

1.5.2 Other greenhouse gasses

Carbon dioxide is not the only gas emitted from soil with the potential to influence the climate. Methane (CH_4) production also occurs as a part of the carbon cycle. It is produced by the soil microbiota under anaerobic conditions through a process known as methanogenesis and is approximately 21 times more potent as a greenhouse gas than CO_2 over a time horizon of 100 years.

Nitrous oxide (N_2O) is produced as a part of the nitrogen (N) cycle through process known as nitrification and denitrification which are carried out by the soil microbiota. Nitrous oxide is 310 times more potent as a greenhouse gas than CO_2 over a time horizon of 100 years (U.S. Environmental Protection Agency, 2002).

Whilst these gases are more potent greenhouse gases than CO_2 , only approximately 8% of emitted greenhouse gases are CH_4 and only 5% are N_2O , with CO_2 making up approximately 83% of the total greenhouse gases emitted. Eighty percent of N_2O and 50% of CH_4 emitted are produced by soil processes in managed ecosystems (US Environmental Protection Agency, 2002). It should be noted that these figures detail total proportions of each greenhouse gas and are not weighted to account for climatic forcing.

In one study, biochar addition to soils has been shown to reduce the emission of both CH_4 and N_2O . Rondon et al. (2005) reported that a near complete suppression of methane upon biochar addition at an application rate of 2% w^{-1} to soil. It was hypothesised that the mechanism leading to reduced emission of CH_4 is increased soil aeration leading to a reduction in frequency and extent of anaerobic conditions under which methanogenesis occurs. Pandolfo et al. (1994) investigated CH_4 adsorption capacity of several activated carbons (from coconut feedstock) in a series of laboratory experiments. Their results showed increased CH_4 'adsorption' with increase

Pandolfo et al. (1994) investigated CH₄ adsorption capacity of several activated carbons (from coconut feedstock) in a series of laboratory experiments. Their results showed increased CH₄ 'adsorption' with increase surface area of the activated carbon, particularly for micropores (<2µm). These charcoal materials were activated using steam or KOH, however, and it remains to be tested how different biochar materials added to soils in the field will interact with methane dynamics. The influence of biochar on SOM dynamics are discussed later in this report (Section 3.2.5).

A reduction in N₂O emissions of 50% in soybean plantations and 80% in grass stands was also reported (Rondon et al. 2005). The authors

hypothesised that the mechanism leading to this reduction in N₂O emissions was due to slower N cycling, possibly as a result of an increase in the C:N ratio. It is also possible that the N that exists within the biochar is not bioavailable when introduced to the soil as it is bound up in heterocyclic form (Camps, 2009; Personal communication). Yanai et al. (2007) measured N₂O emissions from soils after rewetting in the laboratory and found variable results, i.e. an 89% suppression of N₂O emissions at 73-78% water-filled pore

hypothesised that the mechanism leading to this reduction in N₂O emissions was due to slower N cycling, possibly as a result of an increase in the C:N ratio. It is also possible that the N that exists within the biochar is not bioavailable when introduced to the soil as it is bound up in heterocyclic form (Camps, 2009; Personal communication). Yanai et al. (2007) measured N₂O emissions from soils after rewetting in the laboratory and found variable results, i.e. an 89% suppression of N₂O emissions at 73-78% water-filled pore space contrasting to a 51% increase at 83% water-filled pore space. These results indicate that the effect of biochar additions to soils on the N cycle depend greatly on the associated changes in soil hydrology and that thresholds of water content effects on N₂O production may be very important and would have to be studied for a variety of soil-biochar-climate conditions. Furthermore, if biochar addition to soil does slow the N-cycle, this could have possible consequences on soil fertility in the long term. This is because nitrate production in the soil may be slowed beyond the point of plant uptake, meaning that nitrogen availability, often the limiting factor for plant growth in soils, may be reduced leading to concurrent reduction in crop productivity. Yanai et al. (2007) reported that this effect did change over time, but their experiment only ran for 5 days and so extrapolation of the results to the time scales at which biochar is likely to persist in soil is not possible. Further research is therefore needed to better elucidate the effects and allow extrapolation to the necessary time scales.

1.6 Pyrolysis

Pyrolysis is the chemical decomposition of an organic substance by heating in the absence of oxygen. The word is derived from Greek word 'pyro' meaning fire and "lysis" meaning decomposition or breaking down into constituent parts. In practice it is not possible to create a completely oxygen free environment and as such a small amount of oxidation will always occur. However, the degree of oxidation of the organic matter is relatively small when compared to combustion where almost complete oxidation of organic matter occurs, and as such a substantially larger proportion of the carbon in the feedstock remains and is not given off as CO₂. However, with pyrolysis much of the C from the feedstock is still not recovered in charcoal form, but converted to either gas or oil.

Pyrolysis occurs spontaneously at high temperatures (generally above approximately 300°C for wood, with the specific temperature varying with material). It occurs in nature when vegetation is exposed to wildfires or comes into contact with lava from volcanic eruptions. At its most extreme, pyrolysis leaves only carbon as the residue and is called carbonization. The high temperatures used in pyrolysis can induce polymerisation of the molecules within the feedstocks, whereby larger molecules are also produced (including both aromatic and aliphatic compounds), as well as the thermal decomposition of some components of the feedstocks into smaller molecules. This is discussed in more detail in Section 3.2.5.1.

The process of pyrolysis transforms organic materials into three different components, being gas, liquid or solid in different proportions depending upon both the feedstock and the pyrolysis conditions used. Gases which are produced are flammable, including methane and other hydrocarbons which

can be cooled whereby they condense and form an oil/tar residue which generally contains small amounts of water. The gasses (either condenses or in gaseous form) and liquids can be upgraded and used as a fuel for combustion.

The remaining solid component after pyrolysis is charcoal, referred to as biochar when it is produced with the intention of adding it to soil to improve it (see List of Key terms). The physical and chemical properties of biochar are discussed in more detail in Chapter 2.

The process of pyrolysis has been adopted by the chemical industry for the production of a range of compounds including charcoal, activated carbon, methanol and syngas, to turn coal into coke as well as producing other chemicals from wood. It is also used for the breaking down, or 'cracking' of medium-weight hydrocarbons from oil to produce lighter hydrocarbons such as petrol.

A range of compounds in the natural environment are produced by both anthropogenic and non-anthropogenic pyrolysis. These include compounds released from the incomplete burning of petrol and diesel in internal combustion engines, through to particles produced from wood burned in forest fires, for example. These substances are generally referred to as black carbon (see List of Key terms) in the scientific literature and exist in various forms ranging from small particulate matter found in the atmosphere, through to a range of sizes found in soils and sediments where it makes up a significant part of the organic matter (Schmidt et al., 1999; Skjemstad et al., 2002; Preston et al., 2006; Hussain et al. 2008).

1.6.1 The History of Pyrolysis

While it is possible that pyrolysis was first used to make charcoal over 7,000 years ago for the smelting of copper, or even 30,000 years ago for the charcoal drawings of the Chauvet cave (Antal, 2003), the first definitive evidence of pyrolysis for charcoal production comes from over 5,500 years ago in Southern Europe and the Middle East. By 4,000 years ago, the start of the Bronze Age, pyrolysis use for the production of charcoal must have been widespread. This is because only burning charcoal allowed the necessary temperatures to be reached to smelt tin with copper and so produce bronze (Earl, 1995).

A range of compounds can be found in the natural environment that is produced by both anthropogenic and non-anthropogenic pyrolysis. These include compounds released from the incomplete burning of petrol and diesel in internal combustion engines, through to being produced from wood in forest fires for example.

1.6.2 Methods of Pyrolysis

Although the basic process of pyrolysis, that of heating a C-containing feedstock in an limited oxygen environment, is always the same, different methodologies exist, each with different outputs.

Apart from the feedstocks used, which are discussed further in Section 1.7, the main variables that are often manipulated are pyrolysis temperature, and