CIVIMATICS

INTERDISCIPLINARY MATHEMATICAL MODELLING MEETS CIVIC EDUCATION

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A POTENTIAL MODELLING OF EMISSION AND DECOMPOSITION OF METHANE GAS INTO THE ATMOSPHERE (YAEL FLEISCHMANN AND FRODE RØNNING)

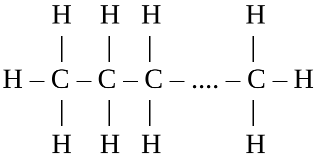
It is claimed that emission of methane gas into the atmosphere is an important factor in causing the greenhouse effect, which in turn is connected to climate change. A generating question for an SRP could be the following:

Q: What is the contribution of methane gas to the greenhouse effect?

To be able to answer this question it is necessary to acquire some knowledge about methane, what is it, how is it generated, and what happens with it when released in the atmosphere. This will lead to a number of subquestions, which we will start by discussing.

Q_1. What is methane and how is it related to other chemical compounds?

Hydrocarbons are compounds consisting only of the elements hydrogen and carbon, and they are considered to be the simplest organic molecules. The least complex hydrocarbons have only single carbon-carbon bounds, and they are called saturated. Furthermore, if there are no carbon cycles, the hydrocarbon is referred to as acyclic. Acyclic, saturated hydrocarbons are called alkenes, and methane is the simplest of all alkenes. The general formula for an alkene is C_nH_{2n+2}. This follows from the fact that all carbon-carbon bounds are simple. When the number of carbon atoms increases ($n \geq 4$), the number of possibilities for creating carbon chains increases. The different versions obtained in this way are referred to as isomers, and the simplest isomer for a given n can be illustrated as below:



$$\begin{array}{ccccccccccc} & & H & & H & & H & & & & H & & \\ & & | & & | & & | & & & & | & & \\ H & - & C & - & C & - & C & - & \ldots & - & C & - & H \\ & & | & & | & & | & & & & | & & \\ & & H & & H & & H & & & & H & & \end{array}$$

Methane has only one carbon atom, hence the formula CH_4.

Alkenes form the basis for a number of other chemical compounds, such as alcohols, aldehyds and organic acids, to which they are transformed in oxidation processes. Removing one hydrogen atom from an alkene, gives a radical, the alkyl group, C_nH_{2n+1} (Kice & Marvell, 1974). This can combine to other groups of atoms (functional groups) giving new compunds. The simplest example is with the methyl group CH_3 as the starting point, to add the hydroxyl group –OH to get CH_3OH, methanol.

Having placed methane in the chemical landscape we will now turn to a discussion of how methane behaves in the atmosphere. This leads to the discussion of how methane is part of a cycle.

Q_2. How can the flow of methane be described as a cycle?

As indicated above, the alkyl groups can combine with various functional groups to form new compunds, which indicates that the alkenes are not stable. The heavier alkenes, such as propane (n=3) and butane (n=4) are commonly used for cooking and heating, since they burn easily, but not as fiercely as methane would do. This means that they oxidise to CO_2 and water. Methane oxidises in the troposphere to CO_2 and water, and according to Wahlen (1993) this constitutes the major sink for methane. Wahlen writes that the atmospheric lifetime for methane is 8-12 years (p. 407). Another, small sink, of methane is due to bacteria comsuming atmotsperic methane. These bacteria, called methanotrophs, constitute a group of bacteria that are capable of utilising single-carbon compounds, and methane is both the energy source and the source of carbon for these bacteria (Bürgmann, XXXX). The oxidation described above is *aerobic* oxidation. Methane is also consumed in *anaerobic* oxidation. This is an oxidation that takes place through reduction of sulfates or nitrites (Conrad, 2009). Chemically this process can be described as

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

with sulfates, or

$$CH_4 + NO_3^- \rightarrow CO_2 + NO_2^- + H_2O$$

with nitrites. Similar processes exist for ammonium (NH_4) instead of methane. The nitrite-driven anaerobic oxidation of ammonium and methane is caused by certain groups of microorganisms. According to Reimann, Jetten and Keltjens (2015) these bacteria were only discovered about 20 years ago.

Wahlen also indicates some important sources of methane:

> Methane is produced by bacteria under anaerobic conditions in wet environments such as wetlands, swamps, bogs, fens, tundra, rice fields, and landfills. It is also produced in the stomachs of ruminants (cattle and other cud-chewing mammals), and possibly by termites. … Other sources of CH_4 are from leakage of natural gas upon drilling and distribution, and from coal mining. A further source is from biomass burning where CH_4 is a product of incomplete combustion. (Wahlen, 1993, p. 408)

Conrad (2009) attributes about 25% of methane sources to mining and combustion of fossil fuels or burning of biomass, about 69% to microbial processes, and about 6% to chemical production of CH_4 from plant material. According to this, microbial processes are the largest source of methane. This covers a wide range of sources, where some sources are more or less directly controllable by humans. Microbial methabolism takes place where organic matter is decomposed in the absence of oxygen or other oxidants. Wetlands are the largest individual source of methane but also rumen fermentation in cattle, sheep and other ruminants are an important source of CH_4 (Conrad, 2009).

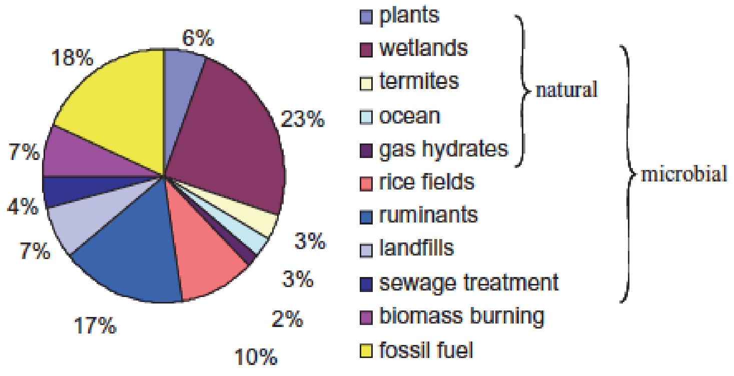


Figure 1. Global methane sources in percent of total.

Figure 1 is taken from Conrad (2009, p. 286) and shows the percentual distribution of methane sources. This shows that close to one quarter of the methane comes from wetlands. Conrad claims that there is little direct human influence on the methane source strength of wetlands. The second largest sources, according to Conrad, are burning of fossil fuels and rumen fermentation, each of the sources accounting for 17-18% of the total. Wahlen presents a table based on four different studies from 1988-1991 (Wahlen, 1993, p. 416). According to this table wetlands account for a share in the range 22-25% and animals (enteric fermentation) account for a share in the range 15-20%.

These figures are seen to be consistent with the figures that Conrad presents in his paper from 2009. Both sources indicate the total emission of methane to be around 500-600 Tg per year. Figure 2 shows a graphic from the website https://unece.org/challenge. We interpret this figure to show the distribution of methane emission stemming from human activities, although this is not explicitly said on the website. It is said, however, that about 60% of global methane emissions are due to human activities.

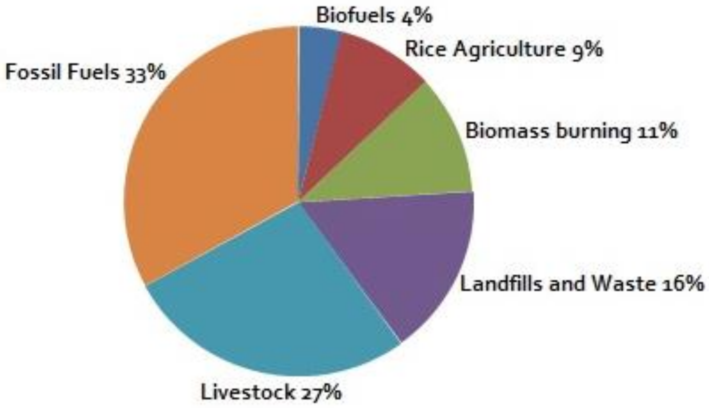


Figure 2. Distribution of methane emission from human activities

Above we have identified some important sources of methane, as well as sinks, the most important sink being the oxidation of methane to CO_2 and water. This interplay between sinks and sources makes it reasonable to talk about methane being part of a cycle. What affects the net emission of methane is obviously the difference between the total sink strength and the total source strength. The total sink strength has for a long time been smaller than the total source strength, causing an increase in the concentration of methane. However, the CH4 sink strength increases proportionally with the increasing CH4 concentration in the atmosphere, which to some extent neutralises the changes in source strength (Conrad, 2009).

Q_3. What is the role of methane as a greenhouse gas?

Conrad (2009) claims that methane is the second most important human caused greenhouse gas, after CO_2 contributing about 30% to the total net human caused radiative forcing of 1.6 W/ m^2. Conrad further claims that the concentration of CH_4 in the atmosphere has been increasing from pre-industrial values of about 715 ppb[1] to currently about 1770 ppb. The growth rate of atmospheric CH_4, was about 12 ppb/year in the 1980s, but has decreased since the early 1990s and with a value of about 4 ppb/year since 1999.

Figure 2 shows the development in the concentration of CO_2 (given in ppm[2]) from 1800 to present. Figure 3 shows the corresponding development in CH_4 (given in ppb) for the same time span (https://www.eea.europa.eu).

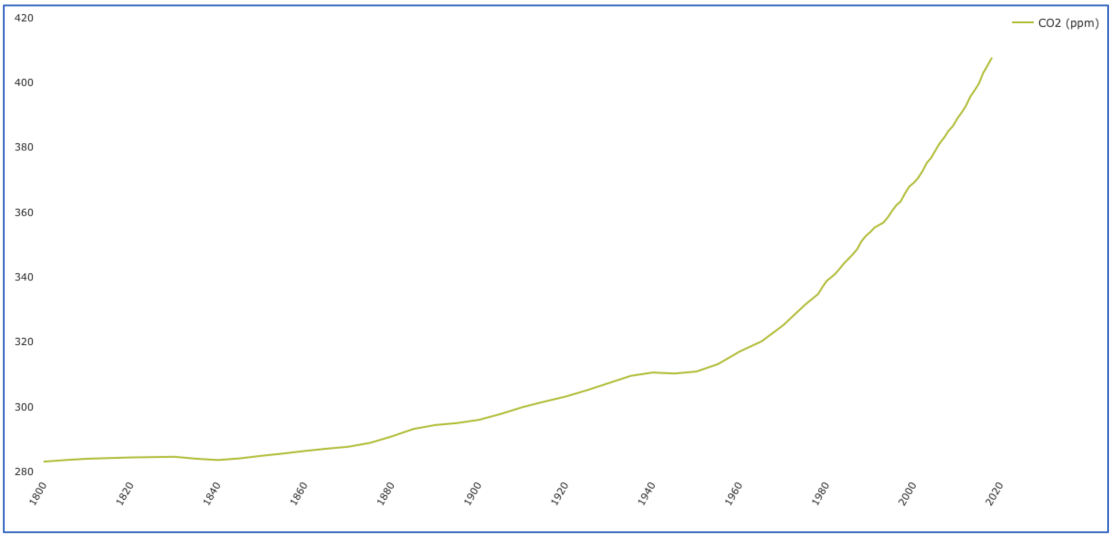


Figure 3. Concentration of CO2 in the atmosphere

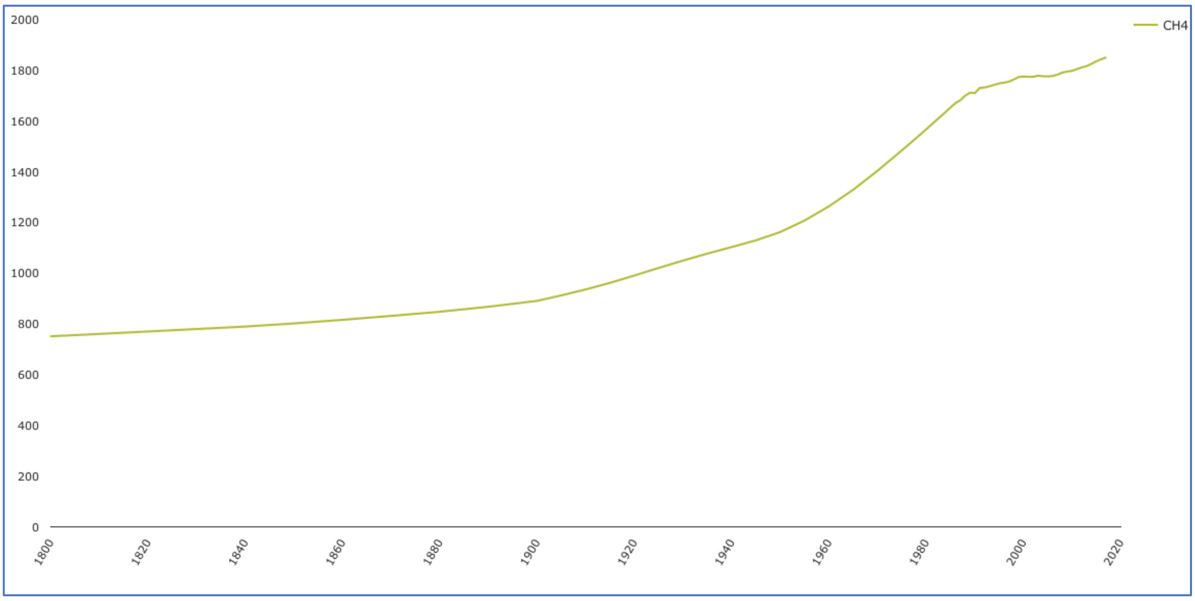


Figure 4. Concentration of CH4 in the atmosphere

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[1] parts per billion (10^9)
[2] parts per million (10^6)

According to https://unece.org/challenge methane has a 100-year global warming potential that is 25 times that of CO_2, and that over a 20-year period it is 84 times more potent as a greenhouse gas than CO_2. However, as Figures 3 and 4 show, the concentration of methane is much lower than the concentration of CO_2.

It appears that much of the knowledge regarding the methane cycle is relatively new. Fung et al. (1991) write that although some major sources have been identified, there are considerable uncertainties in the source strengths. Conrad (2009) lists a number of issues that need to be addressed for better understanding of the ecology of methane-producing or -consuming micro-organisms, and their role in the methane cycle.

Q_4. How is methane produced by ruminants?

Cows, goats, sheep and several other animals belong to a class of animals called ruminants. Ruminants have four stomachs and digest their food in their stomachs instead of in their intestines, as humans do. Ruminants eat food, regurgitate it as cud and eat it again.

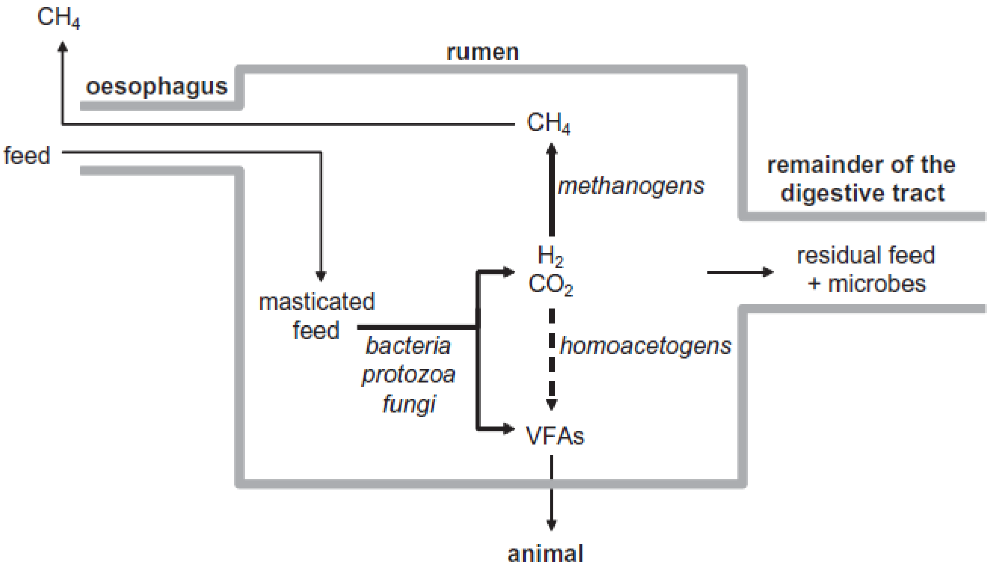

Figure 5 from Buddle et al. 2011

One of the chraracteristics of ruminants that makes them so interesting and advantageous for the human production is that they can convert otherwise indigestible cellulose-rich plant material into meat, milk, wool, and leather. Since they eat plants that humans cannot digest, they do not compete directly with humans for food.

In figure 5, which is taken from Buddle et al. (2011, p. 12), the process of the synthesis of methane in the digestion of a ruminant is shown in more detail. During the fermentation of the feed, several bacterial, protozoal and fungal species derive the energy from the feed in form of volative fatty acids (VFAs) that the animal absorbs. Side products of this process are the gases H2 (hydrogen) and CO2 .In a subsequent step, methagonens use these end products of the the fermentation as substrates, and produce methan at the end of the tropic chain.

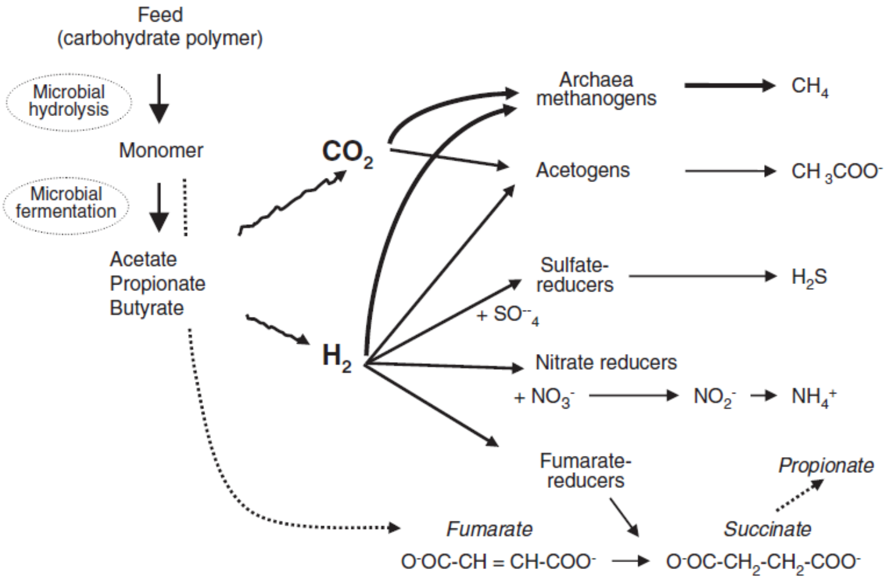

Figure 6 from Morgavi et al 2010

For an even more detailed chain describing the microbial fermentation process of deed polysaccharides and H_2 reduction in the rumen, see Figure 6 from Morgavi et al., 2010.

Q_6. How can production of methane from ruminants be reduced (without reducing the number of ruminants)?

Reducing the microorganisms that produce methane in the cow's digestive system is not only of interest to climate-friendly agriculture but it would also increase cow productivity (between 4 to 10% of the energy in the cow feed is lost through methanogenesis and thus not available for digestion (https://ec.europa.eu/environment/enveco/climate_change/pdf/ecoeva.pdf).

Therefore, the reduction of microogranisms has long been the subject of scientific research. Basically, two approaches have delivered promising results:

- Reduction of enteric methanogenesis
- Adaption of the ruminant’s diet.

In the following we will discuss the most prominent options explored so far.

By reducing the number or activity of methanogens in the rumen a **vaccination against rumen methanogens** can potentially reduce methane emissions. The great advantage of this approach is that it is likely to be inexpensive and one of the few options that would be viable with grazing animals. Vaccination of farm animals is already widely practiced for disease control and the adoption of this technology by veterinarians and farmers could be quick if it were shown to be effective at reducing methane emissions. So far, however, the results are inconclusive, as vaccines are very specific to certain microbial strains and there are differences in efficiency (Patra et al., 2017).

By **adding substances to the cow’s diet**, the entire digesting process can be influenced towards a lower percentage of methanogens and a higher percentage of microbes, which produce more VFAs, as an energy source used by the ruminant.

Probiotics can achieve just that. It has been shown that ionophore antibiotics like Monesin reduce methanogenesis, presumably by shifting the fermentation processes and reducing certain microorganisms (Russell & Houlihan, 2003). However, these findings have been debated and criticized (Odongo et al., 2007; Grainger et al., 2008; Grainger et al., 2010).

In some cases, organic acids such as malate, fumaat or acrylate have also been shown to reduce methane emissions, but the results of these studies vary widely and remain inconclusive (Bates, 2001; Jeyanathan et al., 2014). Many secondary plant compounds such as tannins, saponins or essential oils have been shown to directly reduce methanogens and hydrogen production in the rumen (Hess et al., 2006).

Some oils like coconut oil or garlic powder are considered to be some of the most effective additives for methane control (Kongmun et al., 2010). One advantage of adding fats to the cows is that it reduces methanogenesis without significantly affecting other rumen functions.

Other substances such as bromochloromethane, 3-nitrooxypropanol or nitrates have also been shown to be effective in reducing methane emissions (Van Wesemael et al., 2019).

Although many feed additives have the potential to reduce methane emissions, more research is needed to determine whether they are effective in the long term (or whether the rumen microorganisms adapt to them) and whether there are any potential risks, such as negative effects on the environment.

Recent studies suggest that **replacing a grass-only diet with mixed feeds** may be beneficial, as some plants, such as flowers, may have the potential to lower methane emissions as phytonutrients inhibit methanogenesis (Haque, 2018; Hammond et al., 2015). Tannin-rich legumes like Sainfoin have also been reported to help reduce methane emissions (Stewart et al., 2019). In general, cows fed corn silage emit less methane than cows fed grass silage.

The diet of cows is generally balanced between forage such as grass, hay and energy rich concentrates containing more sugar and starches. The more concentrates the cow feeds on, the lower the production of methane, in relation to the cow's productivity. This is because the main substrate for methanogenesis are fibrous carbohydrates. However, feeding large amounts of concentrates without the addition forage is not without risk and can for example lead to an acidic environment in the rumen which is bad for the cow.

In addition to the options explained above, also selective breeding might have the potential to reduce methane production.

Regardless of their diet, there is variation in the production of methane between individual animals. Depending on the feed efficiency of an animal, the relative amount of methane produced can be lower. There is some evidence that the level of methane production is a heritable trait in cows, which suggests this trait may be selected for breeding (González-Recio et al., 2020). However, the fermentative processes in the digestive system depend on the community of microorganisms, so the extent to which these microorganisms depend on the genetics of the cow, is highly debated.

To be continued…

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