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METHANE FORMATION IN MANGROVE SEDIMENT

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ABSTRAK

PEMBENTUKAN METANA DI SEDIMEN MANGROVE. *Metan adalah salah satu gas rumah kaca yang memiliki kontribusi dalam proses pemanasan global. Sumber utama metana adalah lahan basah yang salah satunya adalah ekosistem mangrove. Metana di ekosistem mangrove dihasilkan dari penguraian bahan organik di dalam sedimen oleh mikrorganisme anaerobik yang dikenal dengan nama bakteri methanogen. Besarnya metana yang dihasilkan dipengaruhi oleh aktivitas mikro-organisme, kondisi lingkungan dan atribut bahan organik. Tulisan ini mengulas tentang atribut-atribut bahan organik dan pengaruhnya terhadap pembentukan metana di sedimen mangrove. Hasilnya menunjukkan bahwa kandungan karbon oganik total (TOC) dalam bahan organik berperan besar sebagai sumber karbon dalam pembentukan metana. Semakin besar kandungan TOC semakin besar pula produksi metana. Rasio unsur karbon dan nitrogen (C/N) dalam bahan organik juga memiliki peran penting. Rasio C/N yang tinggi akan menghambat pertumbuhan bakteri methanogen akibat kurangnya nutrisi sedangkan rasio C/N yang rendah akan menghasilkan amoniak yang bersifat toksik untuk methanogen. Produksi metana yang melimpah dihasilkan dari bahan organic mudah terurai yang mengandung sedikit lignin yang umumnya berasal dari makroalga laut. Selain itu, metana akan banyak dihasilkan jika bahan organik memiliki ukuran pori yang besar dan tidak terlindungi secara kimiawi atau tidak berikatan dengan mineral.*

INTRODUCTION

The increasing level of greenhouse gasses in the atmosphere is believed to have a significant contribution to recent global warming. Much attention has been given to carbon dioxide (CO_2) because it has the highest concentration and its concentration is increasing at a greater rate than other greenhouse gasses. Due to the ability of mangroves to capture carbon dioxide from the atmosphere, mangrove ecosystem restoration and management have been proposed for nature-based approaches to global warming mitigation (Kauffman *et al*., 2014). However, mangroves not only sequester a greenhouse gas from the atmosphere in

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the form of carbon dioxide but also emit another greenhouse gas to the atmosphere in the form of methane (Purvaja & Ramesh, 2001).

Currently, methane (CH_4) has also become a great concern for the science community interested in climate change issues and has been considered as the second most potent greenhouse gas. This consideration is based on the methane capacity to absorb infra-red radiation which is 21 times higher than that of carbon dioxide (El-Fadel & Massoud, 2001). In addition, current methane concentration in the atmosphere has increased to more than twice as much as its concentration before the industrial revolution (Blasing, 2014).

Ramesh *et al*. (1997) stated that the main sources of methane are wetlands including mangrove ecosystem sand that methane is produced from the decomposition of organic matter in the sediment which is mediated by anaerobic microbes called methanogens. It is estimated that microbial process account for almost 70% of global methane production (Conrad, 2009). As methane is produced through anaerobic microbial decomposition of organic matter, it can be concluded that methane production in mangrove sediment is influenced by three factors including microbial activities, environmental conditions and organic matter properties.

This paper is trying to identify what it is within the organic matter that influences methane production in mangrove sediment, and also examine how much organic matter influences methane production. With a better understanding of the contribution of organic matter to methane production, it is expected that we can manipulate organic matter properties in mangrove sediment in order to reduce methane emissions from mangrove ecosystems.

MANGROVES AND METHANE EMISSIONS

Recently, mangrove restoration and management have been proposed in the global warming mitigation framework. This coastal forestation has been suggested not only for CO_2 sequestration but also to protect the coastal from erosion (Van Santen *et al*., 2007). In addition, mangroves are useful for water quality maintenance (Everard *et al*., 2014) and biodiversity conservation (Nagelkerken *et al*., 2008). Moreover, local communities living adjacent to mangrove ecosystems may gain economic benefits from mangroves. To some extent, they may utilize mangrove woods and harvest fish and crustacean as a food source (Alongi, 2002; Warren-Rhodes *et al*., 2011).

Interestingly, mangroves are not only able to capture CO_2- the most potent greenhouse gas contributing to global warming- but they also emit another greenhouse gas in the form of methane (CH_4). Methane emissions from mangrove ecosystems are significant as wetlands are the major source of methane emission to the atmosphere with a contribution at approximately 23% (Figure 1) (Aronson *et al*., 2013). Methane concentration in the atmosphere has increased significantly. It is similar with CO_2 trend. Present atmospheric methane concentration (1762-1893 ppb) is more than twice as much as its pre-industrial revolution concentration (772 ppb). Even though present methane concentration in the atmosphere is still far less than CO_2 concentration (395.4 ppm), methane has higher capacity to absorb infra-red radiation. It is estimated that methane has more than 20 times the global warming potential than CO_2 (El-Fadel & Massoud, 2001; Blasing, 2014). Therefore, methane is classified as the second most potent greenhouse gas after CO_2.

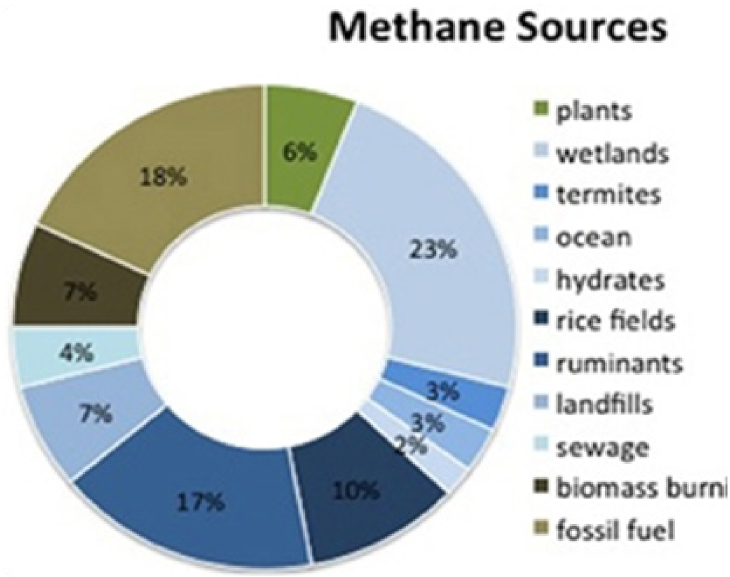

Figure 1. Methane sources (Aronson *et al*., 2013)

In mangrove ecosystems, methane is mainly produced as organic matter in the sediment decomposes. This decomposition process occurs anaerobically which means it occurs in the absence of oxygen. In the presence of oxygen, organic matter completely decomposes and converted to CO_2 instead of methane. In addition, oxygen can also oxidize methane to form CO_2. This oxidation process is mediated by methane-utilizing bacteria called methanotrophs. To reach the atmosphere, methane produced in anaerobic zone of sediment must pass through sediment anaerobic-aerobic interface. During this passing, some may escape but some may be oxidized. Thus, methane emissions in mangrove ecosystems depend on both methane productions in anaerobic zone of sediment and methane oxidation in aerobic zone of sediment. In submerged sediment, emissions depend on methane oxidation in oxygenated water column as well.

METHANE PRODUCTION PATHWAYS

There are a few studies indicating that methane can be produced aerobically in plant leaves and in oxic water columns (Keppler *et al.*, 2006; Reeburg, 2007). However, this mechanism is still debatable and almost all studies show that methane is exclusively produced through organic matter decomposition in anaerobic environment. Methane formation through anaerobic decomposition of organic matter is a very complex process which consists of four inter-correlated stages and every single stage involves specific microbial groups which secrete specific enzymes (Kangle *et al.*, 2012; Adekunle & Okolie, 2015). The four stages in methane formation are shown in Figure 2 below.

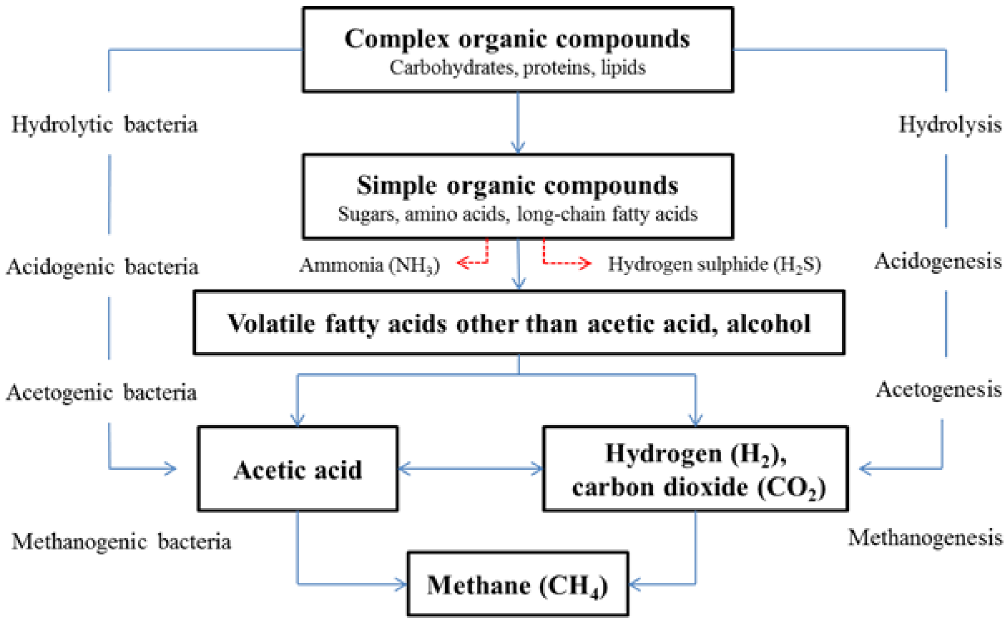

Figure 2.Anaerobic methane formation process.

Hydrolysis is the first stage in anaerobic methane formation where insoluble organic matter is transformed into its soluble building block compounds. During this stage, large polymeric structured complex organic compounds are broken down into their simple monomeric structures. For example, carbohydrates, proteins and lipids are broken down into sugars, amino acids and long-chain fatty acids respectively. Sometimes toxic by products such as complex heterocyclic compounds are formed in this stage as well (Lu *et al.*, 2008). The hydrolysis stage is critical as it determines the next subsequent stages. Thus, it is believed to be the rate-limiting stage of anaerobic methane production.

Acidogenesis is the next stage following hydrolysis. In this stage, monomeric compounds produced in the hydrolysis stage such as sugars, amino acids and long-chain fatty acids are converted into hydrogen (H_2), CO_2, alcohols and volatile fatty acids. Only about 30% of hydrolysis products are converted into alcohols and volatile fatty acids (Angelidaki *et al.* in Kangle *et al.*, 2012). The remaining products are converted into H_2, CO_2 and other compounds which are readily available for methanogens. Acidogenesis also produces by products such as ammonia (NH_3) and hydrogen sulphide (H_2S) which may have toxic effects and inhibit the growth of some types of bacteria during methane formation (Salminen & Rintala, 2002).

Acetogenesis is the next stage after acidogenesis. In this stage, compounds produced in acidogenesis which are not readily available for methanogens such as alcohols and volatile fatty acids are converted into acetate, H_2 and CO_2 which are typical substrates for methanogens. This process is carried out by hydrogen producing bacteria and only occurs in a low H_2 partial pressure environment. Therefore, collaboration between H_2 producing bacteria and methanogens which consume H_2 to produce methane is very critical.

Methanogenesis is the final stage of methane production. In this stage, H_2, CO_2 and acetate produced in acetogenesis or other previous stages are converted to methane by methanogens. There are two main types of methanogenesis based on the substrates used by methanogens, hydrogenotrophic methanogenesis and acetotrophicor aceticlastic methanogenesis. Hydrogenotrophic utilizes H_2 and CO_2 while acetotrophic utilizes acetate. Acetotrophic methanogenesis is more common than hydrogenotrophic with a ratio of 70%:30% (Kangle *et al.*, 2012).

ORGANIC MATTER AND METHANE PRODUCTION

According to the general mechanism of anaerobic methane production above, there are three main factors influencing methane formation in sediment including microbes, environmental conditions and organic matter. Of those three factors, organic matter is the easier one to control in the environment. Therefore, a better understanding on the role of organic matters in the methane formation is important in order to find out appropriate methods in reducing methane production. This section will explore on how organic matters influence methane formation.

There are at least four properties of organic matter that influence methane formation including total organic carbon (TOC) content, carbon-nitrogen ratio (C/N), biochemical and chemical protection and nanoscale structure.

1. Total Organic Carbon (TOC)

Methane contains single carbon element in its structure. This carbon element derives from carbon element contained in larger organic compounds during organic matter decomposition process. Therefore, carbon content in organic matter is the primary carbon source in methane formation. From this illustration, we can assume that the more organic carbon content available, the more the methane is produced. If there is no organic carbon available, no methane will be produced. This assumption was proven by Kumar *et al*. (2016). From observation conducted in wheat agriculture field at Khodiyar Village, Anand Gujarat, they found that TOC and methane flux has a strong positive correlation. The higher the TOC, the higher the methane flux is.

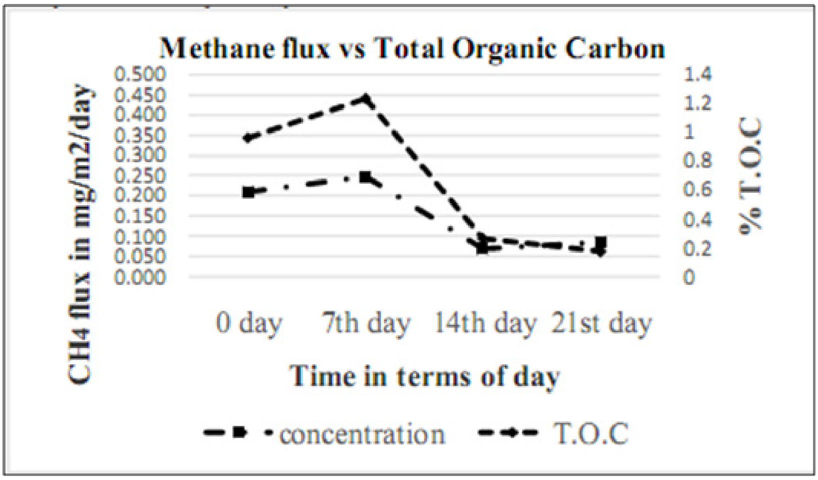

Figure 3. Methane flux variation against TOC value in wheat agriculture field at Khodiyar Village, Anand Gujarat (Kumar *et al*., 2016).

2. C/N ratio

Carbon (C) and nitrogen (N) is essential nutrition for organism growth. Therefore, availability of these elements in organic matter content is critical in determining the magnitude of methane production. If carbon and nitrogen are sufficient to support microbial growth, there will be more active microbes involved in methane production process. Carbon-nitrogen ratio (C/N) is one of parameters indicating the availability of those elements for microbial growth and methane production effectiveness. Kangle *et al*. (2012) mentioned that the optimum C/N ratio in methane production is between 20 and 30. A ratio higher than 30 is an indication that organic matter lacks of nitrogen for protein synthesis during microbial growth. Conversely, a ratio below 20 is an indication that nitrogen content in organic matter is abundant.

Lack of nitrogen simply decreases methane production due to inhibition in microbial growth (Mata-Alvarez *et al*., 2000). However, too much nitrogen available in organic matter does not mean microbial growth will be boosted which in turn increases methane production. Excess of nitrogen in organic matter will produce ammonia in acidogenesis stage in methane formation process instead. Ammonia is a toxic by product which may poison microbes during methane formation process. Therefore, low C/N ratio can inhibit methane production (Kangle *et al*., 2012).

3. Biochemical and chemical protection

Biochemical protection is a terminology to indicate the biodegradability of organic matter due to its chemical compound composition. If organic matter contains more highly biodegradable compounds, it means the organic matter is biochemically unprotected. Conversely, if organic matter contains more low biodegradable compounds, it means that the organic matter is biochemically protected. Therefore, biochemically unprotected organic matter is easily to be decomposed resulting in high methane production. Conversely, biochemically protected organic matter is hard to be decomposed resulting in low methane production. An example of low biodegradable compound is lignin. Organic matter containing high lignin is therefore resistant to microbial degradation (Argyropoulos & Menachem, 1997) resulting in low methane production.

Chemical protection is a terminology to indicate the biodegradability of organic matter due to binding with minerals. Organic matter which is bound with minerals is classified as chemically protected. Mineral binding is very effective to protect organic matter from microbial attacks. Amelung *et al*. (2008) stated that organic matter which is chemically protected could remain in soil for a long time even until 5 centuries even though it contains a lot of highly biodegradable compounds. Thus, organic matter which is chemically protected results in low methane production.

4. Nanoscale structure.

Porosity of organic matter has an important role in bridging contacts between microbial enzymes and the active sites of organic matter which will be broken down in decomposition process. Organic matter porosity which is smaller than the size of microbial enzymes will inhibit contact between enzymes and organic matter. Conversely, large porosity makes organic matter less protected from microbial enzyme attack in hydrolysis stage of methane production (Papa *et al*., 2014). As organic matter is easier to attack, there is a higher probability to degrade organic matter and produce methane. In addition, three dimensional (3D) structure of the organic matter porosity is also important. As enzymes are specific as to the substrate they attack, mismatch between enzyme structure and organic matter porosity structure may inhibit enzyme attack to organic matter which in turn reducing methane production.

Information on how organic matter properties influence methane production above tells us that organic matter has a quite important role in methane formation. Therefore, reduction of methane emission in mangrove ecosystem may be done by minimizing methane production in this ecosystem through manipulating organic matter properties. Manipulation or modification of organic matter properties can be done by preventing riverine input to maintain low TOC, fertilizing mangrove sediment with inorganic nitrogen to create extreme C/N ratio, forestation mangrove ecosystem with species containing high lignin to provide biochemically protected organic matter and mineral addition to mangrove sediment to create chemically protected organic matter. Meanwhile, there is nothing we can do to manipulate nanoscale structure of the organic matter.

So far, there is no study conducted to reduce methane emission in real environment. Sometimes, lab scale and mesocosm experiments give different result with phenomena in the nature. Thus, optional means mentioned above to manipulate organic matter properties do not necessarily reduce methane production in mangrove sediment. It may create a new environmental problem instead. Therefore, it is still unclear which properties of organic matter in mangrove sediment can feasibly be manipulated, or how to modify them so that methane production in mangrove sediment can be reduced.

CONCLUSION

Organic matter properties that influence methane production include TOC, C/N ratio, biochemical and chemical protection, and nanoscale structure.Since the availability of carbon content in organic matter which is represented by TOC is a basic requirement for methane formation; and C/N ratio, biochemical and chemical protection and nanoscale structure of organic matter may limit the microbial activity hence organic matter properties are significant factors in methane production. Total organic carbon (TOC), C/N ratio and biochemical protection have higher possibility to be modified in mangrove ecosystem. However, it is still unclear how to modify them and modifying them may have other environmental impacts instead.

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