

THE IMPACT OF BURNING ON THE NATURE OF SOIL ORGANIC MATTER IN AUSTRALIA

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ABSTRACT

Fire plays an important role in modifying many soil chemical, physical and biological properties. Perhaps the largest consequence of fire is the formation of charcoal from the consumed biomass. This paper focuses on the formation of charcoal, its chemical and physical nature and its impact on soil C dynamics. Because of the high frequency of fire in the tropics, it is highly probable that charcoal plays an important role in predetermining many of the chemical and physical properties of soil organic matter observed in tropical soils, as well as the pathways and rates of carbon cycling.

Key words: charcoal, characterization, C dynamics

RESUMO

O IMPACTO DA QUEIMADA NA NATUREZA DA MATÉRIA ORGÂNICA DO SOLO NA AUSTRÁLIA.

O fogo tem um papel importante na modificação de muitas propriedades físicas, químicas e biológicas do solo. Provavelmente a maior consequência do fogo seja a formação de carvão da biomassa consumida. Esse trabalho enfoca na formação do carvão, sua natureza física e química e seu impacto na dinâmica do C do solo. Por causa da alta frequência do fogo nos trópicos, é altamente provável que o carvão tenha um papel importante na predeterminação de muitas propriedades físicas e químicas da matéria orgânica do solo observada nos solos tropicais, bem como nos caminhos e taxas de ciclagem do carbono.

Palavras-chave: carvão, caracterização, dinâmica do C

INTRODUCTION

All of the vegetated surfaces of the earth are subject to fire irrespective of the climate in which they are found. Deserts, rainforests and all other vegetation types burn. It is only the frequency of the occurrence of fire that varies between vegetation types.

The Australian continent spans approximately thirty-five degrees of latitude, from the tropics of Cape York (10° S) to temperate southern Tasmania (45° S). Fire is experienced across the whole continent, including the central arid core, with characteristic intervals ranging from 1-2 y in the tropics, 10-20 y in the arid centre to 50-100 y in the temperate south. These intervals reflect current landuse, vegetation and climate. Archaeological and historical evidence indicates that while the frequency of fire has changed over the millennia driven by changes in climate and

culture, it has always been present. Today, satellite observations show that it is uncommon for the continent to be without a fire of sufficient size to be detectable from space. For the Australian continent, fire has been and remains ubiquitous.

The impact of fire that is relevant to the nature and dynamics of soil organic matter is primarily determined by two factors, the volume of biomass carbon exposed, and its subsequent fate. The average fire-affected area is approximately 30×10^6 ha/y, of which more than 90% occurs in the tropical savannas of Western Australia, the Northern Territory and Queensland, very few of which are wildfires. The extra-tropical burning comprises management of hazard reduction in forests (approx. 1×10^6 ha/y), and wildfires. Assigning carbon densities to the different fuel loads, we have a mass of approximately 150 MtC/y being burned. The fate of this carbon can then be partitioned into 145 MtC/y

volatilised as CO₂ and 5 MtC/y carbonised to charcoal. By comparison, the current national fossil fuel consumption is approximately 85 MtC/y. Thus, in terms of the anthropogenic fluxes of carbon, fire matters!

The area, carbon density and fate figures used above have some uncertainty associated with them that will be gradually reduced in the future by the increasing use of satellite observations. The fuel loading and fate figures will remain more uncertain for some time yet. Also, consideration must be given to the interannual variation in area and fuel loadings which is both large and non-normally distributed reflecting a lagged response to the driving El Niño Southern Oscillation (ENSO) and anti-ENSO cycles. Moreover, there is persuasive anecdotal evidence of decadal trends in fire regimes in response to changing landuse, both traditional and contemporary. These trends, such as less frequent burning or changed time of burning, are spatially distinct and conflicting in carbon outcomes. Unfortunately, the absence of objective measurements, such as those from satellite observations, currently limits our quantitative assessment of both changes in fire regimes and of their carbon consequences.

Fire has a number of direct impacts on soils. Specifically, heating at the soil surface (300 to 425°C) can cause mineralogical transformations such as the conversion of iron oxides to maghemite in the presence of organic matter (Schwertmann and Taylor, 1989). Soils have low thermal conductivity however, and these effects are usually seen only within the top few millimetres of the soil surface. At lower temperatures (60 to 125°C), heating can effectively sterilize soils and cause hydrophobicity through the replacement of surface water (dehydration) with volatile organics (Savage, 1974). At higher temperatures (200 to 450°C), organic materials (living or dead) become charred and lead to the formation of smoke, soot, charcoal and ash. Smoke and soot particles can travel great distances through the atmosphere where they may have a significant climatic impact (Crutzen and Andreae, 1990). Through gases formed during biomass burning, significant amounts of nitrogen, perhaps as much as 50% of the biomass N, can be lost from an ecosystem causing an overall lowering of landscape fertility (Crutzen and Andreae, 1990). For example, Hurst *et al.* (1994) estimate the annual release of N from Australian savanna fires to be 1.7 Mt, most of which would be lost to the burned landscape. At higher temperatures (>600°C), P may also be lost (Walker *et al.* 1986). Charcoal and ash largely remain where they are formed due to their larger particle size and thus more rapid settling rate (Clark and Patterson, 1997) but may subsequently be transported by erosional processes and redeposited elsewhere in the landscape.

CHEMISTRY OF CHARCOAL AND IMPLICATIONS IN SOIL C DYNAMICS

A number of terms are used in the literature to identify various products of fire and heating. These can be misleading in that the same term may often refer to different materials in different disciplines. Jones *et al.* (1997) define 16 individual products of fire and in this paper, we use the terms charcoal and ash as defined by these authors.

Charcoal is derived from plant material that has had its chemical and ultrastructure altered by heating. Shafizadeh (1984) showed that at about 400°C and above, plant material undergoes considerable chemical change with carbohydrate structures being converted to fused aromatic ring structures with the loss of carbon dioxide/monoxide and water. The fused aromatic rings form basic structural units of three or four graphitic layers, randomly organised to form the charcoal structure, or may form soot as spherical "onion-like" particles in the gaseous phase (Schmidt and Noack, 2000). Despite this significant chemical rearrangement, the plant morphological structure from which the charcoal is formed, remains largely intact. The graphitic structures are not true graphite and can contain other elements such as oxygen and nitrogen that form functional groups within the graphitic structures, such as carboxyl groups and heterocyclics (Skjemstad *et al.*, 1996; Knicker and Skjemstad, 2000).

Despite the relatively simple chemical structure of charcoals, products of incomplete combustion can form a continuum from partially charred plant materials to fully graphitised "black carbon" particles. Methods of analysis therefore, have proven difficult to develop with different methods often determining different portions of this continuum. Many methods have been proposed ranging from optical/microscopic, thermal and chemical. Optical methods rely on the characteristic morphology and sometimes lustre of charcoal pieces. This technique can be reliable for charcoals of larger particle size (>5 mm) but charcoals of smaller particle size can be difficult to identify and therefore to estimate (Schmidt and Noack, 2000). Thermal methods rely on the relative stability of charcoal to heat in an oxidising atmosphere compared with other natural forms of carbon. Thermal separation may be preceded by chemical extractions to remove interfering species (Kuhlbusch, 1998). Chemical methods rely on oxidation of charcoal structures to recognisable chemical units (Glaser *et al.*, 1998b) or the selective removal of other forms of carbon leaving only the charcoal material which can then be estimated. These methods rely on the use of oxidising acids such as nitric (Verardo, 1997) or chromic acid (Bird and Gröcke, 1997) or high-energy ultraviolet photo-oxidation (Skjemstad *et al.*, 1996; Skjemstad *et al.*, 1999). Other rapid indirect methods using FTIR are also being developed (Janik *et al.*, 1998). Schmidt *et al.* (2000) compared a number of these techniques and found that

the estimates could differ by as much as a factor of 500 or more. They concluded that it is essential that a reliable set of standard materials be established for the purpose of testing methods and for interlaboratory comparisons.

Within CSIRO Land and Water, the method used for charcoal estimation is based on the oxidation of more chemically labile materials with photo-oxidation and subsequent analysis of the residue by solid-state ^{13}C NMR. Because of its highly aromatic nature, charcoal can be readily detected with NMR once other aromatic materials such as lignins and tannins are removed. A full description of the method used is given in Skjemstad *et al.* (1999). This methodology has the advantage of concentrating the charcoal material so that other estimates such as the content and nature of nitrogen within the charcoals can also be investigated (Knicker and Skjemstad, 2000). This treatment is also relatively gentle, since no strong oxidizing agents are used, and allows the morphology and particle size of the charcoals to be determined.

Regardless of the method of estimation, it is clear that the highly condensed aromatic structures present in charcoal will be highly resistant to microbial decomposition (Skjemstad *et al.*, 1998) and should persist in soils and sediments for centuries and probably millennia. This recalcitrance has significant implications for the dynamics of carbon in soils, particularly since methods for soil organic carbon estimation cannot effectively discriminate between charcoal and other forms of organic carbon (Skjemstad and Taylor, 1999). Skjemstad *et al.* (2001) showed that in Vertisols under exploitive cultivation, charcoal content did not vary over periods of 50 years or so, despite the fact that other soil carbon fractions significantly decreased over this period. It was also demonstrated that charcoal, which could represent nearly 50% of the total organic carbon, equated well with the inert pool of the Rothamsted soil carbon turnover model (Jenkinson, 1990).

Charcoals maintain a C/N ratio similar to that of the plant material from which they are formed (Knicker *et al.*, 1996). Soils high in charcoal therefore, can contain over 20% of their nitrogen content within the aromatic charcoal structure in the form of nitrogen containing heterocyclic components (Knicker and Skjemstad, 2000). It must be assumed that this nitrogen is as stable and unavailable as the carbon within these aromatic structures. This implies that the charcoal fraction also represents an inert or at least a highly recalcitrant pool of N. Therefore, the importance of charcoal in stabilising both carbon and nitrogen against decomposition in soils and sediments demonstrates the need for a universal and simple method to accurately measure this material in soil carbon turnover studies.

Finely-divided soil charcoal also appears to contain significant amounts of carboxylic acid groups, perhaps as much as 10% (Skjemstad *et al.*, 1996, Glaser *et al.*, 1998a) which may be of importance in enhancing cation

exchange properties of tropical soils which are often low in exchange sites (Gallez *et al.*, 1976).

CHARCOAL PRODUCTION (FORMATION) AND DISTRIBUTION

Despite the interest in fire and charcoal formation, there is very little information on the rates of production of charcoal under natural burning events. Kuhlbusch *et al.* (1996) estimated that between 0.7 and 2.0% of the organic carbon converted to CO_2 during burning was retained as charcoal (black carbon). From these data, they estimated that between 10-26 Tg (Mt) C/yr of black carbon was formed world wide from savanna fires. Our estimates using C/Si ratios of plant material and ash/charcoal deposits from recent fires in northern Australia, suggest that the conversion rate may be much higher, approaching 4.0%, so that annual charcoal deposition, at least in Australia, may be even higher than that estimated by Kuhlbusch *et al.* (1996). It should also be noted that heating of the soil itself is likely to convert some soil organic matter to charcoal. Although soil does not have a high thermal conductivity and this influence is only likely to be significant in the top few millimetres or so, oxygen diffusion would be slower and combustion is likely to be less complete, favouring more efficient charcoal formation. Such high charcoal production rates should lead to increases in charcoal in soil and if charcoal was truly inert, should, in turn, lead to charcoal being the dominant form of carbon in the soil. Goldberg (1985), for example, estimated that without a mechanism for the decomposition of charcoal the Earth's surface carbon pools would be converted to charcoal within 100,000 years. The mechanism for this decomposition of charcoal is not clear but is probably a combination of microbial and chemical oxidation processes.

Other mechanisms lead to the redistribution of charcoal in the landscape. Scanning electron microscopy shows that the highly aryl charcoal residues from photo-oxidation have a plant-like morphology. These charcoal particles can vary considerably in size and morphology, however, ranging from plant-like fragments in the 5-40 mm particle range to sub-micron particles, which are often platy in nature and can be difficult to distinguish morphologically from clay particles. Figure 1 shows an electron micrograph of charcoal extracted by photo-oxidation and treatment with HF from a Rhodoxeralf from South Australia. Virtually all of this finely divided charcoal appears to result from the burning of grasses and understorey vegetation in savannas and open woodlands. Our experience is that charcoal from these sources is highly sensitive to physical impact and is readily reduced in particle size by relatively low inputs of energy, such as those from raindrops or wind. Although nearly all soils

studied have been shown to contain measurable amounts of charcoal, certain soil types always contain significant amounts. For example, soils that are dark in colour but contain relatively low amounts of organic carbon (<3%) invariably contain a high proportion of charcoal. It would appear that finely divided charcoal is significant in determining soil colour, at least in soils that have a low to moderate iron content. Soils formed from alluvium with moderate or high clay contents also often contain significant amounts of charcoal. It is postulated that these finely divided charcoal materials are mobile, behaving in a manner similar to clay and silt and hence accumulate in the same locations where clay and silt materials accumulate. Charcoal is therefore often found in high concentrations and to some depth in soils such as Vertisols, soils formed on riverine plains and deltas and in marine coastal sediments. The distribution of charcoal both laterally and vertically in soils is highly variable and appears to reflect the amount of above-ground biomass susceptible to fire and burning frequency, the clay content and type, as well as the

erosional processes as described above.

Although darkly coloured clayey soils often contain high levels of charcoal, there appears to be no clear general relationship between soil type and charcoal content. For a set of soil samples that we have analysed from across Australia, the charcoal content varied from <0.1 to >80% of the total soil carbon. Recently, we analysed a set of 320 profiles to 1 m forming a 1,700 km transect in the Northern Territory from Darwin (12° 27' S, 130° 50' E) on the north coast to Wauchope (20° 38' S, 134° 13' E) in central Australia for total organic and charcoal carbon content. This transect in tropical Australia represents a mean annual rainfall gradient from about 1,600 mm in the north to <300 mm in the south. The charcoal content varied from below detection to as much as 62% of the total organic carbon in the 1 m profile. On average, the charcoal carbon represented 5.8 tC/ha (15% of the organic carbon) but varied from below detection to 32 tC/ha. In tropical Australia therefore, as much as 2.0 Pg (Gt) of carbon may exist in the form of soil charcoal.

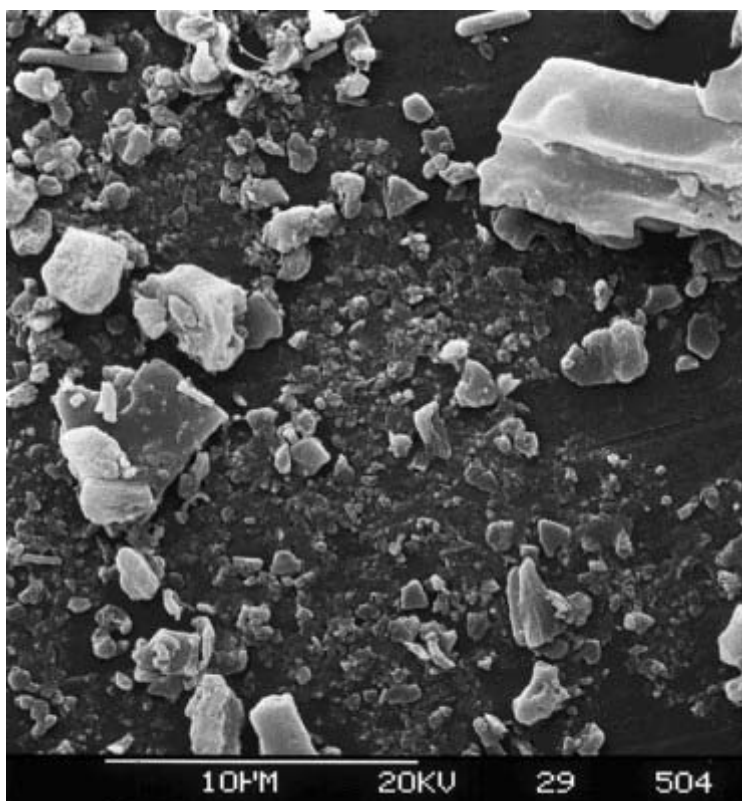


Figure 1- An electron micrograph of charcoal extracted by photo-oxidation and treatment with HF from a Rhodoxeralf from South Australia. EDX analysis showed that all particles, including those that are sub-micron, are charcoal.

Even though this appears to be a large amount of carbon, as indicated earlier, charcoal production rates are also high. If on average 1.0 t of dry matter/ha was consumed annually by fire, this would lead to a production rate of about 20 kg charcoal C/ha/y. In just

1,000 y under this activity, 20 t of charcoal C per hectare would be produced, three times more than the average measured amounts in these soils. It is clear that fire has been part of the tropical landscape for perhaps tens of millennia and so even using much more conservative

estimates, soils can not account for the amount of charcoal that must have been produced during Australia's recent fire history. It is possible that because of its fine particle size, charcoal may move beyond 1 m in deeper profiles or may be deposited in marine sediments through erosion. These processes undoubtedly account for a substantial quantity of "missing" charcoal but it seems unlikely that the necessary tens of Gt of charcoal could be accounted for by these mechanisms. It seems much more likely that charcoal is, in fact, susceptible to long-term oxidation and that production rates are in near-equilibrium with rates of loss. This assumption leads to a turnover rate in the order of 3,000-5,000 y for soil charcoal. This timescale is reinforced by ¹⁴C radiocarbon dating of photo-oxidation resistant material from soil fractions, most of which was charcoal, and was shown to be some 1,400 y older than the soil as a whole (Skjemstad *et al.*, 1993).

CONCLUSIONS

Fire plays an important role in modifying many soil properties, particularly in the tropics where both natural and anthropogenic burning is prevalent. Perhaps the largest impact of fire is through the formation of charcoal. This material is rapidly incorporated into the soil and because of its chemistry and morphology is difficult to distinguish from soil organic carbon formed through normal biological processes.

Charcoal has a highly condensed aromatic structure that is resistant to both chemical and biological oxidation. Charcoal cannot be truly inert however, since current production rates would soon lead to charcoal as the dominant form of carbon in almost all soils and sediments. This is clearly not the case and decomposition processes must occur which result in mean residence times of charcoal in soils of the order of a few millennia. Because of its recalcitrance and relatively large contribution to some soil types, its presence can have a profound impact on soil carbon dynamics and must be accounted for in any soil carbon turnover studies.

At present, there is no recognised method for the determination of charcoal in soils and sediments with a range of methods being used that appear to determine various parts of a continuum of carbonised plant products. Some standardisation is required and a rapid and simple technique for the estimation of charcoal would help advance charcoal research in both soils and sediments.

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