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The Role of Methane Emissions on Ancient and Present Climatic Changes

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1. Introduction

In this Chapter we have reviewed the available literature to discuss how the changes in the atmospheric concentration of methane can affect the future of climate. There is an increasing interest in the exploitation of natural gas for the energy policy by all Countries. In fact its physical properties and its about constant chemical composition (as largely constituted by methane) recommend it to restrict pollutants during combustion processes and to give the best ratio between energetic content and CO_2 emissions, with respect to all other oil derivatives and fossil sources. Moreover natural gas seems to promise more conspicuous reserves than oil, then assuring a "methane peak" more delayed in time than "oil peak".

However, during the last century, we were in the presence of an increasing accumulation of methane in the atmosphere, as never was occurred in the last 800,000 years. Note that methane is much more effective (25 times) as Green House Gas (GHG) than CO_2. The main suspicion about the causes of this accumulation is charged on the leaks of gas that occurs during the extraction and management activities.

On the other hands, the increasing accumulation of methane in the atmosphere could influence the future of the climate because of two dangerous effects: the first is the fast achievement of a no-return threshold, beyond which the Global Warming (GW) become out of human control. This is made easier by a non linear positive feedback, promoted by the increasing of the same GW on the dynamics of emission processes from the natural sources (destabilization of hydrates, stimulation of metabolic production by plants and animals, etc.). For these complex reasons it will need to know better and, if possible, to control the emission mechanisms by natural sources and, besides, to study how ameliorate the present extraction technologies or invent novel ones that will guarantee an about null gas leaks. That needs to prevent the threat for the future of next human generations.

On these purposes we organized the presentation of this Chapter according to the following Sections.

In Section 2 we discuss briefly the biological and thermogenic origins of methane and its biological dynamics in the sediments. In Section 3 are discussed the general characteristics of all the methane sources and the details concerning the natural sources. In Section 4 the anthropogenic sources are presented in details. In Section 5 all data on fluxes are summarized and shortly discussed. In Section 6 the chemical and photochemical dynamics of methane in the atmosphere is discussed and finally its impact on the climatic changes is analyzed in the Conclusions.

Methane (CH_4) is an important Greenhouse gas (GHG) and its concentration in the atmosphere fluctuated during the last million of years between 320 ppbv (nmol/mol of dry air) (during glacial ages) and 780 (warm periods) up to the end of XIX Century, as deduced from the analysis of the composition of deep ice core drilled in the Antarctica (O'Connor et al., 2010; Loulergue et al., 2008). Before the end of the last glaciation, methane concentration diminished up to 380 ppbv (Monnin et al., 2001). It must be remembered that the ice cores extracted by the Greenland glacier show an abrupt change (200 ppbv in a century or 16 ppbv per 1 °C) in concomitance with the fast warming years at the end of last glaciations (Chappellaz et al., 1993; Huber et al., 2006; Wolff et al., 2010).

In the historical age the methane concentration in the atmosphere increased gradually up to 715 ppbv in 1750 (Etheridge et al., 1998) and 780 ppbv at the end of 1800. Finally a very large methane content in the atmosphere has been registered in the last century: the concentration really underwent an acceleration achieving in 2005 the value of 1,774.62 ± 1.22 ppbv (more than double its pre-industrial value) as measured by NOAA in both hemispheres (Forster, 2007) with an increase of about 1,000 ppbv since the beginning of the industrial era in the late 1700's, representing the fastest changes in this gas over at least the last 800,000 years. In 2008 CH_4 achieved 1787 ppbv (Dlugokencky & Bruhwiler, 2009) with an increase of 140 % respect to the start of industrial revolution. This is much higher than the increase of carbon dioxide (CO_2) in the same period (35 %).

Recently, conspicuous emissions of methane were observed from the circum arctic territories and were preliminarily attributed to the anaerobic decomposition of organic sediments on the deep of recent marshes formed by the fusion of permafrost due to the global warming (Walter et al., 2007). Also unexpected methane flows were observed during the 2010 year from the Central and Eastern Siberian Seas (Shakhova et al., 2010). The global warming indeed caused in the last years an abnormal increase in the summer mean temperature (about 4°C) of Siberian rivers and coastal seas.

Other phenomena were observed around the Svalbard Islands An alternative hypothesis concerning the decomposition of the methane hydrates seems more convincing (Barone & Chianese, 2009) in this case.

Moreover other dramatic episodes were registered some time ago in very different environments, as the abrupt emission of a great amount of natural gases near the Namibia coasts, were an animal slaughter occurred (Ward, 2007). This event, however, can be better attributed to a gravitational instability of the deep sea layers, oversaturated by gases produced anaerobically in the marine sediments.

The origin of the present increase, as so as the large changes of concentration of atmospheric methane in the past is discussed in this Chapter. Methane is a long-lived greenhouse gas because it is chemically stable and persists in the atmosphere. The chemical lifetime of CH_4 from removal through reactions with the hydroxyl radical (OH) is estimated at 9.6 years (Folland et al., 2001). Once emitted, however, CH_4 actually remains in the atmosphere for

what is known as a "perturbation lifetime" of approximately 12 years before removal and ultimate conversion to carbon dioxide (CO_2), mainly by chemical oxidation in the lower atmosphere, or troposphere (Solomon et al., 2007). It must be noted that methane is about 25 times more active as greenhouse gas than the CO_2 (O'Connor et al., 2010; Barone & Chianese, 2009; United States Environmental Protection Agency [U.S. EPA], 2010a).

The longer perturbation lifetime of CH_4 is primarily a result of feedbacks between CH_4, OH, and its by-product CO which is also removed by reactions with OH. Minor removal processes include reaction with chlorine in the marine boundary layer, adsorption on soil sinks, and stratospheric reactions. Increasing emissions of CH_4 reduce the concentration of OH, a feedback that may increase the atmospheric lifetime of CH_4 (Solomon, 2007a).

As OH reacts also with other short-lived pollutants, including Volatile Organic Compounds (VOCs), and tropospheric ozone, it interferes with the same VOCs and ozone precursor species and affects the CH_4 lifetime (Wuebbles, 2010).

For this reason, emissions of this gas into the air have a long-term influence on climate. Methane is a light gas and it diffuses and mixes very well throughout the atmosphere, much faster than it is removed: its global concentration can be accurately estimated from data at a few locations (Solomon, 2007b).

In order to understand how the different residence times of different Greenhouse gases, with largely different Radiation Forcing (RF) powers, can affect Global Warming it is important to evaluate their accumulation velocities in the atmosphere. In fact the methane concentration in the atmosphere (amongst those of all other GH gases) is regulated by the dynamical interplay between sources and sinks. Over a period of 100 years, each molecule of CH_4 has 25 times the direct global warming potential of a molecule of CO_2 (Solomon, 2007a).

That implies not only to define the values of the present emissions from the different sources, but also to understand how these values changed along the time in the last century and in the past and how will be possible to forecast next variations. It is likely to discuss two aspects, i.e. how the emissions can change in the next decades, due to new assessments and landuse changes (urbanization, deforestation, infrastructure cementifications, new agriculture and husbandry implementations, spontaneous increase of deserts or wetlands, flooding of coastal lands due to increase of sea level) and how these changes will impact on the climate.

In turn the same kind and intensity of the emission as so as the transformation of land availability and uses will be regulated by Global Warming.

2. Origins of methane

2.1 Recent biological origin of methane

A large portion of CH_4 emissions can be linked to the biological process of anaerobic decomposition, during which some bacteria, the **methanigen**, break organic matter down in the absence of oxygen. They are a specialized group of microbes that produce CH_4 through the process of methanogenesis. Some of the methane can be partly or completely oxidized by another group of bacteria, called methanotrophs, while the remainder can ultimately enter the atmosphere. Microbial production of methane occurs in a variety of settings, some deemed natural and others attributed to anthropogenic activities. For example, methanogenesis can occur both in natural wetlands (a natural source) and in human-influenced wetlands such as rice paddies (an anthropogenic source). Methanogenesis also takes place in other water bodies, submerged sediments, landfills and waste treatment

facilities, and the digestive systems of animals arthropods and ruminants, some of the last domesticated (classified as an anthropogenic source) and some wild (classified as a natural source). Other natural sources of CH_4 include wildfires and geologic processes. Other anthropogenic sources include natural gas handling, biomass burning, and fossil fuel production.

The total flux of CH_4 into the atmosphere from all sources is currently estimated to be 566 Teragrams of CH_4 per year (Tg CH_4/y), which is more than double the pre-industrial value (Solomon, 2007a; U.S. EPA, 2010a). Based on analysis of known methane sources, observed isotopic abundances, and budget modelling, the Intergovernmental Panel on Climate Change (IPCC) estimates that the significant increase in atmospheric CH_4 levels observed over the last two centuries is primarily due to increasing anthropogenic emissions of CH_4, which are currently approximately 1.5 to 2.5 times the magnitude of natural emissions (Forster, 2007). In the same report, a similar estimate is reached by adding together the best estimates for the main natural source categories, which suggest that natural sources contribute 208 Tg CH_4/y to the atmosphere, or 37% of total global emissions. The remainder comes from anthropogenic sources, the largest of which are fossil fuels and natural gas systems exploitation, livestock, waste management and biomass burning (Solomon, 2007b; U.S. EPA, 2007).

2.1.1 Metabolic ways of methanogenesis in the wetland soil and marsh sediments

From complex natural polymers (cellulose, amylase, other polysaccharides and different vegetation proteins) several hydrolytic species of bacteria produce monomers (simple sugars or amino acids. Different fermentative bacteria begin to operate, by means of different fermentation ways, on these materials:

1. Acetate way: is the more direct one, giving acetate a helpful substrate for the *Methanigen bacteria* that produce methane;
2. Long chain fatty acid way (propionate, succinate, butyrate, lactate acids) that in turn can be transformed in acetate; analogously is the ethanol way;
3. Other species of bacteria (*syntrophs bacteria)* can oxidize fatty acids up to CO_2 releasing at mean time H_2 and before that the gas will released, there is the intervention of Homo-*acetogen bacteria* that transform the two molecular species, by an acetogenesis process, in the acetate, thus reconnecting to the first way.

2.2 Ancient (fossil) origins of methane as natural gas and formation of its hydrates

Different mechanisms have been invoked to explain the formation of methane deposits and natural sinks. Methane can originate by both thermo chemical and biochemical processes. In the first case, as other light hydrocarbons, it has the same origins of petroleum through a transformation of organic materials (dead microorganisms, zoo- and phytoplankton, algae, marine animals, and all kinds of life degradation products including dispersed terrestrial pollens). These materials fall on the ocean soundings, continental escarpment seafloor and marine trenches or lacustrine stagnant basins, together with a mixture of clays. This sedimentary mud can be covered by layers of sands and can transform in rock during slow repeated processes under high pressure and temperature.

As consequence of long period geological processes (in Holocene or much more ancient ages), these rocks subside by 2 - 4 or even 6 km depth. Moreover, due to the collision between tectonic plates, the rocks can curl, for the strong side compression forces, and also move from the marine trenches below continental platforms (Figure 1).
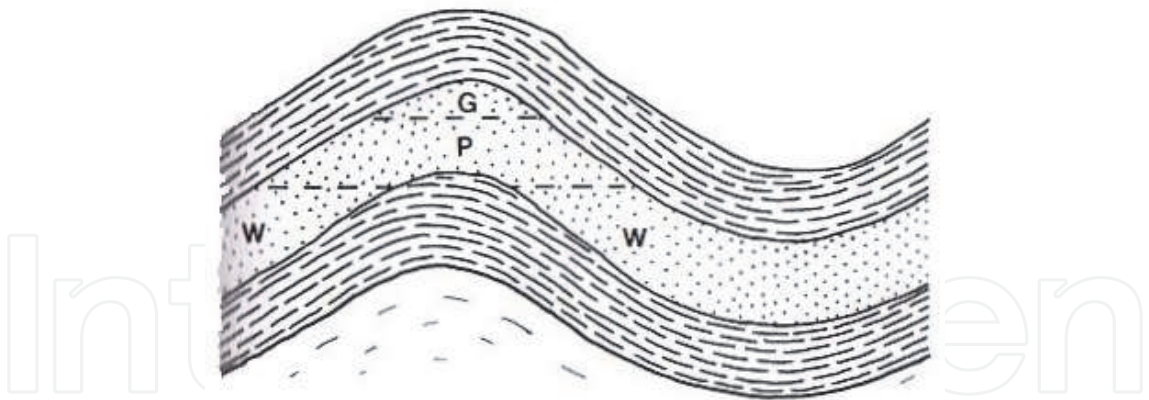
Fig. 1. Curling of layers of rocks containing petroleum reservoirs sealed up and down by other impervious clay rocks: P and G indicate the rock layers sodden (mainly sandstones) of petroleum and gas respectively and W the rock layers in whose interstices predominates water.
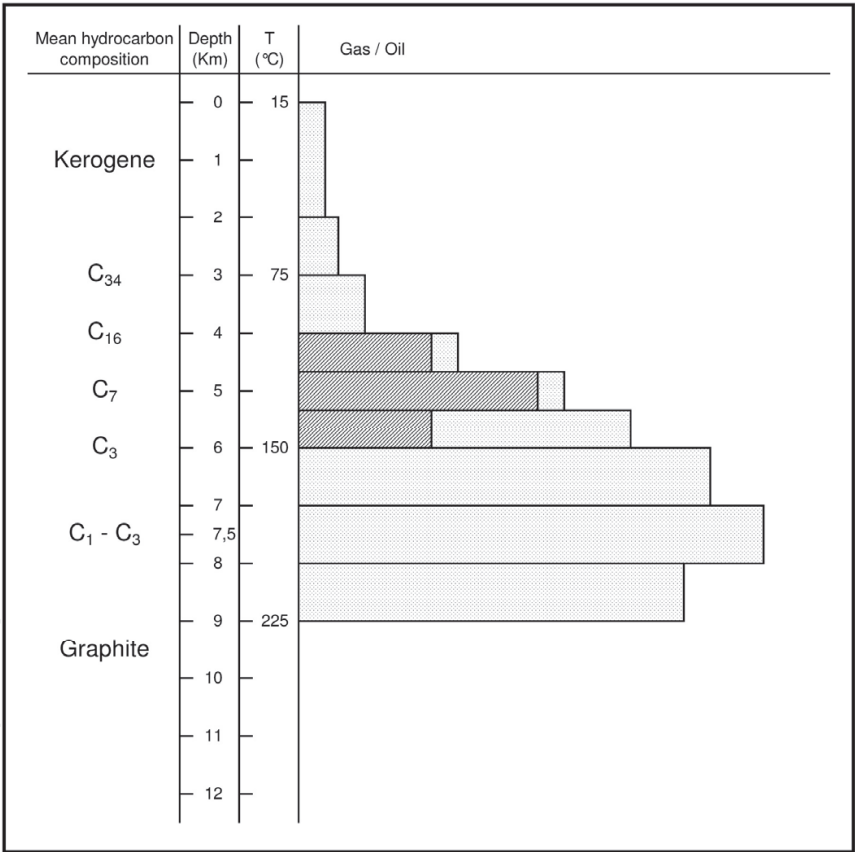

Fig. 2. Natural gas thermogenesis in the deep marine and terrestrial Earth layers. The two central columns report the achieved deep by the organic sediments and the temperatures they experienced. On the first column on the left is reported the mean hydrocarbon composition in which the kerogen blend is transformed, passing from a mixture of solid paraffin's, to crude oil, light oil, gases and finally to a graphite status. The histogram on the right gives a qualitative ratio amongst the gases and oil fractions produced at different temperatures and depths (i.e. pressures).

In both cases the subsided rocks experience temperatures between 80 and 160 °C or even higher. The organic matter in the interstices of these rocks (kerogen) undergoes a thermal degradation, in absence of oxygen, giving rise to a complex mixture constituted mainly by hydrocarbons: so originates a petroleum reservoir. The high temperatures of the deeper layers would promote the thermochemical production of hydrocarbons with small molecular weights (Figure 2).

However, when the rocks are oversaturated, expulsion and migration processes through pores or fractures occur until the oils and gases, blocked on the top and sides by impervious clay layers, encounter geological traps. These traps can be drilled and exploited for the oil extraction and refinement. The gases can remain free on the top of the trap, or solubilized in the oil or finally migrate through other thin geological fractures into other reservoirs, often located very far from the petroleum field.

Here, in the presence of sea water and at low temperatures, about 0 C, and on the high hydrostatic pressure exerted by the column of some kilometers of ocean and by thick layers of overhanging rocks, methane and other gases can be fixed as hydrate crystals (Figure 3).
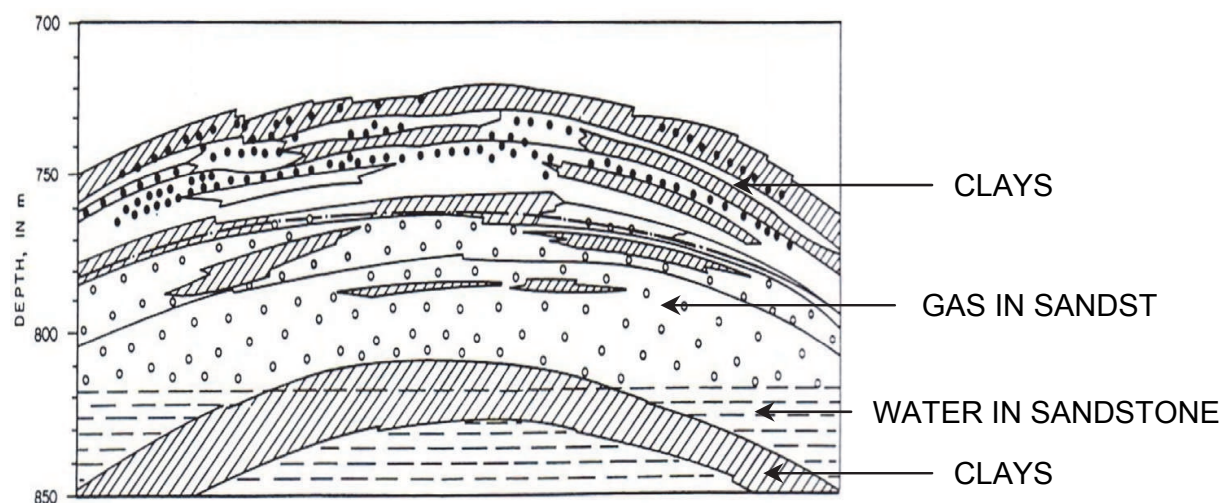

Fig. 3. Structure of a geological trap of natural gas hydrates, originated both by migration from petroleum reservoirs, or by local biological processes. (Adapted and redrawn from Barone & Chianese, 2009; Claypool & Kvenvolden, 1983 and Sloan & Koh, 2008). The filled spots in the upper layers represent gas bubbles eventually seeping trough fractures in the clays or overhanging rocks.

Different is the formation of hydrates under the Arctic permafrost: here the low temperature and high pressure forced the preexisting accumulation of methane and natural gas to transform partially into hydrates. In these areas the extensions of the two fields of hydrates and free gases are geographically partially overwhelmed. In all the less ancient, humid environments (marshes, peat-mosses, anoxic depths of crater-like lakes, and also under permafrost and marine sediments) the biochemical origin of methane seems largely preferred. In these cases the activity of methanigen bacteria is mainly involved in the biochemical transformation of organic sediments accumulated in previous years.

In the case of marine sediments these bacteria use the reduction of sulfate and nitrate as metabolic source of oxygen (Sloan & Koh, 2008). When the biochemical activity occurs on very recent sediments, methane and other gases (frequently H_2S) can gently and slowly seep continuously versus the surface, unless entrapment phenomena create, under high pressure,

instable mixtures of free gases and saturated solutions. The entrapment occurs very often in the upper layers of marine and oceanic sediments (400 - 500 m under the sea floor) and of permafrost (200 - 1000 m under the surface).

When the origins are more ancient, isotopic carbon analysis is not sufficiently accurate for settling between the different hypotheses, even if the presence of ^{13}C can be assumed as a proof for recent biochemical origins. The ratio R = methane versus (ethane plus propane) can better demonstrate the thermo-geochemical (R < 10^2) (Diaconescu e al., 2001; Mazzini et al., 2004; Sassen & Macdonald, 1994; Woodside et al., 2003) or the biochemical (R = 10^3 - 10^5) origin of gases (Claypool & Kvenvolden, 1983).

There are no sufficient proofs to support the hypothesis that origins of methane and its hydrate is a surviving memory of Earth primordial reducing atmosphere. The presence of N_2 together with CH_4 in natural double hydrates could be a weak indication for this hypothesis, as well as the presence of He in the evolved gas; but the last one could originate from the decay of radioactive elements in the neighbor of the trap.

2.3 Biological dynamics of methane in the organic sediments

Besides the methanigen productions, other biochemical transformations occur in the organic sediments that leave to the oxidation of methane. During the natural or human-promoted landfill processes, several aerobic bacteria colonies and associations of species develop and growth. These microorganisms oxidize methane, producing CO_2 that is dispersed in the atmosphere. Chemical transformations also occur in the upland soils and riparian areas, so the dynamic methane balance is negative and these layers act more as a sink, subtracting at all 30 Tg/yr of CH_4 from the atmosphere.

Much more efficient are the biochemical activity of the marine aerobic bacteria colonies and associations of species that develop and growth on the upper layers of the oceanic sediments. In these cases the need of oxygen for the oxidative processes is given by the reduction of nitrate and sulfate ions present in the seawater. It is the same oxygen source utilized by these microorganisms for their own metabolism. The trophic sites of both the anaerobic and aerobic colonies, however, do not have often well defined boundaries.

3. Sources of methane

Natural Sources of methane (about 30%):

-   Wetlands;
-   Upland soils and riparian zones;
-   Vegetation
-   Rivers and estuaries;
-   Lakes;
-   Hydrates from terrestrial and continental shield permafrost
-   Oceans (from biota and organic dissolved or suspended products);
-   Terrestrial and marine geological sources;
-   Wild fires;
-   Wild ruminants;
-   Termites and other arthropods;
-   Hydrates from submarine fields;
-   Natural gas spontaneous emissions from fossil deposits (gas, carbon, petroleum, shale rocks, etc.).

Anthropogenic sources of methane (about 70%):

- Animals husbandry;
- Rice Paddies;
- Landfills
- Biomass combustion;
- Methane from biogenic origins: Waste disposal and waste treatment.
- Gas, petroleum and exploitations and production;
- Coal mining
- Hydrates exploitations;
- Shale rocks.

It is important to note that sometimes there are superposition of source sites (location of permafrost in continental shelves, gas hydrates, and geologic sources), or ambiguity in the definitions (e.g., there are small ponds in natural wetlands that are difficult to distinguish). Field studies may include flux measurements that have contributions from more than one of the sources listed here (O'Connor et al. 2010; U.S. EPA, 2010a).

This Chapter is organized into paragraphs covering natural sources and anthropogenic sources by type. However, the earth is a mosaic of these different source types, the boundaries between these source types are sometimes inexact (e.g., between a wetland and the emergent vegetation of a lake margin), and system changes that affect one source can also affect one or more other sources (O'Connor et al. 2010; U.S. EPA, 2010a).

The issue of methane in permafrost regions exemplifies this interconnectedness. The predicted thawing of permafrost with climate warming may contribute to increased natural source methane emissions to the atmosphere. However, this is a complex system response. There is not a lot of methane frozen into permafrost (unless it is a gas hydrate formation), so permafrost thaw will not release much methane directly. The released methane is probably being oxidized as it diffuses through 1 to 100 meters of thawed soil before reaching the atmosphere. However permafrost thawing implies the formation of marshes or can be associated with thermokarst erosion, which can form (or drain) lakes: in the first two cases the anoxic fermentation of organic sediments can occur giving methane emissions (Walter at al., 2007). Moreover, if gas hydrates are associated with permafrost, then permafrost thawing promotes destabilization of these hydrates, with methane release, potentially in large quantities (Barone & Chianese, 2009).

Another consideration is changes in wetland vegetation and moisture status associated with permafrost thawing; this would be an issue for some, but not all, permafrost landscapes. If the landscape gets wetter and the vegetation composition becomes more dominated by sedges, this could lead to increased methane emissions from a wet landscape - at least for years to decades; however, if the landscape gets drier (or stays relatively dry), then methane emissions would probably stay low (U.S. EPA, 2010a).

3.1 Detailed description of natural sources
3.1.1 Wetlands

Wetlands are ecosystems in which saturation with water is the dominant factor controlling soil development, as well as the species of plants and animals that are present. They are transitional areas, at the interface between upland environments and aquatic systems, and they are concentrated in the high latitudes, where frozen soils can inhibit water drainage, and in the tropics, where precipitation rates are high.

Because saturated soils create anoxic conditions, wetlands are an important natural source of CH_4, which is produced by anaerobic microbial processes that decompose dead plant. They cover about 5 percent of the Earth's surface. Emissions of CH_4 are a minor part of the larger amounts produced and consumed in wetland soils. The different types of bacteria, both producing and consuming it are affected differently by environmental factors (e.g., temperature, water level, and organic matter supply and characteristics). Therefore, a relatively small environmental change can result in a large change in flux by changing the balance between production and consumption (U.S. EPA, 2010a).

In recent years, sophisticated models have been applied for estimating emissions from wetlands. However there are substantial uncertainties affecting the emissions estimates, even if it is possible to estimate fluxes under changing environmental or climate conditions. The 2010 U.S. EPA Report on emission estimates were derived by taking a simple average of the many estimates that have been made since 2004. Flux estimates for high latitude wetlands range from 24 to 72 Tg CH_4/yr, with an average of 43 Tg CH_4/yr. Reported emissions from tropical wetlands range from 81 to 206
Tg CH_4/yr, with an average of 128 Tg CH_4/yr (Table 1). The 2010 U.S. EPA Report estimates a total mean emission value of 170 Tg CH_4/yr with an uncertain range of 108-278 Tg CH_4/yr (compare this estimate with that of: 100 – 230 Tg CH_4/yr (Denman et al., 2007) and the estimate of 225 Tg CH_4/yr (Keppler at al, 2003) that perhaps also encloses emissions from rice paddies. In this chapter the last ones are intrusted to the anthropogenic emissions (see paragraph 4.2).

The overall estimates reflect an increase over the figures from the U.S. EPA 1993 Report (U.S. EPA, 1993), suggesting that emissions from the tropical latitudes made the greatest contribution to global fluxes, achieving about the 75 percent of the total CH_4 emissions from wetlands worldwide.

Changes in land use and climate will affect CH_4 emissions from wetlands, with the potential for both large increases and large decreases. At high latitudes, changes in climate are thought to be the major factors driving changes in CH_4 emissions. For example, models using altered temperatures and rainfall suggest that emissions from northern wetlands could double by the end of the 21st century. In the tropics, changes in land use, such as draining or filling wetlands for other uses, are believed to be the major driver of change (U.S. EPA, 2010a).

3.1.2 Upland soils

Upland soils are well-aerated, not water-saturated, and generally oxidizing sites, with dry soil conditions. These conditions favour microbial processes that make these soils a sink for CH_4. Natural sink include upland soils associated with forests and grasslands under natural vegetation, but not agricultural lands.

Riparian zones, located at the interface of terrestrial and aquatic environments, are often permanently wet and rich in organic matter, with water saturated soil conditions and microbial available carbon that contribute to high rate of CH_4 production.

CH_4 sink capability of soils under natural vegetation (including upland and riparian soils) is estimated at 30 Tg CH_4/yr that are subtracted from the atmosphere (Table 1). Methods of estimating CH_4 budgets (i.e., the balance of sources and sinks) however contain significant uncertainties due to the large spatial and time variability (U.S. EPA, 2010a).

Many interrelated factors determine the sink strength for CH_4. Recent studies have found that the strength depends on oxidation by methanotrophic microbes in the soil, and

therefore is influenced by environmental factors that control this oxidation rate. The primary factor is soil diffusivity, which controls the amount of CH_4 transferred into the soil and, therefore, its availability to methanotrophs. Other factors are soil organic carbon content, vegetation type, pH, bulk density, and drainage. In the future enlargement of these sink areas will depend on the human use of territory and climatic changes.

3.1.3 Water bodies
In all water bodies, microbial processes that occur both in the water column and in sediments produce CH_4. Different aquatic sources, including the deep waters of the open ocean, shallower coastal waters on the continental shelves, freshwater rivers and estuaries, where fresh and salt waters mix are considered.

The **oceans** are believed to be a minor natural source of CH_4. Continental shelf areas, estuaries, and rivers contribute to emissions of CH_4, but they have higher organic inputs and nutrient levels than the open ocean; they are relatively shallow, mixing is active and the gas produced in the sediments is easily transported as surface water and released to the atmosphere.

In the open ocean also, enhanced CH_4 production and flux can be found in upwelling areas, which are areas where the prevailing winds and currents bring nutrient-rich deep water to the sea surface. Upwelling areas tend to have higher rates of primary productivity, which in turn leads to more organic material falling down, depleting oxygen in the depth levels and creating here favourable conditions for methane-producing bacteria.

Open ocean emissions are low and dispersed over large areas, and thus they are difficult to resolve with techniques such as inverse modelling that use changes in atmospheric concentrations to estimate flux. The most recent emissions for the open ocean are estimated as 1.8 Tg CH_4/yr, a weighted average among less of 1 Tg CH_4/yr and about 4 Tg CH_4/yr.

Emissions from the **continental shelves** are somewhat higher than those from the open ocean, even though these environments cover a much smaller area. This difference likely reflects greater organic inputs and an increase in sedimentary contributions. An average of recent estimates gives a total flux of 5.5 Tg CH_4/yr.

Estuaries and rivers cover limited areas, yet they contain much biological activity. They are also sites of active mixing, enabling CH_4 produced in adjacent wetlands and shallow-water environments to be rapidly released to the atmosphere. Averaging the available estimates for estuaries and adding the only available estimate for rivers results in a total flux of 1.85 Tg CH_4/yr.

On overall, natural CH_4 emissions from oceans, estuaries, and rivers are estimated at 9.1 Tg CH_4/yr (U.S. EPA, 2010a) (Table 1). Natural emissions from oceans, estuaries, and rivers represent only about 2 percent of the total global CH_4 emissions to the atmosphere every year. They are expected to remain largely unchanged in the future.

3.1.4 Permafrost
Permafrost is soil, sediment, or detritus that is permanently frozen (temperature < 0°C) for at least two consecutive years. It is widespread and nearly continuous in the arctic, but also exists intermittently in the sub-arctic and boreal regions, and at high elevation. Permafrost is a natural source of CH_4, which could be released as it melts.

Emission estimates are based on measured concentrations of CH_4 in permafrost and estimates of contemporary permafrost degradation rates. Current CH_4 releases from

permafrost are estimated to be 0 to 1 Tg CH_4/yr. There is now strong evidence that permafrost is melting, and that a substantial fraction of permafrost existing now will be melted within the next 100 years due to global climate change. However, it now also seems clear that the permafrost melting will be only a small direct source of CH_4. Indirectly, however, thawing permafrost is already impacting CH_4 emissions from other natural sources, particularly lakes and wetlands. Permafrost can contain ice wedges, which are lenses of frozen water that can be up to several meters thick. As permafrost thaws and ice wedges melt, this water can sometimes drain away, leading to ground subsidence or collapse, which in turn can alter drainage patterns. In this process, known as thermokarst erosion, lakes and wetlands can form or can dry up. This process affects CH_4 emission rates from high latitude lakes and wetlands.

3.1.5 Gas hydrates

Gas hydrates are ice-like crystals formed between water and gas molecules such as CH_4 under high pressure and ambient temperatures. Large quantities of CH_4 are currently trapped in hydrate form, occurring mainly on continental shelves and to a lesser extent below permafrost regions. Gas hydrates can store large amounts of the gases that they trap, and are stable within a specific range of temperature and pressure known as the hydrate stability zone. In Figure 4 thermodynamic stability ranges of methane and lighter hydrocarbons hydrates are reported together the domain of coexistence with liquid water, ice and natural gases.

Under current conditions, the CH_4 emissions from gas hydrates are small (estimated at 2 to 9 Tg CH_4/yr); however, the potential for significant CH_4 release from gas hydrates warrants close examination of this source (U.S. EPA, 2010a). A significant fraction, if not all, of these emissions are expected to be oxidized in the ocean water column (see paragraph 2.3).

Since 1993, there has been limited discussion of the current flux of CH_4 from gas hydrate reservoirs. Oceanic and onshore continental reserves are believed to be stable at present, which means that they are not currently emitting CH_4. Offshore continental shelf reserves are currently unstable, however, and are believed to emit CH_4 (Shakhova, 2010; Barone & Chianese, 2009). Estimates assume that the CH_4 being liberated from the gas hydrate form is released into the atmosphere. It is possible, however, that some or all of this gas is not actually emitted and, instead, it is oxidized or absorbed within the sediment or dissolved into the water column.

Due to their proximity to the Earth's surface (< 2,000 meters) and the sensitivity of the hydrate stability zone, gas hydrates will likely be affected by climate change. Pressure on hydrates is expected to change as a result of sea level rise and the melting of polar ice caps; however, temperature changes are likely to have a far more significant effect. CH_4 emissions from this source are likely to increase as temperature rises. Based on recent research, it is estimated that the increase in methane emissions due to an increase in ocean temperatures may be sufficient to overcome oxidation in the water column and result in significant atmospheric methane emissions. The magnitude of the methane emissions expected to reach the atmosphere due to release from destabilized hydrates upon ocean warming is, however, uncertain. The methane hydrates and their stability will be moreover discussed on paragraph 4.9, referring to the offshore extraction from the deep ocean sediments.
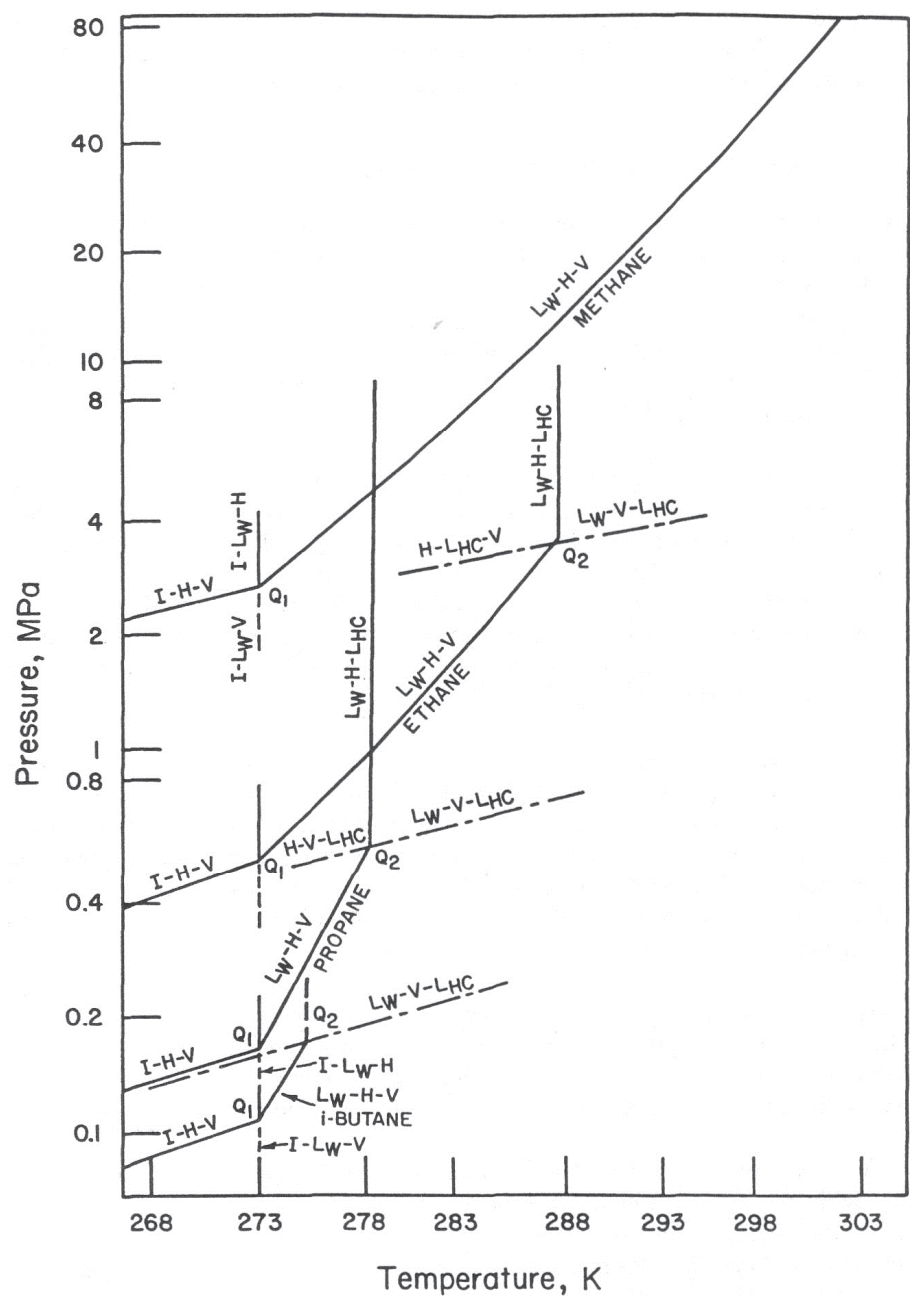
Fig. 4. Phase diagrams of simple natural hydrocarbons forming hydrates (from Barone & Chianese, 2009; adapted and redrawn from Sloan & Koh, 2008). H indicates hydrate, I ice, L_w and liquid water and vapour, L_{HC} liquid light hydrocarbons. Methane hydrate phase diagram presents a quadruple point (Q_1), the other gas hydrates two (Q_1 and Q_2).

3.1.6 Lakes and ponds

Lakes and ponds are naturally formed permanent water bodies dispersed on the land. This source category includes natural freshwater lakes but excludes impoundments and reservoirs (water bodies formed by dams), as greenhouse gas emissions from impoundments, reservoirs, and other engineering works are considered to be anthropogenic (paragraph 4.7).

CH_4 production rates depend on temperature, organic matter availability (food for the bacteria), and isolation from oxygen; these factors are influenced by climate, lake size and depth, and productivity of microscopic and macroscopic plants and animals, which create organic matter for CH_4 production when they die and sink to the bottom. There are four pathways for CH_4 emissions from lakes: bubbling, diffusion, plant-mediated transport, and seasonal overturning. Bubbling has been determined to be the dominant pathway for CH_4 flux, accounting for more than 90 percent of CH_4 emissions from lakes.

Based on recent estimates, lakes emit approximately 30 Tg CH_4/yr to the atmosphere. The number and total area of large lakes is well known, but some uncertainty involves the total surface area of small lakes and ponds. Lakes smaller than

1 km² constitute about 40 percent of the total global lake surface area. Because small lakes and ponds generally emit more CH_4 per unit area than large lakes, uncertainties about total surface area are a major factor in the overall uncertainty of the estimate (U.S. EPA, 2010a).

Climate warming impacts on permafrost and the development of thermokarst lakes could substantially affect future CH_4 emissions from lakes. It is estimated that emissions from lakes north of 45°N will eventually decrease, due to lake area loss and permafrost thaw. Before this long-term decline, though, a period of increased CH_4 emissions, associated with thermokarst lake development in the zone of continuous permafrost, would come. CH_4 emission rates from northern lakes could rise as high as 50 to 100 Tg CH_4/yr during this transitional period, which would last hundreds of years.

3.1.7 Geologic sources

CH_4 and other hydrocarbons can seep naturally from **geologic sources** on the deep Earth's crust. Some geologic CH_4 emissions are produced via what is known as macroseepage, which includes relatively large localized emissions from identified geologic features and events such as mud volcanoes and localized vents. Emissions can also result from diffuse soil exhalation or degassing in volcanically active or other geothermal regions, and from microseepage in petroliferous or hydrocarbon-containing sedimentary basins. Sources include both marine (underwater) and terrestrial (land-based) faults.

Surprisingly white crystal efflorescence formed by the same hydrates found in the oil pipelines were discovered in 1986 on the floor of Caribbean-Mexican Gulf, at 1000-3000 meters depth under the sea level, near the crust fractures from which petroleum emissions drip out (Sassen & Macdonald, 1994). In the following years the same discover was made on other marine floors at different depths. In these conditions high pressure favors the formation of the hydrates from the seeps and endothermic inclusion reactions, that cause a temperature decrease with respect to the deep ocean local temperature (2÷4 °C, almost constant). So, the methane and part of the other gases are selectively trapped in white or even dirty crystals, while the bigger molecules float up to the sea surface (Barone & Chianese, 2009).

Previous estimates of natural sources have either ignored this source or only evaluated "traditional" but actually minor sources such as high temperature magma-producing volcanoes. More recent estimates include emissions from mud volcanoes, other macroseepage locations, terrestrial microseepage, and submarine seeps.

Submarine estimates are extremely uncertain, particularly when estimating the proportion of emissions that are absorbed by ocean water before reaching the surface. In contrast, estimates of onshore emissions can be based on direct measurements and standard emission

factor concepts applied to point sources (for individual features such as mud volcanoes) and more diffuse area sources (for microseepage). "Bottom-up" emissions estimates for both marine and terrestrial sources generally lie in the range of 32 to 74 Tg CH_4/yr. This range largely reflects uncertainty in estimating both the global number of sources and the proportion of emissions that actually reach the atmosphere, rather than being absorbed by ocean water. Recent isotopic constraints on the budget suggest a narrower range of 42 to 64 Tg CH_4/yr, based on the total budget of "fossil" (radiocarbon-free) methane in the atmosphere.

Relatively few climate- or human-related factors are believed to be capable of influencing CH_4 emissions from geologic sources. Some reports suggest decreased emissions associated with large-scale extraction of oil and gas, and increased emissions following deglaciation events and the corresponding increase in seismic activity (i.e., post-glacial rebound). While geologic CH_4 emissions have almost certainly changed in the past and are likely to continue to change in the future, these mechanisms are too speculative to be used as a basis to estimate even the potential direction of future changes in geologic CH_4 emissions.

3.1.8 Wildfires

Wildfires are fires in forests, grasslands, savannas, and shrublands. They can either be ignited by lightning strikes or started accidentally by humans, but do not include deliberate controlled burns for land-clearing activities. As they burn, wildfires release a number of greenhouse gases, particulates, and other air pollutants. When combustion is complete—for example, in dominantly flaming fires—the carbon in biomass is generally converted to CO_2.

When combustion is incomplete, particularly in smouldering fires, some carbon is released in the form of carbon monoxide (CO) and CH_4: smouldering of biomass, consisting of both living and dead organic matter, is the primary source of emissions of CH_4 from wildfires.

Wildfire emissions of CH_4 are estimated to range from 2 to 5 Tg per year. This range depends on the frequency and strength of wildfires, which in turn are determined by a number of factors, including type of vegetation burned, influences from weather (e.g., wind, humidity, temperature) and climate.

Future climate change is likely to lead to enhanced frequency of weather conditions associated with high wildfire risks in many regions of the world. Climate change could affect multiple elements of wildfires, including fire behaviour, ignition, fire management, and vegetation fuels. The recent episodes in Russia and Australia are symptomatic. Currently, no scenarios for future CH_4 emissions from global wildfires exist in the literature.

3.1.9 Plants

Plants, from the tropical forests and other unflooded ecosystems, have long been recognized as important conduits for CH_4 emissions, transporting CH_4 from anaerobic soils and sediments to the atmosphere. However, it is only recently that plants themselves have been considered a possible source of CH_4 production. In 2006, it was reported that plants emit CH_4 through an unidentified process under aerobic conditions, and that this previously unrecognized source could add up to as much as 62 to 236 Tg CH_4/yr, or 10 to 40 percent of

global CH_4 emissions. A significant plant CH_4 source could help explain a number of gaps in the understanding of current and past global CH_4 budgets, including an apparent large unidentified CH_4 source in the tropics.

The initial estimate of the size of a possible plant CH_4 source has since been revised downward in a number of analyses that have either scaled emission rates measured in the laboratory by estimates of global plant production ("bottom-up" estimates) or worked backward from global budgets to determine how large a plant CH_4 source could be reconciled with current estimates of other CH_4 sources ("top-down" estimates). The range of greatest agreement among these estimates is about 20 to 60 Tg CH_4/yr (U:S: EPA, 2010a).

The recently proposed aerobic plant CH_4 source has not yet been incorporated into simulations of future CH_4 emissions. However, future plant emissions would likely depend on changes in the distribution of different vegetation types, as well as changes in environmental factors that might control emission rates. Current estimates attribute 35 to 50 percent of global plant emissions to tropical forests, with the second largest source, tropical savannah and grasslands, contributing about 20 percent. These estimates suggest that future plant emissions will depend largely on changes in climate and land use in the tropics.

3.1.10 Wild animals

CH_4 is also produced by enteric fermentation, a normal digestive process that occurs in ruminant animals such as bison, gnus, deer, elk, mountain goats, and sheep, as well as in some smaller rodent species. Note that IPCC reports do not consider zoogenic emissions. Note also that enteric fermentation occurs in cattle and other domesticated ruminants; however, emissions from livestock are considered anthropogenic, so only estimated emissions from wild animals are reported here. Estimates of emissions from wild animals range from 2 to 15 Tg CH_4/yr (U.S. EPA, 2010a).

Changes to land use, which alter the type of plants available for wild ruminants, could affect the diets of these animals and subsequently their rate of enteric fermentation. As human activity encroaches on wildlife ecosystems, wild animal populations will likely decrease due to habitat unavailability.

3.1.11 Terrestrial arthropods

Termites and other terrestrial arthropods produce CH_4 as a result of microbial degradation of ingested organic matter. In the years some investigation of CH_4 emissions from termites has resulted in more refined estimates of emissions from the various termite species, and has suggested that some CH_4 may be oxidized in termite mounds prior to atmospheric release. The high rates of CH_4 produced by arthropods are due to methanigen (methane-producing) bacteria, which are found in many species of termites. Based on recent research, termites and other terrestrial arthropods continue to be a small but not insignificant contributor to global CH_4 emissions, producing an estimated 2 to 22 Tg CH_4 per year.

The habitats for terrestrial arthropods are also linked to climate effects, resulting in shifting or reduction of dry soil ecosystems (e.g., in more northern environments) or drought, which are likely to decrease populations. Currently, no scenario for future CH_4 emissions from this source exists in the literature.

4. Anthropogenic sources (about 70%)

Anthropogenic sources of methane consist in:

- Rice Cultivation;
- Animals husbandry;
- Landfills;
- Waste disposal and waste treatment;
- Methane from biogenic origins;
- Biomass burning;
- Gas and petroleum refining and production;
- Coal mining
- Exploitation of Gas Hydrates;
- Exploitation of Shale rocks.

4.1 Rice cultivation

Methane is produced during flooded rice paddies by the anaerobic decomposition of organic matter in soils. Flooded soils are ideal environments for methane production because of their high levels of organic substrates, oxygen-depleted conditions, and moisture. The level of emissions varies with soil conditions and production practices as well as climate. The rice paddy global emissions of methane can estimate to be about 100 Tg/yr. The main part of the rice production is concentrated among the 45°N and 10°S in the Asian and Mediterranean countries; the U.S. production is a small part of the total (U.S. EPA, 2010b). From 1980 the production of rice increased of more than 40%, but the emission of methane become less large because of the advanced cultivation technologies. Several cultivation practices have shown promising for reducing methane emissions from rice cultivation: minor use of organic fertilizers, addition of urea and ammonium salts, reducing the ph of the paddies, alternate short drainage periods among them.

4.2 Animal husbandry: Livestock enteric fermentation and manure management

Among domesticated livestock, ruminant animals (cattle's, buffaloes, sheep's, goats, and camels) produce significant amounts of methane as part of their normal digestive processes. In the rumen, a large pre-stomach of these animals, symbiotic bacteria convert vegetation feed (at high cellulose content) by means of microbial fermentation, into products that can be digested and utilized by the animal. This microbial fermentation process, referred to as enteric fermentation, produces methane as a by-product, which can be exhaled by the animal. Methane is also produced in smaller quantities by the digestive processes of other animals, but emissions from these sources are insignificant. EPA and other Agencies have studied options for reducing methane emissions from enteric fermentation and have developed resources and tools to assist in estimating emissions and evaluating mitigation options (U.S. EPA, 2010b).

Methane is produced also during the anaerobic decomposition of organic material in livestock manure management systems. Liquid manure management systems, such as lagoons and holding tanks, can cause significant methane production and these systems are commonly used at larger swine and dairy operations. Manure deposited on fields and pastures, or otherwise handled in a dry form, produces insignificant amounts of methane as

they are easily oxidized at air. On the overall the husbandry of animals introduce about 85 - 115 Tg/yr of methane into the atmosphere (Keppler at al., 2003; U.S. EPA, 2010b).

4.3 Landfills

Landfills are the second–largest human-related source of methane in the U.S., accounting for 23 percent of all methane emissions in 2007. Methane is generated in landfills and large open dumps as waste decomposes under anaerobic conditions. In the last case the favorable conditions occur if the wastes are piled up in high and huge hills without adequate aeration apparatus. The amount of methane created depends on the quantity and moisture content of the waste and the design and management practices at the site.

4.3.1 Waste disposal

Untreated deposits of urban solid wastes can produce methane, besides amines and hydrogen sulphide, if they stay for a long period without sufficient aeration. They can produce up to 25 Tg/yr of methane.

4.3.2 Wastewater treatment

Wastewater from domestic (municipal sewage) and industrial sources is treated to remove soluble organic matter, suspended solids, pathogenic organisms, and chemical contaminants. These treatment processes can produce methane emissions if organic constituents in the wastewater are treated anaerobic ally and if the methane produced is released to the atmosphere. In addition, the sludge produced from some treatment processes may be further biodegraded under anaerobic conditions, resulting in methane emissions. These emissions can be avoided, however, by treating the wastewater and the associated sludge under aerobic conditions or by capturing methane released under anaerobic conditions.

Waste disposal and management can produce up to (25 + 40) Tg/yr on the overall (Keppler et al., 2003).

4.4 Methane from biogenic origins

This is a promising energy source, with the utilization of both biomasses from natural origin and by the gasification or induced fermentation of wastes. The biogenic origins of methane, however, opened a lot of controversies about the real causes of the methane increase in the atmosphere in the last century.

4.5 Biomass burning

About 40 Tg/yr of methane are produced during the incomplete burning of vegetation and organic residues. The quantity of emissions depends on the burning technology, on the temperature of the flames, on the water content and on the carbon content of the biomass (Keppler at al., 2003).

4.6 Fossil fuels ascertained reservoirs

Before to treat the methane emissions from the management of fossil fuels, it is better to remember the estimate of their reservoirs.

The estimates for the Organic Carbon in Earth reservoirs are reported in Table 1.

Reservoir of Organic Carbon in the Earth	Gtons of carbon
Fossil fuels	5000
Gas hydrates	10000
Lands (including soil, biota, peat, detritus)	2790
Ocean (including biota, dissolved or dispersed organics)	983
Atmosphere	3.6

Table 1. Gtons of Organic Carbon in Earth reservoirs.

The estimate of the organic carbon dispersed in rocks and sediments could be equal nearly 1000 times the total known reservoirs.

4.6.1 Natural gas and petroleum systems

Methane is the primary component of natural gas. Methane losses occur during the production, processing, storage, transmission, and distribution of natural gas. Because gas is often found in conjunction with oil, the production, refinement, transportation, and storage of crude oil is also a source of methane emissions. The U.S. inventory report provides a detailed description on methane emissions from natural gas and petroleum systems and how they are estimated for what concern the U.S. reservoirs (U.S. EPA, 2010b).

4.6.2 Coal mining

Methane trapped in coal deposits and in the surrounding strata is released during normal mining operations in both underground and surface mines. In addition, handling of the coal after mining, results in methane emissions.

Overall emissions of methane in the atmosphere from the fossil fuel exploitation, extraction and transport are estimated to be about 110 Tg/yr (Keppler et al., 2003).

4.7 Hydrate exploitation

In this paragraph we discuss with much more details the technology of extraction of methane from the gas hydrates (clathrates) for both the enormous reservoirs, recently discovered, of this source and for the possible peril for the climate if the production will be carried out with not sufficient cautions, especially in the offshore and deep ocean exploitations.

From the middle of '30 years, the engineers, managing petroleum pipelines in the cold regions of Siberia, discovered the formation of some "dirty crystals" incrusting the pipes and often blocking the transmission of oil at temperatures near or below 0°C.

The analysis of these crystals showed that they are an incoherent mixture of crystals of inclusion compounds of methane and other small hydrocarbons in solid water. Actually the blend of crystals is mixed with the mud used for drilling and extraction processes. Similar situations were also observed in Canadian and Alaskan pipelines (Barone & Chianese, 2009; Sloan & Koh 2008). These inclusion compounds of gases in solid water were named gas hydrates and they take part of the large family of clathrate. In particular the methane hydrate (of definite stoichiometric composition: $8CH_4.46H_2O$) is thermodynamically stable around 0°C under a pressure range of few atmospheres (Barone & Chianese, 2009) (see paragraph 3.1.5).

Note that decomposition of 1 m³ of solid methane hydrate (density 912 kg/m³) produces 0.790 m³ of liquid water and 156 m³ at STP of gas (172 m³ at 25 °C).

Extended deposits of gas hydrates, mainly methane hydrates, were discovered in several areas of West Siberia, besides the methane gas reservoirs, located in the depth, under the permafrost layers. The methane hydrate field found at the confluence of Mussayakha and Jennissei/Ob river mouths, offered a large methane source, actually exploited from 1971 up to 1980 (Makogon & Sloan, 1994; Makogon et al., 1996; Sloan & Koh, 2008).

Today the technological interest is devoted to ascertain the consistency and to study the possibility of exploiting the enormous reservoirs of natural gas hydrates present also under the permafrost of circumarctica territories of Alaska and Northwest Territories of Canada, and under the soundings of continental escarpments and oceans. These reservoirs occur near natural gas fields or strictly associated with them (Collett, 1993; Collett, 2007, Collett et al., 1994; Council of Canadian Academies, 2008; Dallimore & Collett, 2005; Ripmeester at al., 2005). Although the permafrost reservoirs (found or estimated and including those extending below the proximate continental margins) represent only the 1% of the offshore fields, the highest accessibility and the possibility to use the existing transport infrastructures, for the natural gas transference, gives much more promising the exploitation of these fields. Intense international collaborative project was developed, involving Institutions and Industries from Canada, Japan, U.S., India and Germany (Collett, 1993; Collett et al., 1994; Collett, 2007; Council of Canadian Academies, 2008; Dallimore & Collett, 2005; Ripmeester at al., 2005).

Extended geophysical researches in marine environments were devoted to the petroleum offshore and deep ocean drilling technologies. The Deep Sea Drilling Project (DSDP) and the successive Oceanic Drilling Program (ODP), ROPOS Project and IODP Project for the petroleum research led to discover the presence of extended deposits of pure hydrocarbon hydrates, in equilibrium with free gases under the wide but tick layers of oceanic sediments. Large deposits of hydrates, mainly methane hydrates, were found out of the east and western coasts of U.S., as so as the western coasts of Mexico, Middle America and Peru and Chile Trenches. In particular on the Blake Bahamas Ridge and on Barklay Canyon out of Vancouver Island, at the Bush Hill in the Green Canyon, at the Tigershark field in Alaminos Canyon and in Mississippi Canyon of Mexican Gulf, on the southern summit of the Hydrate Ridge at the Oregon Margin, on Håkon Mosby site in the Norwegian Sea and around the Shetland islands (Dickens et al., 1997; Lu et al., 2005; Milkov & Sassen, 2002; Milkov & Sassen, 2003a; Milkov & Sassen, 2003b; Milkov et al., 2003; Kvenvolden, 1994).

An intensive effort was undertaken by Japanese Drilling Projects on the Nankai Trough (Okhotsk Sea): this project seems very promising for a possible exploitation and commercialization (Kurihara et al., 2005; Matsumoto et al., 2004; Takahashi et al., 2001; Tsuji et al., 2004; Uchida et al., 2004).

India-U.S. cooperation leads to drilling projects for the location of hydrate accumulation on the Indian continental margin, in particular on the shale fractured area occurring at the Krishna-Godowari basin. Chinese projects were focused on the South China Sea with increasing success. Other Countries of the Asian South East area, on the basis of this success, were encouraged to undertake their own exploration in the same zone. South Korea also tried to explore the Ulleung basin on the East Korean Sea (Fan et al, 2005; Park, 2006).

Recent reviews calculated a total methane volume of 1.2×10^{17} m^3 at STP or 74˙400 Gtons in the oceanic hydrates, of which 4.4×10^{16} m^3 under the continental shelves. These quantities are two or three order of magnitude higher than the known natural free gas (Barone & Chianese, 2009; Klauda & Sandler, 2005; Milkov, 2004; O'Connor et al., 2010).

Note that the clathrate reserves present under the Antarctica permafrost or the North Pole Ocean soundings have not yet been evaluated.

The possibility of exploiting, as new energy sources, the enormous reservoirs of natural gas clathrates present under the permafrost of circumarctica territories and under the soundings of continental escarpments and oceans, has stimulated the interest for many exploitation programs. However, the deep drilling technologies now at disposal could destabilise the hydrate reservoirs and this, besides the drilling and extraction costs, is an actual restraint to the exploitation of this energy sources.

Many efforts also must be made by the mine engineers for improving or developing new available technologies for a safe utilization of these natural reserves without any threat of introducing in the atmosphere relevant and persistent quantities of CH_4. Very interesting is the advanced drilling and extracting technology experimented by Japanese project in the Nankai Trough. In order to not destabilize, with a vertical wall, the hydrate layers during the operation, a 90° bent exploring and extraction wells were successful employed, achieving the deposit by the side (Moridis et al., 2004; Moridis & Reagan, 2007a; Moridis & Reagan, 2007b; Moridis & Sloan, 2007; Moridis, 2008; Takahashi & Tsuji, 2005). This procedure moreover protects the ship bearing the extractive derrick, respect to an abrupt large accidental emission of gas that can cause the sinking of the navy or its fire (remember the Mexico Gulf disaster).

4.8 Shale rocks

Shale are sedimentary rocks enclosing any kind of fine-grained and laminated sheets, consisting at least of 30% of silt- and clay-sized-particles. They also contain substantial amounts of quartz small quantities of carbonates, feldspars, iron oxides, fossils and organic matter. Some organic-rich shales, called oil shales, contain kerogen (see paragraph 2.2) that, when present in large enough quantities, can yields oil if subjected to intense heat.

Shale is the must abundant of the sedimentary rocks, accounting for roughly 70% of this rock type in the Earth crust. They typically are formed in environments where muds, silts and other sediments were deposited by gentle transporting currents and became compacted, as , for example, the deep ocean floor, basins and shallow seas, river floodplains and playas. Most shales occur in extensive sheets several meters thick, though some develop in lenticular formations.

Shales are often found with alternate layers of sandstones or limestone. The laminated structure gives the property defined fissility, id est. they exhibits a tendency to split into thin layers that are usually parallel to the bedding-plane surface. Such physical properties as permeability and plasticity are largely dependent on the grain sizes of constituent minerals. Shales color is determined primarily by the composition: higher the organic content darker is the color; ferric oxides tone to red or purple, ferrous salts impart green or blue; lime turn to gray or yellow.

Shales are commercially important, having applications in the ceramic industry. They are valuable material for tile, brick and pottery manufactures and for Portland cement industry. In addition they were exploited for the extraction of bitumen and liquid petroleum.

In the past the gas extraction from the shale source was utilized by small enterprises and, later on, abandoned for economic reasons. The reservoirs of natural gas embedding the shale rocks are however very promising and can become an important energy source especially for the Countries that do not have direct access to other reservoirs (Howarth et al., 2001).

New technology, analogous to that experienced for the extraction of methane from the hydrates (Takahashi & Tsuji, 2005) was recently proposed for the exploitation and intensive extraction of natural gas from shale rocks as a new important source. In fact very large field

extensions of oil shales are present in the North of United States and Canada, sites that there are not subject to unstable conditions of foreign Countries (U.S. EPA, 2010c). Moreover it is easier to achieve the core of the shale field by means of an oblique coaxial well, without bents, due to the frequent presence of rock formations as hills.

Actually the exploitation of these resources imply the use of pressurized warm water or fluids (hydraulic fracking) to break the shale rocks and made free the gas (or oil). Moreover it is recommended to build up a pipeline, before to bore a new well, in order to avoid gas leaks. This can be not economically favorable and it will result in a discouraging option at the present energy market status (Council of Scientific Society Presidents, 2010). However the U.S. Government decided (2011) to finance research and new technology developments in order to exploit the enormous shale gas reservoirs existing in the North America, with the double goals: renew the U.S. gas reserves and export the gas in the foreign markets with a competitive price.

Moreover the permeability of this kind of shale rocks and the delay in connecting wells with pipelines can favor leaking emissions of gas into the atmosphere up to 200 times respect to the emissions of traditional well exploitation. So that, an intensive exploitation of oil shale for the gas extraction, at the present technological state of art, will cause a true disaster for the environment, especially in the first decades of activity, with a further increase of greenhouse gas concentration and consequent unforeseen perils for the Global Warming (Howarth et al., 2011).

5. Summary of the methane emissions

The literature data discussed in the Paragraphs 3 and 4, are finally collected in the Table 2, where are selected and compared with the results from Keppler et al., 2003; U.S. EPA, 2010a and Whiticar & Schaefer, 2007. The emissions from shales are not considered by EPA and other references quoted here, and not evaluated. Also the fugitive emissions from industries, transport, aviation and other activities are not here considered explicitly and grouped into the total anthropogenic sources (Whiticar & Schaefer, 2007).

Source	(U.S. EPA, 2010a)			(Keppler et al., 2003)
	Emissions estimate (Tg CH_4/year)	Uncertainty Range [a]	$\delta^{13}C(‰)$ [b]	Emissions estimate (Tg CH_4/year)
Wetlands (Total) - Northern/bogs - Tropical swamps	170.3 (42.7) (127.6)	 (27-72) (81-206)	 (-62) (-58.9)	225 (including rice cultivation)
Upland soils and riparian areas	-30[c]	Not available	Not available	
Oceans, rivers and estuaries	9.1	2.3-15.6	-58	15
Permafrost	0.5	0-1		
Lakes	30	10-50	-53.8	
Gas Hydrates		2-9 [d]	-62.5	10
Terrestrial and marine		42-64	-41.8	

Source	(U.S. EPA, 2010a)			(Keppler et al., 2003)
	Emissions estimate (Tg CH$_4$/year)	Uncertainty Range [a]	δ^{13} C(‰) [b]	Emissions estimate (Tg CH$_4$/year)
geological sources				
Wildfires		2-5	-25	
Vegetation		20-60	Not available	
Termites/arthropods	20 [e]	2-22	-63	20
Wild animals	8	2-15	-60.5	30
Total of natural sources	**208**		**-57[f]**	**300 (including rice cultivations)**
All sources (natural plus anthropogenic)	**566 [g] 586[i]**	**503-610[h, i]**	**-54.5[b]**	**610-625**
Rice cultivations				100[j]
Husbandry				85; 88.5 [k]
Coal mining, gas and petroleum exploitation				110; 95 [k]
Biomass burning				40; 21 [k]
Waste disposal + Waste treatment				40+25; 58 [k]
Total of anthropogenic sources				**310-325; 263-281[k] (including other minor sources)**
Natural sources as percent of the total	**37%**			

[a] Ranges presented here may reflect a compilation of several different estimates. Published estimates vary due in part to uncertainty in estimating the global number of point and diffuse sources and the average annual emissions from each individual source or source area.

[b] Mean value from Ref 66 and references therein.

[c] The balance for these sites is in favour of sinks more than sources.

[d] Spontaneous emissions.

[e] Estimates for terrestrial arthropods include termites. It is estimated that other arthropods could contribute up to 100 Tg CH4/year.

[f] From Lassey et al., 2007.

[g] Mean value for anthropogenic emissions (Wuebbles & Hayhoe, 2002).

[h] Because the relative contributions of emissions from each source to the total budget are not independent of each other (i.e., if one source is at the lower end of its estimated range, another may be at the higher), the ranges cannot be summed.

[i] From Denman et al., 2007.

[j] From Stern & Kaufmann, 2000.

[k] From Ungher et al., 2010.

Table 2. Current methane emissions from natural and anthropogenic sources

Several methods have been invoked to separate and determine the contributions of different sources to the atmosphere. One of the methods analyzes the relative abundance of the three principal isotopes of carbon (the stable isotopes ^{12}C and ^{13}C, and the unstable ^{14}C) that can suggest which processes are producing CH$_4$. This is because microbes producing CH$_4$

discriminate against the heavier isotopic form, ^{13}C, giving a gas depleted of this isotope. In contrast, combustion processes (wildfires, biomass burning) do not discriminate. That gives significance to the numbers reported in the fourth column of Table 1 and note [b].

Moreover the ancient sources of CH_4 (coal, oil, natural gas hydrates, geological sources) release gas that lacks radioactive ^{14}C, contrarily to the more modern sources. (This radioactive isotope originates from the action of cosmic rays on the atmospheric CO_2 that in turn can be metabolized by the photosynthetic organisms and enter in the feeding chain of living organisms, but it is not accumulated and rapidly decay at their death). The isotopic composition of each sink accounts for the gas fluxes in atmosphere, giving the isotopic signature of each source. However the signatures of different analogous sources overlap and can change seasonally. The addition of isotopic data however, can be a powerful constraint on possible source budgets.

By analyzing ice cores, it is possible to compare present-day methane concentrations and sources with historical (i.e., pre-industrial) records. This has been helpful in estimating how natural sources respond to changes in the environment before there was a significant anthropogenic input (Chappellaz et al., 1993; Keppler et al., 2003). For instance the pre-industrial total methane emission was estimated 233 Tg/yr mainly from Wetlands and unchanged sources from wild animals, plants, wildfires and oceans (Keppler et al., 2003).

Depletion of ^{14}C isotope in ice cores, as measured by the $\delta^{14}C$(‰) analogous to that reported for ^{13}C in Table 2, can also help to evaluate the fossil CH_4 origin from geological sources.

6. Impact of methane on the climate changes

6.1 Methane as greenhouse gas

Radiative Forcing (RF) is a measure of how the energy balance of the Earth-atmosphere system is influenced when factors that affect climate are changed (solar radiation, Earth albedo, greenhouse gas concentration, aerosol particles). Radiative forcing is usually quantified as the "rate of energy change per unit area of the globe as measured at the top of the atmosphere", and is expressed in units of watts per square meter (W/m²). When radiative forcing from a factor or group of factors is evaluated as positive, the energy of the Earth-atmosphere system will ultimately increase, leading to a warming of the system. In contrast, for a negative radiative forcing, the energy will ultimately decrease, leading to a cooling of the system. As of 2005, atmospheric CH_4 and N_2O are the second- and third-largest contributors to radiative forcing among greenhouse gases, after CO_2 (Forster et al., 2007).

The conspicuous water vapour contribution to the greenhouse effect is not considered in the RF calculations, as its concentration is quite constant, as confined between the defined limits represented by the mean vapour pressure of the ocean and the cold trap at troposphere-stratosphere boundaries. Other minor contributions to the RF became by the halogenated compounds as CFC (negative after Montreal Protocol) and other chlorine or bromine containing compounds and the long living HFC and FC (positive). The increase of RF from 1990 to 2010 was estimated about 0.47 W/m² for CO_2 and about 0.08 W/m² for CH_4 (Butler, 2010).

6.2 The last glaciations

At the end of the last glaciation, the rate of increasing of methane concentration in atmosphere achieved about 200 ppm per year, as proved by the analysis of Greenland ice carrots (Chappellaz et al., 1993; Huber et al., 2006; Wolff et al., 2010). This could be one of

the training effects on the ancient and quite abrupt global warming. The main emission source, at this time, was the decomposition of hydrates from the permafrost on the continental shelves and escarpments, as they remained mainly uncovered by the ocean water, retired for their accumulation into the ice continental shields. The hydrate instability was due to diminished hydrostatic pressure of 6 -10 atmospheres, corresponding to the lowering of 60 – 100 meters of the sea level. Also, it must be considered that the stability zone of methane hydrates is defined both by the thermodynamic phase diagram, as reported in the Figure 4 of this chapter, and the combination of it with the hydrothermal and geothermal gradients, since the stability zone is confined in well defined values of depth (pressure) and temperature of the permafrost layers (Barone & Chianese, 2009; O'Connor et al., 2010). The emission of gas from the destroyed structure of hydrates can be considered a modulating effect of methane, with respect to the astronomical factors, on the bistability of climate in the last million of years (O'Connor et al., 2010). Methane indeed ruled the climate in very ancient eras (hundreds millions or billion of year ago, in very different atmospheric and geologic environments (Pavlov et al., 2000).

6.3 Recent concentration trends in atmosphere

Today the methane effects on climate warming occur in a totally different condition, i.e. at the summit of a warm period. In previous paragraphs and in Table 1 the methane emissions were mainly considered. The unique sinks reprinted from EPA, and reported here, are those of biogeochemical nature, as the upland soils (and riparian areas) that are estimated to subtract from the atmosphere about 30 Tg/y of methane (U.S. EPA, 2010a).

During the last Century the methane concentration in the atmosphere increased rapidly up to decade 1970 - 80; after that the increase was less clear and the concentration is stabilized up to the 2006 (Butler, 2010; Dlugokencky, 2003). Recent evidences, however, indicate that the concentration starts again to increase (Dlugokencky & Bruhwiler, 2009) achieving the value of about 1810 ppm at 2010 (Butler, 2010).

The rapid increase occurred in the last Century can be attributed in large part to the enormous development of mining and oil and gas extraction activities. The increase almost corresponds to the total anthropogenic emissions not balanced by the depletion of methane for the chemical processes in atmosphere. In the years 1980 – 2000 this balance was probably attained, both for the petroleum crisis and the Soviet Union economic collapse, occurred in the previous decades (remember that the estimated life time of CH_4 in atmosphere is about 8-10 years: Folland 2001, Shindell 2006) , and then a delay must occur between the restarting of increased emission and a clear signal of accumulation). In the first years of the new Century, the exploitation of oil and gas gives a new acceleration to the unbalanced accumulation of methane in the troposphere. It is possible that the new increased rate of accumulation could also be due to high precipitation regime on the tropics (increased emissions from wetlands) and by the warm temperatures on the Arctic (emissions from permafrost), both stimulated by the Global Warming (Dlugokencky & Bruhwiler, 2009; Butler, 2010).

In Table 1 the leaking methane emissions from coal mining and gas and petroleum extraction are in fact estimated to be 95 – 110 Tg/y (Keppler et al., 2003; Ungher et al., 2010). Those quantities are due to the incoercible losses from coal mines (especially in those working underground) because they must be continuously aerated in order to avoid dangerous concentrations of CH_4 and/or CO into the galleries, otherwise their moisture can explode spontaneously even in dilute compositions.

A conspicuous quantity of gas is dispersed into the air at the exit of wells for oil extraction (it is too much expensive to trap the gas and it is dispersed in the atmosphere). The loss is high in the case of oil management with high content of light fractions, as for those from Mexican Gulf. In the case of refinery plants for the fractionation of the crude oil, gas is preferentially burned.

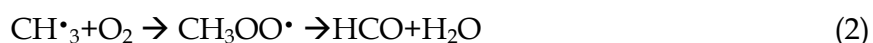## 6.4 Methane chemistry and the dynamics of atmospheric processes

However, in order to properly take into account the short- and long-term effects of this greenhouse gas on the Global Warming, it needs to consider the trend of the accumulation of CH_4 into the atmosphere in a quantitive manner, and not only qualitative as in the previous paragraphs. Actually, the understanding of what happened in the last centuries is object of several controversies. In this paragraph we consider only some simple questions. Any kind of prediction is based on the attempt to delineate the dynamics between the net emission of methane into the atmosphere and all the depletion processes. In this manner it is possible to try some perspective on climate change, based on the evaluation of the increased Radiative Forcing promoted by methane according to different future horizons.

These predictions suffer of the high uncertainty on the emissions factors and of the fact that it is not possible to simply scale down the emission factors: in fact the annual averages cannot be transformed in instant averages, as they results from a combination of fluxes emitted discontinuously during the year and site by site.

An estimate of methane depletion from the troposphere was attempted at 2004 (O'Connor et al., 2010; Lilieveld et al. 2004): the value is about 560 Tg/yr, the 90% (504 Tg/yr), due to fotooxidation initiated by the main radical reaction:

$$CH_4 + OH^{\bullet} \rightarrow CH^{\bullet}_3 + H_2O \tag{1}$$

followed by a cascade of reactions involving the radical $CH^{\bullet}_3$ that give CO_2 at the end:

$$CH^{\bullet}_3 + O_2 \rightarrow CH_3OO^{\bullet} \rightarrow HCO + H_2O \tag{2}$$

$$HCO + OH^{\bullet} + h\nu \rightarrow H_2 + CO_2 \tag{3}$$

The $OH^{\bullet}$ concentration increases proportionally to the low troposphere (Planetary Boundary Layer, PBL) pollution. However the $OH^{\bullet}$ production mainly happens in urban areas, industrial districts and high traffic motorways. Then $OH^{\bullet}$ is partially destroyed before it can be mix with CH_4. Other oxidizing species (ozone, nitrogen oxides, their radical derivatives and the atomic oxygen in its own ground state) react very slowly with methane.

On the other hands CH_4 is a light molecule that can diffuse up to the stratosphere, where very fast reactions occur:

$$CH_4 + O(^1D) \rightarrow CH^{\bullet}_3 + OH^{\bullet} \tag{4}$$

$O(^1D)$ indicates an oxygen atom in its singlet excited state. This species is fast consumed by reaction with water vapour in the troposphere, giving $OH^{\bullet}$ radicals in turn. In the stratosphere the presence of $O(^1D)$ is due to the photo dissociation of molecular oxygen caused by the solar UV radiation:

$$O_2 + h\nu \rightarrow O(^1D) + O(^3P) \tag{5}$$

where $O(^3P)$ represent another electronic excited state of oxygen atom (triplet state) that cannot recombine with $O(^1D)$. The last one can be consumed by reactions with water vapour, giving two $OH^\bullet$, or with molecular oxygen (O_2), giving in turn ozone (O_3).

CH_4 then can also react with $O(^3P)$ and moreover with Cl atoms originated by the photo dissociation of anhydrous HCl (from volcanic activity) or chlorinated species of anthropogenic origins (CFC). In that manner about 25 Tg/yr of CH_4 are consumed into the stratosphere (Ridgwell et al., 1999). Finally about 30 Tg/y are absorbed by dry soils (Table 1).

7. Conclusions

The present accumulation trend of methane in the atmosphere is very alarming for the future of the climate. However, it needs still more accurate research and models for formulating scenarios at all convincing. As we declared in the Introduction Section the trends for the future decades must be referred to three interfering feedbacks and self-accelerating processes: the increased leaks of gas by the extraction activities, the increased emissions by the perturbed natural reservoirs and the depletion reactions in the atmosphere. Really a very rough estimate of the recent unbalanced accumulation in the troposphere, based on emissions rates of 566 – 586 Tg/yr (Table 1) (Denman et al., 2007; Wuebbles & Hayhoe, 2002)   gives a mean value of 16±10 Tg of methane per year. Other references (Bousquet et al., 2006; Keppler et al, 2003), give higher value of methane emissions from which higher accumulation rates can be estimated during the next decades (up to 40 Tg/yr). Then, assuming for the next decade an increasing accumulation of 16 Tg/yr of methane, id est. 0.9% of the present concentration budget, the last will reach 1960 ppm in 2020; if we consider an increase of 40 Tg/yr it will reach 2200 ppm in 2020. Considering a 20 year Time Horizon (TH) from now, i.e. 2030, the methane concentration will reach 2120 or 2600 ppm. At 50 year TH from now, id est. at 2060 and at same increasing trend, methane concentration could achieve 2600 or 3800 ppm, respectively, that will promote a catastrophic climate changes. Other estimates are much more prudent, considering an increase up to 1790 – 1900 ppm only at the end of the century (Ferretti et al., 2005 and other reported in O'Connor et al., 2010).

However for the natural gas extraction wells, there are accepted losses from 1.7% to 6%, in dependence of the employed technology. It has estimated that, during the extraction of gas from the shale rocks, utilizing the fracking process of the layers by means of pressurized water, 3.6 - 7.9% of the gas (respect to the total gas extracted) is dispersed in the atmosphere (in other words from 30% to 400% more than the losses in the case of extraction from the gas fields) (Howarth et al., 2011; Wood et al., 2010). Then, the exploitation of shale rocks as new gas or oil source can open a serious threat, due to the high leaks of gas from these activities.

Very recently (Isaksen et al. 2011) it has been presented a detailed analysis of the feedback contributions to the Global Warming, mainly due to the stimulated methane emissions from the Arctic. These Authors depicted some emission scenarios considering the permafrost thaw, hydrate destabilization and submarine landslides. They use the global-scaled Oslo CTM2 (Chemical Transport model 2), that combines the meteorological inputs from the Reading ECMWF (European Center for Medium Range Weather Forecast) and the Second-Order Moments Scheme for the advecting transport (Prather 1986). The data base for anthropogenic and natural emissions (Oliver and Berdovsky 2001; Muller et al. 1992) were also used. The methane concentrations were calculated as suggested by the ESRL network (Dlugokencky et al. 2010) that has a horizontal resolution of 2.8 x 2.8 degrees and gives 60 vertical layers up to 50 km in the stratosphere. This approach have been validated by several

inter comparisons (Shindell et al. 2006, Isaksen et al. 2005, 2011 and References quoted therein). The strong reciprocal feedbacks of the spontaneous Arctic increasing emissions and Global Warming lead to an accumulation rate of methane from 2.5 to 5.2 (or more) times the present value. This methane burden involves an overall Radiative Forcing 250-400 % times higher than the present one. Moreover those results involve also a strong increase of water vapour and hydroxyl radicals in the stratosphere and ozone in the troposphere.

The conclusions are impressive as it is forecast an increase of the RF of 0.6 Wm^{-2} on a Time Horizon of 50 years for the methane increase alone, that become 0.7 Wm^{-2} considering the life time increase of methane promoted by its own increased concentration and 0.9 Wm^{-2} for the accumulation of CO_2 as final product of the CH_4 oxidation processes. Other contributions must be due to the accumulation of the other GHG.

These scenarios are much more alarming than those based on simple linear extrapolation of methane accumulation trends registered in recent years. They prelude to a "world without ice" (Pasken, 2009). That will be, paradoxically, a world with few fresh waters, furrowed not by rivers, but rather by discontinuous wades, because of the failure of perennial glaciers and springs.

8. Acknowledgements

9. References

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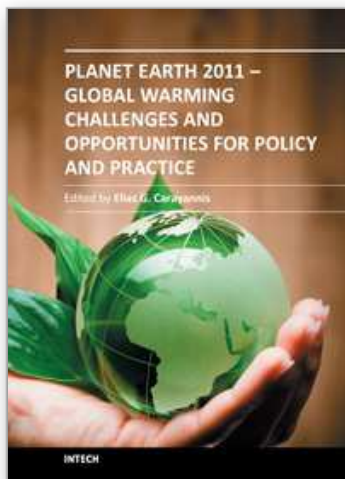
Planet Earth 2011 - Global Warming Challenges and Opportunities for Policy and Practice

Edited by Prof. Elias Carayannis

ISBN 978-953-307-733-8

Hard cover, 646 pages

Publisher InTech

Published online 30, September, 2011

Published in print edition September, 2011

The failure of the UN climate change summit in Copenhagen in December 2009 to effectively reach a global agreement on emission reduction targets, led many within the developing world to view this as a reversal of the Kyoto Protocol and an attempt by the developed nations to shirk out of their responsibility for climate change. The issue of global warming has been at the top of the political agenda for a number of years and has become even more pressing with the rapid industrialization taking place in China and India. This book looks at the effects of climate change throughout different regions of the world and discusses to what extent cleantech and environmental initiatives such as the destruction of fluorinated greenhouse gases, biofuels, and the role of plant breeding and biotechnology. The book concludes with an insight into the socio-religious impact that global warming has, citing Christianity and Islam.

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