

structural composition of the biomass feedstock relates to the chemical and structural composition of the resulting biochar and, therefore, is reflected in its behaviour, function and fate in soils. Secondly, the extent of the physical and chemical alterations undergone by the biomass during pyrolysis (e.g. attrition, cracking, microstructural rearrangements) are dependent on the processing conditions (mainly temperature and residence times). Table 1.2 provides a summary of some of the key components in representative biochar feedstocks.

Table 1.2 Summary of key components (by weight) in biochar feedstocks (adapted from Brown et al., 2009)

	Ash	Lignin (w w ⁻¹)	Cellulose
Wheat straw	11.2	14	38
Maize residue	2.8-6.8	15	39
Switchgrass	6	18	32
Wood (poplar, willow, oak)	0.27 - 1	26 - 30	38 - 45

Cellulose and lignin undergo thermal degradation at temperatures ranging between 240-350°C and 280-500°C, respectively (Sjöström, 1993; Demirbas, 2004). The relative proportion of each component will, therefore, determine the extent to which the biomass structure is retained during pyrolysis, at any given temperature. For example, pyrolysis of wood-based feedstocks generates coarser and more resistant biochars with carbon contents of up to 80%, as the rigid ligninolytic nature of the source material is retained in the biochar residue (Winsley, 2007). Biomass with high lignin contents (e.g. olive husks) have shown to produce some of the highest biochar yields, given the stability of lignin to thermal degradation, as demonstrated by Demirbas (2004). Therefore, for comparable temperatures and residence times, lignin loss is typically less than half of cellulose loss (Demirbas, 2004).

Whereas woody feedstock generally contains low proportions (< 1% by weight) of ash, biomass with high mineral contents such as grass, grain husks and straw residues generally produce ash-rich biochar (Demirbas 2004). These latter feedstocks may contain ash up to 24% or even 41% by weight, such as rice husk (Amonette and Joseph, 2009) and rice hulls (Antal and Grønly, 2003), respectively. The mineral content of the feedstock is largely retained in the resulting biochar, where it concentrates due to the gradual loss of C, hydrogen (H) and oxygen (O) during processing (Demirbas 2004). The mineral ash content of the feedstock can vary widely and evidence seems to suggest a relationship between that and biochar yield (Amonette and Joseph, 2009). Table 1.3 provides an example of the elemental composition of representative feedstocks.

Table 1.3 Examples of the proportions of nutrients (g kg^{-1}) in feedstocks (adapted from Chan and Xu, 2009)

	Ca	Mg	K	P
	(g kg^{-1})			
Wheat straw	7.70	4.30	2.90	0.21
Maize cob	0.18	1.70	9.40	0.45
Maize stalk	4.70	5.90	0.03	2.10
Olive kernel	97.0	20.0	-	-
Forest residue	130	19.0	-	-

In the plant, Ca occurs mainly within cell walls, where it is bound to organic acids, while Mg and P are bound to complex organic compounds within the cell (Marschner, 1995). Potassium is the most abundant cation in higher plants and is involved in plant nutrition, growth and osmoregulation (Schachtman and Schroeder, 1994). Nitrogen, Mn and Fe also occur associated to a number of organic and inorganic forms. During thermal degradation of the biomass, potassium (K), chlorine (Cl) and N vaporize at relatively low temperatures, while calcium (Ca), magnesium (Mg), phosphorus (P) and sulphur (S), due to increased stability, vaporise at temperatures that are considerably higher (Amonette and Joseph, 2009). Other relevant minerals can occur in the biomass, such as silicon (Si), which occurs in the cell walls, mostly in the form of silica (SiO_2).

Many different materials have been proposed as biomass feedstocks for biochar, including wood, grain husks, nut shells, manure and crop residues, while those with the highest carbon contents (e.g. wood, nut shells), abundance and lower associated costs are currently used for the production of activated carbon (e.g. Lua et al., 2004; Martinez et al., 2006; González et al., 2009;). Other feedstocks are potentially available for biochar production, among which biowaste (e.g. sewage sludge, municipal waste, chicken litter) and compost. Nevertheless, a risk is associated to the use of such source materials, mostly linked to the occurrence of hazardous components (e.g. organic pollutants, heavy metals). Crystalline silica has also been found to occur in some biochars. Rice husk and rice straw contain unusually high levels of silica (220 and 170 g kg^{-1}) compared to that in other major crops. High concentrations of calcium carbonate (CaCO_3) can be found in pulp and paper sludge (van Zwieten et al., 2007) and are retained in the ash fraction of some biochars.

Regarding the characteristics of some plant feedstocks, Collison et al. (2009) go further, suggesting that even within a biomass feedstock type, different composition may arise from distinct growing environmental conditions (e.g. soil type, temperature and moisture content) and those relating to the time of harvest. In corroboration, Wingate et al. (2009) have shown that the adsorbing properties of a charcoal for copper ions can be improved 3-fold by carefully selecting the growth conditions of the plant biomass (in this case, stinging nettles). Even within the same plant material, compositional heterogeneity has

also been found to occur among different parts of the same plant (e.g. maize cob and maize stalk, Table 1.3).

Lignocellulosic biomass is an obvious feedstock choice because it is one of the most abundant naturally occurring available materials (Amonette and Joseph, 2009). The spatio-temporal occurrence of biomass feedstock will influence the availability of specific biochars and its economic value (e.g. distance from source to field). For example, in an area with predominantly root crops on calcareous sandy arable soils and a dry climate, biochars that provide more water retention and are mechanically strong (e.g. woody feedstocks) are likely to be substantially more valuable than in an area of predominantly combinable crops on acidic sandy soils and a 'year round' wet climate. In the latter case, biochars with a greater CEC, liming capacity and possibly a lower mechanical strength (e.g. crop residue feedstock) may be more in demand.

In Terra Pretas potential feedstocks were limited to wood from the trees and organic matter from other vegetation. Nowadays any biomass material, including waste, is considered as a feedstock for biochar production. Considering that historical sites contain either biochar (Terra Preta) or BC (from wildfires), chronosequence studies can only give us information about the long term consequences and dynamics of those limited natural feedstocks. This implies an important methodological challenge for the study of the long term dynamics of soils with biochar produced from feedstocks other than natural vegetation. Even for trees and plants, careful consideration needs to be given to specific species that bioaccumulate certain metals, or, in the case of crop residues, that may contain relevant concentrations of herbicides, pesticides, fungicides, and in the case of animal manures that may contain antibiotics or their secondary metabolites. See Section 5.1.5 for a more detailed discussion on the (potential) occurrence of contaminants within biochar.

In addition, chronosequence studies using historic sites are often poor predictors of structural disintegration and concomitant chemical reactivity and mobility of biochars, because they are either not in arable land use, or have not been subject to the intense physical disturbance of modern arable tillage and cultivation (e.g. the power harrow).

A detailed description of all biochar feedstocks is beyond the scope of this report and feedstocks have been reviewed in other works (Collison et al., 2009; Lehmann and Joseph, 2009). The key point is that the suitability of each biomass type as a potential source for biochar, is dependent on a number of chemical, physical, environmental, as well as economic and logistical factors (Collison et al., 2009), as discussed, where appropriate, throughout this report. It is important to stress, however, that for any material to be considered as a feedstock for biochar production, and therefore also for application to soil, a rigorous procedure needs to be developed in order to assess the biochar characteristics and long term dynamics in the range of soil, other environmental conditions, and land use and management factors that are considered for its application.

1.8 Application Strategies

Biochar application strategies have been studied very little, although the way biochar is applied to soils can have a substantial impact on soil processes and functioning, including aspects of the behaviour and fate of biochar particles in soil and the wider environment (Chapter 3) as well as on 'threats to soil' (Chapter 4), occupational health and safety (5.2), and economic considerations (Section 5.4). Broadly speaking there are three main approaches: i) topsoil incorporation, ii) depth application, and iii) top-dressing.

For topsoil incorporation biochar can be applied on its own or combined with composts or manures. The degree of mixing will depend on the cultivation techniques used. In conventional tillage systems the biochar (and compost/manure/slurry) will generally be mixed more or less homogeneously throughout the topsoil (in most arable soils from 0-15/30 cm depth). Water and wind erosion will remove biochar along with other soil material, i.e. that would erode without biochar additions as well, and possibly more biochar will be eroded from the surface because of its low density. Potentially, the application of biochar combined with compost or manure would reduce this risk, but studies evidencing this are lacking. In conservation tillage systems the incorporation depth will be reduced (leading to greater biochar concentrations at equal application rates) and possibly a concentration gradient decreasing with depth. In no-till systems any incorporation would be through natural processes (see top-dressing below). Deep mouldboard ploughing effectively results in (temporary) 'depth application' (see below), with more topsoil homogenisation occurring during subsequent ploughing.

Depth application of biochar has been described mostly as 'deep-banded' application (e.g. Blackwell et al., 2007). The placement of the biochar directly into the rhizosphere is thought to be more beneficial for crop growth and less susceptible to erosion. The application can be either by pneumatic systems, which can operate at high rates, or by applying the biochar in furrows or trenches and subsequently levelling the soil surface. Deep mouldboard ploughing essentially results in temporary 'depth application', although horizontally continuous (unlike the 'deep-banded' application). Subsequent mouldboard ploughing and cultivation will then further homogenise the biochar distribution through the topsoil.

Top-dressing of biochar is the spreading of biochar (dust fraction mostly) to the soil surface and relying on natural processes for the incorporation of the biochar into the topsoil. This form of application is being considered mainly for those situations where mechanical incorporation is not possible, e.g. no-till systems, forests, and pastures. An obvious drawback is the risk of erosion by water and wind, as well as human health (inhalation) and impacts on other ecosystem components (e.g. surface water, leaf surfaces, etc.). It is also largely unknown what the rates of incorporation would be for different soil-climate-land use combinations.

The dust fraction of biochar is an issue for all application strategies during the storing, handling, and applying phases of the biochar (see Sections 2.2.1 and 5.2 for more detailed information about the properties and implications of

biochar's dust fraction). This aspect needs to be investigated thoroughly before implementation. Like any trafficking on soil, there is a risk of (sub)soil compaction during biochar application. This may be particularly the case for the relatively heavy machinery involved in 'depth application'.

Both topsoil incorporation and top-dressing can be applied with a range of frequencies, i.e. a 'one-off' application, every few years, or every year. For specific effects on soil, e.g. nutrient availability (from a feedstock like poultry manure) or liming effect, a more frequent application may be more beneficial to the soil and/or less detrimental to the environment (nitrate leaching).

1.9 Summary

As a concept biochar is defined as 'charcoal (biomass that has been pyrolysed in a zero or low oxygen environment) for which, owing to its inherent properties, scientific consensus exists that application to soil at a specific site is expected to sustainably sequester carbon and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health'. Inspiration is derived from the anthropogenically created Terra Preta soils (Hortic Anthrosols) in Amazonia where charred organic material plus other (organic and mineral) materials appear to have been added purposefully to soil to increase its agronomic quality. Ancient Anthrosols have been found in Europe as well, where organic matter (peat, manure, 'plaggen') was added to soil, but where charcoal additions appear to have been limited or non-existent. Furthermore, charcoal from wildfires (pyrogenic black carbon - BC) has been found in many soils around the world, including European soils where pyrogenic BC can make up a large proportion of total soil organic carbon.

Biochar can be produced from a wide range of organic feedstocks under different pyrolysis conditions and at a range of scales. Many different materials have been proposed as biomass feedstocks for biochar. The suitability of each biomass type for such an application is dependent on a number of chemical, physical, environmental, as well as economic and logistical factors. The original feedstock used, combined with the pyrolysis conditions will determine the properties, both physical and chemical, of the biochar product. It is these differences in physicochemical properties that govern the specific interactions which will occur with the endemic soil biota upon addition of biochar to soil, and hence how soil dependent ecosystem functions and services are affected. The application strategy used to apply biochar to soils is an important factor to consider when evaluating the effects of biochar on soil properties and processes. Furthermore, the biochar loading capacity of soils has not been fully quantified, or even developed conceptually.