CHAPTER - 1

INTRODUCTION

- Preamble
- Objective
- Summary of the research work
Global green house drift and tropical biosphere

During the 570 million years of the Phanerozoic the biosphere has been a varying entity, with several waves of extinctions from controversial causes (Sepkorki, 1987). Glaciations and interglacial have at times been accompanies by sea level changes of 100m, global temperature changes of 5°C and large shifts in atmospheric concentration of CO₂ and other gases (Berner and Lasagen, 1989). Greenhouse gases (H₂O, CO₂, CH₄, O₃, CFCS, N₂O) are radiatively active molecule in the atmosphere; that is, they absorb and re-radiate electromagnetic energy being originating from the sun. The radiatively active molecule, all of which except water vapour are trace gases, absorb thermal energy (infra-radiation) emitted from the earths surface, limiting its escape to space and re-radiating part of it back to the ground. The long term effect has been a warming of the globe by about 33°C, making life possible at the surface of our planet which otherwise would be permanently frozen (Ramanathan, 1988). The global trend of temperature rise is consistent and Levinson (2008) reported a rise of +0.16 ± 0.03°C decade⁻¹ since 1979 and +0.16 ± 0.02°C decade⁻¹ since 1958. Atmospheric concentrations of important greenhouse gas have increased substantially (Table 1.1) since the beginning of the industrial period (from the late 1700s) but at different rates (Rind and Lacis, 1993). A perturbation to the atmospheric concentrations of an important green house gases (or in the distribution of aerosols) induces a radiative forcing that can affect climate. Radiative forcing of a specific gas is to estimate the radiation in infrared radiation leaving earth per unit in area in atmospheric abundance.
Table 1.1: Comparison of atmospheric abundance of different greenhouse gases and solar constant since the pre-industrial time and their respective radiative forcing.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pre-industrial Level</th>
<th>Current Level</th>
<th>Increase since 1750</th>
<th>Radiative forcing (W m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>280 ppmv</td>
<td>383.9 ppmv</td>
<td>104 ppmv</td>
<td>1.66</td>
</tr>
<tr>
<td>Methane</td>
<td>700 ppbv</td>
<td>1,745 ppbv</td>
<td>1,045 ppbv</td>
<td>0.48</td>
</tr>
<tr>
<td>Ozone</td>
<td>25 ppbv</td>
<td>34 ppbv</td>
<td>9 ppbv</td>
<td>0.35</td>
</tr>
<tr>
<td>CFC-12</td>
<td>0</td>
<td>533 pptv</td>
<td>533 pptv</td>
<td>0.17</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>270 ppbv</td>
<td>314 ppbv</td>
<td>44 ppbv</td>
<td>0.15</td>
</tr>
<tr>
<td>Solar constant</td>
<td>Increased by 2%</td>
<td></td>
<td></td>
<td>4.58</td>
</tr>
</tbody>
</table>

The biosphere as an element of the climate regulates the active greenhouse composition of the lower atmosphere to a large degree. There are major uncertainties associated with descriptions of the processes controlling surface-atmosphere trace gas exchange (Andreae and Schimel, 1989). This limits our ability to predict fluxes that are needed for modeling the inventory strength in the regional and global scale. The biosphere and atmosphere are coupled to one another. Micrometeorological conditions, such as insulation, temperature, humidity, wind and precipitation affect the physiological functioning of vegetation, the architecture of plant communities and soil properties. In return, the functional type and extent of vegetation over land surface influence the physical and chemical properties of the atmosphere. Consequently, the production, consumption and transport of atmospheric trace gases are subject to a suite of biotic and abiotic controls and pathways as they travel between the biosphere and atmosphere. Therefore, the biogeochemical cycles of carbon, nitrogen, and water etc. in the biosphere and their feedback in controlling the micrometeorological conditions are of major research interest.

Quantification of the surface-atmosphere exchange of trace gases is recognized as an essential prerequisite for understanding the role of the biosphere in the global climate change. Deposition provides a natural sink for atmospheric trace species that influence
atmospheric chemistry, whilst also acting as a source of nutrients for biological systems. However, in regions where the biogeochemical cycles of many species are grossly perturbed by anthropogenic activities, atmospheric deposition can become an equally important source of toxic substances to the biosphere. The understanding of sources and sinks of trace gases, and of the degree to which they are undergoing change, has benefited from the contributions of a number of disciplines, including atmospheric chemistry, ecology, biogeochemistry, microbiology, soil physics and chemistry, meteorology, hydrology, and oceanography. Exchanges of biogenic trace gases between surfaces and the atmosphere are controlled by the production and consumption of gases by plant, microbial, and chemical processes, the physical transport through soils, sediments, or water, and the flux across the air-surface boundary. These biological and physical processes in turn depend on other biotic and abiotic properties and processes within ecosystems. The unresolved budget for global carbon and the location of the 'missing sink' for carbon is a prime example of the lacuna, which is yet to be, resolved (Schimel, 1995).

**Variability of solar radiation and climate change**

The amount of solar power arriving at the top of the atmosphere is known as the solar constant (1365 w m\(^{-2}\)). However the amount of radiation produced by the Sun is not constant, especially at short wave length, where variations of several percent occur as a function of solar activity. This activity which is related to the changing magnetic structure of the gaseous Sun is manifested in an 11 years cycle in the early observed sun spots and other solar features. They were absent in the 17\(^{th}\) century — period called the “Maunder Minimum” (1645 - 1715). The weak Sun in the 17\(^{th}\) century coincided with the so called Little Ice Age. Throughout the 20\(^{th}\) century the Sun was unusually active, peaking in the
1950s and the late 1980s. Five of the ten most intense solar cycles on record has occurred in the last 50 years. If the earth cools under a quite Sun, then it may be an indication that the increase in the Sun’s activity since the Little Ice Age has been the dominant factor in global temperature rise. That would also mean that the sensitivity of the Earth’s atmosphere to an increase of CO$_2$ during pre-industrial period has been over emphasized. After a prolonged lull in the activity, Sun spots and their associated star storms are on the rise again after a minimum in sun spot activity in December, 2008. A new cycle of solar storms would peak in May 2013 (News on brief, Quite sun enters new sun spot cycle, Nature, vol-459, No. 7244, 14 May, 2009, p-152). However, the global pattern of warming during the past half century is not due to known natural external causes alone, there has been a substantial anthropogenic contribution to surface temperature rise (IPCC, 2007).

The partitioning of the incoming solar radiation in the Earth’s atmosphere depends on the mixing ratios of different greenhouse gases in the atmosphere and their resultant concentration after their exchange from the atmosphere by the biosphere. Physical as well as chemical storage energy contributed by the biosphere plays a major role in the complex energy dynamics of various ecosystems.

Tropical rainforests are among the most important biomes because of their vast amounts of primary productivity, and water and energy exchange with the atmosphere. Although these forests now cover only 12% of the global total land surface (FAO, 1993), they contain about 40% of the carbon in the terrestrial biosphere (Skole and Tucker, 1993) and are responsible for 50% of terrestrial gross primary productivity (Grace et al., 2001). Tropical rainforests are also a major source of global land surface evaporation (Choudhury et al., 1998) and have profound influences on global and regional climates and hydrological cycling (Lean and Warrilow, 1989; Nobre et al., 1991). These large latent energy fluxes from tropical rainforests are known to influence global atmospheric circulation patterns.
In the humid tropics, climate change might drastically alter hydrological regimes, for example, because of altered rainfall patterns and land cover transformation mainly as a result of forest conversion (Bruijnzeel, 1996). Consequently, such alterations might accelerate further global climate changes. The exchange of trace gases such as CO$_2$, CH$_4$, H$_2$O, NO$_x$, O$_3$, etc between the biosphere and atmosphere are controlled by complex interactions between emissions, dry deposition, (photochemical) chemical transformations, and turbulent exchanges, all varying with height within the canopy.

**Brief review of main gases involved in Global Environmental Change**

**Carbon Dioxide (CO$_2$)**

Atmospheric CO$_2$ is an important greenhouse gas, and because of its variable residence time and numerous sources and sinks, it has the potential to regulate climate over a vast range of timescales, from years to millions of years. For example, the 30% rise in atmospheric CO$_2$ concentrations over the past 100 years has been accompanied by significant global warming (Mann et al., 1999; 2003). Most studies incorporating all known climate forcing implicate CO$_2$ as the primary driver for this most recent rise in global temperatures (Mann et al., 1998; Crowley, 2000; Mitchell et al., 2001). Atmospheric CO$_2$ concentration has continued to increase with present growth rate of 4.1 ± 0.1 Gt C yr$^{-1}$ due to the increased rate of fossil fuel burning and cement production from 6.4 ± 0.4 Gt C yr$^{-1}$ in 1990 to 7.2 ± 0.3 Gt C yr$^{-1}$ in 2005 (IPCC, 2007).

The 520 billion tons of carbon that human have added to the atmosphere lie heavily on the world, and the burden swells by at least 9 billion tons a year. If present trends continue, human kind will have emitted a trillion tons of carbon into the atmosphere well before (Paegle, 1987).
2050, and that could be enough to push the planet into the danger zone (Schmidt and Archer, 2009). Cutting back on CO\textsubscript{2} emission would be tougher than we thought. To map the CO\textsubscript{2} out of the air could cost a lot. Geoengineering schemes such as a) whitening the cloud that lie low over the ocean could help to cool the earth. b) turning biomass into charcoal and burying it or by fertilizing plankton blooms (Lenton and Vaughan, 2009). On the research front, the big question is that how quickly green house gas emissions need to be reduced if we are to avoid dangerous climate change.

In nature, carbon is cycled between various atmospheric, oceanic, land biotic, marine biotic and mineral reservoirs. The largest fluxes occur between the atmosphere and terrestrial biota, and between the atmosphere and surface water of the oceans. In the atmosphere, carbon predominantly exists in its oxidized form as CO\textsubscript{2}. Atmospheric carbon dioxide is part of this global carbon cycle, and therefore its fate is a complex function of geochemical and biological processes. Carbon dioxide concentrations in the atmosphere increased from approximately 280 parts per million by volume (ppmv) in pre-industrial times to 379 ppmv in 2005, a 35.3 percent increase (IPCC, 2007). The IPCC notes that “this concentration has not been exceeded during the past 420,000 years, and likely not during the past 20 million years. The rate of increase over the past century is unprecedented, at least during the past 20,000 years”. The IPCC definitively states that “the present atmospheric CO\textsubscript{2} increase is caused by anthropogenic emissions of CO\textsubscript{2}” (IPCC, 2007). Forest clearing, other biomass burning, and some no energy production processes (e.g., cement production) also emit notable quantities of carbon dioxide to the atmosphere. In its second assessment, the IPCC also stated that “the increased amount of carbon dioxide (in the atmosphere) is leading to climate change and will produce, on average, a global warming of the Earth’s surface.
because of its enhanced greenhouse effect - although the magnitude and significance of the
effects are not fully resolved" (IPCC, 1996). Global Warming Potentials (GWPs) are
intended as a quantified measure of the globally averaged relative radiative forcing impacts
of a particular greenhouse gas. It is defined by measuring the radiative forcing of a unit mass
of a given well mixed greenhouse gas in the present day atmosphere integrated over a chosen
time horizon, relative to that of carbon dioxide (IPCC, 2007).

Direct effects occur when the gas itself is a greenhouse gas (e.g. CO₂, CH₄,
N₂O, O₃ etc). Indirect radiative forcing occurs when chemical transformations involving
the original gas (e.g. NO, NO₂ etc) produce a gas or gases that are greenhouse gases, or
when a gas influences other radiatively important processes such as the atmospheric
lifetimes of other gases.

Methane (CH₄)

CH₄ is an atmospheric trace gas that contributes to 15% of the greenhouse effect and it
showed a persistent increase in the global burden throughout the latter part of the twentieth
century (Dlugokencky, et al., 1994; Cunnold et al. 2002; Steele et al., 1992; Matthews,
1994; Houghton et al., 1996) followed by a period of little change since 1999
(Dlugokencky et al., 2003). Following almost a decade with little change in global
atmospheric methane it shows renewed growth starting near the beginning of 2007 (Rigby
et al., 2008). Its average concentration in the atmosphere is largely determined by a
balance between emission from the surface and destruction by hydroxyl free radicals (OH)
in the troposphere. Methane is primarily produced through anaerobic decomposition of
organic matter in biological systems. Agricultural processes such as wetland rice
cultivation, enteric fermentation in animals, and the decomposition of animal wastes emit
CH$_4$, as does the decomposition of municipal solid wastes. The IPCC has estimated that slightly more than half of the current CH$_4$ flux to the atmosphere is anthropogenic, from human activities such as agriculture, fossil fuel use and waste disposal (IPCC, 2001). Methane is removed from the atmosphere by reacting with the hydroxyl radical (OH) and is ultimately converted to CO$_2$. Minor removal processes also include reaction with Cl in the marine boundary layer, a soil sink, and stratospheric reactions. Increasing emissions of methane reduce the concentration of OH, a feedback which may increase methane’s atmospheric lifetime (IPCC, 2001). Increased level of CO due to wildfires, changes in water vapour, cloud cover and temperature (Prinn et al., 2005; Bousquet et al., 2006) could decrease in OH concentration, resulting renewed growth of atmospheric methane.

Methane is involved in a number of chemical and physical processes in the Earth's atmosphere, including global warming. Global warming potential of CH$_4$ is about 25 times higher than that of CO$_2$ on a molecule to molecule basis (Graedel and Crutzen, 1993). Sources of methane are widespread such as wetlands, paddy fields, landfills, natural gas production and consumption, coal burning, biomass burning, termites, etc. Global budget estimates for methane have shown that wetlands are the largest biogenic source of atmospheric methane, accounting for 40–50% of global source strength (Cicerone and Oremland, 1988; Whiting and Chanton, 1993). Thus, a major effort has been made to map wetlands (Matthews and Fung, 1987; Aselmann and Crutzen, 1989) and to determine average fluxes from the biomes. Numerous biogeochemical factors work in conjugation to regulate methane emission from soil and vegetation. Several attempts were made to correlate methane emission with water level (Harriss et al., 1982; Moore et al., 1990; Cui et al., 2005), temperature (Crill et al., 1988; Schutz et al., 1989) and other biogeochemical
properties of soil. However, current global estimates of methane emissions from wetlands are uncertain. This is due to the paucity of measurements of methane flux, an incomplete understanding of the environmental factors that control methane flux, the great differences in geological distributions, soil types, nutrition inputs and vegetation between different wetland types or even between different wetlands classified as the same type. Therefore, it is necessary and urgent to obtain knowledge on methane fluxes from wetlands.

Methane emission in coastal ecosystem can vary with change in seasons, location, tidal amplitude etc even if the other biogeochemical factors remain the same. In addition localized changes in biogeochemical controls such as bacterial methane oxidation, competition between bacteria, substrate availability, etc., may serve to regulate methane flux from sediments and may account for observed high spatial and temporal variations in its flux (Sotomayor et al., 1994).

Methane is formed in soil by microbial breakdown of organic compounds in strictly anaerobic conditions, at a very low redox potential. Methane production in the soil begins only after all the molecular oxygen, nitrate, iron (III), manganese (IV) and sulphate (all that have higher redox potential) get completely reduced (Ponnamperuma, 1972). Such low redox conditions usually require prolonged water logging, high organic load as is common in natural wetlands and flooded rice field as well as lake sediment. The methanogenic food chain is a microbial system that mediates the biodegradation of organic matter in many anaerobic environments. Since methanogenesis is the terminal step in this chain, any perturbation of the chain should be reflected by altered methane production, resulting in the altered methane flux. Therefore, methanogenesis is a key process to study the source of strength methane from wetlands. Methane oxidations at the aerobic part of the soil
sediment are regulated by methanotropic bacteria and play a significant role in quantifying the net CH$_4$ flux to or from the atmosphere.

The CH$_4$ formed in flooded soil and sediments can migrate to the surface and be emitted into the atmosphere by several ways. One of them is by diffusion in the solution towards the surface. During the course of diffusion a substantial proportion of CH$_4$ (10-40% in rice paddies, for example: Kruger et al., 2002) is oxidized. In this oxidation process the electron acceptors that compete with each other to oxidize CH$_4$ inside the soil sediment are mainly SO$_4^{2-}$, Mn (IV)/Fe (III), NO$_3^{-}$, O$_2$ (in contact with the atmosphere).

In the study of methane dynamics it is very important to quantify the role of different factors that dominate over other in a temporal and spatial scale. Keppler et al. (2006) suggest that in pre-industrial times, that is, without anthropogenic emissions, the relative contribution of CH$_4$ to the atmosphere by direct plant emissions may have been even larger than today.

**Water vapor (H$_2$O)**

Water vapor is constantly cycling through the atmosphere, evaporating from the surface, condensing to form clouds blown by the winds, and subsequently returning to the Earth as precipitation. Heat from the Sun is used to evaporate water, and this heat is put into the air when the water condenses into clouds and precipitates. This evaporation-condensation cycle is an important mechanism for transferring heat energy from the Earth's surface to its atmosphere and in moving heat around the Earth. In addition, water vapor is the most abundant of the greenhouse gases in the atmosphere and the most important in establishing the Earth's climate. Greenhouse gases allow much of the Sun's shortwave radiation to pass through them but absorb or trap the long wave, infrared radiation emitted by the Earth's
surface. Water vapour is indeed the most dominant greenhouse gas. The radiative forcing for water is around 75 W m\(^{-2}\) while carbon dioxide contributes 32 W m\(^{-2}\) (Kiehl, 1997). Water vapour is also the dominant positive feedback in our climate system and a major reason why temperature is so sensitive to changes in CO\(_2\). The hydrological cycle describes the movement of water, in all three phases, within and between the Earth's atmosphere, oceans, and continents. In the vapor phase, water moves quickly through the atmosphere and redistributes energy associated with its evaporation and re-condensation.

The movement of water vapor through the hydrological cycle is strongly coupled to precipitation and soil moisture, which have important practical implications. The evapotranspiration process of vegetation plays a vital role in the water cycle over the continents and especially in the tropical forest. Precipitation over the continents (~111,000 km\(^3\) y\(^{-1}\)), some three times the amount of water transported from the oceans the difference is mostly due to water supplied by evapotranspiration. The oceans supply most of the atmosphere's water, but lakes and rivers, moist ground and evapotranspiration from moist vegetations also make contributions.

**Nitrogen Oxides (NOx)**

The largest sources of nitrogen oxides are provided by fossil fuel consumption (20-24 TgN yr\(^{-1}\)) and biomass burning (3-13 TgN yr\(^{-1}\)) where as the release of NO by soils is not well quantified, but could be on the order of 4 - 21 TgN yr\(^{-1}\) (Holland et al., 1999; Jaegle et al., 2005). Other contributions to the sources include lightning discharges (5 TgN yr\(^{-1}\)) and aircraft emissions (0.5 TgN yr\(^{-1}\)) primarily in the upper troposphere. Sinks are provided by wet deposition of nitrates (27 TgN yr\(^{-1}\)) and dry deposition of NOx (16 TgN yr\(^{-1}\)).
The primary climate change effects of nitrogen oxides (i.e. NO and NO$_2$) are indirect and result from their role in promoting the formation of ozone in the troposphere and, to a lesser degree, lower stratosphere, where it has positive radiative forcing effects. Nitrogen oxides are created from lightning, soil microbial activity, biomass burning -- both natural and anthropogenic fires, fuel combustion and in the stratosphere from the photo-degradation of nitrous oxide (N$_2$O). Concentrations of NOx are both relatively short-lived in the atmosphere and spatially variable. Between two species comprising the NOx group, NO$_2$ have more negative effect on the atmospheric health, plays an important role in the photochemical production of Ozone, which has detrimental effect on living cell beside its green house effect in the lower atmosphere. NO$_2$, which is always present along with NO, reacts with OH to form nitric acid (HNO$_3$), removing (OH) from the atmosphere. Again OH radical is known as the detergent of the atmosphere responsible for removing various environmental pollutants (CO, CH$_4$ etc.) from the system.

**Tropospheric Ozone (O$_3$)**

Ozone is not directly released into the atmosphere, but is produced by photochemical reactions, primarily in the stratosphere through photolysis of molecular oxygen (O$_2$). This mechanism does not operate below approximately 20km altitude as the shortwave radiation required to dissociate O$_2$ is absorbed above that level. The presence of ozone in the troposphere results primarily from the intrusion of ozone-rich air through the tropopause. Direct measurements of the corresponding ozone global flux are not available, but indirect estimates or model calculations suggest that this flux ranges from 400 to 800 Tg yr$^{-1}$. The global deposition of ozone on the surface can be inferred from the knowledge of surface ozone concentrations and of dry deposition velocities. The global budget can be closed by
considering an in situ production of ozone in the troposphere ranging from \(-100\) to \(+500\) Tg yr\(^{-1}\). The photochemical theory shows that this net production results from the difference between large production and destruction rates. The photochemical production results from complex chemical chains involving the photo-oxidation of hydrocarbons or of carbon monoxide in the presence of nitrogen oxides. Ozone production is therefore largest in regions with high NOx concentrations, i.e., in regions of intense industrial activities or biomass burning. The ozone destruction is provided by reactions of ozone with OH and HO\(_2\) radicals. The photolysis of ozone followed by the oxidation of water molecules by the resulting oxygen atoms also leads to ozone destruction. Ozone destruction dominates in remote areas (e.g. mangrove forest) and specifically over the oceans. NOx (NO + NO\(_2\)) acts as a catalyst during ozone production by CH\(_4\) and/or CO oxidation cycle (Graedel and Crutzen, 1993). The NOx atmospheric lifetimes are a few days and its principal sources are anthropogenic in nature. Away from urban area the NOx concentrations drop rapidly to very low values and there is a cross over from “high NOx” to low NOx” region. As very low level of NOx in troposphere, hydrocarbon oxidation removes O\(_3\) and consumes OH, while at higher NOx levels, more O\(_3\) and reactive radicals are produced (Andreae, 2002) under pristine condition the biosphere is the dominant source of both hydrocarbon and NOx in the lower and mid troposphere, and their relative amount emitted are such that NOx concentrations are low and consequently the troposphere is in a low Ozone state.

**Hydrogen sulphide (H\(_2\)S)**

The release of biogenic hydrogen sulfide from aquatic and terrestrial environments to the atmosphere is considered to be an essential part of the global sulfur cycle (Friend, 1973). The primary source of H\(_2\)S is decaying vegetation in swamps, bogs, and other land areas.
Hydrogen sulfide is relatively insoluble in water; at 20°C and 1 atmosphere, the solubility is only 0.385g per 100g H₂O. Vegetation or bodies of water therefore will not readily absorb it, nor will it be involved in liquid state reactions in the atmosphere. In fact, the only real mode of 'removal' is the oxidation reactions it so readily becomes involved in. Hydrogen sulfide can be oxidized by O₃, O₂ or O. Cadle and Ledford (1966) have shown that although the oxidation of H₂S by O₃ proceeds quite slowly in a gaseous atmosphere, the reaction is catalyzed by the presence of aerosols. Sulphide plays a major role in aerosol formation. Open ocean acts as source of Dimethyl Sulphide (DMS) that contribute to the formation of aerosol in the lower atmosphere. In mangrove environment where the soil condition is quite anoxic reduction of sulphate can lead to the production of H₂S that can further contribute to the formation of non-sea sulphate aerosol at a regional scale.
OBJECTIVES

Interactions between the tropical mangrove forests and the trace gases

Because of the high levels of UV radiation and water vapour in the tropics, OH concentrations are highest in this zone, and most of the oxidation of CO, CH₄ and other trace gases occurs in the "great tropical reactor" the region of high OH in the tropical troposphere. This region plays a key role not only in regulating physical climate, but also in maintaining the chemical composition of the lower atmosphere. The history of climate and atmospheric composition reveals a tight coupling between biogenic trace gases in the atmosphere and the global climate (Petit et al., 1999). The central role of the biosphere in controlling chemical composition of the atmosphere indicates that the condition of equilibrium between major and minor gases couldn’t persist long without life’s interference.

Mangroves cover about 22 million ha globally, but their area has been decreased by human activity in the last several decades (Tuan et al., 2002) report about 15 million ha (almost 2.4% of tropical rain forest, http://www.fao.org/forestry/mangroves) of mangrove forests remain worldwide. Although mangroves have been exploited for many centuries, our scientific understanding of these wetland forests remained poor until the 1970s (Lugo and Snedaker, 1974; Blasco, 1975; Chapman, 1976). During the past three decades or so, these wetland forests have received increasingly greater attention, which is reflected in an exponential increase in the number of publications (Ellison, 2002). Some studies have emphasized the effects of hydrology on the structure and function of mangrove forests and the relationship between the hydrological regime and soil biogeochemistry and factors that affect the geographical range, zonation, succession and productivity of mangrove forests.
Integrated research on mangrove biogeochemistry and its feedback to the regional climate for understanding the impacts of global climate changes is a newly emerging challenge. Sundarban mangrove, the largest mangrove wetland in the world and located between latitude 21°31'00" N and 22° 30' 00" N and longitude 8°10'00" E and 89° 51'00" E covers an area of about 1m ha, of which 60% is located in Bangladesh and the remaining 40% lies in India (Choudhuri and Choudhury, 1994).

Exchange of CO\textsubscript{2} and CH\textsubscript{4} between the Sundarban mangrove ecosystem and the atmosphere was studied earlier by Mukhopadhyay et al. (2001). However, a better understanding of the complex interactions between the Sundarban mangrove ecosystems and the adjacent atmosphere needs further investigation. Therefore, this study was carried out to examine the role of biosphere-atmosphere exchange of energy (in the form of heat) and material (in the form of trace gases) in the world's largest mangrove ecosystem.

Mangrove forests are highly productive but globally threatened coastal ecosystems, whose role in the carbon and nitrogen budget of the coastal zone has long been debated. The potential impact of mangroves on coastal zone carbon dynamics has been a topic of intense debate during the past decades. Biosphere can play the role of both as sink and source of CO\textsubscript{2} in different biological condition.

In general one has to consider several processes for the estimation of CO\textsubscript{2} balance between the atmosphere, the ocean, and the terrestrial ecosystems (Fig 1.1). In particular, it is needed to understand CO\textsubscript{2} balance between the atmosphere and terrestrial ecosystems.
Fig 1.1 Summary of the major components in mangrove carbon budgets considered: primary production (litter fall, wood and root production) and various sink terms.

Quantification of the exchange rate between the biosphere and the atmosphere of the most important greenhouse gas at a regular basis is quite essential to predict regional level climate change. Aquatic ecosystem dominated by the mangrove ecosystem can have considerable contribution in the regional carbon cycle. Besides quantifying CO$_2$ flux at a temporal scale in Sundarban biosphere reserve the contribution of this important trace gas towards the partitioning of solar energy was also tried to be predicted in this study. Since wetlands are believed to be the single largest source of CH$_4$, extensive effort was made to quantify their emission rates to the atmosphere. Although CH$_4$ production or deposition in wetlands is strictly controlled by the activity of methanogenic (anaerobic) and methanotropic bacteria (aerobic), biosphere (mangrove forest) can regulate this CH$_4$ exchange by various physical as well as biochemical processes. Mukhopadhyay et al. (2001) previously quantified the methane flux in the deep mangrove forest at Sundarban ecosystem. Regular monitoring of CH$_4$ flux along with various physicochemical
parameters that may contribute to the chemistry of atmospheric methane in the atmosphere might be an essential tool to explain any change in regional as well as global climate.

The contribution of water vapour in regional energy budget and the hydrological cycle is not well known at Sundarban mangrove forest ecosystem. Study of temporal variation of H₂O mixing ratio in the atmosphere and its exchange rate with the adjacent biosphere was carried out.

Only limited information is available about effects of atmospheric N deposition on the biosphere-atmosphere exchange of N trace gases in tropical mangrove forest. The role of Mangrove ecosystem in the NOₓ cycle is still not very clear. Microbial activities (nitrification-denitrification) in the mangrove soil along with the dense vegetation cover can have some regulating role to play over the NOₓ exchange with the lower atmosphere. In addition, advection of anthropogenic NOₓ from adjacent metropolis Kolkata and Haldia into the mangrove forest contributes towards the formation of surface layer ozone. Soils are also an important source of reactive nitrogen (NOₓ) due to microbial production of Nitric oxide (NO) by the nitrification and denitrification process and subsequent chemical transformation of the emitted NO. Protein content and nitrate reductase activity in mangrove leaves can indicate stomatal uptake of atmospheric NOₓ and its subsequent conversion by the mangrove plant.

In the Sundarban mangrove ecosystem the biosphere can play an important role in tropospheric ozone chemistry by regulating the production and destruction of nitrogen oxides and other non-methyl hydrocarbon with in the system.

Quantification of the atmospheric mixing ratio of H₂S along with its emission rate from the tropical mangrove soil and other physicochemical controlling factors in a temporal and
spatial scale at Sundarban Mangrove forest could be very useful for the study of biogenic aerosol formation at this land ocean boundary condition.

Biosphere-atmosphere exchange of trace gases in relation to energy dynamics was studied in the Sundarban mangrove forest with the following objectives:

1. To study energy dynamics and its implication to biosphere – atmosphere exchange of CO₂, H₂O and CH₄ in the Sundarban mangrove forest canopy.
2. To measure the Biosphere-Atmosphere exchange of NOₓ at the land ocean boundary condition of Sundarban mangrove forest.
3. To quantify H₂S exchange between the mangrove ecosystem and the atmosphere.
SUMMARY OF THE PRESENT WORK

Climate is influenced by the operation of atmosphere, biosphere, hydrosphere, cryosphere and pedosphere is closely linked to the atmosphere. In order to improve understanding of the climate and environment, effect of biosphere-atmosphere interaction need to be studied.

Change in vegetation type and their seasonal variation affect the albedo of a geographical region, as well as its hydrological cycle. Mangrove cover a significant portion of the land-ocean boundary and changes wrought to them by humanity such as deforestation, reclamation for agriculture and human settlement can have profound effect on climate, locally and globally.

To achieve quantitative understanding of the key biogeochemical and biophysical interactions and feedbacks between the mangrove biosphere and atmosphere it is important to study how this coupled system affects and is affected by the climate and environmental change.

Chapter 1 gives an introductory overview of the trace gases (CO₂, CH₄, H₂O, NOₓ, O₃ and H₂S) and different processes involved in their addition and removal relating it to the biosphere-atmosphere interactions. The objective of the present work is outlined based on present day knowledge.

Chapter 2 describes the physiography of the study area with location of four stations (Station 1, 22.117°N and 88.82°E, Station 2, 22.420° N and 88.420°E, Station 3, 20°16′58.9″ N, 86°43′3.7″ E, Station 4, 20°17′13.8″ N, 86°42′50″ E) along the north east coast of the Bay of Bengal. Micrometeorological conditions for the onset of monsoon are also given.
Chapter 3 deals with the detailed methodology of the sampling techniques and analysis of air, water sediment and plant samples for trace gases, nutrients and biochemical parameters. Micrometeorological methods used for the quantification of biosphere-atmosphere exchange of trace gases and energy partitioning has been discussed in details.

Chapter 4 presents results and discussion under several sections.

- **Section 4.1** depicts the micrometeorological parameters at the land ocean boundary during 2006 and 2008 and inters annual variation of rainfall during 2004 and 2008.

- **Section 4.2** describes the temporal and spatial variation of CO$_2$ exchange flux along the north-east coast of the Bay of Bengal, India. Study of CO$_2$ exchange between the Sundarban mangrove ecosystem and the atmosphere revealed that the ecosystem changes from a net source to a net sink possibly due to the change of seasonal distribution pattern of rainfall during the period from 2000 to 2008. The overall mean annual estimate of carbon dioxide sink strength was estimated to be 24.8 Tg CO$_2$ yr$^{-1}$ for Sundarban mangrove forest. Lower atmospheric CO$_2$ concentration was found in the mangrove-dominated area relative to the area devoid of mangrove.

- **Section 4.3** elaborates the temporal and spatial variation of methane dynamics along the north-east coast of the Bay of Bengal, India. This study revealed that various micrometeorological parameters along with several physicochemical factors act in combination to regulate the biosphere atmosphere exchange of methane. The availability of soil organic carbon, soil moisture and temperature showed positive correlation with methane emission flux. Tidal amplitude, rate of methane oxidation, which is again controlled by SO4/Cl ratio in soil, has negative
control over soil methane flux in this region. In this study the mean annual rate of increase of methane concentration between the time periods from 1998 to 2008 was found to be 0.13%.

- **Section 4.4** gives the Biosphere - atmosphere exchange of H$_2$O in the mangrove forest. The magnitude and seasonal dynamics of evapotranspiration (ET) for a tropical mangrove forest was estimated and it was found that annually 63.82% of total precipitation was consumed by evapotranspiration. Evaporation rate reached maximum in June (0.069 g m$^{-2}$ s$^{-1}$) before the onset of monsoon. Annual mean canopy resistance for daytime and nighttime were found to be 1.78 and 0.68 s cm$^{-1}$, respectively. Evaporation in the mangrove forest was controlled by the amount of available energy and plant physiological activity (i.e. stomata opening and closing). The mangrove forest with two trademarks of low albedo and high surface roughness was poorly coupled to the environment.

- **Section 4.5** critically examines the energy dynamics and its implication to biosphere–atmosphere exchange of CO$_2$, H$_2$O and CH$_4$. Amount of radiant energy (short wave) available to drive biosphere–atmosphere exchange of CO$_2$, H$_2$O, CH$_4$ and its transformation into other forms of energy were determined from January to December. The mean annual incoming short wave radiation (435 ± 32.8 Wm$^{-2}$) was partitioned into 29% sensible heat, 35% latent heat, 4% ground heat, 7% physical storage energy and 10% photosynthetic storage energy. The mean budget closing energy flux (68.96 ± 24.6 Wm$^{-2}$) or, budget error was 15.8% of incoming short wave radiation. In Varimax factor analysis, budget closing energy showed high loading in association with leaf chlorophyll of different mangrove species,
indicating its major role for reflectivity of the surface for short wave. Stepwise multiple regression analysis between storage energy \([\Delta Hs (P)]\) and fluxes of CO\(_2\), CH\(_4\), H (sensible heat), H\(_L\) (latent heat of evaporation), \(\Delta R\) (budget closer energy) showed that the combined explained variability for CO\(_2\) flux, evapotranspiration and budget closer energy (39\%) was less than that of CH\(_4\) and sensible heat flux (46\%). The extent of warming effect by CH\(_4\) and sensible heat flux was predominant over the resultant cooling effect due to the processes such as photosynthesis, evapotranspiration and albedo.

- **Section 4.6** describes the biosphere-atmosphere exchange of NO\(_x\) in the tropical mangrove forest. Biosphere - atmosphere exchange of NO\(_x\) in Sundarban mangrove forest along the northeast coast of the Bay of Bengal, India showed uptake with a rate from \(-0.84\) to \(-1.63\) ng N m\(^{-2}\)s\(^{-1}\) in the day and both uptake and emission with a rate varied between \(-0.36\) and 5.19 ng N m\(^{-2}\)s\(^{-1}\) in the night during September and February. However, emission of NO\(_x\) was observed with a range from 0.34 to 2.13 ng N m\(^{-2}\)s\(^{-1}\) in the day and from 0.88 to 3.26 ng N m\(^{-2}\)s\(^{-1}\) in the night from March to August. NO\(_x\) was up taken by mangroves during the day. This was most likely to be a result of mangroves being more active during daylight, when their stomata were open. Mangroves absorbed nitrogen from both the soil and the atmosphere. Differences in the seasonal and diurnal variations between NO\(_x\) and O\(_3\) could be partly explained by plant growth during the post-monsoon season, when nitrogen uptake was highest. Stomatal uptake of NO\(_x\) could also be an important process for keeping low ozone state at the land ocean boundary of the NE coast of the Bay of Bengal in addition to the NO\(_x\)-O\(_3\) photochemical cycle.
Section 4.7 critically examines the exchange of hydrogen sulphide between Sundarban mangrove ecosystem and atmosphere from January to December. The Sundarban mangrove forest acted as a net emitter of H$_2$S with a mean rate of 32.01 ± 10.51 μg S m$^{-2}$ h$^{-1}$. Dissolved Iron, SO$_4^{2-}$/Cl ratio in the pore water, soil organic carbon etc. showed significant correlation with H$_2$S emission. Emission of H$_2$S from the anoxic mangrove sediment could have significant contribution towards the occurrence of non sea salt sulphate in aerosol. The total turn out of H$_2$S from the Sundarban mangrove ecosystem was calculated to be 1.20 ± 0.58 Tg S y$^{-1}$. 