

METHANE IN THE ENVIRONMENT (a review)

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Abstract. The atmospheric concentration of methane, a potential greenhouse gas, is determined by global balance between sources and sinks. The aim of the paper was to review the recent studies on the natural and anthropogenic sources that are responsible for the increase in the concentration of methane in the atmosphere, focusing on processes of methane formation and oxidation and factors influencing them. Methanotrophic and methanogenic metabolisms are an important part of these researches from the viewpoint of environmental protection. Great variability of soil properties and their interactions affecting the production, consumption and transport of CH₄ makes our understanding of these processes still insufficient. Although most research to date has focused on sources of methane emissions, CH₄ absorption by oxygenated soil is an important process that significantly reduces emission. The paper describes many soil-related factors affecting methanotrophic activity: particle size distribution, humidity, temperature, pH, oxygen concentration, use of nitrogen fertilisers. Land use has a significant effect on CH₄ oxidation in soils, the greatest methanotrophic potential being that of forest soils as compared to meadows, pastures and arable land.

Key words: methane production, methane oxidation, CH₄ emission, soil

Methane (CH₄) is the simplest saturated hydrocarbon. The gas is colourless, odourless, flammable, and explosive when present in the air in a proportion of ca. 1:10. The methane molecule has a tetrahedral shape; the bonds present in this compound are very weakly polarised, which, combined with lack of free electron pairs, results in chemical stability. Methane is lighter than air, and its density at room temperature at 1 atm pressure is 0.657 kg m⁻³ (Bielański 2002, Stepniewska *et al.* 2004). An important aspect of methane in environmental protection is its ability to absorb infrared radiation. Methane has a relatively short lifetime of 10 years in the atmosphere (Stern *et al.* 2007). Atmospheric methane was discovered only in 1948. The first direct measurements of the concentration and content of this gas were performed even later, i.e. in the seventies of the twentieth century (Schlesinger 1997).

Table 1. Estimated sources and sinks of methane in the atmosphere in units of Tg CH₄ yr⁻¹ (Schlesinger 1997)

	Range	Likely
Sources		
<i>Natural</i>		
Wetlands		
Tropics	30-80	65
Northern latitude	20-60	40
Others	5-15	10
Termites	10-50	20
Ocean	5-50	10
Freshwater	1-25	5
Geological	5-15	10
Total	160	
<i>Anthropogenic</i>		
Fossil fuel related		
Coal mines	15-45	30
Natural gas	25-50	40
Petroleum industry	5-30	15
Coal combustion	5-30	15
Waste management system		
Landfills	20-70	40
Animal waste	20-30	25
Domestic sewage treatment	15-80	25
Enteric fermentation	65-100	85
Biomass burning	20-80	40
Rice paddies	20-100	60
Total	375	
Total Sources	535	
Sinks		
Reaction with OH	330-560	445
Removal in stratosphere	25-55	40
Removal by soils	15-45	30
Total Sinks	515	
Atmospheric increase	30-35	30

The global warming potential of CH₄ is 21 times greater than that of carbon dioxide (Dlugokencky *et al.* 1998), and the average content in the atmosphere is 1.7-1.78 ppm (IPCC 2007). The increase is attributed to enormous intensification of emissions from anthropogenic sources, mainly from agriculture and energy industry. The spread of CH₄ in the atmosphere on a global scale is relatively uniform. The average concentration over the more densely populated and more in-

dustrialised northern hemisphere is only about 6% higher than over the southern hemisphere (IPCC 2006).

Methane is released from many natural and anthropogenic sources. Anthropogenic emission comes from biogenic sources including agriculture, livestock enteric fermentation waste (cattle breeding), human waste (landfills and sewage treatment plants), rice fields and biomass burning. Fossil fuels are sources of methane emission as well. Methane is naturally released from wetlands, by termites, wild ruminants, oceans and fresh water reservoirs, and during decomposition of CH₄-hydrate particles in the process of melting of glaciers and volcanic eruptions (Minami and Takata 1997). Estimates of data on emission sources and removal of CH₄ on a global scale are shown in Table 1.

Anthropogenic sources of CH₄ contribute 70% of the total budget. Natural sources (wetlands, oceans, termites) are also large and dominated the global emissions until the 20th century. Increased livestock production and fossil fuel use are the main reasons for the atmospheric increase of CH₄ (IPCC, 2007). Soils are a minor sink for CH₄ and account for approximately 6% of the global budget; the dominant removal process for atmospheric CH₄ is oxidation by OH, mainly in the troposphere (Fowler *et al.* 2009)

SOURCES OF METHANE AND THE PROCESS OF METHANOGENESIS

CH₄ emission, i.e. methanogenesis, occurs primarily during biochemical processes involving microorganisms classified as archaea.

Anaerobic conditions induced by flooding, with soil redox potential (Eh) below -200 mV, allow methanogenic bacteria to produce CH₄ using acetate and CO₂+H₂ which are produced by fermenting and syntrophic bacteria (Conrad, 1999). Acetotrophic methanogenesis (CH₃COOH→CH₄+CO₂) usually contributes more to the total CH₄ production than hydrogenotrophic methanogenesis (4H₂+CO₂→CH₄+2H₂O), but the relative proportions can vary. The contribution of CO₂ reduction to total methanogenesis is rather high (approximately 53-63%) (Conrad *et al.* 2010). About 73% of methanogenic species consume H₂ in hydrogenotrophic methanogenesis (Garcia *et al.* 2000) while, acetotrophy comprises about 10% of methanogenic species (Meronigal *et al.* 2004).

In this type of anaerobic respiration, biologically useful energy is obtained through the transfer of electrons from hydrogen to CO₂. The living environment of organisms should meet strict requirements so that the above-mentioned process could take place: very low oxygen content, high humidity > 50%, and neutral or slightly alkaline reaction (Stepniewska *et al.* 2004). Along with a rise in temperature, the enzyme activity enhances the reaction efficiency. Therefore, the most common habitats for methanogens are wetlands, rice fields, liquid manure, land-

fills containing considerable amounts of organic matter, and the gastrointestinal system of ruminants. This type of organism is also found in the digestive system of termites. Various investigations indicate that methane is also the product of reduction of other carbon compounds. For instance, during methane fermentation, ca. 70% of methane is produced from acetic acid, and approximately 30% from hydrogen and carbon dioxide (Freeman *et al.* 2002).

Wetlands and rice fields as a global source of methane emission

Permanently or temporarily flooded wetlands are considered one of the biologically most productive ecosystems on earth, where both methanogens and methanotrophs are present and active. Wetland rice fields have been considered to be the major abiogenic source for methane emission (Sass *et al.* 1992, Neue *et al.* 1997). After submergence, a complex physicochemical environment develops with an aerobic, methanotrophic surface layer and an anaerobic, methanogenic underlying layer. The loss of methane to the atmosphere is the highest when the concentration of methane dissolved in the soil or sediment pore waters exceeds the hydrostatic pressure of the overlying water, allowing the formation of gas bubbles. These bubbles may provide escape of a large fraction of the methane flux to the atmosphere (Lansdown *et al.* 1992). The loss of CH₄ from the surface of soil or sediments is determined by the balance between methane production at depth and methane oxidation as it diffuses up through zones of higher redox potential. In some marine sediments, anaerobic methane oxidation is also performed by sulphate-reducing bacteria that use CH₄ as a source of reduced carbon (Schlesinger 1997.)

Although wetlands cover only 5% of the Earth's surface, they play an important role in global greenhouse gas emissions. Methane emission from wetlands is estimated to average about 110 Tg year⁻¹ (Kreileman and Bouwman 1994). This makes wetlands the largest natural source of atmospheric methane, accounting for about 20% of the global annual methane emission (Watson and Downing 1992).

Methane release from wetlands is controlled by several environmental parameters and is the net result of both production and consumption. If, upon flooding, appropriate redox conditions occur, substrate supply is the major controlling factor of methane production, which is the final step in anaerobic microbial degradation of organic matter (Boeckx *et al.* 1997). Secondary controls on methanogenesis are soil temperature and pH (Schimel 1995). The flux of methane from wetland soils increases as a function of the height of the water table, and when soils are flooded the flux increases with soil temperature (Schlesinger 1997).

Salinity and sulphate content as well as vegetation and hydrology are also important factors influencing methane emission from wetlands (Wang *et al.* 1996).

When wetland soils and shallow lakes are overgrown by vegetation, the plants may act as conduits for the escape of methane to the atmosphere (Yavit *et al.* 1997). The process is enhanced by the tendency for many of these species, including rice, to have hollow stems composed of aerenchymous tissue, which allows O_2 to reach the roots and acts as a conduit for CH_4 transport to the surface (Kludze *et al.* 1993, Hatano and Lipiec 2004).

Global methanogenesis has increased with the increasing cultivation of rice which now accounts for a half of the global production of methane from wetlands (Aselman and Crutzen 1989). Rice is the world's most important food source and its cultivation area has increased from 104 million ha to 148 million ha over the last half century (Xu *et al.* 2007, Aulakh *et al.* 2001). Methane produced in rice paddy soils is emitted to the atmosphere by three pathways: molecular diffusion, ebullition as gas bubbles, and rice-mediated transport (Hosono and Nouchi 1997). The methane produced in soils may be subjected to oxidation in the rhizosphere, either aerobically by oxygen released from plant roots or anaerobically by other electron acceptors such as indigenous ferric iron or sulphate (Min *et al.* 2002). Emission of methane from rice paddies is affected by a variety of agronomic and environmental factors including physiological characteristics of rice cultivars (Bodelier *et al.* 2000).

Approximately 90% of the world rice production is located in Asia, with as many as 60% – in China and India. However, production of methane in rice fields is a global problem; as a greenhouse gas it exerts a warming effect on the entire planet (Dubey 2005).

Landfills as a source of anthropogenic methane emission

The intensity of methane production in the waste layer is largely dependent on the quantitative and qualitative composition of waste and on the conditions of the degradation process. Landfill surface emissions measurements quantify the net result of CH_4 transport from the anaerobic waste and methanotrophic oxidation through aerobic soil covers (Baran and Turski 1999). The potential range of percentage oxidation in landfill soils spans from negligible to 100%, with an average value of around 40% estimated with current methodologies (Chanton *et al.* 2009). Recent measurements (Yamada *et al.* 2011) with combination of flux measurements and gas profiles in the landfill cover soil allowed to calculate oxidation factors that were ranging from 0.10 to 0.58, values greater than the default value in IPCC Waste Model equal to 0.10. Variability of soil properties determining gas flow partly corresponds to high spatial variability of methanotrophic activity ranging from 0.17 to 9.80 g CH_4 m⁻² h⁻¹ as it was shown in Röwer *et al.* (2011) studies on landfill covers in Germany.

The need to reduce CH₄ emissions from landfills is essential not only for the reduction of the global warming effects, but also for the prevention of fires and explosions caused by release of methane. There are two strategies of reducing CH₄ emissions from landfills. One method involves reducing contact of the waste layer with the atmosphere by using impermeable cover material facilitating recovery of the biogas. It is estimated that 50-85% of CH₄ produced in a landfill can be utilised as an energy source or as a feedstock to produce hydrogen for the technology of hydrogen fuel cells. This strategy is also implemented by use of a layer of soil overburden, which plays the role of a biofilter for gases produced in the landfill (Nozhevnikova and Lebedev 1995).

Another means of limiting the release of the biogas from landfills is the method of CH₄ inhibition by maintaining aerobic conditions in the component waste layer and reducing organic matter. Theoretically, emission can be thus reduced by 87% (Pawłowska 1999). It seems possible that in the future more extensive search for alternative energy sources will be focused on maximisation of recovery of CH₄ as a renewable fuel (Peer *et al.* 1993).

Emission of methane obtained in breeding of ruminants

Livestock methane emission is estimated at 80 Mt per year and can vary in the range of 65-100 Mt year⁻¹ (IPCC 1995, Reay 2001). Emissions from ruminant animals make up approximately 75% of total livestock emissions (Clark *et al.* 2011). A particularly significant impact of agriculture on methane emission is recorded in Poland (Zaliwski and Purchała 2007). The use and disposal of manure is an inherent element of cattle rearing. Methane from this source is formed during manure decomposition under anaerobic conditions, which are most commonly provided in animal production characterised by high density of animals in a small space. The volume of methane emission from manure is calculated by multiplying the species-specific emission coefficient by the number of livestock animals. Emission coefficients depend mainly on the consistency of manure and its management. The liquid form of manure provides anaerobic conditions; therefore, it exhibits the highest coefficients (Zaliwski 2005, Zaliwski and Purchała 2007).

Emission of methane in Poland

Burning of fossil fuels as well as garbage dumps and landfills are the largest contributors of methane emissions in Poland (47.1% and 27.5%, respectively). Agriculture (24.6%) also takes a substantial share, while industry is responsible for the remaining emission volume (0.8%) (IPCC 2006).

In 2003, 24.6% of methane emissions in Poland originated from agricultural sources. The two primary agricultural sources include enteric fermentation (89.9%) and animal faeces (9.9%). The third source is crop residue burning, which contributes to air pollution to a much smaller extent (0.2%) (IPCC 2006).

METHANE OXIDATION IN SOIL

Although most investigations so far have been focused on the sources of methane emission, it should be emphasised that aerated soils may be a sink of methane. Aerobic soils are an important sink for methane, contributing up to 15% of annual global CH₄ destruction (Minami and Takata 1997). Methane is subjected to the aerobic oxidation by methanotrophic bacteria when it diffuses across an anoxic-oxic interface before escaping to the atmosphere (King and Adamsen 1992).

The methanotrophic ability of soil is related to the presence of microorganisms utilising CH₄ as a carbon and energy source. As a result of intracellular metabolism, CH₄ – a simple organic compound – is transformed into inorganic CO₂ and organic substances incorporated into microbial cells. Owing to its methanotrophic abilities, soil plays an important role in preventing global climate changes by reduction of CH₄ emission into the atmosphere.

Microorganisms that may oxidise CH₄ under aerobic conditions were first described and isolated from soil in the proximity of a natural gas leak by Söngen in 1906 (Pawłowska 1999).

Methanotrophic microorganisms are mainly bacteria; the ability to oxidise CH₄ has also been detected in two yeast species: *Rhodotorula glutinis*, and *Sporobolomyces roseus*, and other fungi identified probably as *Penicillium jahtinellum* (Higgins *et al.* 1981). Almost all known methanotrophs can use not only methane but also methanol as a carbon and energy source, although not all methanol-utilising bacteria exhibit the ability to oxidise methane (Mancinelli 1995, Pawłowska 1999).

The methanotrophic bacteria identified so far have been classified into 5 types and 20 species. These include *Methylococcus capsulatus*, *Methylomonas albus*, *Methylomonas capsulatus*, *Methylobacter chroococcum*, *Methylomonas methanica*, *Methylobacter bovis*, *Methylobacter Capsulatus*, *Methylosinus sporium*, *Methylosinus*, *Trichosporium*, *Methylocistis parvus*, *Mcs. Minimus*, *Mcs. Methanolicus*, *Mcs. Puriformis*, and *Mc. echinoides* (Dubey 2005). Investigations conducted so far have demonstrated that type I methanotrophs, belonging to the γ -subclass of *Proteobacteria*, include the following genera: *Methylomonas*, *Methylobacter*, *Methylococcus*, *Methylomicrobium*, *Metylocaldum* and *Methylosphaera*. Type II methanotrophs belong to the α -subclass of *Proteobacteria* and comprise the genera *Methylosinus*, *Methylocystis* and *Methylocella* (Murrell and Radajewski, 2000). There is growing evidence that the two groups also differ ecologically. Type I methanotrophs prefer

a somewhat lower CH₄ concentration than type II methanotrophs (Amaral and Knowles 1995).

The aerobic oxidation of methane by methanotrophic bacteria, expressing only the ratio of substrates and products, proceeds according to the overall equation: CH₄ + 2 O₂ → CO₂ + 2 H₂O + 883 kJ mol⁻¹. Stoichiometrically, oxidation of 1 mole of CH₄ with 2 moles of O₂ yields 1 mole of CO₂. In practice, O₂ consumption and CO₂ yield per unit volume of CH₄ are lower than those indicated by the reaction formula. This is the result of binding a certain amount of carbon derived from CH₄ in the cell biomass, which is referred to as oxidation of methane via assimilation. The volume of the assimilated methane is variable and depends on the developmental stage of the microbial population (Brzezińska *et al.* 2004). Methane oxidation is evidently an exoergic process. The energy released may be used for biochemical synthesis of the cellular material.

Almost all species of methanotrophs isolated so far live in an environment with pH > 5 and belong to mesophilic organisms (> 15°C); yet, pure cultures of psychophilic methanotrophs have been isolated from tundra soil. They are referred to as the *Methylobacter psychophilus* species (Dubey 2005).

Effect of physical and physicochemical factors on methane oxidation

Particle size distribution of soil material

The size and shape of the structural elements of soil material exerts an impact on its methanotrophic ability through porosity and the size of surface area available to micro-organisms. Texture and compaction of soil determine the pore size distribution effective for both water retention and gas transport, thus determining the rate at which methane and atmospheric oxygen become available to the methane-oxidising micro-organisms.

Soil compaction not only decreases total porosity but may also change the pore size distribution by mainly affecting wide coarse pores which predominantly control gas transport. Secondary macropores formed by the processes of soil aggregation, rootage or animal burrows can greatly increase the diffusivity and permeability inherent in the primary soil properties, providing pathways for preferential gas (Allaire *et al.* 2008) and water (Gebhardt *et al.* 2009) flow.

The study of soils of different texture showed that the mean methanotrophic activity in soils with high sand (≥65%) and low clay content (≤18%) was one order of magnitude higher than in soils having more than 35% of clay (Dörr *et al.* 1993). High oxidative capabilities characteristic for soil with predominance of coarse sand (coarse sand 70%, fine sand 18 %, silt/clay 12%) and sandy soil with predominance of fine sand (coarse sand 16%, fine sand 68 %, silt/clay 16%) were

also observed in soil from landfills (Pawłowska *et al.* 2003). Methanotrophic capacity of clay and silt soils is mainly limited by gas diffusion (Dörr *et al.* 1993).

Soil moisture

Changes in soil water content have profound effects on microbial activity that, in turn, alter the composition of soil microbial populations. The water content of soil regulates methane oxidation by affecting gas transport through soil (i.e. gas-phase molecular diffusion occurring in moist soil is faster than aqueous diffusion) and through the physiological requirement by methanotrophs for water to oxidise methane. When landfill, temperate and subarctic soils were saturated with water (40-50% H₂O), the soil methane oxidation rate decreased. However, when the soil moisture content was between 5 and 15%, the methane oxidation rate was much greater. These results are consistent with the observations made by Wahlen and Reeburgh (1996), who demonstrated a decrease in methanotrophic activity in this range of moisture in soils that were not affected by permanent excessive moisture. Experiments conducted on sandy and sandy-clay soils used as a landfill cover show that the oxidation rate was the highest when moisture was within the 11-20% w/w range (Boeckx and Van Cleemput 1997). Optimum moisture for methane oxidation was demonstrated to be close to half the value of soil water capacity. Stein and Hettiarachi (2001) found the same optimum moisture content, which ranged between 15.6 and 18.8% (gravimetric), for a landfill cover soil (Fig. 1). Both the increase and decrease in soil moisture beyond the optimum value caused a decrease in soil methanotrophic capabilities (Pawłowska 1999).

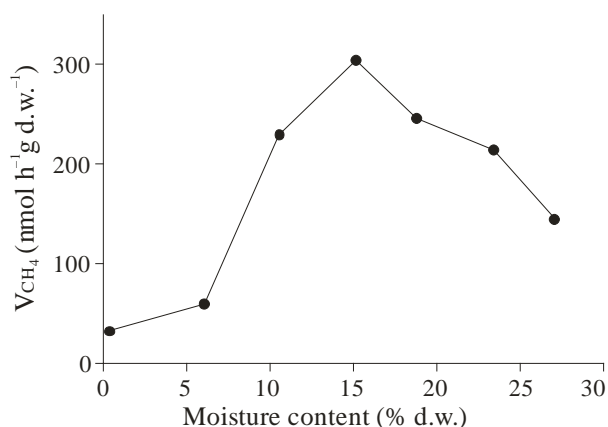


Fig. 1. Effect of soil moisture on methanotrophic activity (Stein and Hettiarachi 2001)

The decrease in methane oxidation in the water-saturated soil probably resulted from slower diffusion of the methane and oxygen through the soil to the microorganisms. (Mancinelli 1995). The data obtained in the field and laboratory studies indicate that soil moisture, and thus water potential, are important factors regulating methane oxidation.

Soil temperature

In addition to soil texture and moisture content, methane turnover rates heavily depend on temperature. The temperature optimum for individual methanotrophic species can vary; in terms of temperature requirements, soil microorganisms are divided into kryophiles, mesophiles and thermophiles. Each of these groups has its own temperature optimum below 20°C, 20-40°C and above 40°C, respectively. Some psychrophilic cultures have their optimum temperature much lower than 20°C, so methane oxidation can also occur in temperate or colder regions. Whalen *et al.* (1990) observed a nearly doubled CH₄ oxidation rate when temperature was raised from 15 to 25°C (Fig. 2). Park *et al.* (2005) found a correlation between temperature and CH₄ oxidation rate.

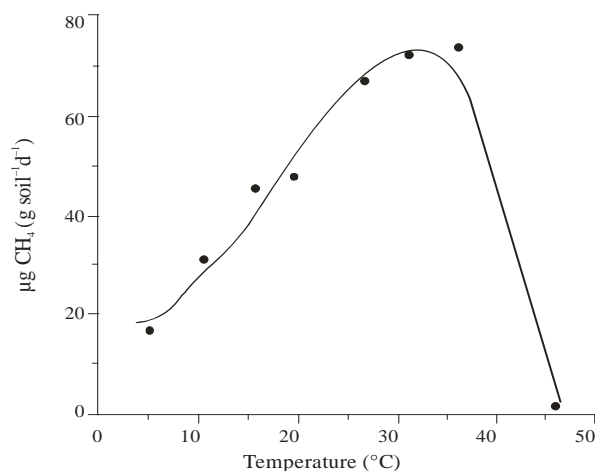


Fig. 2. Effect of soil temperature on methanotrophic activity (Whalen *et al.* 1990)

Soil pH

The activity of soil microorganisms depends on pH of reaction environment. In terms of the degree of microbial sensitivity to acidification, the following groups can be distinguished: pH-insensitive, requiring neutral reaction (pH 7),

acidophilic (optimum pH 2.0-3.5), and basophilic, developing at high pH (minimum pH 8). A significant change in soil pH, e.g. caused by nutrient take-up, nutrient leaching from soils or soil acidification due to industrial pollution, may significantly affect the methanotrophic and methanogenic soil activity by exerting an effect on the composition and abundance of microorganisms (Stepniewski *et al.* 2003). Methanotrophic bacteria living in various ecosystems display diverse affinities for methane and various oxidation rates of this gas. This is associated with environmental conditions prevailing in their habitats, particularly availability of CH_4 .

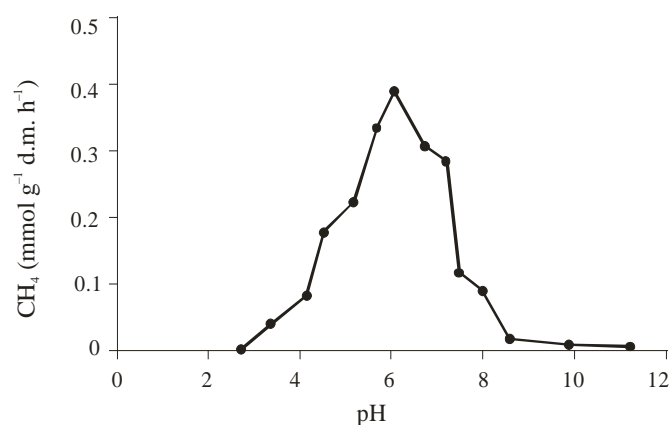


Fig. 3. Effect of different pH on the activity of methane oxidation in soil incubated at 28°C (Min *et al.* 2002)

Methanotrophic activity of different soil types sometimes differs by several orders of magnitude. It depends on the physical, chemical, biological and climatic conditions, and on soil management practices (Murrell and Radajewski 2000, Sigmund and Olsen 1998).

Effect of CH_4 and O_2 concentrations on methane oxidation

As shown in many laboratory studies, there is a strong effect of CH_4 concentration on oxidative soil capabilities. Methanotrophic activity of cultivated soils measured at CH_4 concentrations of 2 and 10 ppm was increasing by the same ratio as the initial CH_4 concentration. Methanotrophic capability of clay soils taken from a landfill cover increased more than four times along with the increase in CH_4 concentration from 1.7 to 84 000 ppm (Bogner *et al.* 1997).

Many results showed a linear increase in methanotrophic activity accompanying a CH_4 increase, which may indicate that CH_4 concentrations were below the

saturation value. No saturation was observed in forest soils in the range of 1.7-1000 ppm, however, some reports indicate that saturation occurs below 160ppm (Benstead and King 1997, Roslev *et al.* 1997). Oxidation of CH₄ in soils starts when the concentration of this gas reaches the threshold value, which is often reported within the 0.1-0.3 ppm range (Heipieper and Debont 1997). The threshold value depends on many factors. Ammonium fertilisation may cause an increase in the threshold value up to 10ppm (Adamsen and King 1993).

The effect of oxygen concentration on methane oxidation is relatively poorly studied. Reported results show that a decrease in O₂ concentration from ambient down to 2 and 0.2% was accompanied by a decrease in the methanotrophic activity of forest soil (Schnell and King 1996).

Effect of nitrogen fertilisers

N input to ecosystems is severely increasing due to human activities such as the use of N fertilisers in agriculture, fossil fuel combustion and cultivation of N-fixing plants (Galloway *et al.* 2008, Stiehl-Braun *et al.* 2011). Nitrogen, especially in the form of ammonium ion, has drawn much attention for its inhibitory effects on methane oxidation, because methane monooxygenases (MMOs), which oxidize methane to methanol, can oxidize not only CH₄ but also ammonium ions in soil (Bradford *et al.* 2001, Wang and Ineson 2003). The results of Bender and Conrad (1995) demonstrated that soils that were exposed to low CH₄ concentrations (forest luvisol) did not respond to NH₄ concentration changes, but soils at high CH₄ concentrations (meadow cambisol, cultivated cambisol and paddy soil) showed inhibited uptake rates.

Adding to agricultural sandy loam soils the dose (0.21 g kg⁻¹) of nitrogen in the form of NH₄ resulted in complete inhibition of the oxidation of CH₄ (Hütsch *et al.* 1996). Smaller amounts of N 0.025 g kg⁻¹ in the form of NH₄ Cl reduced the methanotrophic capacity of loamy sand by about 78-89% (Bronson and Mosier, 1994). There are observations from many studies where the addition of N fertiliser did not inhibit, or even increased, soil CH₄ uptake. There are many examples that applications of organic manures leading to the release of large amounts of NH₄ had no (Hütsch, 1996) or even a positive effect (Willison *et al.* 1996) on the soil CH₄ sink in long-term agricultural trials. It further seems that methanotrophic species differ in their sensitivity to N additions (Mohanty *et al.* 2006). Bender and Conrad (1995) observed a beneficial effect of low concentrations of NH₄⁺, while reducing the rate of oxidation found beyond a certain dose.

NO₃ ions have inhibitory effects on CH₄ oxidation as well. For example, Xu and Inubushi (2004) and Reay and Nedwell (2004) have shown a negative corre-

lation between NO_3 concentrations and CH_4 oxidation rates in temperate forest soils, but the mechanism for such effects is still unclear (Stiehl-Braun *et al.* 2011).

CH_4 oxidation in soils fertilised with nitrogen in the form of KNO_3 or NaNO_3 was weaker as compared to non-fertilised soils in experiments conducted on forest and grassland soils, and in laboratory experiments conducted with agricultural and subarctic soils (Mosier *et al.* 1991, Castro *et al.* 1993, Powelson *et al.* 1997). Complete disappearance of methanotrophic activity in sandy soils was observed after the addition of NaNO_3 in the amount equivalent to 0.21 g N kg^{-1} . The same quantity of nitrogen in forest soils did not restrain the process. This may be due to the combined effect of fertilisation and soil granulometric composition (Hütsch *et al.* 1996).

Influence of soil usage

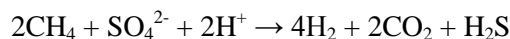
The effect of the use of soils is related to the physical and chemical agents. CH_4 consumption generally dominates in well-drained oxic upland soils, and these soils therefore act as net sinks for atmospheric CH_4 (Hatano and Lipiec 2004). Boeckx *et al.* (1997) found that forest soils compared to the respondents (arable land, meadows, pastures) showed greater ability to oxidise methane.

In native grassland, N fertilisation decreased CH_4 uptake rate by about 35%. Cultivation of soil causes further decreased consumption by an additional 15%. In cultivated and fertilised, irrigated fields of maize and wheat, further decrease CH_4 consumption (85-90%) was observed, however lower than in native grassland (Bronson and Mosier 1994). Keller *et al.* (1993) found that conversion of forest to cattle pasture transformed a net sink of $330 \text{ mg CH}_4\text{-C m}^{-2} \text{ y}^{-1}$ to a net source of $180 \text{ mg CH}_4\text{-C m}^{-2} \text{ y}^{-1}$.

Methane consumption has also proven to be very sensitive to cultivation. Cultivated soils generally show much lower CH_4 uptake rates than soils under native vegetation (Mossier *et al.* 1997). Paustian *et al.* 1995 found that CH_4 uptake in conventionally-tilled soybean was only about 1/8 as much as the uptake in a native grassland. The total impact of cultivation on CH_4 oxidation probably involves factors such as: desiccation of surface soils, reduction in available carbon resources, and changes in the soil physical structure acting simultaneously (Ojima *et al.* 1993). It is assumed that in general the CH_4 sink strength of different land management follows the order of: woodland, grassland, arable land (Willison *et al.* 1996).

Anaerobic oxidation of methane

The methanotrophic bacteria colonising sea and ocean depths are capable of living on energy derived from methane oxidation using SO_4^{2-} (sulphate) ions as the electron acceptor.



Anaerobic methanotrophs have never been found in environments lacking sulphates. Bacteria involved in this process primarily colonise deep sedimentary layers and uptake sufficient amounts of essential ions from the seawater solution (Reinoud, 1998). For the ocean, which covers 70% of the Earth's surface, an annual rate of methanogenesis of 85-300 Tg CH₄ year⁻¹ has been estimated, of which >90% is consumed by anaerobic oxidation of methane (AOM) (Hinrichs and Boetius 2002, Reeburgh 2007). This accounts for 7-25% of the total global methane production. AOM efficiently controls the atmospheric methane efflux from the ocean (<2% of the global flux) (Reeburgh 2007), because almost all the methane produced in ocean sediments is consumed by AOM within the sulphate-penetrated seafloor zones (Knittel and Boetius 2009).

Raghoebarsing *et al.* (2006) showed that some consortia of archaea and bacteria are able to oxidise methane with nitrate instead of sulphate, but this nitrate-reducing process coupled to methane oxidation can also be performed by a single bacterium without the need for an archaeal partner (Włodarczyk 2011). Anaerobic methane oxidation coupled to denitrification was recently assigned to bacteria belonging to the uncultured phylum NC10. Ettwig *et al.* (2009) enriched NC10 bacteria from eutrophic ditch sediment. The enrichment culture oxidised methane and reduced nitrite to dinitrogen gas.

CONCLUSION

Most methane on Earth is produced by methanogenesis, the final step in the fermentation of organic matter, which takes place in rice fields, the guts of animals, soils, wetlands and landfills, as well as in freshwater and marine sediments. Methanotrops appear to play an important role in maintaining low levels of methane in the atmosphere and, consequently, play an important role regulating the Earth's environment. Physical and physicochemical factors like: particle size distribution, water content, temperature, pH, the availability of nutrients, oxygen concentration, and soil diffusivity are important factors regulating both methane production and oxidation in soil. The largest sources of atmospheric methane are anaerobic wetlands and rice fields. Methane emissions are very sensitive to spatial and temporal variability of soil and crop parameters which are largely influenced by climatic conditions, land use and agricultural practices. Generally, upland soils have a potential to absorb methane, however, the balance of sink and production in these soils depends on air filled porosity and fertilisation. Many studies indicate that the highest uptake of methane occurs in forest soils.

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METAN W ŚRODOWISKU (artykuł przeglądowy)

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Streszczenie. Bilans źródeł i pochłaniaczy metanu determinuje stężenie metanu w atmosferze, gazu o dużym potencjale cieplarnianym. Celem pracy było przedstawienie najnowszych badań dotyczących naturalnych i antropogenicznych źródeł, odpowiedzialnych za wzrost stężenia metanu w atmosferze, oraz przegląd głównych czynników regulujących procesy powstawania i utleniania metanu w środowisku. Metanogeniczny i metanotroficzny metabolizm jest ważnym elementem badań z punktu widzenia ochrony środowiska. Duża zmienność właściwości gleby i jej interakcje wpływają na produkcję, konsumpcję i transport CH₄, co sprawia, że nasze zrozumienie tych procesów jest wciąż niewystarczające. Chociaż większość dotychczasowych badań koncentrowała się na źródłach emisji metanu, absorpcja CH₄ przez natlenione gleby jest ważnym procesem, znacznie zmniejszającym uwalnianie CH₄ do atmosfery. Praca opisuje wiele czynników glebowych wpływających na metanotroficzne przemiany: skład granulometryczny, wilgotność, temperaturę, pH, stężenie tlenu, stosowanie nawozów azotowych. Znaczący wpływ na utlenianie CH₄ w glebach ma użytkowanie gruntów, największy potencjał metanotroficzny posiadają gleby leśne w stosunku do łąk, pastwisk i gruntów ornych.

Słowa kluczowe: Wydzielanie metanu, utlenianie metanu, emisja CH₄, gleba