

2. PHYSICOCHEMICAL PROPERTIES OF BIOCHAR

This chapter provides an overview of the physical and chemical properties of biochar, as determined mainly by feedstock and the pyrolysis operational conditions. The combined heterogeneity of the feedstock and the wide range of chemical reactions which occur during processing, give rise to a biochar product with a unique set of structural and chemical characteristics (Antal and Gronli, 2003; Demirbas, 2004). A primary focus was given to those characteristics that are more likely to impact on soil properties and processes when biochar is incorporated into soil. The implications of such characteristics in the context of the biochar-soil mixture are discussed in Chapter 3. More detailed information on a wider range of biochar properties can be found in the relevant scientific literature (e.g. Lehmann and Joseph, 2009; and others).

2.1 Structural and Chemical Composition

2.1.1 Structural composition

Thermal degradation of cellulose between 250 and 350°C results in considerable mass loss in the form of volatiles, leaving behind a rigid amorphous C matrix. As the pyrolysis temperature increases, so thus the proportion of aromatic carbon in the biochar, due to the relative increase in the loss of volatile matter (initially water, followed by hydrocarbons, tarry vapours, H₂, CO and CO₂), and the conversion of alkyl and O-alkyl C to aryl C (Baldock and Smernik, 2002; Demirbas 2004). Around 330°C, polyaromatic graphene sheets begin to grow laterally, at the expense of the amorphous C phase, and eventually coalesce. Above 600°C, carbonization becomes the dominant process. Carbonization is marked by the removal of most remaining non-C atoms and consequent relative increase of the C content, which can be up to 90% (by weight) in biochars from woody feedstocks (Antal and Gronli, 2003; Demirbas, 2004).

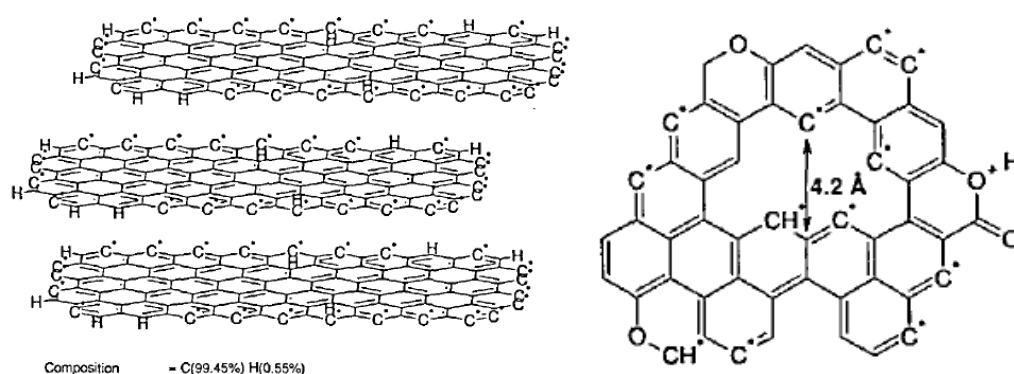


Figure 2.1 Putative structure of charcoal (adopted from Bourke et al., 2007). A model of a microcrystalline graphitic structure is shown on the left and an aromatic structure containing oxygen and carbon free radicals on the right

It is commonly accepted that each biochar particle comprises of two main structural fractions: stacked crystalline graphene sheets and randomly

ordered amorphous aromatic structures (Figure 2.1). Hydrogen, O, N, P and S are found predominantly incorporated within the aromatic rings as heteroatoms (Bourke et al., 2007). The presence of heteroatoms is thought to be a great contribution to the highly heterogeneous surface chemistry and reactivity of biochar (see the next section).

2.1.2 Chemical composition and surface chemistry

Biochar composition is highly heterogeneous, containing both stable and labile components (Sohi et al., 2009). Carbon, volatile matter, mineral matter (ash) and moisture are generally regarded as its major constituents (Antal and Gronli, 2003). Table 2.1 summarizes their relative proportion ranges in biochar as commonly found for a variety of source materials and pyrolysis conditions (Antal and Gronli, 2003; Brown, 2009).

Table 2.1 Relative proportion range of the four main components of biochar (weight percentage) as commonly found for a variety of source materials and pyrolysis conditions (adapted from Brown, 2009; Antal and Gronli, 2003)

Component	Proportion (w w⁻¹)
Fixed carbon	50-90
Volatile matter (e.g. tars)	0-40
Moisture	1-15
Ash (mineral matter)	0.5-5

The relative proportion of biochar components determines the chemical and physical behaviour and function of biochar as a whole (Brown, 2009), which in turn determines its suitability for a site specific application, as well as transport and fate in the environment (Downie, 2009). For example, coarser and more resistant biochars are generated by pyrolysis of wood-based feedstocks (Winsley, 2007). In contrast, biochars produced from crop residues (e.g. rye, maize), manures and seaweed are generally finer and less robust (lower mechanical strength). The latter are also nutrient-rich, and therefore, more readily degradable by microbial communities in the environment (Sohi et al., 2009). The ash content of biochar is dependent on the ash content of the biomass feedstock. Grass, grain husks, straw residues and manures generally produce biochar with high ash contents, in contrast to that from woody feedstocks (Demirbas 2004). For instance, manure (e.g. chicken litter) biochars can contain 45% (by weight) as ash (Amonette and Joseph, 2009). Moisture is another critical component of biochar (Antal and Gronli, 2003), as higher moisture contents increase the costs of biochar production and transportation for unit of biochar produced. Keeping the moisture content up to 10% (by weight) appears to be desirable (Collison et al., 2009). In order for this to be achieved, pre-drying the biomass feedstock may be a necessity, which can be a challenge in biochar production.

Despite the feasibility of biochar being produced from a wide range of feedstocks under different pyrolysis conditions, its high carbon content and strongly aromatic structure are constant features (Sohi et al., 2009). According to Sohi et al. (2009), these features largely account for its chemical stability. Similarly, pH shows little variability between biochars, and is typically

1.5 Carbon sequestration potential

Globally, soil is estimated to hold more organic carbon (1,100 Gt; 1 Gt=1,000,000,000 tonnes) than the atmosphere (750 Gt) and the terrestrial biosphere (560 Gt) (Post et al., 1990; Sundquist, 1993). In the Kyoto Protocol on Climate Change of 1997, which was adopted in the United Nations Framework Convention on Climate Change, Article 3.4 allows organic carbon stored in arable soils to be included in calculations of net carbon emissions. It speaks of the possibility of subtracting the amounts of CO₂ removed from the atmosphere into agricultural sinks, from the assigned target reductions for individual countries. SOC sequestration in arable agriculture has been researched (Schlesinger, 1999; Smith et al., 2000a, b; Freibauer et al., 2002; West & Post, 2002; Sleutel et al., 2003; Janzen, 2004; King et al., 2004; Lal, 2004) against the background of organic carbon (OC) credit trading schemes (Brown et al., 2001; Johnson & Heinen, 2004). However, fundamental knowledge on attainable SOC contents (relative to variation in environmental factors) is still in its infancy, and it is mostly approached by modelling (Falloon et al., 1998; Pendall et al., 2004).

The principle of using biochar for carbon (C) sequestration is related to the role of soils in the C-cycle (Figure 1.7). As Figure 1.7 shows, the global flux of CO₂ from soils to the atmosphere is in the region of 60 Gt of C per year. This CO₂ is mainly the result of microbial respiration within the soil system as the microbes decompose soil organic matter (SOM). Components of biochar are proposed to be considerably more recalcitrant than SOM and as such are only decomposed very slowly, over a time frame which can be measured in

hundreds or thousands of years. This means that biochar allows carbon input into soil to be increased greatly compared to the carbon output through soil microbial respiration, and it is this that is the basis behind biochar's possible carbon negativity and hence its potential for climate change mitigation.

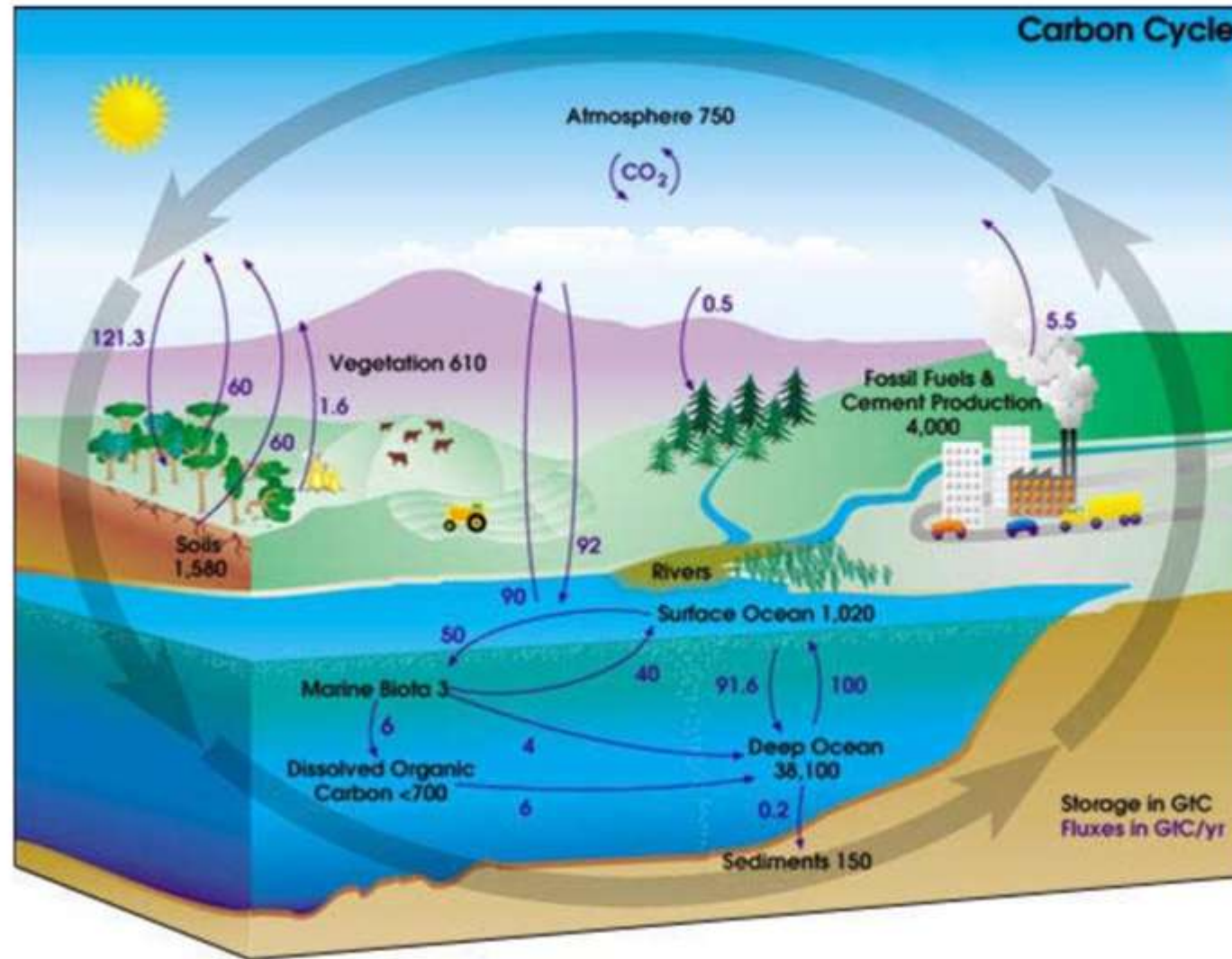


Figure 1.7 Diagram of the carbon cycle. The black numbers indicate how much carbon is stored in various reservoirs, in billions of tons (GtC = Gigatons of Carbon and figures are circa 2004). The purple numbers indicate how much carbon moves between reservoirs each year, i.e. the fluxes. The sediments, as defined in this diagram, do not include the ~70 million GtC of

It is for this reason that the relatively small flux of CO₂ from anthropogenic sources (5.5 Gt C per year) is of such consequence as it turns the overall C flux from the atmosphere from a *loss* of 1.75 Gt per year, to a *net gain* of 3.75 Gt C per year. This is in relatively close agreement with the predicted rate of CO₂ increase of about 3 Gt of C per year (IPCC, 2001). It is mitigation of this net gain of CO₂ to the atmosphere that biochar's addition to soil is posited for.

Lehmann et al. (2006) estimate a potential global C-sequestration of 0.16 Gt yr⁻¹ using current forestry and agricultural wastes, such as forest residues, mill residues, field crop residues, and urban wastes for biochar production. Using

projections of renewable fuels by 2100, the same authors estimate sequestration to reach a potential range of 5.5-9.5 Gt yr⁻¹, thereby exceeding current fossil fuel emissions. However, the use of biochar for climate change mitigation is beyond the scope of this report that focuses on the effects of biochar addition to soils with regard to physical, chemical and biological effects, as well as related effects on soil and ecosystem functioning.

1.5.1 Biochar loading capacity

Terra Preta soils have been shown to contain about 50 t C ha⁻¹ in the form of BC, down to a depth of approximately 1 meter (approximately double the amount relative to pre-existing soil), and these soils are highly fertile when compared to the surrounding soils. This has led to the idea of biochar being applied to soil to sequester carbon and maintain or improve the soil production function (e.g. crop yields), as well as the regulation function and habitat function of soils. Controlled experiments have been undertaken to look at the effects of different application rates of biochar to soils.

At present, however, it is not clear whether there is a maximum amount of C, in the form of biochar, which can be safely added to soils without compromising other soil functions or the wider environment; that is, what is the 'biochar loading capacity' (BLC) of a given soil? It will be important to determine if the BLC varies between soil types and whether it is influenced by the crop type grown on the soil. In order to maximise the amount of biochar which can be stored in soils without impacting negatively on other soil functions, the biochar loading capacity of different soils exposed to different environmental and climatic conditions specific to the site will have to be quantified for different types of biochar.