Methanogenesis and Methane Emission

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Introduction

Methanogenesis happens in both natural and anthropogenic environments, from wetland to landfill, to ricefield and livestock production. Methanogenesis involves a series of microrganisms to complete the process. Methanogen is the most important population which use either organic low-weight carbon compounds or inorganic carbon molecule (CO_2) as electron acceptor to produce methane. Methanogenesis has specialized environmental requirements to perform, from temperature to pH and alkalinity, to soil type and the availability of organic carbon. Though a large portion of methane produced by methanogenesis is removed by methanotrophs in the soil, the strong greenhouse gas effect, and increased anthropogenic emission of methane an important component in global climate and carbon cycle. Therefore, understanding methanogenesis will improve our knowledge in the process of methane production.

Reactions and Organisms involved

In general, methanogenesis requires four populations of microbes to successively break down complex molecules (Le Mer and Roger 2001). Hydrolytic microflora first break down polymers into monomers in either aerobic, facultatively, or strictly anaerobic environment. Then, fermentative microflora transform monomers and intermediary compounds formed during fermentation into acids. After that, syntrophic or homoacetogenic microflora might further transform the acids into acetones. Lastly, methanogens can produce methane from the simple compounds where they use carbon as the electron acceptor. All known methanogens belong to the domain Archaea (Woese et al. 1978) with more than 60 species from 26 genera are described (Garcia et al. 2000). However, there still remains a large proportion of methanogens unknown. Methanogenesis also require coenzyme and cofactors such as F420, coenzyme B, coenzyme M, methanofuran family in Archaea group, and methanopterin in the process. Particularly, F420 is common in redox reactions and coenzyme M involved with metal transfer.

The five most common compound groups methanogens use as carbon sources are CO_2 (coupled with H_2), acetate, formate, methylated compounds, and primary and secondary alcohols. The two most common pathways are $CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$ and $CH3COOH \longrightarrow CH_4 + CO_2$, H_2 is usually produced during ethanol fermentation. Based on their trophic groups, methanogens can be classified into five groups: hydrogenotrophs, acetotrophs, formatotrophs, methylotrophs, and alcoholotrophs (Le Mer and Roger 2001). About 77% of methanogenic species are hydrogenotrophic. Most hydrogenotrophs are cocci and robs with few sarcinae. 60% of hydrogenotrophs are also formatotrophs which are all cocci or robs. 14 % of methanogens are acetotrophic, which are corresponding to genera *Mathanosarcina* and

Methanosaeta. M*ethanosaeta* has sheath while the other two species from Mathanosarcina are cocci. 28% of methanogens are methylotrophs, all of which are sarcinae with four genera cocci. For alcoholotrophs, there are a few rods and a few sarcinae.

Conducive environmental conditions

Methanogenesis favors anaerobic environment. Oxygen can inhibit the growth of methanogens even at trace level except for *Candidates* Methanothrix paradoxum which can persist in oxygenated soil (in 't Zandt et al. 2018). Methanogenesis prefers temperature between 30 and 40 °C. Low temperatures can decrease the activity of methanogens and other bacteria involved in methanogenesis(Conrad et al. 1987). A study of peatland soil in Canada found methane emission increased by nearly 7 times when temperature was elevated from 10 to 23 °C (L 143). Therefore, soil temperature can induce seasonal variations of methane emission in either temperate or subtropical zones (Boon and Mitchell 1995, Klinger et al. 1994, Prieme 1994). Though limited, methane emission can still present in wetland under the snow or swamps in winter when the rate of emission was quite low due to low temperature (Dise 1992).

Methanogenesis happens in soils absent of ferric iron (Fe(III)) reducers and sulphate reducers most of the time (Chidthaisong and Conrad 2000). Ferric iron can oxidize carbon source into CO_2 rather than leave it to perform as electron acceptor for methanogens. Reduced ferric iron can be reoxidized by oxygen released by root into oxidizing form to continue the process. This cyclic process will delay organic matter from becoming available for methanogenesis (Wassmann and Rennenbeerg 1993). On the other side, sulphate reducers will compete with methanogens for H_2, which is the reactant in the most common pathway of methanogenesis. In addition, sulphate in soil may also lower rice productivity and reduce the amount of organic carbon source for methanogenesis.

Soil submersion can reduce the size of oxidized zones and allows the development of methanogenic community while inhibiting the methanotrophic activities (Le Mer and Roger 2001). Therefore, environment with deeper water is more conducive to methanogenesis given enough organic carbon storage (Klinger et al. 1994, Shannon and White 1994). While favoring anaerobic environment, the capacity of methanogenesis strongly decrease with depth of soil with the top 5 meters contribute about 70% of the total methane produced (Van den Pol-van Dasselaar and Oenemaa 1999). This is because methanogens rely on recent plant residues as the major substrate.

Methanogens prefer neutral or slightly alkaline conditions and are very sensitive to variations in soil pH (Garcia et al. 2000, Wang et al. 1993). They require a minimum pH of around 5.6. Acidic soil in general has less stable structures, therefore produce less methane than neutral soil (Sass et al. 1990). Experiments in ricefields showed that increasing soil salinity by 0.66 kg per m^2 can decrease the amount of methane production by three to four times and reduce methane emission by 25% (Van der Gon and Neue 1995).

Soil texture also creates conducive environmental conditions for methanogenesis. It helps establish the anaerobiosis for methenogenesis, protect organic matter from decomposition through other redox pathways, transfer and store produced methane, and affect the depth of soil with methanotrophs. For example, in marshland, methane production rates are highest in clay, followed by clayed silt, gravel, and sand in order. Clay soils are poorly drained and prone to anaerobiosis, which makes it suitable for methanogenesis (Le Mer and Roger 2001). There are more active methanogenesis in soil rich in swelling clay than sandy, silty, or kaolinite-rich soil because the density of swelling clay soil increases after submersion, which diminishes variations of pH and Eh and decomposition of organic matter (Neue et al. 1990).

Habitats with high net primary productivity provide sufficient carbon sources for methanogens. A study in Florida Everglades found methanogens possess nifH gene would actively express it for nitrogen fixation to boost the primary productivity when the environment like peatlands was limited by the availability of nitrogen (Bea et al. 2018).

Process rate

Anthropogenic activities are responsible for about 70% of total methane emission. Though agriculture is the main anthropic source of methane, ricefield is the most widely studied environment of methanogenesis. About 0 - 78 kg CH_4 are produced every hectare everyday in ricefield soil by methanogens (Le Mer and Roger 2001). In rice soils enriched with straw, the value can increase to 128 kg CH_4 per hectare per day. A bibliographic survey summarized 127 estimations of ricefeild methane emission from 36 references and concluded emission rates range from 0 to 80 mg CH_4 per m^2 per hour (LeMer 140). The median of the 127 estimations is 9.6 mg CH_4 per m^2 per hour with a 95% confidence interval of -27% to +37%.

About 30% of total methane emission is from natural activities. Wetland is the largest natural source of methane (Heilig 1994). Swamps and peat soils produced 0 - 50 kg CH_4 per hectare per day by methanogens. Though the magnitude of methane production in peatland is not as as high as in ricefield, it covers 3% of land surface and contains one third of carbon in soil. In total, wetland soils, including swamps, bogs, peatland, and so on, release 100-200 Tg of methane each year.

Global significance

Emission of methane from soil is a balance between methanogenesis and methanotrophy. Methanotrophy is the process where methane is oxidized by microbes in soil. The balance between the production and oxidation of methane is usually positive in ricefield, peatland, and landfill, meaning there are more methane produced than removed in such anaerobiosis carbon rich environment (LeMer 204 and

238). Methane can also be eliminated naturally in troposphere by hydroxyl radicals or in stratosphere by chlorine originated from chloro-fluoro carbons (CFCs).

Methane is considered the second or third greenhouse gas after CO_2 and CFCs (LeMer 121 and 138). Though being a trace gas, methane has global warming potentials 104 times greater than CO_2. The methane concentration level in 1994 has already doubled that of the preindustrial level, less than 700 ppb (Heilig 1994). By 2019, the concentration of methane has reached about 1876 ppb (ESRL 2019). The rate of concentration change has been the highest in at least 800,000 years (IPCC 2013).

In addition to its greenhouse gas effect, methane in troposphere reacting with hydroxyl radicals can reduce its oxidative capacity and limit its ability to eliminate pollutants such as CFCs while also producing other greenhouse gases like ozone, CO, and CO_2 (Le Mer and Roger 2001). In stratosphere, methane also react with hydroxyl radicals to produce about half of the water vapor in stratosphere. But the process also destruct ozone layer which acts as the natural barrier against solar radiations (Le Mer and Roger 2001).

Conclusion

Methanogenesis has been widely studied from the microbes to environment and its global warming effects. However, the knowledge of microflora involved in the process is still understudied. Among multiple factors influencing the emission of methane by soil, the effects of competition and predation on methanogenic population remain unstudied. Also, with scientist having discovered the first species that can persist in aerobic environment, more studies are needed to understand the complexity and diversity of the microflora. Besides, the data of methane emission from soils other than ricefield are very limited. The complexity of methanotrophy coupled with methanogenesis makes the measurement of process rate more complicated. What's more, the pathway of alcoholtrophs, such as from methanol to methane, has not yet been understood. In addition, water management techniques have been adapted in agricultural practices to control methanogenesis while saving irrigation water. However, the effect of such adaptations remain undetermined.

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