eg. *Rhizophora* spp.), traps more sediments compare to other mangrove species (Furukawa and Wolanski 1996; Kathiresan 2003). Bird and Barson
(1977) estimated the annual sedimentation rate in mangrove from different areas, ranges between 1 - 8 mm. The main sources of particulate sediment into coastal areas are fluvial discharge, dumping of dredged material and re-suspension of bottom sediment by waves and ship movements (Wolanski 1994). Coastal mangrove forests are mostly connected to the sea via tidal creeks. Sediment transport mechanisms in mangrove creeks are mainly dependent on hydrodynamic processes such as asymmetry of the tidal currents, baroclinic circulation, tidal pumping and shear-induced destruction of flocs (Wolanski 1995).

1.9.2 Role of Estuaries in Sedimentation

Estuaries are recognized as a trap for fine, cohesive coastal sediments (FitzGerald and Knight 2005; Syvitski et al 2005). Coastal sedimentary processes are inherently dynamic but major changes have been related to anthropogenic activities in upland areas (Syvitski et al 2005). Estuaries are associated with rivers or other forms of runoff from land. They are the immediate recipients of sediment carried by those rivers, as manifest by the formation of river deltas. In the long term, sediment build-up in estuaries are limited by a dynamic balance between the effects of tides, waves and rivers on sediment inputs and outputs in different parts of an estuary. Estuarine export of fine and coarse sediment is poorly understood because of the tidal pumping mechanism involved in estuarine sediment import (Woodroffe 2003; Wolanski 2006).

The Hooghly is a macro-tidal estuary, receives high sediment loads from the river Ganges, majorly filled with fluvial sediments. Particle settling in this estuary can be enhanced by the change from fresh to salt water, the rise and fall of the water level with the tides, and the presence of turbidity maxima during slack tides.
1.10 BIOGEOCHEMICAL CYCLING OF TRACE METALS IN COASTAL SEDIMENTS

Trace metals are designated as a group of metals exist in minute quantities, typically occur at concentrations of $<1$ ppb (part per billion) or $<1 \, \mu g \, L^{-1}$, also reported in molar units in natural systems and acts as micronutrients for many organisms but elevated concentrations can be toxic to living organisms (Donat and Bruland 1995). Several studies have been carried out in coastal environment on cycling of trace metals, because of their toxicity, bioaccumulation capacity, and persistent nature, and ultimately, it was proven that coastal ecosystems act as sinks for anthropogenic contaminants in tropical and subtropical areas (Banerjee et al 2012 and references there in). The prevalent tribulations with trace metals are that they are persistent, and they bioaccumulate in the time periods (Passos et al 2010). So, in addition to posing a threat to various coastal ecosystems around the world, toxic metals may directly jeopardize the development, reproduction, or life of the coastal organisms (Valette-Silver 1993) and also pose a long-term public health risk, especially for the human population that relies on fishery resources (Eimers et al 2001; Nobi et al 2010). One particularly important distinguishing feature of trace metals is their ability to bond reversibly to a broad spectrum of compounds (Benjamin and Honeyman 2000). Thus, the major inputs of trace metals to coastal areas are derived from riverine, atmospheric, and anthropogenic sources. Trace metal enrichment in soil, water, and air may result from natural sources (like weathering of rocks and volcanic activities) and/or anthropogenic activities such as smelting, mining, agricultural, and waste disposal technologies (Farkas et al 2007).

Sediments represent an important sink for trace metals in aquatic systems, and metal concentrations in sediment can be several orders of magnitude greater than in the overlying water (Johnson et al 1997). Trace
metal dynamics is more complex in the estuarine system compared to other aquatic systems due to strong gradients in chemical composition of the water, variable suspended matter concentrations and complex hydro-dynamic processes (Morel et al 1991; Millward and Turner 1995). The partitioning of trace metals between the dissolved and particulate fractions, and their transport in estuaries can be affected by variability of in-situ processes such as coagulation and flocculation in the Estuarine Turbidity Maximum (ETM), re-suspension events (of sediments and pore waters), bioturbation, burial (Santschi et al 1997; Bianchi 2007), redox, ionic strength abundance of adsorbing surfaces, and pH chemistry of soil (Wen et al 1999; Bianchi 2007). The cycling of trace metals in mangrove ecosystems has a specific interest in scientific community because of their potential role in the abatement of trace metal pollution (Lacerda 1998). Mangrove plants can remediate metal pollutants from the sediments, mainly in two ways: (1) phyto-stabilization, in which plants convert pollutants to a less bioavailable form and/or prevent pollutants’ dispersal by wind erosion or leaching; and (2) phyto-extraction, in which plants accumulate pollutants in their harvestable tissues, thus decreasing the concentration of the pollutants in the soil. High sedimentation rates in mangrove environments, along with anaerobic and reduced sediment condition, rich in sulfide and organic matter content, facilitates rapid accumulation and burial of trace metals in the sediments (Lacerda 1998; Janaki-Raman et al 2007). Thus, mangroves can act as biogeochemical barriers to trace metal transport in coastal waters (Lacerda et al 1999).

1.11 OBJECTIVE OF THE STUDY

The biogeochemical properties of mangroves are the least understood of the ecological processes, along the transition from upland to coastal margin ecosystems. The purpose of the proposed research work is to
understand the coastal and oceanic fluxes of elements through the Hooghly estuarine and the Sundarbans mangrove ecosystems. This work is motivated by the observation that human activities are significantly altering coastal ecosystems worldwide by changing the flows of sediment, carbon, and nutrients to the coastal ocean with likely consequences for the sequestration or emission of anthropogenic CO$_2$ (Borges 2005) and ultimately threatening the system. As environmental alterations may be registered in the substrate of sediments, changes in grain size as well as trace metal concentration in sediments could be used to evaluate human impact in the coastal ecosystems. In an area like the Sundarbans, which is known as one of the biodiversity hot spots of India, where the lives of people have higher dependency on the waters surrounding them either by fishing or other related activities, even a small variation in the mangrove surrounding waters can cause severe impact on their lives and properties. It is necessary, therefore, to identify the major anthropogenic activities impacting on the Sundarbans mangroves and the adjoining macro-tidal Hooghly estuary, including the most serious stress factors such as nutrient fluxes, OC loading and trace gas emissions. It is worth examining these in detail in order to develop effective management strategies to mitigate their impacts. As mentioned above, this study addresses a few key global change problems on regional mangrove and estuarine ecosystem level, emphasizing their interactions with sediments, water and atmosphere.

This study focuses on the following hypotheses: (1) There are noteworthy differences in the magnitude of nutrient fluxes between the various system studied on seasonal basis (2) Coastal waters are significant sources of CO$_2$ and CH$_4$ to the atmosphere and have considerable seasonal variations (3) Accumulation of sediment in the coastal environments depends on their internal system energy.
The following are the objectives of the present study that have been focussed in the context of local changes in environmental biogeochemistry:

- Study of spatial and seasonal scale variation of various forms of dissolved inorganic and organic nutrients in surface waters of the Hooghly estuarine and the Sundarbans mangrove ecosystems.

- Application of the biogeochemical model (LOICZ - Land Ocean Interactions in Coastal Zone) for C-N-P-Si fluxes on the seasonal basis, using a case study of the Hooghly estuary to understand the biogeochemical processes of nutrients.

- Seasonal and spatial scale measurement of dissolved CO$_2$ and CH$_4$ and their air-sea exchange processes (fluxes) from the estuarine and mangrove waters.

- Determination of the rate of sediment accretion in the Hooghly estuarine and the Sundarbans mangrove ecosystems.

- Estimation of the rate of accumulation of trace metals in the estuarine and mangrove sediments and find out the possible sources of metal input to the system.

- Spatial scale measurement of trace metals in the bed sediments and assess the current status of trace metal pollution in these coastal ecosystems using different environmental indices.

In view of the complex nature of the processes occurring in the coastal ecosystems, a multi-disciplinary effort is necessary to find a holistic solution for their management and the present research work is a step forward in this direction.