CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The composition of the global atmosphere is predominantly a product of the activity of the biosphere. The global atmosphere is chemically complex and evolving, possessing fundamental chemical connections to the oceans, land and the biota. It is this ‘biosphere-atmosphere-hydrosphere’ interaction, that collectively determines the composition of the global environment and its susceptibility to change (Fig. 1.1). The earth's atmosphere is a vital resource and until recently appeared unaffected by human activities, except on local scales. However, during the past decade it has become abundantly clear that anthropogenic activities have significant impacts on the Earth's atmosphere, hydrosphere and the biosphere. The rates of these transfers are now so large and the products of the chemical reactions are so hazardous that the atmosphere, land and ocean can no longer cope with this assault. The overall aim of this research work is to describe, evaluate and understand the interactive physical chemical and biological processes that regulate the Earth system, the changes that are occurring in this system and the manner in which they are influenced by human actions, based on a micro level case study on mangrove ecosystem.

1.2 COASTAL WETLAND ECOSYSTEMS

Ocean margins, which comprise, estuaries, coastal wetlands and similar marginal ecosystems, are globally critical ‘Land-Ocean interfaces’, controlling the anthropogenic and terrestrial fluxes and fate of
chemicals and biological production to the open ocean. The coastal region include ecosystems from the upper intertidal regions (including tidal freshwater ecosystems) to the outer edges of the continental shelves. These areas are sites where terrigenous materials are introduced into the ocean, where productive wetlands have developed and biogenic zones in near shore waters are the most productive regions of the oceans. Ocean margin ecosystems, have been used throughout human history as a depository for waste materials and currently several new and potentially toxic materials are continuously added to these systems. Of great ecological and socio-economic concern today are the tropical coastal wetlands that face severe environmental threats due to human mediated disturbances, altering the fundamental ecostructure and chemistry of these fragile ecosystems.

In spite of the global attention currently focused on the wetland ecosystem, there is yet no single, universally accepted definition of a wetland. The main cause of this, is the wide diversity in wetland types and the difficulty in demarcating the boundaries of this ecosystem, which lies at the interface between dry land and open water. The 1971 Ramsar Convention defines wetlands as "areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water, the depth of which at low tide does not exceed six meters". In addition, wetlands "may incorporate riparian and coastal zones adjacent to wetlands, and islands or bodies of marine water deeper than six meters at low tide lying within the wetlands" (WWF 1992). India, by virtue of its extensive geographical stretch and varied terrain and climate, supports a rich diversity of inland and coastal wetland habitats. India's 7500 km long coastline has numerous lagoons, estuaries and mangrove swamps, with rich species diversity.
1.3 MANGROVE ECOSYSTEMS

Tropical coastal ecosystems are dominated by forested wetlands in the intertidal zone known as 'Mangroves', influenced by the neritic waters of the tropical coastal oceans and inflow of freshwater from major riverine systems. Mangroves are widely distributed in the subtropical and pantropical areas and their geographical distribution as well as species diversity are shown in Fig.1.2. The mangroves characterize a unique ecosystem with rich biological diversity and genetic variability, similar to the tropical rainforest. In a mangrove ecosystem, the trees and shrubs form the basic component. These communities of salt-tolerant intertidal vegetation with their peculiar morphological and physiological adaptations to thrive in muddy and swampy soils, act as protective barriers between the land and sea. Further, the most extensive stands of mangrove, tend to develop in alluvial and tidal plains, although coastal barrier and lagoon systems may support complex mangrove communities in areas without human interference. The distribution of mangrove forests are also associated with sources of terrigenous sediment, relatively high freshwater inputs and protected or rapidly prograding shore-lines. The mangrove ecosystem provide shelter and abundant food for a variety of fauna and serve as nurseries for the juveniles of crustaceans, molluscs and fishes. Further, the continuous flow of nutrients and particulate organic matter from the mangrove ecosystem into the coastal waters, enriches the productivity of these waters.

1.3.1 Geographical Properties of Mangroves

*Regional Classification:* Thom (1982) proposed that the combination of geophysical energies with the geomorphology of the coastal zone, is important to establish the ecological characteristics of mangroves. According to Thom, the landform characteristics of a coastal region, together with environmental processes control the basic patterns in the structure of
Fig. 1.2  Global distribution of mangroves with species diversity

Adopted from Chapman (1975)
coastal forests. He identified five basic types of environmental settings where mangroves occur, based on the relative influence of rainfall, river discharge, tidal amplitude, turbidity and wave power. These geophysical energies are the dominant forcing functions of mangroves and collectively represent the ‘energy signature’ of mangroves. The regional scale description of mangrove environments using geomorphology and geophysical processes can be further separated into ecological classification systems as either ‘fringe’, ‘basin’ or ‘dwarf forests’ to describe the microtopographic effects of hydrology on the formation of these forest types (Lugo and Snedaker 1974). Within the regional boundaries of an environmental setting, there may exist all three ecological types of mangrove forest, depending on the local effects of tides, waves and river flow. The geomorphological type of the coastal environments can constrain the function, as well as structure of mangrove ecosystems (Twiley et al. 1992). Linking ecological processes with specific types of environmental conditions should help to develop a greater understanding of the biogeochemical processes and cycling occurring in the mangrove ecosystems.

1.3.2 Global distribution of mangroves

Information on the distribution of mangroves gathered from World Resources 1986, claims that there are 24 x 10^6 ha of mangroves in the tropics that dominate the river delta, lagoon and estuarine-coastal environments. Other estimates of mangrove area range from 15.47 to 30 x 10^6 ha, with an average of 21.8 x 10^6 ha (Lugo et al. 1990). The largest area of mangroves occur in the 0° to 10° zone with 10.07 x 10^6 ha compared to only 0.25 x 10^6 ha in the 30° to 40° latitudes. In the present study, a global extent of 16.25 x 10^6 ha based on the report prepared by Pernetta (1993) has been used to develop the global estimates of trace gas fluxes from the mangrove ecosystems of the world.
1.3.3 Mangrove Ecosystems of India

Recent estimates by Jagtap et al. (1993) suggest that India has a mangrove cover of 3150 m$^2$, over 80% of which occurs along the east coast and Andaman group of Islands. Distribution of mangroves is mainly governed by topography, tidal amplitude, substratum and salinity. Deltaic environments on India's east coast support extensive mangrove formation due to gradual intertidal slope and heavy impact of siltation (Untawale and Jagtap 1992). The western coastline has narrow intertidal belts which support the fringing mangroves.

The zonation of mangroves is mainly influenced by salinity. Polyhaline and Mesohaline zones support the maximum number of species. Limited flora like Kandelia candal, Sonneratia caseolaris, and Heretiera spp. occur in the upstream and low salinity zones (0.05 - 5 %). Along the mainland coast, Avicennia marina, A.alba, A. officinalis, Rhizophora mucronata, and Suaeda maritima are the dominant species. Generally, the luxuriant mangroves occur in the intertidal zones with regular inundations. The supralittoral zone is mainly composed of scrubby vegetation.

1.3.3.1 Ecological characteristics

Structure and Adaptations: Mangroves share a number of characteristic features that allow them to live in shallow marine waters. They are first of all shallow rooted, with their roots spreading widely or else with peculiar prop roots from the trunk and or branches. The shallow roots of Avicennia spp., often send up extensions, called 'pneumatophores', to the surface of the substrate that allow the roots to receive oxygen in the otherwise anoxic mud, in which these trees grow. The leaves are tough and succulent and have salt glands, which help to maintain the osmotic balance by secreting salt. Others exclude salt and separate fresh water from salt water at the roots by a 'reverse osmosis' process. One of the most significant
adaptations of mangroves include *viviparous* development of the embryo, followed by its dispersal by water. This condition is particularly well developed in *Rhizophora spp.*

The above overview provides an evaluation of the potential importance of mangrove ecosystems in the coastal zone. Degradation of mangrove habitat renders them increasingly susceptible to the adverse effects of climatic change and sea level rise and reduces their capacity to provide environmental goods and services in a sustainable basis. It can be observed from the Fig. 1.2 that the majority of the World’s mangrove forests are distributed along the coastlines of the developing countries, where species degradation occurs at a rapid rate due to human interferences, in addition to naturally occurring geomorphological changes. Such natural and anthropogenic alterations of the mangrove ecosystem has large-scale implications on the global biogeochemical cycling of carbon, nitrogen, oxygen, phosphorus and sulphur which are critical for the sustenance of life. The amplitude and rate of change of the global chemical cycling processes has increased erratically and indefinitely over the past few decades and it must be recognized that there is a critical threshold, beyond which the earth’s system shifts to a mode of negative feedback mechanism.

Anthropogenic interferences to the mangrove and other wetland ecosystems [which are vital links between the atmosphere, hydrosphere and the biosphere] have accelerated the mobilization of elements such as C, N, O, P, S and a few trace elements from the inert and sequestered forms into chemical species that can impact critical biogeochemical processes (Fig. 1.1). These include changes in ecosystem productivity, environmental toxicity, atmospheric energy adsorption and photochemistry. Fluxes of trace gases and nutrients from the sediment - water interface are intimately connected to the atmospheric chemical composition and eventually to global climate. Further, the complexity of trace element contamination and its adverse consequences, on the biosphere adds a positive ‘human dimension’ to alter
biogeochemical balance of this delicate ecosystem. In the present study, an attempt is made to investigate the biogeochemical fluxes of natural and human-made elements in the mangrove ecosystems and focuses on the linkage of land based activities to atmospheric dynamics. This research work aims to understand the large uncertainties and bridge the gaps in wetland biogeochemical fluxes at the biosphere - atmosphere interface with special emphasis on their impact on present and future climate change scenario.

Presented below is a collection of classical works carried out by researchers world-wide, on diverse aspects of wetland and mangrove ecosystem studies, and provides information on the topics of current concern. This will facilitate in highlighting the existing knowledge as well as the lacuna in our search for reducing uncertainties.

1.4 GREENHOUSE GASES OF CONCERN

Current concerns about climate change rest first and foremost on the documented fact that the atmospheric concentrations of a number of long-lived greenhouse gases are increasing today at rates, which projected into future could lead to significant global and regional climate change. Trace gases like carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), ozone (O$_3$) and the chlorofluoro carbons (CFCs) are very effective greenhouse gases that alter the energy balance of our planet and hence its climate. World-wide, the amount of these chemicals are increasing above their natural background levels in the atmosphere, of special importance are: CO$_2$, CH$_4$ and N$_2$O. Such chemicals present in minute amounts, are now known to have important influences far beyond what their small amounts in the air would suggest. In recent years, we have become increasingly aware of how strongly the physical and chemical properties of the Earth's atmosphere are influenced by emissions from the biosphere and by uptake of trace gases by biota. Plants also emit numerous trace gases viz. ammonia, hydrogen sulphide, and hydrocarbons (eg. CH$_4$). On the other
hand, their surfaces are major sinks for many atmospheric constituents, including pollutants such as \( \text{SO}_2 \) and \( \text{HNO}_3 \). It is obvious that the interactions between the biosphere and the atmosphere are part of a complex interconnected system (Fig. 1.1). The emission and uptake of atmospheric components by the biota, influence the chemical and physical climate through the Earth’s radiation budget.

In spite of the indisputable importance of the atmosphere-biosphere exchange for the composition of the atmosphere, the processes which control the flux rates and the magnitude of the fluxes from diverse sources remain poorly quantified. This is due to both the complexity of the biological and physico-chemical systems involved, and to the difficulty of actually measuring exchange fluxes in the field. Flux measurement of a trace gas such as methane was selected for the present study, because of its complex biogeochemical interactions with the biosphere and their importance in controlling the global climate. The fact that their atmospheric concentrations are increasing as a result of human activity, provides further complexity and interest to their study.

1.4.1 Methane Paradigm

Methane is a very important greenhouse gas for three reasons: i) its large trend of increasing concentrations, ii) its strong absorption and emission of infrared radiation and iii) the location of its absorption and emission bands at regions where \( \text{CO}_2 \) and water vapor do not absorb (so-called "Window Regions"). Global increases in the concentration of the greenhouse gases over the last 200 years are about 20\% for \( \text{CO}_2 \), 8\% for \( \text{N}_2\text{O} \) and over 200\% for \( \text{CH}_4 \) (Lorius 1988). Methane accounts for about 15\% of the radiative forcing added to the atmosphere as opposed to 55\% for \( \text{CO}_2 \), 6\% for \( \text{N}_2\text{O} \) and 24\% for the synthetic CFC (Houghton et al. 1990). The strong ability of \( \text{CH}_4 \) to absorb infrared radiation, reradiated by the Earth’s surface and its relatively short atmospheric life time of 8 - 12 years,
combined with the fact that a large fraction of the atmospheric CH₄ originates from marshes, swamps and wetland soils, makes the possibility of CH₄ control an important option for addressing global climate change.

Methane, has major natural and anthropogenic sources and both its sources and sinks are strongly influenced by human activities. Atmospheric concentrations of CH₄ currently increase by about 0.6% per year (Houghton et al. 1992), a reduction from about 1% per year in the mid 1980s (Khalil and Rasmussen 1987), with current average atmospheric concentration at ~ 1.7 ppm (Houghton et al. 1992). In addition to enhancing global warming, CH₄ is destroyed in the troposphere by oxidation with free OH radicals, producing carbon monoxide and hydrogen. Not only are CH₄ and CO the dominant consumers of tropospheric OH, OH is the major sink for CH₄ and CO. Thus, a sort of feed back can be envisioned: more CO → less OH, less OH → more CH₄ and more CH₄ → less OH and so on. Differences revealed by the global CH₄ budgets by Cicerone and Oremland (1988), Crutzen (1991) and Houghton et al. (1990, 1992) show that an accurate quantification of the individual contribution from various sources and sinks remains a challenge. Here, the budget of Houghton et al. (1992) is taken as the best available estimate and is presented in Table 1.1. It is realized that the present sources and sinks and corresponding strengths are liable to change as research progresses, for instance, the importance of methane-oxidizing bacteria in controlling emission from various natural sources is yet to be quantified (Conrad and Rothfuss 1991, Oremland and Culberston 1992). It can also be noted from the Table, that wetlands are the largest natural sources of methane to the atmosphere, produced by the metabolism of microbes called "methanogens" living in oxygen poor environments (Prinn 1994).
Table 1.1: Estimated sources and sinks of methane

<table>
<thead>
<tr>
<th>Source / Sink</th>
<th>$\text{CH}_4$ $(10^{12} \text{ g CH}_4/\text{yr})$</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SOURCES</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wetlands</td>
<td>115</td>
<td>(100-200)</td>
</tr>
<tr>
<td>Termites</td>
<td>20</td>
<td>(10-50)</td>
</tr>
<tr>
<td>Ocean</td>
<td>10</td>
<td>(5-20)</td>
</tr>
<tr>
<td>Freshwater</td>
<td>5</td>
<td>(1-25)</td>
</tr>
<tr>
<td>$\text{CH}_4$ Hydrate</td>
<td>5</td>
<td>(0-5)</td>
</tr>
<tr>
<td><strong>Anthropogenic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal mining, Natural gas and</td>
<td>100</td>
<td>(70-120)</td>
</tr>
<tr>
<td>Petroleum industry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice paddies</td>
<td>60</td>
<td>(20-150)</td>
</tr>
<tr>
<td>Enteric fermentation</td>
<td>80</td>
<td>(65-100)</td>
</tr>
<tr>
<td>Domestic Sewage Treatment</td>
<td>25</td>
<td>?</td>
</tr>
<tr>
<td>Landfills</td>
<td>30</td>
<td>(20-70)</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>40</td>
<td>(20-80)</td>
</tr>
<tr>
<td><strong>SINKS</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atmospheric removal</td>
<td>470</td>
<td>(420-520)</td>
</tr>
<tr>
<td>(tropospheric + stratospheric)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Removal by soils</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Atmospheric increase</strong></td>
<td>32</td>
<td>(28-37)</td>
</tr>
</tbody>
</table>

*From: Houghton et al. (1992)*
1.4.2 Review of methane emission from wetlands

Natural wetlands and irrigated rice lands are important source of atmospheric methane (Aselmann and Crützen 1990, Mathews and Fung 1987), accounting for about one third of the total methane sources of 515 Tg CH$_4$/yr (Houghton et al. 1992). The range in emissions calculated for these two sources remain large, being a factor of 7 for rice paddies (20 -150 Tg CH$_4$/yr) and a factor of 2 for the natural wetlands (100 - 200 Tg CH$_4$/yr). The differences in calculated global releases reported are the consequence of the large hourly, daily and seasonal variations in measured CH$_4$ emissions, uncertainty about the relative importance of the respective process, controlling factors such as soil type, gas transport by plants, interaction among plants and soil bacterial populations, soil nutrient content, soil texture and hydroperiod have not been considered. Finally the subsequent extrapolation of these flux measurements, are often obtained for short-term periods to areas and time spans for which they need not be representative.

1.4.2.1 Processes

Net emissions of CH$_4$ from the soils to the atmosphere are mainly determined by three processes: production, consumption and transfer of the gas. Both production and consumption of CH$_4$ in soils are biologically mediated (Oremland 1988 and Conrad 1989). Methanogenesis occurs in all anaerobic environments in which organic matter undergoes decomposition (Batjes and Bridges 1994). Although microbial methanogenesis has been known atleast since 1876, (Hoppeseyler 1876), elucidation of the biochemistry of the process dates from the 1930s (Barker 1936, 1956). Much of the history of the detection of atmospheric CH$_4$ and of the earliest systematic measurement data has been reviewed by Ehhalt (1974) and Wofsy (1976). These include lakes wetlands, paddy soils and the digestive tracts of termites and ruminants. These strict anaerobes, convert
fermentation products formed by other microorganisms notably CO₂, H₂ and esters and salts of methanoic acid (HCOOH) into CH₄, but other substrates may be used (Oremland 1988, Conrad 1989, Neue and Roger 1992). Alternatively, under aerobic conditions, methanotrophs can use CH₄ and other carbon substrates such as methanol (Papen and Rennenberg 1990), whereby freely drained soils can act as a sink for atmosphere CH₄ (Seiler 1984, Schütz et al. 1990). There is also experimental evidence that CH₄ oxidation may occur in some anaerobic sediments (Yavitt et al. 1988, Kimura 1992) complicating the overall picture. The anaerobic, sulphate-dependent oxidation of CH₄ has to be elucidated (Oremland 1988). Whalen and Reeburg (1990) report that sub-surface CH₄ oxidizing activity is important in controlling upward CH₄ fluxes in tundra soils where vascular plants are absent. Alternatively some of the CH₄ produced in wetland soils is lost through seepage (Kimura 1992). With reference to atmospheric CH₄ soils can act principally in two different ways: i) aerated soils can act as sinks for tropospheric CH₄ (Crill 1991, Mosier et al. 1991, Bender and Conrad 1992, Dorr et al. 1993, Koschorreck and Conrad 1993, or ii) they act as a biofiller for microbially produced CH₄ in anoxic soil or sediment compartments, which reduces the CH₄ emissions to the atmosphere (Galchenko et al. 1989, Reeburgh et al. 1993).

The main transfer processes of CH₄ to the atmosphere are ebullition, diffusion and transport through the aerenchyma of vascular plants (Bouman 1990, Batjes 1992a). The amount of CH₄ emitted through the rice plants varies between soil types (Inubushi et al. 1990) and also with the rice cultivation (Parashar et al. 1991, 1994).

1.4.2.2 Controlling Factors

In view of the variety of soils, climatic conditions and local forcing factors internationally, it remains difficult to establish unambiguous relationships between the various abiotic factors controlling CH₄ emission
from the soils. Comprehensive reviews of the environmental and agricultural (for rice-paddy wetlands) factors that could serve to explain the observed spatial and temporal variability in the rate and magnitude of CH$_4$ fluxes, have been prepared by several authors including Bouman 1990, Kimura 1992, Batjes and Bridges 1992a and Batjes and Bridges 1994). In the following section, the focus is on the importance of soil-related properties, so as to permit the correlation of similar factors that have been considered in the present study.

Yagi and Minami (1990) and Parashar et al. (1991) have insisted that organic matter supply and substrate quality are the important determinants of CH$_4$ production and emission in wetland paddy soils. They state that very high addition however, may suppress CH$_4$ emission possibly by forming toxic metabolic end products. Soil and flood water regimes interact with climate through temperature effects, changes in reflectivity, heat capacity and thermal conductivity, incoming water temperature and water flow (Neue et al. 1990). Although a temperature of 30°-35°C seems optimum for CH$_4$ production (Inubushi et al. 1990), annual CH$_4$ emissions estimated from field measurements are in the same order of magnitude (1-200 g/m$^2$/yr) for tropical, cool temperate and sub-arctic environments (Bouman 1990). Correlation of CH$_4$ emissions with temperature reflects not only the direct response of the methanogens but also an effect on CH$_4$ diffusion, which increases with soil temperature (Parashar et al. 1991). However, Yavitt et al. (1988) state that CH$_4$ production will not respond to increasing temperature if one or more of the other environmental factors is limiting.

Methane production seems to be favoured by a pH of 6.0 to 7.7 (DeLaune et al. 1986), with the optimum influenced by the soil type, soil temperature and strain of methanogens (Kimura 1992). The effect of seasonality of the hydrologic regime on soil pH and redox potential is thus important (Ponnemperuma 1984). Neue et al. (1990) indicate that a redox
potential (Eh) below -150 to -190 mV, corrected to pH 7, is required for methanogenesis. Two stages have been recognized in the sequence of reduction processes occurring in soils upon flooding (Takai and Kamura 1966). During the first stage O₂, NO₃, Mn⁴⁺ and Fe³⁺ are reduced by facultative or obligate anaerobes. Subsequently, in the second stage, obligate anaerobes reduce the sulphate present, after which methane formation can start (Batjes and Bridges 1994).

Soil texture and mineralogy through their effect on puddling, affect percolation rates and thereby the net emission of CH₄ in waterlogged paddy soils (Neue et al. 1990). According to them, heavy clay soils may crack upon drying, facilitating the rapid release of entrapped CH₄, while in slowly cracking soils, they may be more time for CH₄ to be oxidized in the soil. Nothing is known about the localization of CH₄ oxidation activities on different grain size fractions of a soil layer until the studies by Bender and Conrad (1994) showed that bulk of the CH₄ oxidizing activity was attached to the smaller mineral fractions (clay, silt and fine sand). Within the mineral fractions greater particles had higher specific activities of CH₄ oxidation than smaller particles. A significant correlation exists between the CO₂/CH₄ ratio and the content of free iron in soil and the amount of NH₄ produced during incubation (Kimura 1992). Incubation experiments have shown that soils can be ranked according to their CH₄-producing capacity (Bachelet and Neue 1993). A complicating factor in interpreting various sites is that because CH₄ flux is a function of a variety of processes and release mechanisms, which may vary seasonally and among ecosystems, simple correlation with factors such as temperature provide only an approximation of the true dynamics of methane fluxes (Wilson et al. 1989). Negative, simple linear correlations were found with Eh, electrical conductivity (EC), chloride and sulfate content and with C/N ratio and a positive correlation with pH (Conrad 1989, Neue and Roger 1992) was observed. Studies on methanogenesis in marine sediments and sulphate-rich environments has been carried out by Oremland et al. (1988). The
methanogenic bacterial population in the sediments of the Pichavaram mangrove ecosystem was studied in detail by Mohanraju (1991).

Some diurnal periodicity in CH$_4$ production has been reported by several researchers (Holzapfel-Pschorr and Seiler 1986, Yagi and Minami 1990, Khalil and Rasmussen 1991, Cicerone et al. 1992 and Yao and Chen 1994). Cicerone et al. (1992) suggest that methane release occurs largely through the vegetation and that stomatal opening may be a factor. According to them, diurnal variation could also be influenced by diurnal changes in methane oxidation rates.

It is clearly evident from the literature survey, that the tropospheric abundance of CH$_4$ has been steadily increasing in the past decades through diverse sources. Craig and Chou (1982) suggest that the methane levels are roughly three times higher than the concentration, 100 years ago. Because of the long atmospheric residence time and the high infrared absorption capacity, the warming efficiency of CH$_4$ is 20 - 32 times that of CO$_2$ (Blake and Rowland 1988). Hence an understanding and accurate quantification of CH$_4$ emission from individual sources seems to be an immediate requirement to reduce assumptions. Global extrapolations of emission rates from wetland rice fields based on few reported measurements imply great constraints (Wassmann et al. 1994). The US EPA estimates of 30 Tg CH$_4$/yr for Indian rice paddies was refined to 3-4 Tg CH$_4$/yr, based on the actual field measurements in India by Parashar et al. (1991, 1994) and Mitra 1992. This strongly suggests that global extrapolations can provide only an approximate estimate of the strength of individual sources. However, this baseline data is most essential to arrive at an accurate database or refining the previous estimates.

The preceding review clearly reflects the uncertainties that remain in assessing the relative importance of coastal wetlands such as the mangrove ecosystems in CH$_4$ production and emission dynamics.
Mangroves, can be considered as probable sources for methane, since they possess characteristics, that are typical of a methane producing environment (viz. anoxicity, high organic matter content and soil properties). They could also act as CH$_4$ inhibitors/sinks due to the presence of high salinity and sulphate. It would thus be challenging to understand the competitive inhibitions and interactions of CH$_4$ from the mangrove ecosystems and the factors that determine the time-varying fluxes of this trace gas to the atmosphere.

1.5 BIOGEOCHEMICAL INTERACTIONS AND GLOBAL CLIMATE CHANGE

The biogeochemical cycles of carbon, nitrogen, phosphorus and sulphur are intimately linked to each other through biological productivity and subsequently to problems of global environmental change. In the broadest sense "global change" encompasses both changes to the status of the large, globally connected atmosphere, oceanic and terrestrial environments (eg. tropospheric temperature increase) and change occurring as a result of nearly simultaneous local changes in many regions of the world (eg. eutrophication). The natural global earth-surface system - the atmosphere, hydrosphere, biosphere, and the shallow crust- and the coupled cycles of C, N, P and S are in a continuous state of disturbance and fluctuation. Human activities are interfering in the "workings" of the global earth surface system and the functioning of the C, N, P and S biogeochemical cycles. Agricultural, industrial and urbanization activities are adding "new" disturbances to the system, changing the rates at which C, N, P, S and other natural materials circulate in the environment (Mackenzie et al. 1993) and are resulting in addition of new and synthetic chemicals. Substances like N and P compounds, organic carbon and other organic compounds such as pesticides and trace metals (often connected to the cycles of C, N, P and S because of their bioessential nature) like Co, V and Zn, are modifying the chemistry of the aquatic system. It is this
interaction between the nutrients and trace elements that modify the biogeochemical cycles of C, N, P and S and in turn these affect other cycles and the environment as a whole. The present research work discusses how the interactive web of C, N, P and S and trace element biogeochemical cycling has been affected by human activities and its implications on global change.

1.5.1 Review of biogeochemical cycling of nutrients in wetlands

During the last two decades, the global biogeochemical cycles of elements have been investigated in considerable detail. Much effort has been invested in the nutrient cycling of carbon, nitrogen, phosphorus and sulphur. Interest in these cycles and others, like those of trace metals, has been heightened by problems associated with global, regional and local environmental problems and their effect on the atmosphere (Mackenzie et al. 1993). Peierls et al. (1991) have shown recently, an important relationship between density of humans and both concentration and export of nutrients in major rivers of the world. They reported that excessive nitrate levels in surface coastal waters can lead to algal blooms and toxicity. Increased nitrogen content in surface waters have numerous sources: animal (including man) waste discharges (Moody 1990), atmospheric deposition (Fisher and Oppenheimer 1991), application of nitrogen fertilizers to forested lands (Edwards et al. 1991), deforestation (Likens et al. 1970) and industrial effluents (Moody 1990). Thus various human activities in various combinations - can cause the enrichment of nutrients in aquatic ecosystems, but it would appear that increasing size of the human population is the root cause (Likens 1992).

Land derived carbon, nutrients, freshwater and sediments, all enter the coastal zone at point inputs, the river mouths. Changes in these inputs have major consequences not only for the mixing zone between fresh and sea water, but also for the entire sediment, carbon and nutrient balance of the
coastal zone (Pernetta 1994). Pernetta further states that in shallow water, nutrients can be recycled many times, before becoming finally fixed in the sediments or being exported to the open ocean.

Mangrove ecosystems generally trap various micro nutrients and trace elements from water by the action of prop roots, algal fine root system and micro algae. Robertson (1993) indicates that mangrove ecosystems trap, transform and export nutrients to the coastal zone. According to him, major advances have been made with regard to the role of sediment bacteria in nutrient (carbon, nitrogen, phosphorus) transformation within the mangrove forests. It is believed that the growth of mangroves may be limited by both N and P supply and that the mangrove forest and their sediments may be major sinks for these nutrients.

Another significant source of nutrients to the mangrove waters, is the mineralization of organic detritus from mangrove plants. Odum and Heald (1972) showed that the degradation of mangrove litter contributed substantial amount of nutrients to the coastal waters. Studies have also revealed that major elements such as Na and Mg are not limiting factors in a mangrove environment, since they occur in large quantities in sea water, but, phosphate and nitrate are considered as limiting factors for mangrove and phytoplankton production in mangroves.

The export of detritus and dissolved elements from the mangroves have long been considered as an important support for offshore biological production. Mass balance studies (Lee 1993) have yielded equivocal conclusions regarding the direction of flow of materials to or from the mangrove and tracer methods using mangrove - specific stable isotopes or other signatures have suggested that out-welling may be much less significant than expected. Further, earlier studies have focused on particulate matters, while it is increasingly apparent that dissolved inorganics may play a more important role in material exchange between
mangrove and offshore ecosystems. Nixon (1980) showed that there was no out-welling of nutrients from mangrove environment to the adjacent water bodies.

The role of mangroves in the estuarine and inshore productivity via the detritus based energy pathway has been studied by Gwada and Slim (1993). Odum and Heald (1972) identified that besides mangrove vegetation themselves, phytoplankton can also be a major component of primary production in the mangrove ecosystems. Lugo and Snedaker (1974) have reviewed the biological processes occurring in mangrove ecosystems and the manner in which the plant species sustain their high levels of production. They further state that the flushing efficiency of the tides determine the quantity of detritus exported out of the mangrove area to the coastal waters.

In the Pichavaram mangroves of South India, a distinct seasonal variation in nutrient concentration was recorded by Ramamurthy (1985), and Mohanraju (1991). Nutrient production showed significant increase during monsoon, due to the enrichment by monsoonal floods (Chandran and Ramamurthy 1984 and Mohanraju 1991). Different aspects of research on nutrients and primary productivity in the Pichavaram mangroves have been carried out by Krishnamurthy (1971), Sundararaj and Krishnamurthy (1975), Krishnamurthy and Sundararaj (1973), Muniyandi (1985), and Vasantha (1989). All the above works report on high nutrient concentration and primary productivity in the Pichavaram mangroves. It becomes very essential to quantify the fluxes because, due to the shallow depth of the coastal area, a very significant part of the primary production is transferred to the sediments (Wollast 1993). As the high rate of sedimentation of detrital material increases, the rate of preservation of organic carbon in the sediments also increases. The important transfer of organic matter to the sediments also enhances the biological activity. As a consequence, a large part of the remineralization of nutrients occurs in the upper layers of the sediments, which may then act as an important source of dissolved N, P and
Si to the water column. Except for a few detailed studies, (Walsh 1988) some of the key fluxes of these biogeochemically active elements are poorly known. Thus, in the framework of the concern developed nowadays for the evaluation of future global environmental change, it is of primary interest to evaluate the relative strength and the various causes and components involved in the high production of the coastal zone.

1.5.2 Review of biogeochemical cycling of major elements in wetlands

Mangroves are perfect examples of plants that complete their life cycles in a saline or brackish water environment. Their wetland habitats are often complex, with the concentration and variety of salts encountered from fresh water and marine sources. Mangroves can survive in concentrations of major electrolytes (such as Na, Mg, Ca, K, Sr, Cl, SO₄ and Br) ranging from those found in freshwater to those that are equivalent to two or three times the strength in sea water. Studies on plant-nutrient relationship in mangrove areas by Hardjowigeno et al. (1993) show that besides N and P, elements such as Ca and Mg are extremely important for the growth of mangrove vegetation. The aspect of uptake, retention, return and turn over of N, P, K, Ca, Mg, Na and Cl element cycles in a Chinese mangrove ecosystem was studied by Lin (1993) and report that all these elements are critical in the energy flow of these tidal forests. Research on porewater chemistry of mangroves along the west coast of India, shows that the sediment contain higher amounts of iron, Mg, Ca, sulphates in comparison to porewaters of all the mangrove plants studied (Kanvinde and Bhosale 1993). Hence, a detailed examination of the interrelationship, distribution, retention and flux of the major elements has been a primary consideration in this research work.

It is proved beyond assumption that a major pathway for the entry of materials to the coastal zone, is through input from rivers. Much in
contrast to the mangrove ecosystems, the major ion chemistry of the sources points (i.e.) river basins and their estuaries have been studied in great detail by several researchers (Martin and Meybeck 1979, Subramanian 1987, Ramesh and Subramanian 1988b, Ramesh and Subramanian 1993). Dissolved constituents of continental waters have been investigated to understand the nature and composition of the matter transported by rivers to the oceans (Gibbs 1972) and to determine the geochemical balances. The conservative and non-conservative behaviour of major elements in marginal marine ecosystems has been extensively reviewed by Berner and Berner (1987). Preliminary and broad investigations of the chemical composition of the Indian rivers and estuaries have been periodically reported by Subramanian (1983). The chemical and sediment transport of individual river basins has also been studied by several workers for example, Godavari (Biksham 1985), Cauvery (Ramanathan et al. 1993, 1994 and Ganges (Abbas and Subramanian 1984) and Krishna (Ramesh and Subramanian 1988a,b and 1993, Ramesh et al. 1989).

From the above review, it is quite obvious that research on the chemical composition and importance of major elements in the mangroves is still rudimentary. However, there is strong consensus on the fact that the survival of the mangrove ecosystem is intimately linked to the biogeochemical cycles of major elements.

1.5.3 Review of biogeochemical cycling of trace elements in wetlands

Similar to nutrients and major elements, trace element biogeochemistry is linked to the biospheric components in a mangrove ecosystem. It is believed that the predicted future inputs of nutrients to ocean margins are estimated to increase their efficiency as sinks for trace elements of riverine and oceanic origin (Martin and Windom 1991). This along with predicted global changes will lead to an increasing role of ocean
margins in the marine biogeochemical cycling of trace elements. Heavy metals associated with particulate matter are scavenged by the sediments in the estuarine areas (Showronek et al. 1994).

The role of mangrove forests in heavy metal cycling in coastal zones is poorly known (Lacerda et al. 1988). Studies on the metallic composition of these plants are scarce and deals mostly with the macronutrients (Lacerda et al. 1985, Snedaker and Brown 1981). However, from the results obtained in temperate salt marshes (Lacerda et al. 1979, Nixon 1980) two hypotheses can be advanced: a) mangroves may be long-term sinks for metals by immobilizing them in sediments, consequently decreasing environmental risk or b) deposited metals may be remobilized through plant uptake and eventually exported with plant detritus, increasing the possibility of metals entering the coastal food chains.

Both hypotheses have been proved to occur in temperate salt marshes and in few tropical areas, but the dominance of one over the other seems to be dependent upon local environmental characteristics and the metal species (Nixon 1980, Lacerda and Abrão 1984, and Harbison 1986). The balance between input and output of metals in estuarine areas is mostly dependent on the balance of suspended matter load and its metal content (Salomons and Förstner 1984) and this is also true in areas dominated by mangrove ecosystems (Lacerda and Rezende 1984). The characterization of suspended matter during tidal cycles, in order to understand the metal balances in mangrove ecosystems was carried out by Lacerda et al. (1988). Their studies showed that a complex interaction among different parameters control metal fluxes through the system. Changes in water pH and Eh and manganese precipitation also account for peak trace element concentrations during a tidal cycle. They concluded that the possible net accumulation of metals in mangrove occurs by immobilization mechanism by the fine roots and the quantities of suspended matter entering and leaving the system. These results further indicate that there is a great difference in metal
concentration between marine and mangrove sediments. The availability of heavy metals in mangrove soils may decrease due to flooding, which subsequently reduce their uptake in plant tissues (Chiu and Chou 1991).

The present status of trace elements such as Cu, Zn and Pb in water and sediments of different estuarine systems along the east and west coasts of India were studied by Mohapatra et al. (1994). Based on the available reports, the mean values of Cu, Zn and Pb in water of almost all centres were found to be below the US Environmental Protection Agency’s (EPA) ‘Safe Limits’ except for some localized pollution. In sediments, more than 100 ppm (mean) Cu and Zn concentrations were reported for Cauvery, Cochin backwaters, Ennore Creek and Krishna estuaries.

The distribution of Mn, Cu, Zn, Ni, Co and Cd in the Parangipettai and Cuddalore marine environs of South India, was studied by Ananthan et al. (1993). Studies on contamination of trace elements in various Indian rivers and estuaries have been carried out for Krishna (Ramesh and Subramanian 1987, 1990), for the Ganges estuary by Subramanian (1993), for the Mahanadi river basin by Chakrapani and Subramanian (1993), and by Vaithiyathan et al. (1988, 1993) Ramanathan et al. (1993) in the Cauvery estuarine systems.

1.5.4 Review of sediment characteristics and mineralogy in wetlands

Substrate characteristics are probably the most important factor in terms of sustenance of the mangrove ecosystems. Increased land needs by rising human populations have led to the destruction of many tropical mangrove forests in recent years and this has resulted in appreciable shoreline erosion (Nittrouer 1994). Actions to reverse this situation require an understanding of how mangrove colonization is linked to nutrient and sediment fluxes. Spitzy and Leenheer (1991) indicate that the dissolved and
suspended loads of wet tropical rivers are important sources of organic carbon - over 65% of the world total. Estuarine processes operating adjacent to tropical river mouths, control the fate of these materials by trapping, bypassing or transforming them on the continental margins (Nittrouer 1994).

Tropical weathering produce sediments that have a fine grain size, such as silt and clay as well as characteristic mineralogies. High fluxes of these cohesive sediments, can be trapped by coastal mangrove forests, leading to stabilized and prograding shorelines (Nittrouer 1994). He further emphasizes that the consolidated muds in mangrove forests are resistant to coastal erosion. Mangroves flourish on fine alluvial muds composed of predominantly silt and clay particles (Rajagopalan 1992). It has also been observed that mangroves promote shoreline accretion by accelerating the rate of sedimentation. The pneumatophores of species such as Avicennia are specially effective in trapping river-borne sediments.

The mineralogy and texture of mangrove soils of India, have been described by a few researchers (Blasco 1975, Untawale 1987). The zonation of the mangroves along the central and west coast of India, based on substratum preference was given by Untawale (1985). Based on the limited information available on the mineralogical composition, sediment deposition and characterization in the mangrove ecosystem, it is obvious that scant attention has been given to understand the nature and type of sediments entering the mangrove and adjacent estuarine ecosystems from the river systems. Hence, in order to understand the fate of the delivered materials in this freshwater-seawater interface, further studies are required in this direction.

Despite their potential importance, only few researchers have directed their attention towards studying the mineralogical composition in mangrove ecosystems (Untawale 1985). Thus, attention needs to be focussed towards understanding the processes governing the river-ocean interactions,
the fluxes of materials in the coastal zone, which is being severely altered by human activities. From the preceding review on the status and current trends in mangrove ecosystem studies, one can realize the importance of this ecosystem in being a gateway for terrestrial materials entering the ocean.

1.6 GENERAL OBJECTIVES

The earth’s atmosphere is both a part of and a product of the biosphere. The chemical composition of the atmosphere is to a large degree determined by the uptake and release of a variety of trace gases by the biosphere. In turn, the earth’s climate and the deposition of chemical compounds containing essential elements (such as C, N, P, S) are of critical importance for the sustainability of the biosphere.

Coastal wetlands, consisting primarily of the mangrove ecosystems in the tropics, link all the vital components of the biosphere and hydrosphere with the atmosphere. Globally significant biogeochemical processes and transformations take place in this ecosystem, induced both naturally and to a large degree by anthropogenic forcing, causing major shifts to the constancy in chemical composition of air, water and soil. The biogeochemical cycles in the mangrove ecosystems are driven by complex physical, chemical and biological processes and the problem of possible change in climate due to emission of trace gases to the atmosphere, cannot be considered in isolation. The emission characteristics are regulated by natural and human-induced forcing functions, such as changes in ecosystem productivity and environmental pollution by organic and trace element contaminations. Such human impacts will inevitably intensify in the next few decades, with a strong likelihood that they will cause disruptive changes to the ecosystem, climate and other global functions. Thus, assessing and quantifying the exchange of elements across the coastal wetland boundary is of fundamental importance to the regional and global circulation of elements and energy within the biosphere and the atmosphere.
This research work addresses a few key global change problems on a coastal wetland ecosystem level, emphasizing on their interactions with the oceans on one side and the atmosphere on the other. While a complete understanding of every aspect of this biospheric-atmospheric interaction is unrealistic, a concerted effort with the following overall objectives, will significantly reduce uncertainties in predicting future consequences of current trends. Presented below, are a few immediate priorities and realistic goals that have been focussed in the context of local changes in environmental biogeochemistry and their regional and global implications. These include:

♦ estimation of the greenhouse gas - CH$_4$ concentration from the mangrove environments of Pichavaram, Ennore Creek and Adyar estuary

♦ determine the monthly variation of CH$_4$ with regard to changing environmental conditions

♦ intercomparison of variation in fluxes from unpolluted (Pichavaram) and polluted (Ennore Creek and Adyar Estuary) mangrove ecosystems to delineate the natural variability and anthropogenic forcing on these ecosystems

♦ provide a first order CH$_4$ emission inventory, by predicting a range in emission from the mangroves along the Indian subcontinent and the tropical coastlines of the world, in order to provide a basic database for mangroves as possible CH$_4$ sources

♦ measure the spatial and temporal variation in concentration of various forms of inorganic nutrients in water and their accumulation in the bed sediments of the mangrove ecosystems
and the impacts of 'added' nutrient sources on the primary productivity

- quantify the flux of nutrients from the Vellar-Coleroon estuarine complex to the Bay of Bengal, and to understand the nutrient recycling dynamics in the Pichavaram mangrove ecosystem

- assess the dispersion, migration and flux of major elements in water and their subsequent accumulation in the bed sediments of the Vellar-Coleroon estuarine region and the Bay of Bengal, in addition to understanding the spatial variation in suspended sediment concentration and bulk mineralogy

- estimate the intensity of toxic trace metal pollution in the water and sediments of the Vellar-Coleroon estuarine region, in order to assess the current status of trace metal pollution in this coastal ecosystem

- to assess the impact of such changes in biogeochemistry on the functioning of the mangrove ecosystems.

In view of the complex nature of the processes occurring in the mangrove 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.