

## METHANE

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**Keywords:** Wetlands, animal waste, fossil fuel, hydroxyl, greenhouse effect, concentration, trend

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### Summary

The various anthropogenic and natural surface sources of methane are discussed, and their expert estimations are considered. The scheme illustrates the photochemical oxidation of atmospheric methane. The vertical profile of methane mixing ratio based on few rocket and balloon measurements is presented. The difference between tropospheric methane content of the Northern and Southern hemispheres is small enough (about 6% in 1992) because of its well mixing throughout in the troposphere. The methane concentration evolution is discussed: the relevant paleodata from the Antarctic and Greenland ice cores and the results of recent measurements at various global locations are used. Methane is a greenhouse gas. Thus, its contribution in global warming is briefly considered. Methane controls partly hydroxyl radical tropospheric content and affects on the ozonosphere formation, the relevant atmospheric photochemical reactions are denoted. Some opinions about the possible methane sources and content behavior in the future are expressed.

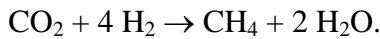
### 1. Introduction

Methane (CH<sub>4</sub>) is a simple saturated hydrocarbon. It is a colorless and odorless gas. The gaseous methane density relative to atmospheric air is about 0.554. Its temperatures of boiling and melting are -164.5 and -182.5 °C respectively and igniting temperature has a range of 650 to 750 °C. Methane with air forms explosive mixtures with methane percentage between 5 and 15 (by volume). Methane is a basic component of natural (77-99% by volume), simultaneous by oil (31-90%), mines (34-40%) and marsh gases. It is contained in the generator and coke gases too. Because of its explosive and fire hazards,

methane has been the cause of many tragedies in mineral mining, throughout the history of humankind. Methane is used in general as a fuel but also as a raw material for the chemical industry (production of acetylene, methyl spirit, hydrocyanic acid and so on).

## 2. Methane sources

Since a large quantity of energy is needed in its production, methane is not generated chemically in the atmosphere. The CH<sub>4</sub> generation occurs mainly in the rice paddies and various types of bogs where the anaerobic decomposition of organic material takes place. Approximately this process may be written as



The essential molecular hydrogen is given off usually by the bacteria developing in the same environment but generating CH<sub>4</sub> directly. Often apart from the fodder supply provision for microorganisms the higher plants and animals create optimal conditions of existence of these microorganisms. Methane from higher animals arises owing to the microbes activity in bowels. The indirect evidence of biological origin of methane is in fact that the ratio between carbon isotopes C<sup>12</sup> and C<sup>14</sup> in atmospheric CH<sub>4</sub> is the same as in the natural biological substances. The gas leakage from natural repositories of fossil fuel may be considered as other atmospheric methane source though its supply from this source is lower than from the decay processes.

Unfortunately, the estrangement of methane sources and their heterogeneous character make their exact estimation difficult. As a result, the existing expert evaluations are based often on the inverse problem solutions (i.e. model reconstruction of methane sources intensity from its observed concentration) but to a lesser extent on the relevant emission measurements. And thus the significant ranges of these estimations are made.

According to the modern ideas, about two-thirds of methane penetrating into the atmosphere has anthropogenic origin. Here it is worth to mention that some parts of anthropogenic source exist as the constituents of wild nature, e.g. animals or rice fields. But during last decades these constituents have been subjected to significant influence due to human activity, e.g. the increase of total number of domestic cattle or rice fields area (the United Nations Food and Agriculture Organization testifies these sources growth by a factor of two to three during the last century) or rise of mining deposits. The above sources can also be considered as anthropogenic ones.

The CH<sub>4</sub> emissions are a function of latitude. The largest methane emissions are between 20-40° N, where there are many rice paddies. The CH<sub>4</sub> source between 50-80° N is due to the wetlands and its sources in the tropical zone are defined by marshes and biomass burning.

The basic types of methane sources and the best estimates and range of their intensity are presented in Table 1, where Other Natural Sources include the methane sources from volcano eruptions, hydrothermal emissions and carbohydrates. Approximately 280 Tg yr<sup>-1</sup> (1 Tg = 1×10<sup>12</sup> g) of the Total methane source (i.e. 54.4%) is in the northern

hemisphere. The upper limit of total range of methane sources in Table 1 exceeds the lower one by about 2.8 times. Therefore, the evaluations of CH<sub>4</sub> source intensity need the essential verification because of their large uncertainty factor.

Source		Range	Likely	Totals	
Natural	Wetlands	Tropics	30-80	60	155
		Northern Latitudes	20-60	40	
		Others	5-10	10	
	Termites	10-50	20		
	Ocean	5-50	10		
	Freshwater	1-25	5		
	Others	8-13	10		
Anthropogenic	Fossil fuel related	Coal Mines	15-45	100	360
		Natural Gas	25-50		
		Petroleum Industry	5-30		
		Coal Combustion	7-30		
	Waste management systems	Landfills	20-70	30	
		Animal Waste	20-30	25	
		Domestic Sewage Treatment	?	25	
	Enteric fermentation	65-100	80		
	Biomass burning	20-80	40		
	Rice paddies	20-100	60		
<b>All Sources</b>				<b>515</b>	

From: Scientific Assessment of Ozone Depletion: 1994 (1994). *WMO Global Ozone Research and Monitoring Project*, Report No. 37, Geneva, Switzerland, 542p.

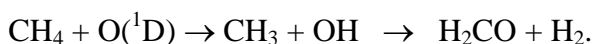
Table 1. Estimated sources of methane (Tg CH<sub>4</sub> per year).

### 3. Methane sinks

Among the atmospheric photochemical reactions of methane destruction the main one is



It controls both the methane and hydroxyl contents in atmospheric air. In the methane photochemical sink this reaction almost has not competitors in the troposphere but in the stratosphere its contribution is about 90%. The same reaction is a second one in the OH photochemical sink by significance (after the OH destruction by carbon monoxide) and responsible for 10-20% of hydroxyl decay. The much lesser influence on methane concentration in the atmosphere has its reaction with excited oxygen



The above mentioned reactions are the first stage of methane oxidation cycle in the atmosphere that is shown by the approximate scheme in Figure 1.

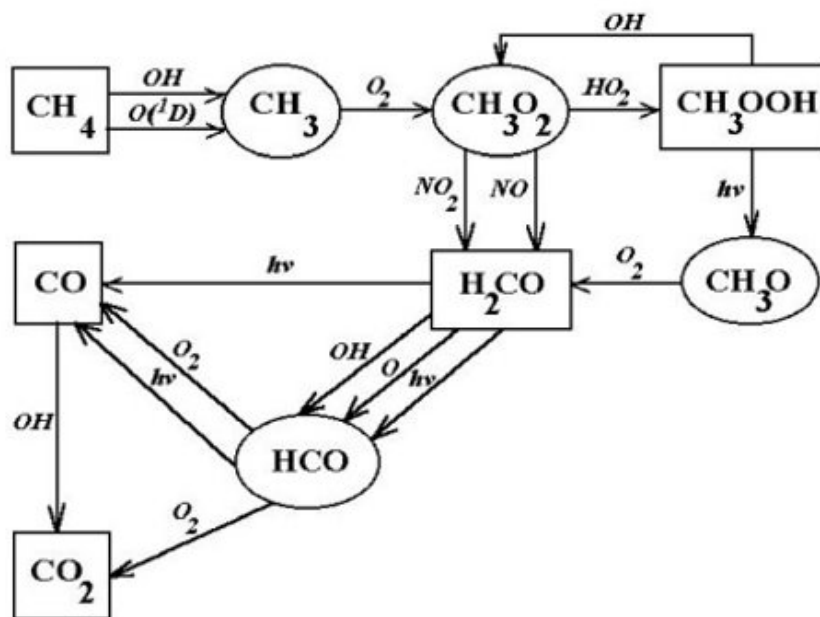
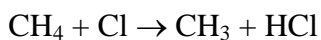
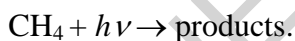


Figure 1. The scheme of methane oxidation in the atmosphere. Symbol “ $h\nu$ ” indicates the specie destruction by sun light (reaction of photodissociation). Radicals in ovals live in the atmosphere a few minutes. Species in rectangles have the “life time” of days or more.

In the stratosphere, in addition, methane is destroyed in its reaction with atomic chlorine



and by sunlight (photolysis reaction)



The first of them is important for the stratospheric ozone balance as it transforms the ozone active atomic chlorine into the ozone passive hydrogen chloride. The contribution of  $\text{CH}_4$  photolysis is relatively small and thus often it is not considered in the relevant studies. The  $\text{CH}_4$  removal in the stratosphere by all reactions except OH is estimated as  $25\text{-}55 \text{ Tg yr}^{-1}$  against the removal of  $330\text{-}560 \text{ Tg yr}^{-1}$  in the reaction throughout with OH.

The other way of methane loss is its removal by soils. According to the available evaluations, soils swallow up about  $15\text{-}45 \text{ Tg yr}^{-1}$ . As a rule, the absorbers of methane are dry soils. The swallowing intensity in the dry subtropical forests is higher than in more moist temperate or tropical belts.

The “life time” of methane (the mean time of its presence in the atmosphere) depends significantly on the hydroxyl content there. In accordance with the current estimates,  $\text{CH}_4$  lasts in the atmosphere from its appearance to decay moment for 8-10 years. In the

middle atmosphere the methane typical “life time” is comparable with time of relevant transport by the meridional winds and vertical turbulent diffusion there. Therefore methane is a good tracer of atmospheric transport processes.

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### Biographical Sketches

**I.L. Karol** was born on 27 July 1927 in Leningrad, USSR. In 1944 he entered the Hydrodynamics Dept. of Leningrad State University, Mathematics and Mechanics Faculty, graduating in 1949. He passed postgraduate studies from 1949 to 1952, when he received a scientific degree of Candidate in Maths & Physics. After three years of lecturing in mathematics at the Ural University in Sverdlovsk, in 1956 he entered the Institute of applied Geophysics USSR Academy of Sciences in Moscow as a senior scientist. In 1959 he was transferred to Institute of Experimental Meteorology of USSR Hydrometeorological Service in Obninsk, near Moscow, where he was nominated as chief of laboratory in 1970. Since 1972 he has been with Main Geophysical Observatory of USSR Hydrometeorological Service in Leningrad (now St. Petersburg) after receiving the USSR scientific degree of Doctor of Math & Physics, presenting in 1970 his theses, which was published in 1972 as a book by Gidrometeoizdat Publishing House "Radioactive isotopes and global transport in the atmosphere". This book was translated into English and published in 1974. Since 1953 I.L. Karol has published 10 scientific monographs and more than 140

papers individually or with co-authors. The original papers are dealing with modeling of global atmospheric composition and climate changes due to natural and anthropogenic causes. During several periods he served as a member of various international commissions and committees of the International Association of Meteorology and Atmospheric Physics, of the World Meteorological Organization, of the World Climate Research Program Joint Scientific Committee. Since 1974 he has been the USSR (now Russian) co-leader of the joint project: "Composition of the atmosphere and climate changes" of the US-Russian Cooperation in Environmental Protection. He was the author or co-author of numerous scientific reports, which he presented at international and national scientific meetings throughout his scientific career.

**A.A. Kiselev** was born on 26 April 1953 in Leningrad, USSR. In 1970 he entered and in 1975 he graduated from the Hydrodynamics Dept. of Leningrad State University. From 1977 to 1981 he passed postgraduate studies at the Mathematics and Mechanics Faculty. In 1986 he received scientific degree of Candidate in Maths & Physics after presenting the candidate theses in geophysics. In 1975 he entered in the Main Geophysical Observatory of USSR Hydrometeorological Service in Leningrad as a junior scientist. Since 1990 he took position of senior research scientist in Main Geophysical Observatory. Since 1975 A.A. Kiselev has published about 30 papers individually and with coauthors. He is a contributor to the Intergovernmental Panel on Climate Change Reports of 1990 and 1999. The original papers are dealing with modeling of photochemical processes in the atmosphere, of global atmospheric composition change due to natural and anthropogenic causes.