

Atmospheric Chemistry in the Anthropocene Era

A. Jayaraman¹

Abstract

The composition of the atmosphere has undergone systematic changes during the course of the earth's history. The changes are mainly driven by the rate at which different gases are emitted into the atmosphere and the rate at which they are removed by chemical reactions and other physical processes. The primitive atmosphere had H₂O, CO₂ and N₂ in abundance, H₂O condensed to form oceans and CO₂ dissolved in ocean water and reacted with crustal rocks to form carbonates. N₂ being less reactive stayed in gas form and becomes the most dominant component (78%) of the present atmosphere. Prior to the origin of life, it is the chemical and physical processes that governed the composition of the atmosphere and this period, in the evolution of the atmosphere is termed as the *chemical era*. After the origin of life, biological evolution has made an important influence in the atmosphere, as living creatures have removed some gases from the atmosphere and have emitted other gases. Molecular Oxygen (O₂) has come mainly from photosynthesis processes in plants and algae, resulting in an increase in its concentration from about 1% to 21% during the last 600 Myr. This period, when biological processes played a major role in determining the atmospheric composition is termed as the *microbial era*. During the last 100 million years are so, the distribution of continents changed from one super continent, resulting in changes in global average temperature, in the total length of shore line, weather pattern etc. Thus, following the microbial era, it is the geological factors that were responsible for producing changes in the atmospheric composition and we call this stage as the *geological era*. In this history of atmospheric evolution now we have a new driver, the humankind, changing the composition of the atmosphere, more rapidly than ever before, by

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various anthropogenic (human-made) activities. We call this era, the *anthropocene era*.

Human influence of the atmosphere has started only recently, during the last 200 years are so with the dawn of industrialization, but the rate at which we are changing the composition is rapidly increasing. In many cases the human activities are out-competing the natural processes. Since pre-industrial period the CO₂ content has steadily increased from about 280ppm to the present level of about 372 ppm, primarily due to fossil fuel and biomass burning. The increase is correlated with a rise in global mean temperature of about 0.6°C. We created Chlorofluorocarbons (CFCs) for use as refrigerants and aerosol propellants that became responsible for the Antarctic ozone hole. The increasing particulate content is another major threat to the environment, causing acid rain and regional climate change. The Intergovernmental Panel on Climate Change (IPCC) in its third assessment report released in 2001 states, "There is new and stronger evidence that most of the warming observed over the last 50 years is attributable to human activities" and "Observed changes in regional climate have affected many physical and biological systems, and there are preliminary indications that social and economic systems have been affected".

In India, the Indian Middle Atmosphere Program (I-MAP) that got initiated in early eighties have helped many research laboratories, the India Meteorological Department and several University research groups to come together to study vertical profiles of ozone, aerosols and other trace gases and their seasonal and long-term variations over India. With funding from the Indian Space Research Organization (ISRO), new rocket and balloon techniques were developed and several new projects related to atmospheric chemistry and radiation were initiated. Early 1990 saw the initiation of the ISRO's Geosphere Biosphere Program, which helped in taking forward some of the I-MAP research studies pertaining to ozone and aerosol studies and new disciplines related to global change studies were included. The recently concluded Indian Ocean Experiment (INDOEX), an international field experiment, has helped in establishing quantitatively the anthropogenic aerosols as the major component in the regional

scale radiative forcing of the climate. Key results from some of these programs and experiments will be presented and new research activities being planned for the coming years will be outlined.

Methane and Nitrous Oxide Emission from Livestock Waste Management Practices in India in Relation to Global Climate Change

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Abstract

Global climate change, due to increase in greenhouse gases (GHGs) and because of anthropogenic activities, has become a cause of concern. United nations framework convention on climate change (UNFCCC) has made it mandatory for nations to communicate inventories of GHGs, viz. methane (CH₄), nitrous oxide (N₂O) and carbon dioxide (CO₂), according to IPCC methodology from various sectors like Energy & Industry, Agriculture, Land use-Land use change (LULUC) and Forestry, and Waste. Agriculture sector GHG emissions include livestock, rice cultivation, residue burning and agricultural soils. Among these livestock, which consists of CH₄ emission from ruminating animals and CH₄ & N₂O emission from manure management practices, has maximum share of GHG emissions. Manure management practices from livestock sector are important and vary, in different climatic regions of India, depending upon the need of the fuel viz. dung cake and manure as well as other available fuel resources.

In the present study, extensive measurements for methane and nitrous oxide emission from livestock manure management practices have been made using closed chamber technique, in Delhi region during various climatic seasons round the year. Spatial variability of methane and nitrous oxide flux, within and between different sites and seasons has been observed due to manure compaction, temperature, and moisture content. Formation of dry surface crust over manure pit reduces methane emission. Total dung production from cattle and buffalo in India has been estimated using gross energy intake and average digestibility of

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Indian cattle feed according to IPCC good practice guidance. Gross energy intake was estimated considering energy value of feed and fodder to be equivalent to 18.45 MJ/ kg dry matter. Methane and nitrous oxide emission, from Indian manure management system of cattle & buffalo using IPCC good practice guidance, had been estimated for the year 1994 to be around 0.86Tg, which has also been compared with the experimental results of the present study. The methane emission reduction or mitigation from manure management practices may involve aerobic decomposition, recovery of methane to be used as a source of energy, and incorporation of higher digestibility diet.

How Important are Greenhouse Gas Emissions from the Coastal Zone?

R.C. Upstill-Goddard¹

Abstract

Carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) together account for ~75% of enhanced greenhouse forcing, and their atmospheric partial pressures are all currently increasing at significant rates through various global-scale processes. In addition, both CH₄ and N₂O play key roles in atmospheric chemistry. Importantly, all three have significant yet insufficiently quantified coastal marine sources. For CO₂ these can be important regionally, but for CH₄ and N₂O they could have wider global significance.

Relevant research effort has increased substantially in recent years and important new data have been published. However, by far the greatest effort has focused on temperate coasts, even though the evidence available from the comparatively small number of tropical studies implies that the latter environments are at least as, if not more, important. This is in large part a consequence of the huge anthropogenic pressures that are often brought to bear on such regions, especially in emerging economies. Available evidence is for highly modified trace gas production and associated sea-air exchange in coastal waters adjacent to regions undergoing land use change and/or agricultural intensification.

In order to meet international obligations under the Kyoto protocol and future such international agreements, the concept of “full greenhouse gas accounting” at regional and even national levels is beginning to emerge. Such an approach will take account not only of human induced changes, but also of natural biospheric sources and sinks, to include the role played by coastal environments.

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New data will be required as inputs to inverse atmospheric models that will provide the basis for future contingencies.

In this presentation I summarise the current state of knowledge regarding the atmospheric fluxes of CO₂, CH₄ and N₂O from coastal systems, and highlight future research requirements in this area.

Anthropogenic Impacts on Coastal Marine Ecosystems and Consequences for N₂O Production

Jonathan Barnes¹

Abstract

Two temperate estuaries (Humber and Tay, UK) and subtropical mangroves (India) are examined in the context of anthropogenic pressures and their production of the globally important trace gas nitrous oxide (N₂O). N₂O currently contributes ~ 6% of the enhanced "greenhouse" effect and is involved in the destruction of stratospheric ozone. The Humber and Tay are geomorphologically similar and are the two largest estuaries in the UK. The Humber drains a catchment of 25,000 km² (>20% of the area of England) with a freshwater flow of 250 m³ s⁻¹. Catchment use consists mainly of intensive agriculture and industry and this is reflected in the high nutrient concentrations observed within the estuary (Nitrate ~ 600 μM). As a result of N transformations in the estuary, observed N₂O concentrations are consistently supersaturated indicating the estuary is a significant source of atmospheric N₂O (typically 1000 kg N₂O d⁻¹). In contrast the Tay with a freshwater flow of 200 m³ s⁻¹ drains a relatively pristine upland mountainous catchment of 5,372 km² and consequently nutrient concentrations are lower (Nitrate ~100 μM). As a result observed N₂O emissions are ~ 2 orders of magnitude lower than the Humber (typically 10 kg N₂O d⁻¹). Similar differences are observed between relatively pristine mangroves observed in the Andaman Islands and the impacted mangroves on the east coast of India (Muthupet, Pichavaram). These data suggest that elevation of nutrients due to inputs through industry/sewage/agriculture/aquaculture may accelerate the production of trace gases in coastal marine ecosystems. Such ecosystems are often viewed as a "panacea" for the "ills" of coastal eutrophication however it is clear that these systems could have a detrimental role in global climate change.

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Methane Emission from Subtropical and Tropical Wetlands: Rice, Swamps & Mangroves

Peter Frenzel¹

Abstract

Methane is an atmospheric trace gas that increased constantly during the last 300 years, reaching now a mixing ratio of ca. 1.8 ppm_v. It is a greenhouse gas and about 10-20 times as effective as carbon dioxide. We review here the results obtained from the best-studied model system, the flooded rice field, and focus on two aspects: (i) on microbial processes and populations involved in methane production and oxidation, and (ii) on the dual role of the rice plant as a source for methanogenic substrates and as a conduit for gases, respectively.

Few data are available from tropical freshwater swamps, and we will summarize what is known, what research is in need, and which future studies are most promising. Mangroves are coastal wetlands that have been rated for a long time as a minor methane source. However, recent reports have shown that polluted mangroves may emit substantial amounts of methane. We report on the methane emission from an unpolluted Indian mangrove that accounted for a methane emission of 10 g CH₄ · year⁻¹. This rate is of the same order of magnitude as that found in Northern wetlands. Methane emission from a freshwater-influenced area was higher, but lower from a c, respectively. Methane emission was mediated by the pneumatophores of *Avicennia*. This was consistent with the methane concentration in the aerenchyma that decreased on average from 350 ppm_v in the cable roots to 10 ppm_v in the emergent part of the pneumatophores. However, the number of pneumatophores varied seasonally with the minimum number during the monsoon, reducing methane emissions largely. In addition, ebullition from unvegetated mudflats may become important at least during monsoon when occasionally measured bubble fluxes were about five times as high as pneumatophore-mediated emissions.

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The Influences of the North Atlantic, Indian and Pacific Ocean Regions on Late Quaternary Environments in Monsoonal Australia

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Abstract

Until recently, little research had been undertaken on the northern Australian region with a view to documenting and understanding the development of the present landscape and patterns of change within it. Emphasis had been concentrated on the humid tropics region of northeastern Australia and it had been assumed that results from this region were applicable to the whole of the northern part of the continent that included arid as well as very seasonal environments.

In order to provide a more comprehensive picture of the region as a whole, we have been constructing long Quaternary records from available marine cores off the whole of the northern Australian coast, extending into the Indonesian region. The major analytical tools are pollen and charcoal analysis that provide a broad picture of terrestrial and coastal vegetation and biomass burning on adjacent land, and allow inferences about patterns of climate change and human impact on the landscapes. All marine cores used have had oxygen isotope records produced from analysis of contained tests of ocean-dwelling foraminifera. These isotope records reflect predominantly global ice volume changes in the North Atlantic Ocean region and are used as a basis for dating and correlation of marine records throughout the world. There is some variation in the records resulting from local sea surface temperature conditions. An advantage of marine cores, additional to that of providing well-dated records, is that sedimentation is continuous and allows record construction for those areas where suitable

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sediments on land, such as those in lakes and swamps, do not exist or are frequently destroyed.

Three pollen records, covering the last 170,000 to 500,000 years, provide a good indication of patterns and causes of change and variability within the region. They are long enough to determine how climate and vegetation have responded to orbital scale forcing that is responsible for glacial-interglacial cyclicality, detect any long term trends in climate and vegetation that may allow prediction of future trends, and determination of the nature and extent of any human impact on the landscape since the arrival of *Homo sapiens* within the region. The major plant groups identified from the pollen are rainforest angiosperms that represent complex rainforest existing under wet conditions, rainforest conifers that indicate cooler rainforest in the Indonesian region and drier rainforest in Australia, sclerophyll trees, composed largely of *Eucalyptus* and *Casuarinaceae*, that are extensive canopy dominants of seasonal climates in Australia, *Poaceae* that is representative of open sclerophyll woodlands and grasslands, ferns that indicate wet conditions and *Rhizophoraceae* that is the best indicator of mangroves.

A record from the Banda Sea provides details of the last 170,000 years. Although situated within Indonesian waters, between Sulawesi and New Guinea, it records changes in Australian sclerophyll vegetation as well as Indonesian rainforest. The record reflects strongly patterns of ice volume change largely through its influence on sea levels. During interglacial periods like that of today, the extensive Sunda and Sahul continental shelves support warm shallow water that aids in maintaining high rainfall and expanded rainforest distribution in Indonesia and sclerophyll forest in Australia, During glacial periods when much sea water is locked up in ice, the continental shelves are exposed and the area is much drier with reduced rainforest representation and colonization of the continental shelves by grassland. However, the tropical mountains remained wet and the higher representation of conifer pollen indicates also that tropical temperatures were reduced, probably by at least 4°C, during glacial periods. Burning of the vegetation was more extensive during the drier glacial periods, but increased values for charcoal, combined with evidence for destruction of rainforest and

expansion of grassland from about 37,000 years ago, could mark initial human impact within the area.

A 250,000 year record from the continental slope off the coast of northeastern Australia provides evidence of changing representation of complex rainforest, drier conifer forest and sclerophyll woodland. Although the global pattern is evident with interglacial periods showing higher rainfall with expanded complex rainforest and glacials being drier with expansion of conifer and sclerophyll vegetation, this cyclicity is overshadowed by a trend towards the sustained expansion of sclerophyll forests and virtual elimination of conifer forests. The cause of this replacement appears to be increased burning, and major fire events can be related to proposed times of major El Niño-Southern Oscillation (ENSO) activity. Burning was most effective at the height of the penultimate glacial period, about 130,000 years ago, when there was correspondence between very dry conditions and high ENSO activity, and about 45,000 years ago when it appears high ENSO activity coincided with the presence of people on the continent. The development of the ENSO phenomenon may have been very late in geological time and related to oceanic and atmospheric changes associated with the constriction of water movement through the Indonesian throughflow from the Pacific to the Indian Ocean. The build up of warm water in the west Pacific, known as the West Pacific Warm Pool, would have been a necessary prerequisite for ENSO variability.

The third record, covering the last 500,000 years, is from off the coast of the Kimberleys in northwestern Australia, within the heart of the monsoon tropics. It is dominated by eucalypts and grasses. These show little variation in relation to glacial-interglacial cycles during the last 300,000 years, but marked 20,000 year cyclicity in relation to precessionally-controlled direct solar heating of the southern hemisphere tropics. It is considered that at times of high solar energy, the sea surface temperatures of the southern Indian Ocean are raised providing a high moisture source for rainfall in this region. Prior to 300,000 years ago the pattern was different. There was no response to precession and the eucalypts and grasses responded primarily to global ice volume, as is the case with the

Asian monsoons today. Despite the different pattern of vegetation change to that in northeastern Australia, the pattern of burning shows marked similarities, including an increase about 45,000 years ago accompanied by the destruction of patches of drier rainforest.

These three records demonstrate the dominance of global ice forcing of the North Atlantic region, ENSO forcing of the Pacific Ocean and monsoon forcing of the Indian Ocean on the climate and vegetation of different parts of the monsoon region of northern Australia. However, not all vegetation components conform to the dominant forcing at a particular site. For example, all three sites indicate strong ice volume control over mangrove variation because of the close relationship of this vegetation community with sea level variation. In all records, mangroves expand at times of marine transgression from glacial to interglacial periods. They do not respond markedly to rainfall levels as has often been assumed.

In relation to management of coastal, wetland and also terrestrial ecosystems, I think the major lessons from the long term approach are that specific areas and specific components of ecosystems are likely to respond to environmental change in different ways. These lessons are highly relevant under present conditions of rapid climate change.

Northern Wetlands as a Source for Atmospheric Methane: Microbial Processes & Controls of Emission.

Peter Frenzel¹

Abstract

Natural wetlands are the most prominent single source for atmospheric methane. As such, they contribute to the warming of the earth's atmosphere. However, the Northern wetlands in particular accumulate often peat (plant fragments) to such an extent that they become on the long term a sink for atmospheric carbon dioxide. While the respective importance of the source and sink terms is a matter of current research and discussion, we will give an overview about what is known about processes and controls of methane emission.

Methane emission depends on two processes: production in the deeper anoxic layers of a wetland and methane oxidation near to the surface where oxygen is available. Hence, one can write:

emission = production – oxidation.

However, emission (and the underlying processes) vary widely, depending on the microtopography of a wetland. Tussocks of vascular plants have been shown to be major point sources of methane in wetlands. At least in one case it has been demonstrated that no methane oxidation occurred on the roots of these plants, an association otherwise quite common in wetland plants. This missing process may be one reason for the high point emissions. However, the moss layer supports a significant methane oxidation that may consume more than 90% of the methane that otherwise would have been emitted to the atmosphere. Methane oxidizing bacteria are similarly active in the millimeter-thick surface layer of bare peat areas.

We have focussed on the microbial populations involved, and on the environmental conditions in the microsites where methane oxidation occurs,

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These results allow us now to understand why previous methane oxidation measurements failed or gave conflicting results, and to recommend a strategy for the quantification of methane oxidation in these wetlands.