

## MICROBIAL MITIGATION OF GREENHOUSE GAS EMISSIONS FROM LANDFILL COVER SOILS

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### ABSTRACT

*Methane (CH<sub>4</sub>), a potent greenhouse gas (GHG) with a global warming potential (GWP) ~23 times higher than that of carbon dioxide (CO<sub>2</sub>) is produced by Landfills. There is urgent need to prevent methane emissions from large landfills. Methanotrophs are a group of bacteria that consume methane and prevent fugitive methane emissions. In present scenario two general research techniques are performed to prevent methane emissions. First, a dimensionless number method developed based on Michaelis-Menten kinetics. Second, effects of nutrient amendments on methane oxidation and nitrous oxide production by constructing soil microcosms using landfill cover soils. Methanotrophic activity and community structure can be differentially affected by both landfill gas composition and amendments thus provides insights for best manipulation of methanotrophic processes for better mitigation of GHG emission.*

### INTRODUCTION

Methane, a major greenhouse gas (GHG) that contributes to global warming, has a global warming potential (GWP) ~23 times higher than that of CO<sub>2</sub> (Gebert et al., 2004). Specifically, GWP is an index that provides the relative impact a specific gas could have on global climate over a defined time scale. However, because CH<sub>4</sub> has a short life (~8 years) relative to other GHGs such as CO<sub>2</sub> (50-200 years) N<sub>2</sub>O (120 years), controlling emission of CH<sub>4</sub> seems likely to be favourable in terms of short-term control of global warming (Dedysh et al., 2007). Methane is produced through decomposition of organic wastes in landfills along with CO<sub>2</sub>. Typically, CH<sub>4</sub> and CO<sub>2</sub> comprise the majority of landfill gas, as shown in Table 1.

### METHANE CAPTURE STRATEGIES IN LANDFILLS

There are two general types of systems to collect gas from landfills in order to meet regulations, I) passive, and II) active gas collection systems. The general concept of a passive gas collection system is to provide avenues for soil gases to be emitted into the atmosphere without the use of mechanical equipment (Allen et al., 1997). Passive gas collection systems are relatively inexpensive but as it vents soil gas directly

into atmosphere, it can pose some environmental risk.

Alternatively, active gas collection systems utilize mechanical equipment such as blowers and pumps to enhance the gas collection rate. Such gas collection systems are now enforced by the Landfill Rule (New Source Performance Standards and Emissions Guidelines) promulgated under the Clean Air Act in March 1996 and amended in June 1998 (Holmes, et al., 1995). These rules require landfill gases to be collected and either flared or utilized at landfills that have either a design capacity larger than 2.5 million metric tons and 2.5 million cubic meters or emit more than 50 metric tons of nonmethane organic compounds. Because of the Landfill Rule, landfills that must meet its criteria have either flaring or CH<sub>4</sub> recovery systems following the active gas collection system (DeJournett et al., 2007).

Some effective strategies have been formulated to prevent methane emissions from large landfills, many landfills allow CH<sub>4</sub> to be freely emitted in atmosphere (Gebert et al., 2004). In such situations, it is often proposed to stimulate growth of methanotrophs, a group of bacteria that consume methane, in cover soil to prevent fugitive methane emissions. Several factors, however, must be addressed to make such

a biogenic removal mechanism effective. First, methanotrophic activity can be inhibited by nonmethane organic compounds (NMOCs) that are commonly found in landfill soil gas. Second is addition of addition of nitrogenous fertilizers (Amaral and Knowles, 1995; Eklund et al., 1998).

**Table 1: Typical constituents in municipal solid waste landfill gas**

Components	%
CH <sub>4</sub>	45-58
CO <sub>2</sub>	35-45
N <sub>2</sub>	<1-20
O <sub>2</sub>	<1-5
H <sub>2</sub>	<1-5
H <sub>2</sub> O	1-5
Trace constituents (e.g nonmethane organic compounds, H <sub>2</sub> S etc.)	<1-3

#### Sinks of CH<sub>4</sub>

Natural sinks of CH<sub>4</sub> consist of reaction with OH radicals in the troposphere, OH, Cl, and O (<sup>1</sup>D) radicals in the stratosphere, and soil microbes. The major sink of atmospheric CH<sub>4</sub> is the reaction of CH<sub>4</sub> initially reacts with OH radical to produce CH<sub>3</sub>. CH<sub>3</sub> then further undergoes chemical reaction and produces CO, CO<sub>2</sub>, H<sub>2</sub>O among other compounds (Gebert et al., 2004).

Another sink of CH<sub>4</sub> is via soil microbial activity. In soils, CH<sub>4</sub> can be oxidized into other forms of carbon via microorganisms, i.e., methanotrophs. Methanotrophs are a group of bacteria that utilize CH<sub>4</sub> as its sole carbon and energy source in the presence of O<sub>2</sub>. It has been estimated that anywhere from 10-100% of CH<sub>4</sub> generated in landfills is oxidized by methanotrophs. Therefore, stimulating activities of such bacteria in landfill cover soils could possibly reduce emission of CH<sub>4</sub> from landfills, especially in landfills where active gas collection is not required (Bateman and Baggs, 2005).

The additions of nitrogen-based fertilizers have been used to stimulate CH<sub>4</sub> oxidation in soils as nitrogenous fertilizers are used as nitrogen sources by the soil microorganisms. However, addition of

nitrogen-based fertilizers to soils generally stimulates the production of another greenhouse gas N<sub>2</sub>O, which has a GWP ~300 times greater than that of CO<sub>2</sub>. Thus a strategy to mitigate one greenhouse gas, CH<sub>4</sub> could result in production of a relatively more potent greenhouse gas i.e. N<sub>2</sub>O (Amaral and Knowles, 1995; Bender and Conrad, 1995).

To consider these issues, two general areas of research are prevailing. First, a dimensionless number method based on Michaelis-Menten kinetics that describes effects of presence of multiple NMOCs on methanotrophic growth and survival. This model can be validated via experimental measurements of methanotrophic growth in presence of varying amounts of NMOCs. Second, effects of nutrient amendments on methane oxidation and nitrous oxide production by constructing soil microcosms using landfill cover soil (Eklund et al., 1998). These experiments suggests that methanotrophic activity and community structure can be differentially affected by both landfill gas composition and amendments, thus providing insights as how best to manipulate methanotrophic processes to have better mitigation of GHG emissions (Barlaz et al., 2004).

#### BIOGENIC N<sub>2</sub>O PRODUCTION

Nitrous oxide can be produced through biological and abiotic processes. Many groups of microorganisms have ability to produce N<sub>2</sub>O but bacterial-mediated nitrification and denitrification appear to be predominant sources of N<sub>2</sub>O production. Microbial production of nitrous oxide can be achieved through different processes such as by-product of nitrification and/ or denitrification (Amaral and Knowles, 1995).

Barlaz et al., 2004 reported substantial activity of particulate methane monooxygenase (pMMO) - expressing methanotrophs and suggested that methanotrophs were responsible for nitrous oxide production.

## NONMETHANE ORGANIC COMPOUNDS

Nonmethane organic compounds (NMOCs) are emitted from landfill cover soils. NMOCs include compounds such as alkanes, alkenes, halogenated hydrocarbons, aromatic hydrocarbons and sulphur compounds (Felsenstein, J. 1985). NMOCs are reported to pose risk on human health as some of these compounds are considered carcinogenic/mutagenic. Another important issue is that some compounds categorized as NMOCs can inhibit CH<sub>4</sub> oxidation since methanotrophs are capable of co-metabolizing compounds such as vinyl chloride, dichloroethylene, and trichloroethylene. Thus, understanding effects of NMOCs on methanotrophs will be crucial in mitigation of both CH<sub>4</sub> (Bogner et al., 1995).

### EFFECT OF NONMETHANE ORGANIC COMPOUNDS (NMOCS) ON METHANOTROPHS

**Culture conditions:** Nitrate mineral salt (NMS) medium can be used for growth of organisms at optimized laboratory conditions. CH<sub>4</sub>:air ratio is generally kept 1:2 (Costello and Lidstrom, 1999). For pMMO-expressing conditions 20 µM copper is used to prevent limitations of copper during entire growth period. Copper is added in form of CuCl<sub>2</sub> after autoclaving media. For soluble methane monooxygenase (sMMO) expressing conditions, addition of copper is not required (Cebon et al., 2007).

Analysis of methanotrophic diversity can be performed by replacing number of species with number of probes having positive signals. Whereas number of abundance of each species can be replaced with relative signals of each probes (Graham et al., 1993).

**Substrate and product toxicity:** To determine either substrate or product toxicity associated with chlorinated ethylenes on growth of pMMO- and sMMO-expressing cells experiments are required to be performed in presence and absence of acetylene, as acetylene is known as potent inhibitor of methane monooxygenase (MMO) activity (Chanton et al., 1999). Methanol can be used instead of CH<sub>4</sub> substrate to

prevent any competitive binding to either pMMO or sMMO that could obfuscate the findings. Formate can also be added in media to prevent any limitation of reducing equivalents occurring during oxidation of chlorinated ethylene (De Visscher et al., 2001).

Addition of ammonium in presence of phenyl acetylene stimulated methane oxidation and inhibit nitrous oxide production. DNA microarray and transcript analyses methods can also be used in addition to various media components to understand methanotrophic community structure and activity (Aziz et al., 1999).

King and Schnell (1994), reported methanotrophic-mediated removal of NMOCs specifically chlorinated ethylenes and/or other compounds that could be co-oxidized via MMO, make sMMO an ideal enzyme when primary objective is to remove NMOCs. Although a great deal of research has examined how cells, when grown under sMMO-expressing conditions (i.e., no added copper) degrade a wide range of halogenated hydrocarbons, both separately and in mixtures, there have been no empirical data showing how methanotrophs, when expressing either sMMO or pMMO, grow in presence of mixtures of chlorinated solvents, and if degradation of such compounds is limited over time due to poor growth (King and Schnell, 1994).

In landfill cover soils where primary substrate CH<sub>4</sub> and co metabolites in the form of NMOCs are present in mixtures, those cells expressing pMMO may actually be predominant as they are better able to tolerate the presence of co-metabolites, and may play a significant role in consuming CH<sub>4</sub> and preventing NMOCs from exiting the system, particularly if the initial concentrations of co-metabolic substrates are high. In landfill cover soils where naturally occurring CH<sub>4</sub> and chlorinated ethylene coexist, consumption will be inhibited by presence of chlorinated ethylene; pMMO-expressing methanotrophic community could be relatively effective in CH<sub>4</sub> consumption compared to sMMO-expressing methanotrophic community while reducing the concentrations of chlorinated ethylene.

## CONCLUSION

To study microbial mitigation of CH<sub>4</sub> in landfill cover soils it is important to understand the factors affecting CH<sub>4</sub> oxidation by methanotrophs. Effect of NMOCs on methanotrophic growth is necessary for this. When NMOCs which are commonly found in landfill gas can bind to MMOs without providing any benefits to the methanotrophs, it can be hypothesized that presence of NMOCs will inhibit methanotrophic growth. MMOs can be found in two different forms, pMMO and sMMO. Dimensionless number can be used to predict the inhibitory effects of NMOCs on methanotrophic growth. The effects of

the presence of NMOCs on growth of methanotrophs expressing either form of MMO can be examined using custom-designed vials enabling both measurement of growth and degradation of NMOCs. Increased concentration or type of NMOCs effects the growth of methanotrophs expressing either form of MMO.

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