Applications for Brown Coal in Australian agriculture

Literature Review

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March 2016

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Important disclaimer

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Executive Summary

Since European settlement, the concentration of soil organic carbon (SOC) in Australian soils has fallen, by as much as 60% in some areas, through reduced inputs and increased loss rates. In many areas, SOC concentrations are below the level needed for optimum productivity and soil health.

A healthy level of SOC improves potential plant yields, through improved nutrient supply and water availability, increased ion exchange capacity, the ability to retain nutrients within the root zone, improved soil structure and porosity, and increased biological activity.

A decline in SOC stocks has occurred worldwide and it is vital that this trend be reversed. In recognition of this problem, Australia was the first of 25 nations to endorse the "4/1000 Initiative: Soils for Food Security and Climate" in December 2015. The '4/1000 Initiative' represents a shared commitment to increasing the global SOC reserve by 0.4% annually. It aims to improve agricultural productivity and help feed a growing world population, and to assist in slowing the rate of global warming by 'locking up' carbon from atmospheric CO_2 in the soil.

The main focus of efforts under the '4/1000 Initiative' in Australia will be on improving the SOC stocks of actively managed agricultural land. There are recommended soil management options that are proven to increase SOC in cropping-based farming systems, but this report shows that, even with the most determined efforts, it will not be possible to meet the '4/1000 Initiative' target using these measures alone. At best, there will be a shortfall of 29 million tonnes of carbon each year, which will have to be provided through supplementary soil amendments.

While Australian soils are generally poor in organic carbon, Victoria is blessed with abundant deposits of ancient decomposed plant matter, which make up its massive brown coal reserve. This friable, soft material has a similar structure to soil carbon and contains low levels of mineral impurities. In principle, Victorian brown coal is ideal for boosting the carbon content of soils across Australia, which would increase their agricultural productivity and boost the rate of carbon dioxide capture from the atmosphere. The challenge is to transform the coal resource into commercial products that can cost-effectively be transported and utilised on farming land across Australia.

This report has been written to inform BCIA members of the opportunities that exist for utilisation of brown coal in Australian agriculture. It was written in response to feedback from a BCIA-run workshop in December 2015, 'Agricultural applications for brown coal', which involved the majority of industry, academic and regulatory experts known to have an interest in this area.

The aim of this report is to summarise the available literature and to illustrate the broad range of potential agricultural products that can be derived from brown coal. It is shown that there is a range of potential uses for brown coal in Australian agriculture. Coal or extracted humic substances can be used as soil amendments and in organomineral fertilisers. Coal itself can be used as a carrier for microbial biofertilisers and to reduce ammonia and N_2O emissions from beef cattle feedlots and other intensive animal-rearing systems. Humic acids can be used as animal feed supplements to improve animal health and growth rates.

It will be a challenge to transform the coal into commercial products that are suitable for long-distance transport and application in the field at an acceptable price. While this process must be led by industry, the credibility of the products will depend upon the availability of high quality supporting data. Farmers will expect to see a quantifiable benefit from their investment in order to make repeat purchases. This report includes recommendations of the further research needed to ensure the quality and reliability of new agricultural products based on Victorian brown coal.

One of the main challenges that this report identifies is that there is currently no well-defined way to quantify the financial benefits of increased soil organic carbon (SOC). This makes it difficult to assign a meaningful value to the benefits provided by brown coal as a soil amendment. To address this knowledge gap, it is recommended that a modelling tool be developed to use the best available information to quantify the value to farmers of increasing SOC on their properties.

As a soil amendment, brown coal can help to build soil carbon, improve productivity and increase profitability. The conceptually simplest way to increase SOC with brown coal is to apply it in bulk (i.e. in the order of tonnes per hectare). Products could be formulated to address the needs of specific problem soils, e.g. coal + lime for acidic soils, coal + gypsum for saline/sodic soils, coal + rock dust for sandy soils, etc. There are a number of strategies that can be employed to increase the rate at which brown coal is converted to SOC. These include chemical processes, such as oxidation with nitric acid or gaseous ozone, as well as biological processes such as composting or inoculation with specific coal-solubilising microorganisms. Industry-led research will be needed to cost-effective product formulations, accompanied by high quality field trials to establish the full value proposition for these products.

Organomineral fertiliser products represent an attractive market opportunity. Organomineral fertilisers are based on blends of brown coal and/or humic substances with proven fertiliser ingredients (either chemical or biological). There is good scientific support for the use of such products to increase the efficiency of N and P fertilisers, which makes for a simple value proposition. This area provides scope for the existence for a number of new manufacturing businesses. Further research will be needed to optimise the formulation of such products and to validate their performance through field trials.

Brown coal can be used as a carrier for microbial biofertilisers, although it is likely that this will remain a niche market in Australia for the foreseeable future. While this is a relatively high-value application, it does not represent a market for large quantities of brown coal.

At the present time, humic substances represent the main agricultural market for coal-derived products, both in Australia and elsewhere. Humic substances represent the ‘active ingredient’ in brown coal and, in dry form, are much cheaper to transport. Even so, their total market size is relatively small, which is probably because they are expensive to produce, expensive to transport in liquid solution, and give unreliable responses in the field. These factors suggest that humic substances will continue be regarded as premium, high-performance ingredients in specific applications, e.g. foliar sprays, fertigation. It is recommended that applications for humic substances should be supported by peer-reviewed scientific research, to create a premium image to match the premium price.

In particular, humic substances show great potential for use as animal feed supplements, where they are reported to improve stock health, growth rates and feed conversion efficiency. This is a premium application with great potential significance for Australian agriculture. Further research is needed to understand the regulatory issues that relate to using humic substances in this manner, and to produce the additional supporting performance data that is sure to be required.

Less expensive, bulk brown coal products can be used to reduce ammonia emissions from intensive animal rearing operations, such as beef cattle feedlots. Since most Australian beef cattle feedlots are in NSW and Queensland, making transportation costs an issue, it is recommended that opportunities be investigated in related industries (e.g. poultry, pork) in Victoria. There is potential for a ‘virtuous circle' to be established, with bulk coal being sent out and returned in the form of nutrient-rich coal and manure, which could then be composted for inclusion in an organomineral fertiliser blend and sold into other markets. Further research is needed to generate trial data to develop a business case for this process.

This report also considers potential agricultural uses for Latrobe Valley fly ash, a by-product of electricity production from brown coal. Applications for the fly ash are generally limited because of its strong alkalinity and high concentration of boron (B). It is suggested that there may be potential agricultural applications in areas of high rainfall and/or acidic soils, where B deficiency is likely to be a problem. In these areas, the high B content of fly ash would be an advantage. Further research is required to investigate the potential for applications in such areas.

The production of value-added agricultural inputs represents the 'low-hanging fruit' of the potential range of products that can be derived from Victorian brown coal. The capital and processing costs are relatively low, and there is a large potential market. There is definitely a role for the use of brown coal in boosting the organic carbon content (hence productivity and profitability) of Australian agricultural soils. Innovative, cost-effective new products are needed to achieve this, along with performance data that establishes a clear value proposition for the farmer. Industry needs to take the lead in developing these opportunities, supported by the academic expertise that is already in place. The information provided in this review should assist with this task, and will hopefully provide the inspiration for new manufacturing opportunities based on Victorian brown coal.

1. Introduction

Australia is a vast and ancient land, with soils that have been subjected to weathering for millions of years. The depletion of nutrients in the soil and the buildup of salts, coupled with limited water availability, have limited abundant plant growth to the temperate margins of the continent. This, in turn, limits the amount of plant biomass recycled to the soil carbon pool. Consequently, most of Australia has naturally low levels of soil organic carbon, which have been reduced further through the introduction of European farming methods.

With a growing recognition of the threat posed by increasing levels of carbon dioxide in the atmosphere, international attention has been given to the potential for sequestering additional carbon in the soil through increased plant photosynthesis. Australia committed to playing an active role in this effort by signing up to the “4/1000 Initiative: Soils for Food Security and Climate” in December 2015.

While Australian soils are generally poor in organic carbon, Victoria is blessed with abundant deposits of ancient decomposed plant matter, which make up its massive brown coal reserve. This friable, soft material has a similar structure to soil carbon and contains low levels of mineral impurities. In principle, Victorian brown coal is ideal for boosting the carbon content of soils across Australia, which would increase their agricultural productivity and boost the rate of carbon dioxide capture from the atmosphere. The challenge is to transform the coal resource into commercial products that can cost-effectively be transported and utilised on farming land across Australia.

This report has been written to inform BCIA members of the opportunities that exist for utilisation of brown coal in Australian agriculture. It was written in response to feedback from a BCIA-run workshop in December 2015, ‘Agricultural applications for brown coal’, which involved the majority of industry, academic and regulatory experts known to have an interest in this area.

This report provides a broad overview of the benefits and value of increasing soil organic carbon (SOC), the agricultural practices that are regarded as useful for building SOC. The implications of the ‘4/1000 Initiative’ target in Australia are set out, and it is explained why the standard agricultural practices will not be enough to increase SOC sufficiently. It is shown that the only way that the objective of the ‘4/1000 Initiative’ can be met in Australia is through the widespread use of brown coal products as supplementary soil amendments.

The report includes an extensive review of the scientific and patent literature, to illustrate the broad range of potential agricultural products derived from brown coal. Research has been undertaken on agricultural applications for Victorian brown coal over the past 40 years, but to date there have been few commercial spin-offs. In this report, efforts have been made to unearth the prior research that has been done in Victoria, in the hope that it may provide inspiration for a range of new products.

Overseas, countries with substantial brown coal deposits have also been active in developing and commercialising new agricultural products. These are highlighted to indicate the potential for other commercial opportunities in Australia.

While the development of new products to boost Australian agricultural productivity must be led by industry, the credibility of the business will depend upon the availability of high quality supporting data. This report includes recommendations of the further research needed to ensure the quality and reliability of new agricultural products based on Victorian brown coal.

2. The need for increased soil organic carbon

2.1. The value of soil organic carbon

The United Nations declared 2015 as the International Year of Soils, in recognition of the important role of soil for food security and the need to maintain this vital resource for future generations[1]. The most important indicator of soil fertility and productivity is soil organic carbon (SOC). The principal functions of SOC in the soil are[2]:

(i) Source and sink of principal plant nutrients (e.g. N, P, S, Zn, Mo);
(ii) Source of charge density and responsible for ion exchange;
(iii) Absorbent of water at low moisture potentials leading to increase in plant available water capacity;
(iv) Promoter of soil aggregation that improves soil tilth;
(v) Cause of high water infiltration capacity and low losses due to surface runoff;
(vi) Substrate for energy for soil biota leading to increase in soil biodiversity;
(vii) Source of strength for soil aggregates leading to reduction in susceptibility to erosion;
(viii) Cause of high nutrient and water use efficiency because of reduction in losses by drainage, evaporation and volatilisation;
(ix) Buffer against sudden fluctuations in soil reaction (pH) due to application of agricultural chemicals; and
(x) Moderator of soil temperature through its effect on soil colour and albedo.

There are also broader benefits from the SOC pool, which have both economic and environmental significance. Important among these are[3]:

(i) Reduces sediment loads in streams and rivers;
(ii) Filters pollutants of agricultural chemicals; Reactors for biodegradation of contaminants; and
(iii) Buffers the emissions of greenhouse gases from soils to the atmosphere.

SOC stocks are generally highest in cool/cold, humid climate regions. Typically, arable soils contain around 1-3% of SOC, whilst grassland and forest soils usually contain more. Globally, the quantity of carbon stored in the soil (2,344 Gt) is second only to that in the ocean (38,400 Gt), and is more than four times larger than the terrestrial biotic C pool (~560 Gt)[4].

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[1] Stockmann *et al.* 2015

[2] Lal 2004

[3] *Ibid.*

[4] Stockmann *et al*. 2013

2.2. Australian SOC stocks

The total stock of SOC in the 0-30 cm layer of soil for the Australian continent is 24.97 Gt. The SOC is not uniformly distributed, with values of around 5.9 t/ha in the centre of Australia and increasing gradually towards the coast in the north, south-west and east, to around 230 t/ha in the high-temperate regions in south-eastern Australia and in the cool, wet regions of western Tasmania. Overall, the average amount of SOC in Australian topsoil is estimated to be 29.7 t/ha[5].

The agricultural sector uses approximately 60% of the land area of Australia. 80% of that area (368 Mha) is used for low-density gazing of natural vegetation, and 98 Mha of land is actively managed, primarily for grazing of modified pastures and various cropping systems[6].

The total SOC stock of Australian agricultural land has been estimated as 13.18 Gt, with an average concentration of 28.3 t/ha (0.67%) in the 0-30 cm layer of soil. This value is lower than the national average, reflecting the large area of land used for grazing on native vegetation, with an average SOC of 24.3 t/ha (0.58%). The actively managed agricultural land has a higher average SOC level, at 43.2 t/ha (1.03%)[7].

2.3. Depletion of soil organic carbon

Cultivation of a soil that previously supported native vegetation or pasture generally leads to a reduced level of SOC. Historically, approximately 78 Gt of SOC has been lost from the global soil pool due to land-use conversion for agriculture, with approximately 26 Gt attributed to erosion and 52 Gt attributed to mineralisation[8].

Conversion of native forest and pasture to cropland has been found to reduce SOC stocks by an average of 42% and 59%, respectively[9]. The reasons for the nearly universally observed reduction in SOC stocks that accompany clearing of native land for agriculture are thought to be well known. These reasons fall into two broad categories: 1) reduced inputs due to harvest and stubble burning; and 2) increased loss rates[10].

Cultivation may increase decomposition rates by creating an environment for more active microbial degradation of SOC. Fallow periods following harvest reduces the viable microbial biomass, converting organic carbon into CO_2 which escapes to the atmosphere. Fallow periods also create favourable conditions for additional loss of SOC through wind and water erosion.

There is strong evidence indicating that some of the SOC loss can be attributed to widespread and sustained use of synthetic N fertilisers. Nitrogen fertilisers tend to be applied at rates in excess of crop N requirements, with an effective efficiency of only 33-36%. The excess N is metabolised by soil microbes which decompose plant residues as a source of carbon. The overall result is a net reduction of SOC[11].

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[5] Viscarra Rossel *et al.* 2014
[6] *Ibid*.
[7] *Ibid*.
[8] Lal 2004
[9] Guo and Gifford 2002
[10] Sanderman *et al*. 2010
[11] Khan *et al.* 2007; Mulvaney *et al*. 2009

It has been suggested that where SOC concentrations are reduced below some critical limit, soil nutrient and water holding capacity will be impeded and physical degradation is likely to occur through fragmentation of soil aggregates and increased susceptibility to soil surface crusting and erosion. Research suggests that the critical SOC concentration is in the range of 1-2% (equating to 42-84 tonnes C/ha in the 0-30 cm soil layer), although the impact on crop productivity will be affected by a range of factors, such as soil mineral composition, climate and fertilisation practices[12].

Australian soils are geologically old, meaning that many weathering-derived nutrients have been exhausted and salts have accumulated. Key agricultural nutrients are often deficient, especially phosphorus and micronutrients such as copper, zinc and molybdenum[13]. The average SOC values for Australian agricultural soils range from 0.58% in the vast areas of grazed native vegetation to 1.03% in the actively managed agricultural land. In places, as much as 60% of the pre-settlement SOC has been lost[14]. Current SOC concentrations are below the critical level needed for optimum productivity and soil health.

2.4. Soil carbon sequestration under the 4/1000 Initiative

The process of removing atmospheric CO_2 by plants and fixing in the soil as SOC is known as "soil carbon sequestration". The strategy aims to increase SOC density in the soil, improve depth distribution of SOC and stabilise SOC by encapsulating it within stable soil micro-aggregates[15]. The aim of soil carbon sequestration is to 'lock up' carbon from atmospheric CO_2, either long term or permanently (i.e. 100 years), through the accumulation of very long lived SOC pools.

Each year, ~9 Gt of C is added to the atmosphere by global human activity, from fossil fuel sources (coal, oil and gas) and through ecosystem degradation[16]. Hypothetically, the entire mass of these C emissions could be sequestered by increasing the global SOC reserve (2,344 Gt) by 0.4% annually. In practice, this is an impossible goal to achieve, but any progress in this direction would assist in reducing the atmospheric CO_2 concentration.

In recognition of this, the French Minister for Agriculture launched the "4/1000 Initiative: Soils for Food Security and Climate" in March 2015, and challenged the world to meet this ambitious goal[17]. A 0.4% annual increase in the global soil carbon stock would make it possible to offset the rise in atmospheric CO_2. The 4/1000 Initiative aims to improve the organic matter content and promote carbon sequestration in soils through the application of agricultural practices adapted to local situations. This initiative is intended to complement other global efforts to reduce greenhouse gas emissions[18].

In December 2015, Australia was the first of 25 nations to endorse the 4/1000 Initiative at COP21 in Paris. Through this commitment, the Australian Government has agreed to provide support for soil carbon sequestration activities, which may include financial support for development projects.

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[12] Stockmann *et al*. 2015

[13] Sanderman et al. 2010

[14] Dalal and Chan 2001

[15] Lal 2004

[16] Stockmann *et al*. 2013

[17] http://newsroom.unfccc.int/lpaa/agriculture/join-the-41000-initiative-soils-for-food-security-and-climate/

[18] *Ibid*.

The current total stock of SOC in Australian soils has been estimated as 24.97 Gt.[19] Increasing the SOC stock by 0.4% would require sequestration of 100 Mt C, or 328 Mt CO_2 annually. In contrast, Australia's annual greenhouse gas (GHG) emissions for 2014-15 were estimated to be 549.3 Mt CO_2-e[20].

It is clear that actions taken under the 4/1000 Initiative will be insufficient to offset Australia's GHG emissions, even if the SOC content were to be increased across the entire continental surface. Nevertheless, soil carbon sequestration has a potentially important role to play in helping to reduce the costs of decarbonising the Australian economy and limiting global warming to less than 2 °C.

2.5. Financial benefits of increased SOC

The ecosystem services provided by SOC are tangible and undisputed. Soil carbon is generally agreed to improve potential yields, through improved nutrient supply and water availability, increased ion exchange capacity, the ability to retain nutrients within the root zone, improved soil structure and porosity, and increased biological activity.

Australian agricultural land is generally poor in SOC, but this is not the only limitation to productivity. Much of Australian agricultural production is water limited, and large areas are affected by salinity and/or low pH. While these factors will continue to acts as constraints on productivity, in general farmers may expect to see the following benefits from increased SOC:

- Increased crop tolerance to water stress, due to larger root volume;
- Increased fertiliser use efficiency, resulting in either higher yields or lower fertiliser costs;
- Reduced fuel costs during cultivation, due to the soil being more friable.
- Reduced yield losses associated with disease, due to better biological diversity in the soil.

At present, it is not possible to quantify the direct financial benefits associated with increased SOC. There have been a number of published attempts to estimate the on-farm value of SOC, as shown in Table 1 below, but the results cannot be readily compared. In all cases, though, there is a net financial gain to the farmer associated with adopting practices that increase SOC.

Benefit obtained	Estimated value	Reference
Fertiliser replacement value	USD 11.6/ha/year	Wander and Nissen 2004
Conversion from cropping to dairy pasture	Value of environmental benefits was 40-70 times greater than cost of lost production	Sparling *et al*. 2006
N, P and S supplied by soil organic matter	USD 227/ha	Rice *et al*. 2007
Improved pasture productivity	AUD 26-95/ha/year	Meyer *et al*. 2015

Table 1: Estimated on-farm value of increased SOC

As well as direct on-farm ecosystem service benefits, there are also indirect ecosystem service benefits associated with higher SOC. These include improved water storage and release, erosion control, higher

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[19] Viscarra Rossel *et al.* 2014

[20] Quarterly Update of Australia's National Greenhouse Gas Inventory: June 2015. Australian Government, Department of the Environment, 2015.

biodiversity, retention of contaminants, and faster degradation of wastes[21]. Through improved soil properties, increased SOC helps to mitigate losses of fertiliser and chemical residues through leaching into groundwater, surface runoff, dust storms and erosion, and thus helps to protect the broader environment.

There is a significant private and societal value associated with increasing SOC on agricultural land, which cannot currently be adequately quantified. Efforts to quantify this value would serve to incentivise individual efforts to build the national SOC stock.

2.6. Strategies for increasing SOC

Since Australian soils are relatively deficient in SOC, in principle it should be easier to boost SOC levels than in soils in other countries that are closer to SOC saturation. However, the majority of Australian agricultural land is used for grazing on native vegetation (3,678,668 km^2) and is remote and marginal, while the area of actively managed agricultural land is comparatively small (977,875 km^2).[22]

Unimproved grazing land contains 8.96 Gt of SOC, which is 35% of the Australian total[23]. Globally, grazing lands are estimated to contain 10-30% of the world's SOC[24], so Australia has potentially more to gain than most by increasing SOC on its grazing land.

The total stock of SOC in the 3,678,668 km^2 dedicated to grazing on native vegetation is 8.96 Gt[25], giving an overall average of 24.35 t/ha. Therefore, achieving the objective of the 4/1000 Initiative on Australia's unimproved grazing land would require that SOC be increased by 0.1 t/ha annually.

It is thought that well managed grazing stimulates the growth of herbaceous species and improves nutrient cycling in grassland ecosystems, resulting in higher SOC. In the USA, annual burning and grazing of tallgrass prairie for 10 years increased SOC by 0.22 t/ha/year. N fertilisation of the tallgrass prairie increased SOC by 1.6 t/ha in a single year. It has been estimated that SOC in the 183 million ha of US rangelands could be increased at the rate of 0.1 t/ha/year through improved management practices[26].

In Australia, modelling results published by the CRC for Greenhouse Accounting have shown that SOC is strongly dependent upon stocking rates and the frequency of drought events. Using historical climate data from 1889-1999 and 1997 stocking rates, the modelling suggested a continued decrease in SOC at ~0.04 – 0.08 t/ha/year, with large regional differences[27].

Currently, efforts are under way to introduce or re-establish salt- and drought-tolerant palatable plants, such as saltbush and tagasaste, to improve the soil health of marginal and degraded lands while allowing for stocking densities to be maintained. Given the prevailing lack of water across vast swathes of Australian grazing land, there appears to be limited scope for significant increases in SOC in these areas[28].

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[21] Sparling *et al*. 2006

[22] Viscarra Rossel *et al.* 2014

[23] *Ibid*.

[24] Schuman *et al*. 2002

[25] Viscarra Rossel *et al.* 2014

[26] Schuman *et al*. 2002

[27] Hill *et al*. 2006

[28] Sanderman *et al*. 2010

In Australia, the main emphasis under the 4/1000 Initiative will need to be on improving the SOC stocks of actively managed land. The total stock of SOC in the 977,875 km^2 dedicated to horticulture, cropping and improved grazing is 4.23 Gt[29], giving an overall average of 43.23 t/ha. Therefore, achieving the objective of the 4/1000 Initiative on Australia's actively managed agricultural land would require that SOC be increased by 0.17 t/ha annually.

In general, any practice that increases crop yields, as long as the harvest index and/or grazing pressure remains steady, should result in increased C inputs to the soil. However, practices such as irrigation and fertilisation will also stimulate microbial activity, leading to increased decomposition rates. The balance between increased inputs and increased decomposition will dictate how much, if any, C will be sequestered under these management practices.[30]

There is a range of recommended strategies for increasing SOC levels in existing cropland. Table 2 below provides a comparison between traditional and recommended management practices.

Traditional methods	**Recommended management practices**
Biomass burning and residue removal	Residue returned as surface mulch
Conventional tillage and clean cultivation	Conservation tillage, no till and mulch farming
Bare/idle fallow	Growing cover crops during the off-season
Continuous monoculture	Crop rotations with high diversity
Low input subsistence farming and soil fertility mining	Judicious use of off-farm input
Intensive use of chemical fertilisers	Integrated nutrient management with compost, biosolids and nutrient cycling, precision farming
Intensive cropping	Integrating trees and livestock with crop production
Surface flood irrigation	Drip, furrow or sub-irrigation
Indiscriminate use of pesticides	Integrated pest management
Cultivating marginal soils	Conservation reserve program, restoration of degraded soils through land use change

Table 2: Traditional farming versus recommended practices for increasing SOC[31]

A meta-analysis of 74 publications[32] on the effects of land use changes on SOC stocks found that SOC was reduced by: changes from pasture to plantation (-10%), native forest to plantation (-13%), native forest to crop (-42%) and pasture to crop (-59%). On the other hand, SOC stocks were increased by: changes from native forest to pasture (+8%), crop to pasture (+19%), crop to plantation (+18%) and crop to secondary forest (+53%). A reasonable summary is that changing land use from cropland to pasture or cropland to permanent forest result in the greatest gains of SOC[33].

Table 3 below shows the SOC accumulation rates that have been reported by application of the recommended management practices in Australia.

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[29] Viscarra Rossel *et al.* 2014

[30] Sanderman *et al*. 2010

[31] Table 7 from Lal 2004

[32] Guo and Gifford 2002

[33] Stockmann *et al*. 2013

Agricultural system/Management practice		**SOC sequestration rate**	**Reference**
No-till, stubble retained		0.024 t C/ha/year	Dalal & Chan 2001[34]
Improved ley pasture		0.14 t C/ha/year	
Sugarcane trash retention		0.14 t C/ha/year	
Cotton		0.07 t C/ha/year	
Manure application		0.27 t C/ha/year	
Average over all cropping systems		0.14 t C/ha/year	
Long fallow wheat-sorghum rotation	No-till	No change	Young *et al*. 2009[35]
Continuous winter cereal	No-till	No change	
Intensive cropping (>1 crop/year)	No-till	Some accumulation of SOC observed	
Perennial pasture		~0.35 t C/ha/year[36]	Sanderman *et al*. 2010[37]
Crop rotation		Ave 0.18 t C/ha/year (range 0 – 0.51)	
Stubble retention		Ave 0.13 t C/ha/year (range -0.56 – 0.90)	
Reduced tillage		Ave 0.25 t C/ha/year (range -0.08 – 0.77)	
Cropping to pasture		0.30-0.60 t C/ha/year	

Table 3: SOC accumulation rates from recommended management practices in Australia

The Sanderman *et al*. (2010) study represents the most comprehensive review available of published field trial data in Australia. It is noteworthy that the average SOC accumulation rates listed for crop rotation, stubble retention and reduced tillage are derived from a very broad range of actual crop responses, from a loss of SOC through to dramatic gains. Further analysis of the data reveals that the dramatic gains were achieved with (a) cotton, where stubble incorporation was used instead of burning, and (b) sugarcane, where trash blanketing was used instead of burning. That is, the highest SOC gains were made with retention of crop residues with high water availability.

This review ranked the management options in terms of their potential to build SOC, from lowest to highest, as shown in Table 4 below.

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[34] For rainfed cropping systems in the Australian wheat belt, including cotton and sugarcane.

[35] Replicated field experiments from 1994 to 2000.

[36] Single trial in sandy soil of Western Australia

[37] Review of Australian agroecosystems.

Management option	SOC benefit	Justification
Reduced tillage	0	Reduced till has shown little SOC benefit
Stubble retention	+	Greater return to the soil should increase SOC stocks
Crop rotation	+	Cover crops mitigate C losses during fallow periods
Cropping to pasture	+/++	Pastures generally return more C to soil than crops
Perennial pasture	++	Perennial grasses return C throughout the year, but studies lacking
Organic matter and other offsite additions	++/+++	Direct input of C, often in a more stable form, into the soil; additional stimulation of plant productivity
Restoration of degraded land	+++	Active management to replant native species often results in large C gains

Table 4: Effectiveness ranking of recommended management practices[38]

For cropping-based farming systems, management options such as stubble retention, reduced tillage and crop rotation are unlikely to achieve the increases of SOC called for under the 4/1000 Initiative. The exceptions to this are trash retention in cotton and sugarcane systems.

If plant photosynthesis is used as the sole means of drawing down C from the atmosphere, then the best results will be achieved if crops are converted to continuous pasture and degraded land is restored by planting native vegetation. Neither of these options are readily applicable to cropping-based farming systems.

The evidence suggests that the most effective strategy for building SOC in cropping-based farming systems is to provide supplementary C in the form of manure or other C-rich offsite additions.

The modelling work done by Dalal and Chan (2001) that the application of all the recommended management practices in Australian rainfed cropping systems could achieve an average soil C sequestration rate of 0.14 t/ha/year (see Table 3 above). This is an optimistic estimate, as the actual rates will be constrained by local environmental conditions.

At best, this implies a shortfall of 0.3 t/ha/year from the 4/1000 Initiative target, which would have to be provided through supplementary soil amendments. With 977,875 km^2 of actively managed land to be treated, this implies that at least 29 million tonnes of extra C will need to be provided each year Australia-wide. This represents a significant market opportunity for efficient C-building soil amendments.

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[38] Sanderman *et al*. (2010)

2.7. Constraints on building SOC in Australia

The productivity of many Australian agricultural soils are constrained by chemical factors such as acidity, alkalinity, salinity and sodicity. Soil pH is a very important factor affecting productivity, through its influence of the availability of nutrients to both plants and soil micro-organisms. For most plants, the ideal soil pH is 6 - 7.5, although many will tolerate pH 5.5 - 8.5. Strongly acidic soils reduce plant growth through aluminium and/or manganese toxicity and an inability to utilise molybdenum and phosphorus. Alkaline soils are associated with induced deficiencies of zinc and iron.

2.7.1. Acidic soils

Naturally acidic soils generally occur in areas where rainfall exceeds 450 mm/year, affecting some of the most productive agricultural land in Australia. Estimates suggest that 33 million ha of land have a pH of less than 4.8, with about half of these soils occurring in New South Wales and Victoria[39].

The pH of the surface soils in Victoria ranges from pH 4 to pH 10, as shown in Figure 1 below. Surface soil pH is generally acidic in the Eastern and western Uplands, the Strzelecki and Otway Ranges and north-eastern Victoria. Soil pH is high and alkaline in north-western Victoria, i.e. Mallee and Wimmera. These extremes in acidity and alkalinity present problems for the production of many agriculturally important plant species in Victoria.

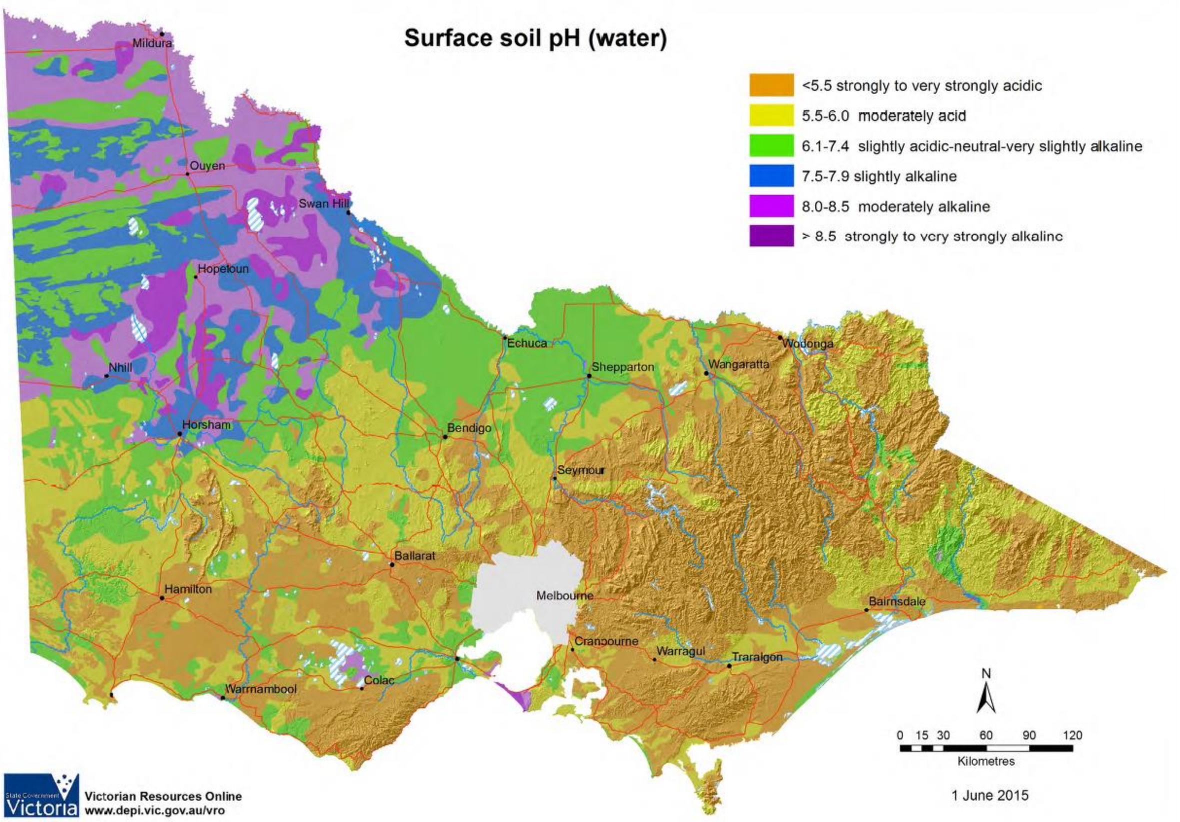

Figure 1: Surface soil pH (water) in Victoria[40]

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[39] Scott *et al*. 2000

[40] http://vro.agriculture.vic.gov.au/dpi/vro/vrosite.nsf/pages/surface-soil-pH

The application of limestone (lime) to ameliorate soil acidity is an established practice. Lime is also used to neutralise the acidity of fertilisers such as elemental sulphur and ammonium fertilisers. The requirement for lime addition to adjust the soil pH can be substantial, generally 3-5 t/ha. Neutralisation of fertilisers requires additional lime, at the rate of 0-3 kg/kg S applied or 0-7 kg/kg N applied. The high cost of lime applications and the low profitability of grazing enterprises has resulted in poor adoption of liming by graziers[41].

2.7.2. Alkaline sodic soils

There is a close relationship between high pH and high exchangeable sodium percentage (ESP) in soils. A simplified sequence of events leading to soil alkalinity is as follows: Sodium ions (Na) in ground water or irrigation waters, combined with and excess of evaporation over precipitation, causes an increase in salt concentrations in soil solution and in the exchangeable Na. Subsequent dilution of the soil solution by rain water or irrigation causes desorption and hydrolysis of the weakly adsorbed Na with a rise in pH[42].

The constraints to crop production on the alkaline to neutral soils in Australia principally include salinity, sodicity, high concentrations of soluble boron (B) and alkalinity. However, alkalinity itself is not usually a direct constraint, although it does influence pH-dependent factors such as nutrient availability[43].

In **saline** soils, sodium joins with chlorine to form a salt, NaCl. The presence of salt in the soils reduces the availability of water to plants and, at high enough concentrations, can kill them. In **sodic** soils, much of the chlorine has been washed away, leaving behind the sodium ions attached to clay particles in the soil. Soils can be saline and sodic at the same time.

Soils are considered sodic when their exchangeable sodium percentage (ESP) is more than 6%. Sodium ions cause dispersion of soil aggregates and a collapse of the pore structure, resulting in hard-setting, crusting soils that reduce water infiltration and increase water runoff, erosion and surface waterlogging[44]. Crop productivity is reduced through poor seed germination and crop establishment, and water stress due to decreased water intake into the soil. A large proportion (86.2%) of sodic soils in Australia have dense alkaline subsoils that present a barrier to root growth[45].

In Australia, it is estimated that salinity affects an estimated 17 million ha, while sodicity affects approximately 340 million ha of land[46], or about 28% of the land surface[47]. In Victoria, sodic soils are estimated to occupy at least 13.4 million ha, representing at least 73% of the agricultural land. The distribution of the major sodic soil classes in Victoria is illustrated in Figure 2 below.

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[41] Scott *et al*. 2000

[42] Mashhady and Rowell 1978

[43] Adcock *et al*. 2007

[44] Foster *et al*. 1993

[45] Rengasamy and Olsson 1991

[46] Wong *et al*. 2010

[47] Jayawardane and Chan 1994

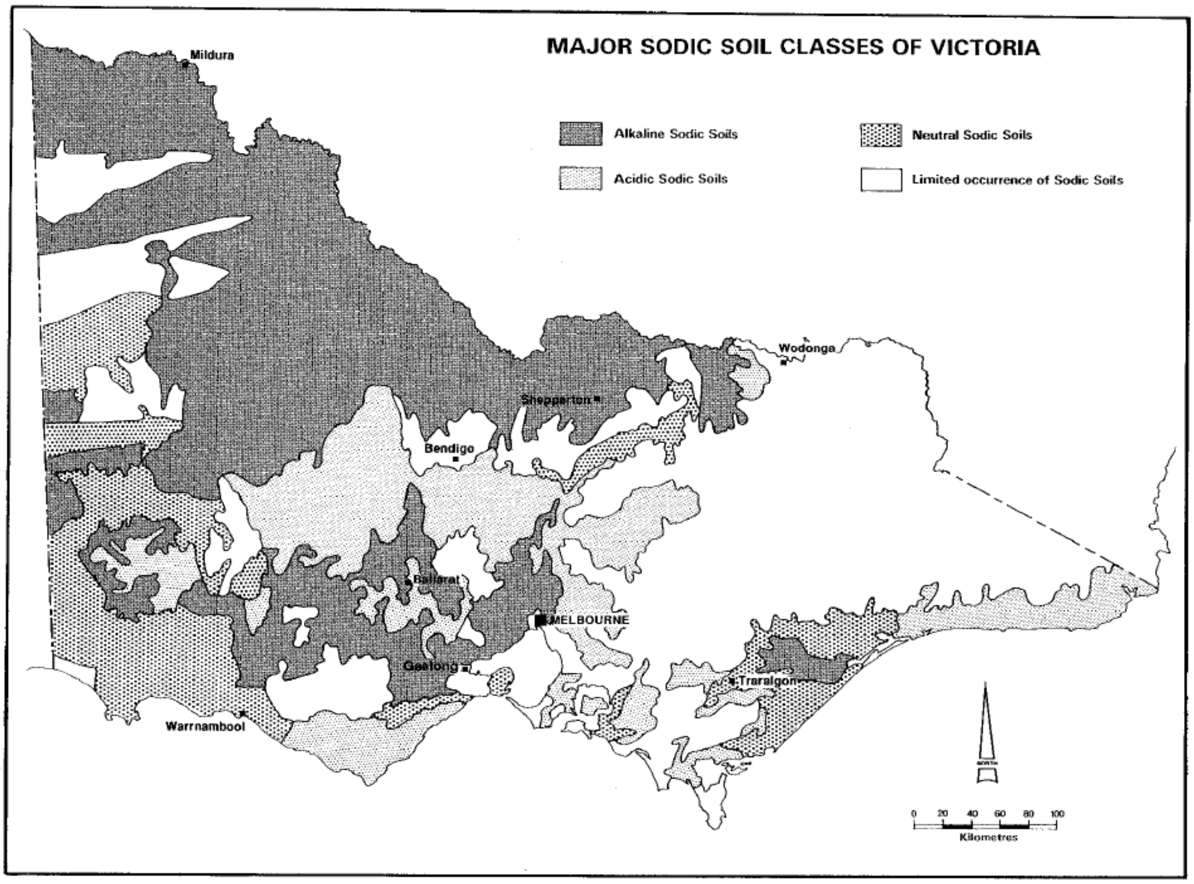

Figure 2: Distribution of sodic soils in Victoria[48]

The standard method to ameliorate soil sodicity is through the application of gypsum (calcium sulphate). The calcium ions of gypsum displace the sodium ions in the soil and help to restore soil structure. However, the commonly recommended application rates (2-5 t/ha) correspond to the minimum quantity required to achieve complete surface coverage, and are inadequate to achieve permanent results. Consequently, repeated gypsum applications are required[49].

Sodic soils can also be improved using surface amendments of organic materials, such as cereal straw, piggery bedding litter and composted feedlot manure. It has been suggested that the improved soil structure was due to complexation of sodium ions by soluble organic materials leaching from the surface amendments[50].

It has been demonstrated that the most effective way to improve sodic soils is through a combination of gypsum and organic matter[51]. The interaction of calcium with soluble organic compounds forms ‘Ca-humates’ which increase the SOC and stabilise the soil structure[52]. The most rapid structural improvement is achieved using organic matter with the greatest capacity to stimulate microbial activity, as measured by soil respiration. The total cumulative soil respiration, as opposed to the rate of soil respiration, appears to be important for the formation of stable soil aggregates. Organic

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[48] Foster *et al*. 1993

[49] Jayawardane and Chan 1994

[50] Adcock *et al*. 2007

[51] Clark *et al*. 2009

[52] Muneer and Oades 1989

materials of low C/N ratio decompose quickly and provide a rapid but ephemeral effect on soil structure, while materials that are more resistant to decomposition take longer to form aggregates but are more likely to have a prolonged effect[53].

2.7.3. Water availability

In addition to constraints by soil chemical factors, the productivity of Australian soils is also limited by water availability. Figure 3 below shows that, over the past 16 years (the period of the current millennium), record low rainfall has been experienced over most of South West Western Australia, with serious to severe deficiencies widespread in northern and central Victoria, neighbouring parts of South Australia and New South Wales, and northern and western Tasmania. Patchy deficiencies are also evident in Queensland, most notably in western parts of the Darling Downs[54].

Research suggests that the long-term drying trend over southern Australia cannot be explained by natural variability alone, suggesting the need for adaptive agricultural practices.

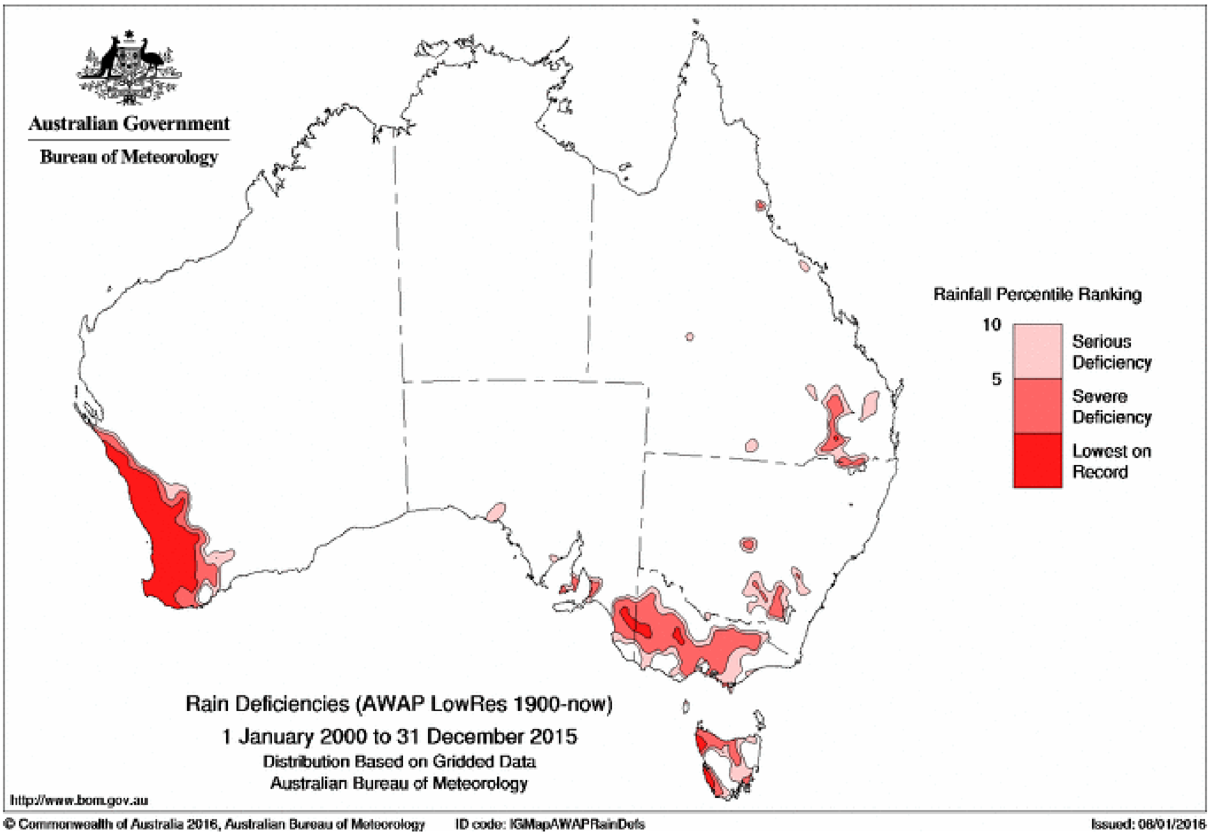

Figure 3: Areas of long-term rainfall deficiency in Australia[55]

In areas of long-term rainfall deficiency, water scarcity hinders plant growth and the input of organic matter is minimal. Under such nutrient limitation, the activity of the soil microbial community is highly

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[53] Clark *et al*. 2009

[54] http://www.bom.gov.au/climate/drought/

[55] *Ibid*.

compromised, as is the biogeochemical cycling of nutrients. As well as reducing the productivity of agricultural soils, these factors also cause severe soil degradation and desertification[56].

Agriculture under increasingly arid conditions requires the more efficient use of available water. It is well established that the water-holding capacity of soil increases with increasing SOC[57] and that amendment of soils with carbon-rich materials (e.g. compost, paper waste, poultry litter, peat, pine bark, lignite and biochar) can improve water availability and crop productivity under arid conditions[58]. The main barrier to large-scale deployment of such amendments is the costs associated with their production and transport.

Given that the productivity of Australian agriculture is constrained by soil chemistry (e.g. acidity, alkalinity, salinity, sodicity) and climate (e.g. drought), it is unlikely that application of the recommended management practices will be sufficient to deliver the desired carbon sequestration rates. Some areas may achieve higher than expected sequestration rates, but others will fall well below expectations.

This suggests the need for innovative new strategies to boost the rate of soil carbon sequestration above those achievable using practices such as those mentioned above. A promising approach is the "judicious use of off-farm inputs", as allowed in the recommended management practices, to accelerate the accumulation of SOC.

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[56] Bastida *et al*. 2015

[57] Rawls *et al*. 2003

[58] Warren and Fonteno 1993; Foley and Cooperband 2002; Mylavarapu and Zinati 2009; Uzoma *et al*. 2011

3. Victorian brown coal as a source of SOC

3.1. Victoria's brown coal resource

Victoria has one of the world's largest reserves of brown coal, estimated at 430 billion tonnes, of which 33 billion tonnes are considered potentially economic. This equates to a 500 year supply of economic brown coal at current usage rates[59]. Victorian brown coal is very clean compared to other international deposits, containing very low levels of ash (1-4%). It is also located close to the surface, so that the cost of mining is low.

Victorian brown coal has many physical and chemical properties in common with soil organic matter, including high water holding capacity, high humic content and good nutrient holding capacity. This is not surprising, as brown coal is a geologically young form of fossilised plant biomass.

The thick deposits of brown coal in the Gippsland Basin of Victoria were formed by progressive growth and subsidence of swamplands during the opening of Bass Strait, which took place between the Late Eocene (38-33.9 Ma) and Middle Miocene (16-11.6 Ma) epochs[60]. Victorian brown coal is regarded as an immature form of lignite, a soft brown combustible sedimentary rock formed from naturally compressed peat.

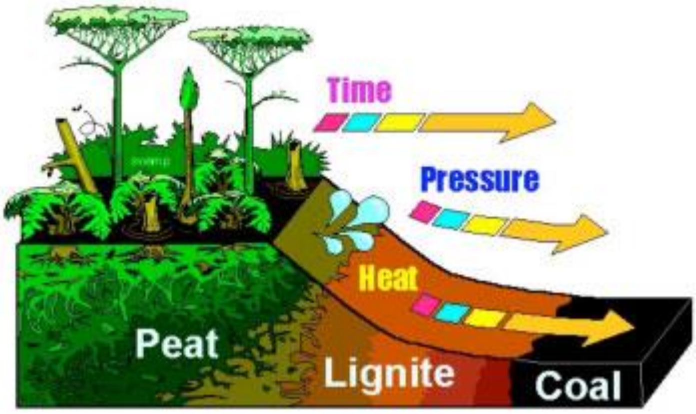

Figure 4: The coalification process[61]

The transformation of plant material into coal occurs through a process known as 'humification'. The principal changes that occur during humification are[62]:

(a) Reduction of the total water content.
(b) Increase in specific gravity.
(c) Increase of compaction.
(d) Decrease of pore space.
(e) Increase in the degree of decomposition.
(f) Colour changes towards dark brown and black.

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[59] Department of Primary Industries (2008). *Strategic policy framework for near zero emissions from Victoria's fossil fuels.* Victorian Government Position Paper October 2008

[60] Gloe and Holdgate 1991

[61] Source: https://reichchemistry.wikispaces.com/file/view/Ed_coal_formation.jpg/107175921/Ed_coal_formation.jpg

[62] Lüttig 1986

(g) Increase of the calorific value.

During the humification process, plant biomolecules (including lignin, polyphenols, melanin, cutin and proteins) are transformed by secondary synthesis reactions into humic substances. These humic substances comprise an extraordinarily complex, amorphous mixture of highly heterogeneous, chemically reactive yet refractory molecules[63].

The humification process also occurs in soil, transforming organic carbon into humic substances such as humic acid and humin. Rather than being high molecular weight polymers as previously believed, humic substances are associations of small heterogeneous molecules held together by relatively weak hydrophobic forces into only apparently high molecular sizes[64]. These humic substances represent the most persistent pool of SOC, with mean residence times of several hundred years[65]. The process of conversion of refractory plant biomolecules into humic substances is poorly understood, but is known to be dependent on degradation and transformation by white rot and litter decomposing fungi, in the presence of other easily degradable C sources[66].

Brown coals are reported to contain up to 80% of extractable humic material[67], with structures very similar to those found in soil. As-mined brown coal contains about 65% moisture, making it uneconomic to transport over significant distances. As an agricultural input, however, the coal would be dried to about 15% moisture, at which point it would contain 55% carbon. In dried form, Victorian brown coal is a highly concentrated form of the humified carbon that is widely deficient in Australian soils.

3.2. Building SOC with brown coal

The ultimate goal of using brown coal to increase SOC is to permanently sequester atmospheric CO_2, so as to contribute to a reduction in global warming. In order to achieve this, the following two objectives must be met:

a) There must be an overall net increase in the amount of C stored in the ecosystem; and
b) The extra C must be stable in the soil for long periods of time, preferably permanently.

In 2011, the Novel CO_2 Capture Task Force evaluated the potential for sequestering atmospheric CO_2 using humic/fulvic soil amendments. The Task Force concluded that "*the most effective and persistent method for increasing SOC is to removing any constraints to a naturally high net primary productivity (NPP). If these methods are not suitable or have already been implemented, addition of exogenous carbon may be considered. The energy and carbon balance and CO_2 life cycle analysis of exogenous carbon addition must be evaluated first, including the production and transportation of the exogenous carbon source itself. The impact of the exogenous carbon source on the… soil carbon rates of change and equilibrium must also be evaluated through R&D and soil carbon measurement activities.*"[68]

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[63] Grinhut *et al*. 2007
[64] Spaccini *et al*. 2002
[65] Piccolo 1996
[66] Grinhut *et al*. 2007
[67] Verheyen and Johns 1981
[68] Burgess et al. 2011, p. 29

This conclusion remains valid, although some new information has become available in the intervening years. The following sections provide the most up-to-date information available relating to the effectiveness of organic matter amendments for building SOC stocks.

3.2.1. Improvements to net primary productivity

In principle, using brown coal as a soil amendment can potentially accelerate the accumulation of SOC in two ways. In the short term, the quality of the soil will be improved, with better water-holding capacity and nutrient retention. This will lead to increased plant yields, and overall more photosynthesis and stabilisation of atmospheric CO_2 as SOC. Over the longer term, the coal will eventually be incorporated into the SOC pool, further increasing plant growth and photosynthesis.

In practice, however, there has been no research undertaken to investigate either the rate of SOC increase by brown coal amendments, or how much the productivity of plant growth may be increased.

In fact, there seems to have been only one study in which these questions were considered, involving compost addition to grassland soils in California. The study included the two dominant grassland types in California: (i) the valley grasslands of the hot, dry interior and (ii) the grasslands of the milder, wetter coastal region. An organic green waste compost was applied at 14.2 t C/ha, and SOC and NPP were monitored over the following 3 years.

It was found that the organic matter amendments significantly increased total NPP by 2.0 ± 0.8 t C/ha at the coastal grassland and 4.7 ± 0.7 t C/ha at the valley grassland over the 3 year study period. Surface application of compost increased both above- and below-ground productivity over the three growing seasons, leading to greater annual C inputs from vegetation. The positive plant production response showed no signs of diminishing over time.[69]

Three years after a single application of composted green waste, the SOC was increased by 26% at the valley grassland and by 37% at the coastal grassland. Organic matter amendments decreased the rate of C loss, so the rate of net ecosystem C storage increased by 25-70%. When including C added in the compost, the amended plots showed an increase in net ecosystem C storage of 17.7 ± 1.4 and 13.8 ± 1.8 t C/ha at the valley and coastal grassland, respectively. A large proportion (65-88%) of the additional ecosystem C was due to the direct addition of C from the compost amendment.[70]

This study provides compelling evidence that organic carbon amendments can increase SOC by both (i) direct C addition and (ii) increased vegetation input resulting from enhanced plant productivity. It seems reasonable to assume that similar results could be achieved using brown coal amendments, although research is needed to confirm this.

3.2.2. Rate of accumulation of SOC

The stock of organic carbon in the soil is not a static reservoir, but rather is a dynamic pool in constant flux. At any point in time, the rate of accumulation of SOC is the difference between the rate of input and the rate of output. In undisturbed biosystems, a balance is reached between inputs and outputs,

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[69] Ryals *et al*. 2014

[70] Ryals and Silver 2013

and the SOC stabilises at a particular level. Any change of land use shifts the balance and the SOC stabilises at a new level.

For example, if the rate of C input reduces, then the SOC will gradually decline and will eventually reach a new steady state. This process is illustrated in Figure 5 below.

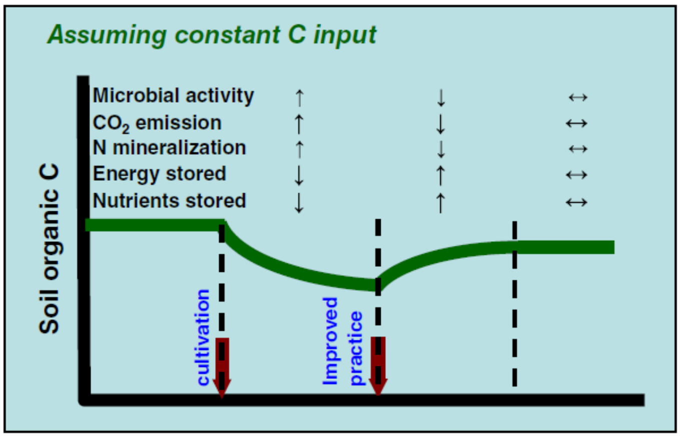

Figure 5: Dynamic response of SOC to changing C inputs[71]

If the rate of C input is increased the SOC will rise again. However, the supply of additional C must be maintained over time if a higher steady state SOC level is to be achieved.

There has been very little research done to investigate the effectiveness of C amendments to boost SOC levels, or the timeframes involved. The best example is provided by the Broadbalk Experiment at Rothamsted, UK, where farmyard manure was added to winter-wheat cropping fields for over 150 years. Two separate experiments are still under way, with one having started in 1843 and the other in 1885. In both cases, farmyard manure (FYM) was/is applied at the rate of 35 t/ha annually. The resulting increase in SOC is illustrated in Figure 6 below.

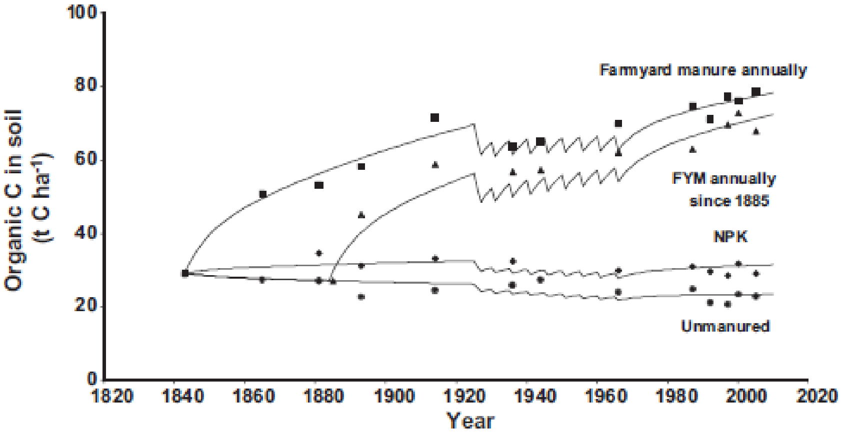

Figure 6: Changes in SOC (0-23 cm) on Broadbalk, for plots given 35 t/ha farm yard manure (FYM) annually since 1843 (■) or 1885 (▲), and those given mineral fertilisers only (◆), and the unmanured control (●). Solid lines derived from RothC model[72]**.**

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[71] Figure 3 from Janzen 2015

[72] Figure 2 from Powlson *et al*. 2012

In both experiments, the SOC increased continuously until 1920, although the greatest rate of SOC increase occurred over the first 20 years. During the period 1926-1966 all the plots on Broadbalk were bare-fallowed one year in five, to control weeds. There was a small decline in SOC during this period, but SOC levels rose again when regular FYM applications were resumed, and were still rising in 2005. If the soil had not had fallow years, the annual rate of SOC increase in latter years would almost certainly have been less[73].

The results of the Broadbalk experiment demonstrate that it takes many years to build the SOC stock to a new equilibrium level, and that the SOC level can fall quickly if regular amendments with additional C are not maintained.

3.2.3. Persistence of SOC from brown coal amendments

As well as being dependent on the rate of carbon amendments added to the soil, the equilibrium SOC concentration also depends on the rate at which the carbon is converted back to CO_2. If the SOC is relatively persistent in the soil, then a higher equilibrium SOC concentration can be achieved for a given rate of input.

Previously, it was thought that the decomposition of SOC was largely determined by the molecular structure of the organic compounds. Simple sugars and aliphatic groups that are readily metabolised by soil microbes were regarded as 'labile', while more resistant compounds such as lignin were regarded as 'recalcitrant'. It was thought that the SOC pool could be increased by selectively increasing the proportion of recalcitrant carbon material in the soil.

However, a new scientific view of SOC dynamics has emerged over the past decade, as summarised in Figure 7 below.

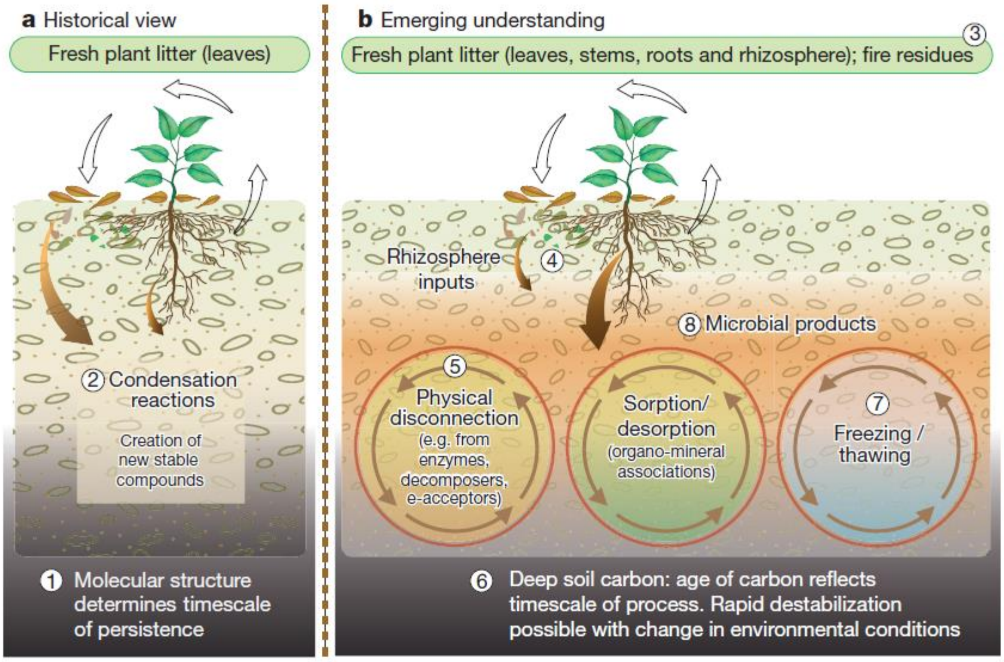

Figure 7: Comparison of historical and emerging views of soil carbon cycling[74]

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[73] Powlson *et al*. 2012

[74] Figure 3 from Schmidt *et al*. 2011

The explanation for this diagram by the original authors is reproduced as follows:

> *The historical view **(a)** has emphasized above-ground plant carbon inputs and organic matter in the top 30 cm of soil. Stable organic matter is seen to comprise mainly selectively preserved plant inputs and de novo synthesis products like humic acids, whose chemical complexity and composition render them nearly inert relative to microbial degradation.*
>
> *The emerging understanding **(b)** is that the molecular structure of organic material does not necessarily determine its stability in soil (1; molecular structure). Rather SOC cycling is governed by multiple processes (5) shaped by environmental conditions (such as physical heterogeneity). Plant roots and rhizosphere inputs (4; roots) make a large contribution to SOC, which is mainly partial degradation and microbial products and fire residues (3) rather than humic substances (2). The vulnerability of deep soil carbon (6; deep carbon) to microbial degradation (8; soil micro-organisms) in a changing environment, such as thawing permafrost (7; thawing permafrost) remains a key uncertainty.*[75]

These insights suggest that the molecular structure of plant inputs and organic matter has a secondary role in determining carbon residence times over the longer term, and that carbon persistence instead arises through interactions between compound chemistry, reactive mineral surfaces, climate, water availability, soil acidity, soil redox state and the presence of potential degraders in the immediate microenvironment. This does not mean that compound chemistry is not important for decomposition rates, just that its influence depends on environmental factors.[76]

It has been established that German brown coal is both mineralised and humified by soil micro-organisms, and progressively adds to the SOC pool[77]. The rate at which this occurs will depend on a wide range of factors, as listed above. Stimulation of soil microbes that can degrade brown coal is an important factor, as discussed in the following section.

The information available suggests that brown coal can be converted to SOC in a relatively short time. The persistence of the organic carbon in the soil will then depend upon the way that the land is managed. Any change to the carbon inputs and outputs will affect the balance of carbon in the soil. Changes to land use can include managed conditions such as tillage, fertilisation, irrigation, etc., and uncontrolled conditions such as fire, flood and drought[78].

In any particular location and set of land management conditions, long-term experimental studies are needed in order to properly understand the persistence of organic carbon in that soil.

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[75] Schmidt *et al*. 2011

[76] *Ibid*.

[77] Rumpel and Kögel-Knabner 2002

[78] Burgess *et al*. 2011

3.2.4. Conversion of brown coal to SOC

i) Physical degradation of brown coal

Brown coal is a poorly unconsolidated mass of plant remains that has very low mechanical strength. As shown in Figures 8 and 9 below, lumps of freshly-mined brown coal exposed to the air for several months will crumble to small particles, through a repeated process of drying, shrinking and cracking.

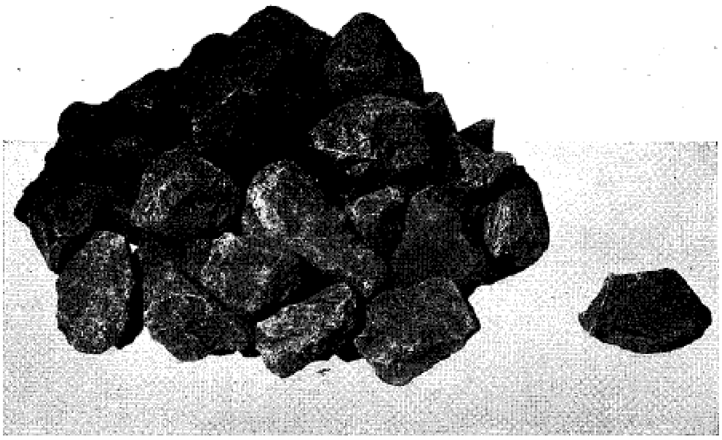

Figure 8: Brown coal from North Yallourn open cut, freshly mined (50- to 75-mm lumps)[79]

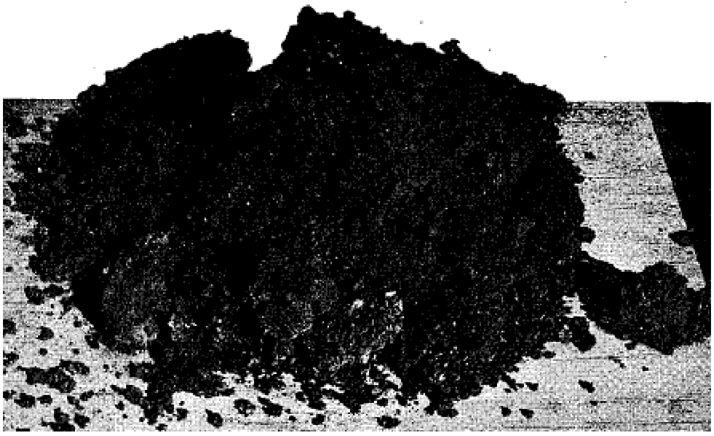

Figure 9: Coal heap shown in Figure 5 after exposure in open air for 64 days[80]

A similar process occurs when brown coal is incorporated into the soil, through repeated cycles of wetting and drying.

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[79] Figure 2 from Herman 1952

[80] Figure 4 from Herman 1952

ii) Microbial degradation of brown coal

SOC is derived from two main groups of input materials: plant materials (and exudates) and microbial residues (and exudates). Plant-C inputs generally are degraded, assimilated and then biosynthesised by microbes prior to long-term SOC stabilisation. Microbial biomolecules such as carbohydrates and proteins initiate the formation of the organomineral-associations that stabilise and protect C in the soil, and are associated with the majority of organic C in the soil[81]. The amount of C that is ultimately stabilised depends on both protection of C within the soil matrix and how effectively the decomposer community converts C to biomass, relative to how much is lost in gaseous (CO_2 and CH_4) or soluble form[82].

Despite the fact that Victorian brown coal deposits are tens of millions years old, it is incorrect to think that they are resistant to microbial degradation. In nature, biodegradation of lignite occurs most rapidly where there is a thriving diversity of microbes in the soil, stimulated by the presence of readily-degraded plant litter[83]. Lignite is transformed into SOC at a rate dependent on the intensity of microbial activity in the soil[84]. In Poland, it was found that a single application of brown coal (5 t C/ha) increased the SOC from 7.6 g/kg to 15.3 g/kg in 10 years[85].

In Canada, it was found that a mixture of oxidised brown coal and green waste compost substantially increased SOC over a 2 year period, while oxidised brown coal alone had no effect on SOC concentration[86]. The difference can be attributed to the stimulating effect of the compost on the soil microbial community.

Brown coal can be biodegraded by a wide range of soil microorganisms, the most efficient of which are the litter-decomposing and white rot fungi. These fungi produce non-specific oxidising enzymes such as manganese peroxidase, lignin peroxidase and laccase which degrade the coal structure. In addition, bacterial species are able to solubilise brown coal through the production of alkaline metabolic products or the production of chelating compounds[87]. Under the right circumstances, the degradation process can be quite rapid. For example, it has been demonstrated that the fungus *Trichoderma atroviride* could solubilise 140 g of 1.5 kg German lignite in 40 days in an optimised bioreactor[88].

In the biodegradation process, the brown coal is not completely consumed by soil microbes. If this were the case, there would be a risk that the carbon could be lost as CO_2 to the atmosphere through microbial respiration. Instead, the coal is broken down into tiny but discrete particles that form part of the SOC. The microscopic brown coal particles are functional as SOC, and are similar in chemical composition to plant-derived SOC, but contain a relatively higher proportion of aliphatic carbon[89].

Thus, brown coal does not remain inert in the soil but is eventually broken down by soil microbes to become part of the SOC pool. Supplementing C-deficient soils with brown coal is an effective way to rapidly build SOC stocks. For example, in a field trial conducted by the Victorian Department of Primary Industries. Brown coal was applied at the rate of 10 t C/ha on two sequential crops of broccoli. At the

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[81] Ludwig *et al*. 2015

[82] Manzoni *et al*. 2012

[83] Rumpel and Kögel-Knabner 2004

[84] Rumpel and Kögel-Knabner 2004; Clouard *et al*. 2014

[85] Kwiatkowska-Malina 2011

[86] Bekele *et al*. 2015

[87] Ghani *et al*. 2015

[88] Hölker and Höfer 2002

[89] Schmidt *et al*. 1996

end of the trial, it was found that the brown coal treatment had significantly increased the SOC beyond that achievable with ‘standard grower practice’, whereas treatments with chicken litter, green organic compost and silage did not produce statistically significant increases[90].

The humic substances produced by biodegradation of brown coal play a crucial role in the formation of stable SOC. It is commonly believed that the accumulation of atmospheric CO_2 can be effectively offset by increasing the rate of photosynthetic CO_2 uptake by plants. However, C derived from CO_2 fixations exists mainly in rapidly cycling plant and soil carbon pools rather than being stabilised in the humus fractions[91]. The labile C is susceptible to further metabolism by soil microbes and eventually being returned to the atmosphere as CO_2. It has been demonstrated that these labile C compounds can be effectively stabilised as SOC through interactions with the highly hydrophobic humic substances derived from brown coal[92].

Thus, the humic substances released through microbial degradation of brown coal contribute to SOC in two ways, both by adding additional organic carbon to the SOC pool, and by increasing the proportion of photosynthesis-derived carbon that is stabilised as SOC.

3.2.5. Acceleration of biodegradation

The key to quickly converting brown coal to SOC is to actively minimise the bottlenecks to the microbial transformation process. Since biodegradation of brown coal requires intense microbial activity, the best results will be achieved when (i) the coal structure is susceptible to microbial degradation, (ii) the right microorganisms are present in abundance and (iii) their growth is not limited by other nutritional factors. Each of these factors is discussed below.

i) Use of oxidised coal

It has been observed that oxidation of coal allows it to be broken down more quickly by soil microorganisms[93]. Oxidation of brown coal involves the attack of aliphatic groups by oxygen, with the production of carboxyl, carbonyl and phenolic functional groups, as well as carbon dioxide and water. The oxidation process involves free radicals that also promote degradation of the coal structure[94]. As a result, oxidation increases the content of readily-extractable humic acid in the coal, making it more like soil organic material.

In general, the rate of microbial degradation on the same source of coal decreases from well-weathered to air-exposed to unexposed coals[95]. Well-weathered brown coal or lignite is known as ‘leonardite’, so this observation is consistent with the fact that leonardite has been used as a soil conditioner and organic fertiliser for many years.

Researchers have found that microbial degradation of coal can also be enhanced by controlled oxidation using a nitric acid solution or ozone[96]. These processes are discussed in detail in Section 4.

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[90] O’Halloran *et al*. 2011

[91] Piccolo *et al*. 1999

[92] Spaccini *et al*. 2002

[93] Scott *et al*. 1986

[94] Mulcahy *et al*. 1991

[95] Scott *et al*. 1986

[96] *Ibid*.

ii) Use of coal-solubilising microorganisms

Soils will generally contain a diverse population of microorganisms capable use using brown coal as a carbon source. However, if their presence has not been stimulated by the availability of lignin-rich plant litter, they may only be present at very low numbers, or in a dormant state. If so, and especially if other conditions are not favourable, it may take many years for the population of coal-solubilising microorganisms to slowly build to a thriving state.

Biodegradation of lignite can be accelerated by deliberately introducing microbial species that have been isolated from natural lignite exposures and mine sites. For example, selection of coal-solubilising microbes from the Morwell brown coal mine yielded 56 isolates which could utilise coal as a sole carbon and energy source, including fungi, bacteria and actinomycetes[97]. There has been a large amount of work done to isolate and utilise such microorganisms to liquefy coal in bioreactors, whereas only one recent publication, in 2015, as looked at co-application of lignite and coal-solubilising bacteria in soil[98].

The practical challenge is that coal-solubilising microorganisms represent a highly specialised, expensive input ingredient. The facilities required to produce bulk quantities of the microbial strains involved may not exist in Australia.

A more cost-effective approach may be to generate a mixed microbial population by composting brown coal with sawdust or mulch, thus using naturally occurring wood-decomposing microorganisms. This would have to be done as an actively monitored process, with controlled air flow to prevent overheating and death of the target microorganisms, but this can be accomplished in a fairly rudimentary manner.

Further research is required to quantify the costs and benefits associated with the use of selected coal-solubilising microorganisms to enhance the rate of SOC formation from brown coal.

iii) Supplementation with essential trace elements

Coal-degrading fungi utilise the enzymes manganese peroxidase, lignin peroxidase and laccase to attack the coal structure. Each of these enzymes requires metal ions either as part of their structure or as a co-factor: both lignin peroxidase and manganese peroxidase contain Fe^{3+} heme groups; manganese peroxide additionally requires Mn^{3+} as a co-factor; and laccase contains Cu^{3+}.[99]

The biodegradation of lignite can be accelerated to adding specific trace elements to assist the production and activity of lignolytic enzymes. For example, the degradation of lignite by the fungus *Trichoderma harzianum* was accelerated by supplementation with chelated forms of Fe, Mn, Zn, Cu, Co, Ca and Mg[100].

The elements Fe, Mn and Cu are also essential plant micronutrients, which means that they are considered to be essential to the growth of plants at low concentrations. The incidence of micronutrient deficiencies in crops has increased markedly in recent decades due to intensive

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[97] Ralph and Catcheside 1994

[98] Cubillos-Hinojosa *et al*. 2015

[99] Fakoussa and Hofrichter 1999

[100] Angelova *et al*. 2009

cropping, loss of top soil by erosion, losses of micronutrients through leaching, liming of acid soils, decreased proportions of farmyard manure compared to chemical fertilizers, increased purity of chemical fertilizers, and use of marginal lands for crop production. Micronutrient deficiency problems are also aggravated by the high demand of modern crop cultivars[101]. In Australia, deficiencies of Mn and Cu are common in sandy soils, and Fe deficiency occurs in soils enriched with calcium carbonate (e.g. Mallee soils)[102].

In normal cropping soils, it may be assumed that biodegradation of brown coal will be inhibited by competition by plants for essential trace elements. It is likely that supplementation with trace elements will be required to accelerate the conversion of brown coal to SOC, although research is required to confirm this.

iv) Provision of additional N, P and S

It has been found that the organic matter in soils around the world exhibits a fairly constant ratio of C: N: P: S[103]. There is a growing body of evidence that this stable soil organic matter originates from microbial detritus rather than directly from recalcitrant plant material, implying that C-rich soil inputs can only be transformed to stable SOC when there is a sufficient supply of N, P and S to support microbial growth. It has been demonstrated that addition of adequate nutrients to incorporated C-rich crop residues can increase the amount of new SOC formed by up to three-fold[104].

It has been estimated that sequestration of 10,000 kg C in humus requires the provision of 833 kg N, 200 kg P and 143 kg S[105]. Victorian brown coal contains very low levels of these elements, so they would have to be added in the form of supplementary fertiliser to avoid reducing the nutrient supply to plants.

A cautionary example of this issue is provided by a field trial conducted by the Victorian Department of Primary Industries. Brown coal was applied at the rate of 10 t C/ha on two sequential crops of broccoli. At the end of the trial, it was found that the brown coal treatment had significantly increased the SOC beyond that achievable with ‘standard grower practice’, whereas treatments with chicken litter, green organic compost and silage did not produce statistically significant increases. However, the brown coal applications resulted in reduced yields of broccoli. It was suggested that incorporation of brown coal had reduced the supply of nutrients to the plants[106]. This indicates that microbial activity was converting the brown coal to SOC, but in doing so was using nutrients at the expense of the crop.

If the aim of the 4/1000 Initiative is to increase the SOC of Australia’s actively managed agricultural soils by an average of 170 kg/ha annually, it will be necessary to add extra N, P and S fertiliser along with the brown coal, to ensure that crop yields are not detrimentally affected. 170 kg C equates to about 300 kg as-mined brown coal[107], so at a minimum it would be necessary to add 14.2 kg/ha N, 3.4 kg/ha P and 2.4 kg/ha S.

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[101] Fageria *et al*. 2002

[102] Holloway *et al*. 2008

[103] Kirkby *et al*. 2011

[104] Kirkby *et al*. 2014

[105] Himes 1998

[106] O’Halloran *et al*. 2011

[107] Dry mass content 350-400 kg/tonne FW; C content 68% DW

Thus, for optimum conversion of brown coal to SOC, it will be necessary to add a tailored fertiliser blend to ensure that crop yields are not affected. This suggests the potential for manufacturing a blended brown coal product specifically for building SOC in agricultural soils, containing N, P and S fertilisers, and ideally coal-solubilising microorganisms and trace elements as well.

3.3. Competitiveness of brown coal for building SOC

As explained in Section 1.6, it is unlikely that the target set by the 4/1000 Initiative will be achieved by relying on plant photosynthesis alone. The most effective way to increase SOC at the rates required is through the use of supplementary C-rich soil amendments. Conservatively, it was estimated that at least 29 million tonnes of extra C will need to be provided each year.

The common assumption is that compost is the best type of supplementary soil amendment. In Australia, the majority of commercially-available compost is produced at beef feedlots. Manure production from intensive cattle production is estimated at 0.9 tonne DM/head/year, and total manure production in Australia is approximately 1 million tonnes annually[108].

The farm gate price for feedlot compost from Australia's largest producer, Rivcow Environmental, ranges from $21.70/tonne at Charlton, Victoria[109] to $27.00 per tonne at Tabbita, NSW[110]. On average, the compost contains 31.2% moisture and 41.3% C (d.b.)[111], so the cost of C from feedlot compost is in the order of $76-95/tonne.

In contrast, Victoria has 33 billion tonnes of potentially economic brown coal, at a typical moisture content of 60-65% and 48% C (d.b.)[112]. The factory door cost for as-mined coal is about $10/tonne, so the cost of C from Victorian brown coal is about $52-60/tonne. Thus, brown coal is a far more economical source of C than feedlot compost.

Apart from cost, availability is also an important factor. Only around 1 million tonnes of feedlot manure is produced each year, which is far less than the quantity needed to achieve the target set by the 4/1000 Initiative. In contrast, there is enough brown coal available to supply 300 tonnes to every hectare of Australia's actively managed agricultural land.

There is simply no way that compost can be regarded as a viable way to increase SOC on Australian agricultural land at any significant scale. The only source of carbon that is available at sufficient scale, at an acceptable price, is the huge reserve of fossil carbon in Victorian brown coal.

Victorian brown coal is the best resource in Australia for rapidly building up the stock of organic carbon in agricultural soils. The challenge is to transform the coal into commercial products and deliver them to farmers at an acceptable price. There is potentially a huge market opportunity for businesses that can successfully meet this challenge.

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[108] Davis *et al*. 2012

[109] http://www.rivcow.com.au/Sites/Charlton_Site__VIC_/Pricing___Distributors.aspx

[110] http://www.rivcow.com.au/Sites/Tabbita_Site__NSW_/Pricing___Distributors.aspx

[111] Watts *et al*. 2011, Table 18, page 50

[112] Brockway and Higgins 1991

4. Agricultural uses for raw brown coal

Victorian brown coal is a relatively immature form of lignite, containing a naturally high proportion of humic substances. That is, it is a fossil reserve of well-humified plant material, making it very similar to the organic matter in soil. This section describes four agricultural applications for which as-mined brown coal can be used with minimal further processing: as a soil amendment, as a component in organomineral fertilisers, as a carrier for microbial biofertilisers, and for mitigation of feedlot emissions. Subsequent sections describe agricultural uses for oxidised brown coal, extracts of brown coal and brown coal fly ash.

4.1. Brown coal as a soil amendment

Brown coal has many desirable attributes for use as a soil amendment, including improved water-holding capacity and nutrient retention, and for improvement of acidic and sodic soils. These properties have been known for some time, but their commercial exploitation has only occurred at a relatively small scale:

- After work done at the Horticultural Research Institute in Knoxfield during the 1970s and '80s, Victorian brown coal was included in a patented potting mix marketed by Debco[113], where it is used to improve the water-holding capacity of the soil.
- A product known as 'Humus Plus 4', a 50:50 blend of Bacchus Marsh brown coal and shredded paper, is produced by the Calleja Group[114]. 'Humus Plus 4' is said to improve the availability of soil P, improve germination and root growth, and increase cereal yields[115]. 'Humus Plus 4' has been evaluated as a peat replacement in the horticulture industry. Positive results were obtained for mushroom production and as a horticultural potting mix. Further commercial development was reported to be under way[116].

The scientific basis for the use of brown coal as a soil amendment is reviewed below.

4.1.1. Improved water-holding capacity

Brown coal has been shown to increase the water-holding capacity of soil in proportion to the coal content[117]. In pot trials, the high level of water held by brown coal helped to prevent plants wilting under water stress conditions[118].

The effect of brown coal on water-holding capacity in a sandy soil was examined in field trials with lettuces. Fresh plant yields were found to be increased by up to 40% over the control and the soils were found not to dry out as quickly[119].

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[113] Drysdale and Nichols 1993

[114] http://maddingleybrowncoal.com.au/the-calleja-group

[115] http://humusplus4.com.au

[116] Molphy *et al*. 2001

[117] Sharma *et al*. 1993

[118] Beardsell *et al*. 1979

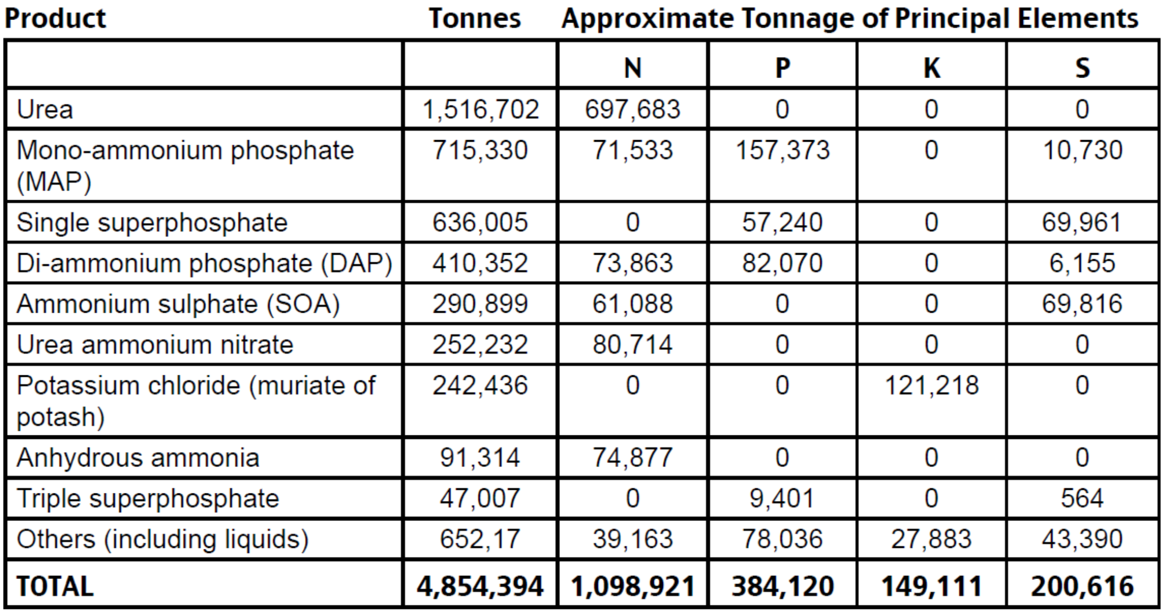
[119] Cullen 1971, cited in Heng *et al*. 1984

4.1.2. Improved nutrient retention

The organic matter in soil possesses a high cation exchange capacity (CEC). Cation exchange is a mechanism that facilitates the availability of nutrients for plant uptake. Hydrogen ions from the root hairs and soil micro-organisms replace nutrient cations from the exchange sites[120].

Brown coal has a high CEC and can effectively enhance soil fertility by helping to retain the available nutrients in the vicinity of plant roots. In pot trials, increased growth of tomato plants was observed in potting mixes amended with brown coal, which was attributed to its high CEC[121].

The retention of plant nutrients by brown coal offers the potential for more efficient use of chemical fertilisers. This is an area of great interest to Australian farmers, who collectively invest more than $3 billion in fertiliser each year[122]. Total sales of fertiliser in 2011 was 4,854,394 tonnes, as shown in Table 5 below.



Product	Tonnes	Approximate Tonnage of Principal Elements			
		N	P	K	S
Urea	1,516,702	697,683	0	0	0
Mono-ammonium phosphate (MAP)	715,330	71,533	157,373	0	10,730
Single superphosphate	636,005	0	57,240	0	69,961
Di-ammonium phosphate (DAP)	410,352	73,863	82,070	0	6,155
Ammonium sulphate (SOA)	290,899	61,088	0	0	69,816
Urea ammonium nitrate	252,232	80,714	0	0	0
Potassium chloride (muriate of potash)	242,436	0	0	121,218	0
Anhydrous ammonia	91,314	74,877	0	0	0
Triple superphosphate	47,007	0	9,401	0	564
Others (including liquids)	652,17	39,163	78,036	27,883	43,390
TOTAL	**4,854,394**	**1,098,921**	**384,120**	**149,111**	**200,616**

Table 5: Australian fertiliser sales in 2011[123]

The two most significant fertiliser elements used in Australia are phosphorus (P) and nitrogen (N) fertilisers. Research has indicated that the efficiency of these types of fertiliser can be increased by amending the soil with brown coal.

i) P fertilisers

Australia's ancient soils are generally poor in P, so the use of P fertilisers has been a necessary, widespread and long-term practice. However, the majority of the soluble P reacts with soil constituents and is 'fixed' as adsorbed P, sparingly-soluble precipitates of P, and organic P, some of

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[120] Heng *et al*. 1984

[121] Richards *et al*. 1986

[122] Dent 2010

[123] FIFA 2011

which is recalcitrant to mineralisation. Consequently, only 10-20% of applied P is directly used by plants in the year of application, and subsequent use of the residual P rarely exceeds 50%[124]. This means that more than half the P fertiliser applied each year is not available to plants and is effectively wasted. Significant improvements in P use efficiency would increase the profitability of the Australian agricultural industry.

Research effort over many years has established that carboxylic acid groups, such as those abundantly present in brown coal, increase phosphorus availability by changing the surrounding chemical environment, whereby carboxylic acids bind preferentially with solid-phase cations (including aluminium), decreasing the number of sites available for P sorption[125].

Researchers at Monash University have demonstrated the benefit of using brown coal amendments in acidic soils to decrease sorption of P fertilisers. It was found that the improved availability of the P fertiliser was due to a combination of factors relating to the brown coal structure, including increased local pH, reducing the number of sites for P sorption and increased microbial activity[126].

BCIA is currently supporting a PhD project at Monash University to further investigate the potential of Victorian brown coal to improve the utilisation efficiency of P fertilisers. To date, it has been demonstrated that a blend of triple superphosphate (TSP) with Victorian brown coal released more water-soluble P in an acidic Ferrosol soil than TSP alone[127]. Further research is ongoing.

ii) N fertilisers

Worldwide, the utilisation efficiency of N fertilisers is low, at only 33 to 36% for cereal grain production. N application rates often exceed crop N requirements because (i) soil N availability is not adequately accounted for and (ii) fertiliser form, placement, or timing does not synchronise with soil and crop N dynamics[128]. Unused mineral N does not accumulate in the soil, but is lost to the wider environment in the form of groundwater pollution and greenhouse gas emissions[129]:

- Surface applied ammonium and urea fertilisers can be converted to ammonia (NH_3), a volatile gas, particularly on calcareous and alkaline soils. Ammonia volatilisation is controlled by many soil and environmental factors but is directly proportional to ammonium (NH_4^+) concentration in soil solution. Ammonia has negative effects on the environment through deposition on neighbouring ecosystems and conversion to nitric acid.
- Microbial activity oxidises mineral N to nitrate (NO_3^-), which is very mobile in the soil and readily leached from the root zone into surface and ground water.
- Microbial activity further denitrifies nitrate to form nitrous oxide (N_2O), which is a potent greenhouse gas.

The loss of N fertiliser as N_2O is of particular concern, because its global warming potential is ~300 times greater than that of CO_2 and 12 times greater than that of methane. Typically, only about 1% of applied N fertiliser is lost as N_2O, but at a fertiliser application rate of 150 kg N/ha/year this equates to a greenhouse gas emission of 700 kg CO_2-eq/ha/year[130]. If agriculture is to play a role in reducing

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[124] Cornish 2009

[125] Schefe and Tymms 2013

[126] Schefe *et al*. 2008a,b,c

[127] Kargosha *et al*. 2014

[128] Mulvaney *et al*. 2009

[129] Shaviv and Mikkelsen 1993

[130] Venterea *et al*. 2012

global greenhouse gas emissions, it will be important to employ strategies to reduce N_2O emissions from N fertiliser use.

In soils, the primary mechanism of retention of NH_3 is through its acquisition of a proton and then subsequently being adsorbed as NH_4^+ on cation exchange sites on soil organic matter and clay[131].

Research with New Zealand brown coals has demonstrated that coals with high CEC can absorb NH_4^+, with sorption increasing at higher pH. It was suggested that this property may result in prolonged retention of N in the plant root zone, allowing greater plant uptake and reduced N leaching[132].

In 2009, the Birchip Cropping Group conducted a preliminary field trial to assess whether application of brown coal would allow less use of chemical fertiliser. The indicative results were promising, leading to a larger trial at Jil Jil in 2010. Replicated trials with wheat at two separate sites showed that a combination of brown coal (40-150 kg/ha) and 28 kg/ha monoammonium phosphate (MAP) resulted in statistically identical yields as the control with 40 kg/ha MAP[133].

BCIA is currently supporting a PhD project at Monash University to further investigate the potential of Victorian brown coal to improve the utilisation efficiency of N fertilisers. Preliminary soil column trials with urea-brown coal blends showed that ammonia gas release was suppressed. Furthermore, brown coal-urea blends showed a remarkable decrease in the daily emissions of N_2O from soil columns, compared to urea. The blends that included brown coal had lower N_2O and NH_3 emissions and maintained higher mineral N in soil. These results suggest that blending of urea with the coal can reduce gaseous NH_3 and N_2O emissions and retain more mineralised N in the soil, thus providing greater amounts of available N to crops[134].

Monash University is currently conducting field trials of urea-brown coal blends in conjunction with the NSW Department of Primary Industries.

4.1.3. Adjustment of soil pH buffering capacity

Brown coal contains high levels of acidic carboxylic and phenolic groups, which can be utilised to increase the pH buffering capacity of the soil[135].

The pH of Victorian brown coals varies from one coal field to another, ranging from pH 3.5 at Rosedale to pH 6.5 (Bacchus Marsh), as shown in Figure 10 below.

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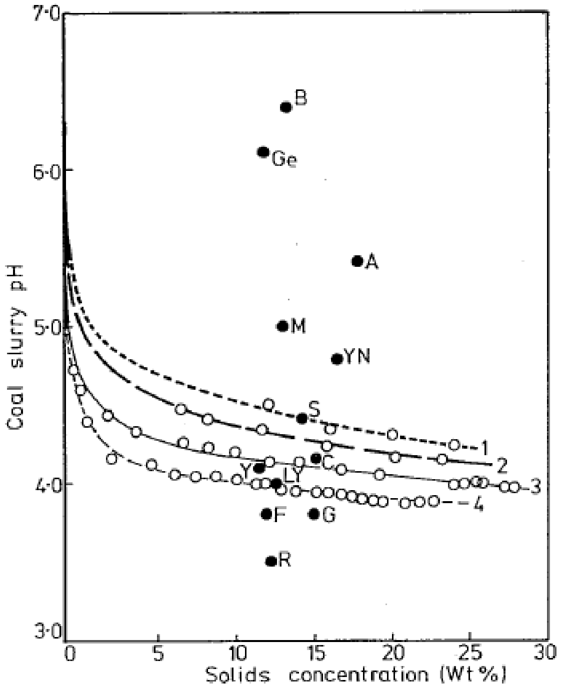
[131] Nommik and Vahdras 1982

[132] Paramashivam *et al*. 2016

[133] McClelland 2011

[134] Patti 2015

[135] Imbufe *et al*. 2004



● Field average results (33% suspensions)

A Anglesea B Bacchus Marsh
C Coolungoolun F Flynn
G Gormandale Ge Gelliondale
LY Loy Yang M Morwell
R Rosedale S Stradbroke
Y Yallourn YN Yallourn North

○ Morwell bulk sample measurements

1 Feb 1980 2 Jan 1982
3 Oct 1983 4 Apr 1987

Figure 10: pH variation of Victorian brown coals from different localities[136]

The outcome of using brown coal as an amendment will depend on the soil pH (pH_{soil}) If the brown coal pH is higher than pH_{soil}, then the coal will be expected to raise the overall pH of the soil. If the brown coal pH is lower than pH_{soil}, then amending with brown coal will make the soil more acidic[137].

An important consequence of soil acidity is Al phytotoxicity, which causes stunted root growth and reduced cop yields. In pot trials with wheat in a yellow sand from Carrabin in Western Australia, with a pH of 4.3, amendment of the soil with Victorian brown coal (pH 4.4) ameliorated the effect of acidity and Al toxicity, increasing root growth. Neither Banko coal from Indonesia (pH 3.8) nor Collie coal from Western Australia (pH 3.4) had any beneficial effect[138].

This suggests that brown coals from Bacchus Marsh and Gelliondale would be useful as an amendment on acidic soils, while all Victorian brown coals would be beneficial on alkaline soils.

On neutral soils, plant growth can be adversely affected by the low pH of brown coals. For example, in pot trials with tomato, marigold and corn plants, it was found that addition of coals to a fertile soil from Thorpdale gave enhanced plant growth over the soil alone. The healthiest growth occurred in the coal from the Gelliondale field (pH 5.4), while the worst was with coal from Loy Yang (pH 3.8). The addition of coal was observed to result in prolific root development[139].

Victorian brown coals can profitably be used on neutral soils if the acidity of the coal is neutralised by co-application with an alkaline agent. For example, the addition of lime has been shown to improve plant growth in a soil amended with Loy Yang coal[140]. Potentially, brown coal fly ash, which is strongly alkaline, could also be used to offset the low pH of brown coal. In Germany, brown coal fly ash has

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[136] Figure 4.5 from Woskoboenko *et al.* 1991

[137] Simmler *et al.* 2013

[138] Yazawa *et al.* 2000

[139] Heng *et al.* 1984

[140] *Ibid.*

been used for many years in the rehabilitation of brown coal mine sites, where the soil is rich in coal particles and sulphur-rich pyrite, with a pH of 1.7-3.5. It has been found that slow weathering of the ash (especially if it contains Ca-silicates) and a lasting release of bases results in a sustained liming effect. Moreover, the ash contains considerable amounts of magnesium and potassium and thus improves the nutrient supply in the soil[141].

4.1.4. Amelioration of sodic soils

Potentially, the structure of sodic soils can be improved by amendment with brown coal, simply through complexation of sodium ions by the carboxylic acid functional groups associated with the high CEC capacity of the coal. However, this benefit is likely to be transient, as the sodium ions will be displaced by acids released from growing plant roots.

Support for this is provided by results from a pot trial in which tomato, marigold and corn plants were grown in a saline soil from Bairnsdale. The high salinity of this soil meant that it was poorly suited to supporting plant growth. The addition of Gelliondale coal to the Bairnsdale soil gave little or no improvement in growth conditions. However, the life of the plants was generally prolonged in the presence of Gelliondale coal[142].

As discussed above, the most effective way to improve sodic soils is through a combination of gypsum and organic matter, particularly when the organic matter is readily degraded by soil microbes[143].

Researchers in Columbia have recently shown that lignite and coal-solubilising bacteria was more effective for amelioration of saline-sodic soil than lignite alone. The greenhouse experiment involved growing star grass on a saline-sodic soil, to simulate natural pasture. The soil was amended with 1% lignite (pH 5.6) together with coal-solubilising bacteria (CSB) isolated from lignite deposits. It was found that the addition of lignite markedly stimulated soil respiration, which was attributed to the high specific surface area and porosity of the coal promoting a favourable habitat for the growth and activity of soil microbes. The addition of CSB led to measurable increases in the concentrations of lignolytic enzymes and increased CEC. The exchangeable sodium potential (ESP), a measure of the sodicity of the soil, was reduced the most when a combination of lignite and CSB was applied[144].

This evidence suggests that there is potential to utilise a combination of brown coal and gypsum for the improvement of sodic soils, and that more effective results may be expected when selected CSB are applied at the same time.

4.2. Brown coal in organomineral fertilisers

Research in countries with large brown coal deposits – Poland, Romania, Turkey and Greece – suggests that are good opportunities for production of ‘organomineral’ fertilisers, incorporating brown coal and either organic or inorganic fertiliser ingredients.

In Poland, numerous experiments carried out over many years have proved the suitability of brown coal for the improvement of physical and chemical properties of light soils and for increasing crop

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[141] Katzur and Haubold-Rosar 1996

[142] Heng *et al*. 1984

[143] Clark *et al*. 2009

[144] Cubillos-Hinojosa *et al*. 2015

production[145]. Combinations of brown coal with chemical N fertiliser[146] and agricultural waste materials (e.g. turkey droppings, potato processing waste)[147] have been demonstrated with positive outcomes. A commercial product called 'Rekulter' (comprising 85% brown coal, 10% peat, 4% brown coal fly ash and 1% mineral fertiliser) was demonstrated to significantly increase SOC levels 7 years after application[148].

In Greece, organomineral fertilisers are being developed using brown coal from the Megalopolis Basin. These products utilise the high CEC capacity of the coal as a carrier for essential trace elements needed by plants. Research at the University of Athens has led to a spin-off company producing trial batches of fertiliser at a pilot plant facility. Field trials with the product have demonstrated "higher agronomical value compared with conventional chemical fertilisers containing the same nutritional elements"[149].

In Romania, organomineral fertilisers based on lignite have been investigated since the 1970s. In 2008, a pilot production facility was installed to allow production of 6 types of lignite-based fertiliser, with a capacity of more than 7,000 tonnes per year[150]. Two types of organomineral fertiliser have been reported[151]:

- Organomineral fertilisers obtained by activating lignite dust with phosphoric acid or sulphuric acid, followed by neutralisation with ammonia and granulation with urea-formaldehyde.
- Organomineral fertilisers comprising mixtures of coal dust and urea, or urea plus ammonium phosphates, granulated with urea solution.

The first type of organomineral fertiliser can be manufactured in large scale fertiliser facilities at a cost comparable to conventional chemical fertilisers. The second type can be viably produced in smaller facilities, with a cost 25-30% lower than conventional chemical fertilisers. Field trials with irrigated maize grown on soils with low SOC demonstrated that the organomineral fertilisers could achieve higher yields and significantly increased humus production than the conventional controls[152].

In the past, attempts have been made to develop similar organomineral fertiliser products in Victoria. During the 1970s, Scientific and Applied Processes Pty Ltd in Morwell patented a process to produce a slow-release N fertiliser from brown coal. The process involved dissolution of dry urea into as-mined brown coal, then oxidisation with hydrogen peroxide and neutralisation with alkali[153]. No public information is available regarding the efficacy of the product, and it is unclear whether it was ever commercialised.

During the 1980s, the Coal Corporation of Victoria developed and patented a compound fertiliser based on Victorian brown coal. The process involved blending organic or inorganic nutrients with brown coal, then digesting the mixture with acidic or alkaline material to improve the binding

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[145] Karczewska *et al*. 1996

[146] Kolota *et al*. 1991

[147] Hoffmann and Hoffmann 2007, Huculak-Mä Czka *et al*. 2010

[148] Kwiatkowska *et al*. 2008

[149] Chassapis *et al*. 2009

[150] Dorneau *et al*. 2010

[151] Dorneau *et al*. 2013

[152] *Ibid*.

[153] Vale 1977

properties and release rate of the nutrients[154]. No public information on the effectiveness of such products is available and the process was not commercialised.

Currently, Vicmill Natural Fertilizers, at Invergordon in northern Victoria, produces a range of blended organic and chemical fertiliser products which include powdered brown coal as a source of humates[155].

The research projects at Monash University currently being supported by BCIA have the developing the knowledge needed to optimise the performance of N- and P-containing organomineral fertilisers, to assist in the development of new commercial products.

There is clearly potential for a range of new organomineral fertilisers based on Victorian brown coal, and the scientific support exists to support such developments. Commercialisation of such products depends on having support from industry to undertake field trials to demonstrate the benefits to farmers from the use of such products.

4.3. Brown coal for mitigation of feedlot emissions

The high cation exchange capacity of Victorian brown coal has proven to be useful in reducing volatile gaseous emissions from beef feedlots, simply through application on the surface of the holding pens.

In Australia, beef cattle account for an estimated 58% of livestock GHG emissions, or 7% of total national emissions. Of a national beef cattle population of about 28.8 million, some 680,000 animals are on a feedlot at any one time[156]. Mass balance modelling that 86% of N in feedlot cattle rations is excreted onto the feedpad in urine and manure, and 62% of the intake N is volatilised from the feedpad to the atmosphere as ammonia, N_2O and other N compounds[157].

Ammonia is a toxic gas with a distinctive odour. Emissions of ammonia from feedlots are damaging to the environment, both aesthetically and through toxic effects to local vegetation through deposition. A small proportion of ammonia is converted to N_2O (1.25% is the standard IPCC conversion factor). This small proportion converts into a significant GHG impact when it is considered that average ammonia emissions from feedlots are 176 g/head/day and N_2O is 298 times more potent as a GHG than CO_2. The N_2O derived from feedlot ammonia emissions in Australia amount to ~163,000 t CO_2-eq annually, which is about 52% of the total feedlot CO_2-eq emissions[158]. Hence, mitigation of ammonia emissions from beef cattle feedlots would have a significant effect in the GHG footprint of this sector of Australian agriculture.

Researchers at the University of Melbourne have demonstrated that application of Yallourn brown coal on a beef feedlot pen, at the rate of 4.5 kg/m^2, decreased ammonia loss by 66%. It was estimated that the value of the retained N nutrient in the feedlot manure was $37/head/year[159]. Nationally, this represents about $25 million of reduced N fertiliser input costs to the farming sector, while significantly reducing the GHG emissions from beef cattle feedlots.

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[154] Heng and Perry 1989

[155] http://www.vicmill.com.au

[156] Denmead *et al*. 2014

[157] Watts *et al*. 2011

[158] Muir 2011

[159] Chen *et al*. 2015

Further work is justified to develop cost-effective brown coal products that can be utilised in beef cattle feedlots, which are predominantly in NSW and Queensland. Research is also required to determine whether similar benefits could be achieved in reducing ammonia emissions from other intensive animal husbandry industries, e.g. poultry and pork.

4.4. Brown coal as a carrier for biofertilisers

Biofertilisers are microbial preparations containing living cells of different microorganisms that colonise plants and increase the availability of plant nutrients and/or provide a growth stimulus. Biofertilisers are sold as live formulations of microorganism for application to the soil or to plant seeds or roots. The use of biofertilisers was first developed in Russia during WW2 and later the technology was transferred to India. The major use of biofertilisers in Australia is to promote nodulation of legume crops, through inoculation of seeds with nitrogen-fixing bacteria.

Biofertilisers are usually packaged with a solid carrier which helps to maintain a sufficient shelf life. The best carrier material is acknowledged to be peat, followed by lignite, charcoal and manure[160]. Peat is currently used in Australia, although good supplies are limited. In India, where peat is not available, lignite has been used as the main carrier since 1971[161]. There, calcium carbonate is used to neutralise the pH of the lignite (NIIR 2004).

As part of a BCIA-funded project at Monash University, the potential of Victorian brown coal was investigated as a carrier for a commercial biofertiliser product. It found shown that brown coal supported survival of nitrogen fixing bacteria during a 3-month storage period to almost the same level as a conventional peat carrier. A glasshouse pot trial with rice showed significant differences between treatments, with Victorian brown coal having the most positive effect on plant growth, particularly when inoculated with nitrogen fixing bacteria. The coal preparation also outperformed a conventional peat carrier as shown in Figure 11 below.

Figure 11: 30 day-old rice plants treated with microbial inoculant on peat or brown coal carriers[162]

Further research is required to assess the potential for commercial use of brown coal as a carrier for microbial biofertiliser products.

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[160] Bhattacharjee and Dey 2014

[161] Saranya *et al*. 2011

[162] Patti 2015

5. Agricultural uses for oxidised brown coal

As noted in Section 2.2.3 above, oxidation of brown coal increases the proportion of readily-extractable humic substances, making the coal more similar to soil organic matter and making it more readily degraded by soil microorganisms. Oxidation of coal can occur either naturally or through industrial processing, as described in the sections below.

It should be noted that there is no evidence to indicate whether the agricultural utility of Victorian brown coal is likely to be enhanced through deliberate oxidation. Victorian brown coal is younger and softer than many lignites found overseas, and may not require the extra processing needed elsewhere. It is currently unclear whether extra costs involved in chemical coal oxidation can be justified.

5.1. Naturally oxidised brown coal

Brown coal deposits in the shallow subsurface are slowly oxidised by air penetration of by oxidising ground water. This weathered brown coal is generally known as leonardite, named after A.G. Leonard, who did much of the early work on lignite outcrops in North Dakota. In general, leonardite differs from the parent coal deposit by containing higher amounts of ash and oxygen, and a higher proportion of base-soluble humic acids. Another difference is that leonardite does not readily burn[163].

In Victoria there are large areas where brown coals occur less than 100 m underground. Leonardite is likely to be found near the top of the coal seams, especially where the seam is closest to the surface. As shown in Figure 7 above, the brown coals found at Bacchus Marsh and Gelliondale both have pH >6, indicating that they have been exposed to leaching by groundwater. During leaching, they would also have been exposed to dissolved oxygen, so they may be more oxidised than coals from other locations.

Extraction of humic acid from Victorian brown coals (0.5M NaOH, 98 °C, 20 hrs) revealed that Bacchus Marsh coal contained more humic acid (68.6%) than Yallourn coal (41.1%) but less than Loy Yang coal (74.3%). This does not suggest that Bacchus Marsh brown coal can be classed as leonardite.

It is possible that genuine leonardite may be present at specific locations around Victoria where the coal seams are closest to the surface, but these have not yet been formally identified.

Leonardite has been used as a soil conditioner and organic fertiliser for many years[164]. As described in Section 3.1 above, as-mined brown coal is also a good soil conditioner. As described below, oxidation of Victorian brown coal can increase the proportion of readily-extractable humic acids. However, further research is required to determine whether such treatment would have sufficient functional benefits to warrant the extra costs involved.

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[163] Youngs *et al*. 1963, Broughton 1972

[164] Youngs *et al*. 1963

5.2. Oxidation with nitric acid

During the 1930s – before the widespread availability of ammonia produced by the Haber-Bosch process (“the detonator of the population explosion”[165]) – efforts were made to develop coal-based fertilisers by oxidation followed by treatment with ammonia. The advantages of such products were considered to be[166]:

- Good control and conditioning of the soil properties (mechanical properties, pH, retention of nutrient ions, microorganism activity, and heat capacity of the soil); and
- Controlled release of nitrogen.

It was found that, in some processes, a high nitrogen content could be achieved (~20%), but the fertiliser was unable to release N into the soil. This was attributed to the stable configurations of the fixed N, which were of the amidine or isoindol type[167]. The best results were obtained by oxidising lignite with nitric acid (20% by weight) and then ammoniation at 100 °C. This produced a product containing 10-12% N, of which 45% could be mineralised to nitrate in the soil[168].

After treatment of brown coal with nitric oxide the main constituents in the coal structure are polycarboxylic acids, nitrohydroxy and/or quinonoid acids. The result of the ammoniation reaction depends on the reaction temperature. In the scheme shown in Figure 12 below, at temperatures below 100 °C the reaction will be I → II, i.e. the corresponding ammonium salt is formed and the lactone ring remains unaffected. At higher temperatures reactions II → III → IV → V will take place.

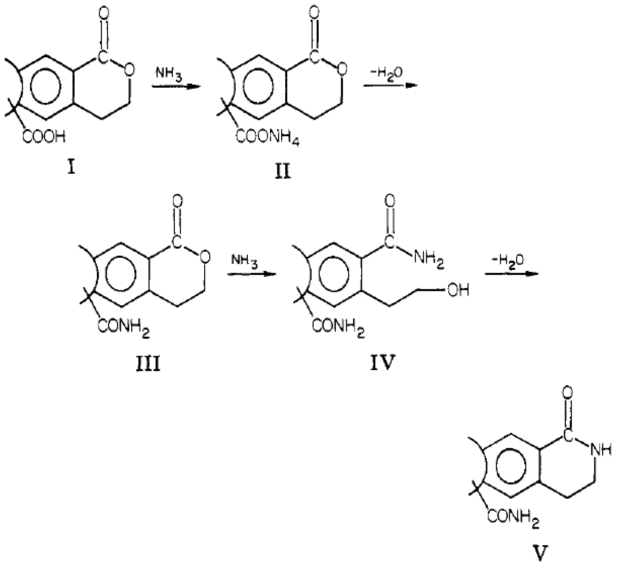

Figure 12: Potential ammoniation reactions with brown coal[169]

Oxidation with nitric acid increases the humic acid content of brown coal. For example, oxidation of a brown coal from Malaysia with 10% nitric acid increased the humic acid content from 20% to 80%[170].

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[165] Smil 1999

[166] Coca *et al.* 1984

[167] *Ibid*.

[168] *Ibid.*

[169] *Ibid.*

[170] Fong *et al.* 2006

Treatment of a Chinese lignite with 10% nitric acid increased the humic acid content from 46% to 60%[171]. The CEC of the lignite was also increased by this treatment. Oxidation of brown coal with nitric acid has been found to make the coal structure more amenable to degradation by soil microorganisms[172].

The product obtained by oxidation of brown coal with nitric acid is known as 'nitrohumic acid'. In Japan, nitrohumic acid from brown coal has been available commercially for many years and is used as a soil conditioner[173]. Nitrohumic acid products, mainly produced in China, are readily available today[174].

Brown coals from the Latrobe Valley are reported to contain up to 80% of humic material using exhaustive solvent extraction[175], but the yield of humates extracted by the usual alkaline extraction process depends on the time and temperature of extraction[176]. Under similar mild alkali extractions as those used to extract the Chinese lignite referenced above[177], Victorian brown coals yielded 12-15% humates. Extraction at near-boiling alkali conditions for 24 hours gave humic acid yields of 41% for Yallourn coal, 68% for Bacchus Marsh coal and 74% for Loy Yang coal[178].

Therefore, based on the experiences with Malaysian and Chinese lignites, it may be expected that nitric acid oxidation of Victorian brown coal would increase the proportion of readily-extractable humic materials. In turn, this would make the coal structure more accessible to soil microorganisms and increase the rate at which it is transformed into soil organic carbon (SOC).

Loy Yang coal has been converted to nitrohumic acid by reaction with 6M nitric acid at 50 °C for 30-45 minutes. The product was obtained at 90% yield and was found to contain 3-5% fixed N. Reaction with nitric acid significantly degraded phenolic groups in the coal and added N in the form of nitro groups[179].

The effects of nitrohumic acid from Loy Yang coal on urea-N uptake and dry matter production by wheat plants were studied in pot experiments. Results indicated that when pellets made by incorporating nitrohumic acid with urea were applied to plants grown on a Rhodoxeralf (a fertile reddish-brown soil), no significant benefits occurred that could not be attributed to urea alone. When similar pellets were applied to plants growing on a Calciorthid (a yellowish-grey, alkaline, nutrient-poor soil), some increases in N uptake and dry weight of plants occurred due to the presence of nitrohumic acid. Part of this effect was due to the N content of the nitrohumic acid[180].

No effort appears to have been made to develop a commercial nitrohumic acid product in Victoria. Further research is required to evaluate the costs and benefits associated with such a product.

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[171] Liu *et al*. 2011

[172] Scott *et al*. 1986

[173] Sakai *et al*. 1987, cited in Liu *et al*. 2011

[174] For example, see: http://www.humicacidcn.com/PRODUCTS/ShowArticle.asp?ArticleID=59

[175] Verheyen and Johns 1981

[176] Pang *et al*. 1990

[177] Liu *et al*. 2011

[178] Pang *et al*. 1990

[179] Patti *et al*. 1992

[180] Wang *et al*. 1995

5.3. Oxidation with hydrogen peroxide

A potential disadvantage of the use of nitric acid for coal oxidation is the fact that the coal has to be washed free of acid before it can be used as a soil amendment. Despite the fact that the acid can be re-used[181], the losses and wastes produced will add to the production cost.

As an alternative, hydrogen peroxide (H_2O_2) can be used to oxidise brown coal, and has also been shown to increase the humic acid content and render the coal more susceptible to microbial breakdown[182]. The advantage of this approach is that the H_2O_2 breaks down to water, so there is no need to wash the coal before it can be used. However, under aqueous reaction conditions, H_2O_2 attacks the coal aggressively, breaking it down to low molecular weight compounds and resulting in high losses. For example, treatment of a Texas lignite in 30% (w/w) hydrogen peroxide for 48 hours resulted in a 87.3% loss of solids, whereas treatment in 8M (35% w/w) nitric acid resulted in only 13.2% losses[183].

5.4. Oxidation with ozone

An alternative approach is to treat the coal with gaseous ozone. Ozone treatment of lignite has been shown to increase the concentration of carbonyl and carboxyl groups and reduce the concentration of hydroxyl groups, increasing the humic acid content and the CEC. X-ray spectral analysis showed that the treatment loosened the lignite molecular structure any disordering the aromatic molecular layers[184].

Russian researchers have demonstrated the rapid gas-phase ozonisation of brown coal in a rotating reactor. Exposure of intensively-mixed coal to a continuous stream of 1 – 1.5% ozone in oxygen (!) at 25 ^{o}C resulted in complete reaction within 1 hour. It was found that the concentration of carbonyl and carboxyl groups was increased and, because the reaction did not involve a liquid reactant phase, there was no loss of solids[185].

There does not appear to have been any subsequent work on gas-phase ozone treatment of brown coal. Further investigation of the feasibility of this approach with Victorian brown coal seems warranted.

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[181] Fong *et al*. 2007

[182] Scott *et al*. 1986, Peiris *et al*. 2002

[183] Moolick *et al*. 1989

[184] Sharypov *et al*. 1999

[185] Semenova *et al*. 2008

6. Agricultural uses for brown coal humic substances

6.1. Analytical extraction of humic substances

Humic substances are complex mixtures of many different acids containing carboxyl and phenolate groups. They are produced by biodegradation of dead organic matter and are present in coal, peat, soil and other natural materials.

Despite many years of research efforts, the structure of humic substances remains poorly defined. Initial analytical studies were focussed on the problem of separating organic complexes from the inorganic material in soil. Caustic alkali has been used almost exclusively since 'humic acid' was first isolated in 1786. Generally dilute (0.5M) solutions of sodium, potassium, or ammonium hydroxides or carbonates are used, but more concentrated solutions have often been employed. Caustic alkali is a drastic reagent, causing substantial alterations to the physico-chemical properties of the organic complexes[186].

Milder extraction methods were developed following the discovery that the organic matter of the soil is bound up as insoluble complexes with calcium, iron, aluminium and other heavy metals. It was found that the humic material could be extracted by solutions of the salts of acids that formed either insoluble precipitates or soluble coordination complexes with calcium ions, such as sodium pyrophosphate, oxalate, citrate. However, these reagents are less efficient extractants than caustic alkali[187]. The efficiency could be increased by pretreating the substrate with acid, followed by leaching with water, to displace calcium ions and disrupt soluble complexes.

Figure 13 below demonstrates that the extraction procedure used has a strong influence on the composition of the humic material recovered. It is well established that the use of strong and hot alkaline or acidic solutions causes substantial degradation and alteration of the structure of soil organic material[188].

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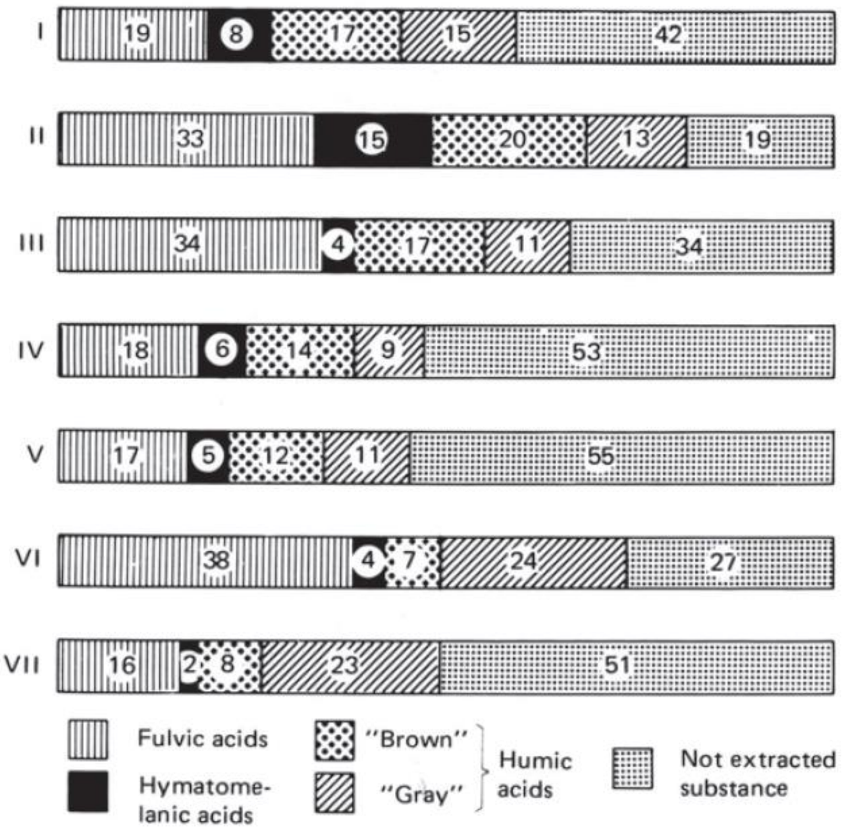
[186] Bremner and Lees 1949

[187] *Ibid*.

[188] Flaig *et al*. 1975



I = 2% HCl cold, 1% NaOH, cold: Nehring [1955], Tyurin [1937].
II = 5% HCl, 70°C, 0.5% NaOH, boiling: } Springer [1938].
III = 5% HCl, 70°C, 1% NaOH, cold: } Springer [1938].
IV = 0.1 M $Na_4P_2O_7$, 0.1 N NaOH, 16 hours, cold: Kononova and Belchikova [1961].
V = 0.1 N $Na_4P_2O_7$, 0.1 N NaOH, 16 hours, cold: } Welte [1956].
VI = 0.1 N $Na_4P_2O_7$, 8 hours, boiling: } Welte [1956].
VII = 0.1 N $Na_4P_2O_7$, 5% hydrazinehydrate, 16 hours, cold: } Welte [1956].

Figure 13: Comparison of different extractants (data is percentage of total C)[189]

The fact that the structure and composition of the humic substances extracted are strongly dependent on the extraction conditions is conveniently ignored by everyone except analytical chemists.

It is conventional to divide humic substances into three main fractions (humic acids, fulvic acids, and humin), based on extraction in alkali. Extraction using a strongly alkaline aqueous solution yields a solution containing humic and fulvic acids, with the humin as the insoluble residue. Humic acid is the component that is precipitated when the pH of the solution is lowered to 1, while fulvic acid is the component that remains in solution.

Strictly speaking, nitrohumic acid is classed as a humic acid because it is soluble in alkali. For example, nitrohumic acid produced from Loy Yang coal was almost completely soluble (or colloidally suspended) in ammonia solution at pH 10[190]. However, nitrohumic acids are treated as a separate type of product

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[189] Figure 10 of Flaig *et al*. 1975

[190] Patti *et al*. 1992

in this report because they are not produced by alkaline extraction. In this section, the term 'humic acids' is used for materials produced from brown coal by processes involving extraction in alkali.

Humic acid is regarded as a network of aromatic rings which are joined by long-chain alkyl structures to form a flexible network. The structure contains voids of various dimensions which can trap and bind other organic components such as carbohydrates, proteins and lipids[191]. A chemical structure for the basic skeleton of humic acid is shown in Figure 14 below. The structure of humic acid is further complicated by the fact that individual networks and segments of networks are linked by hydrophobic bonding, with additional interactions through hydrophilic side groups. Perusal of this structure makes it easier to understand why different extraction conditions result in different product compositions.

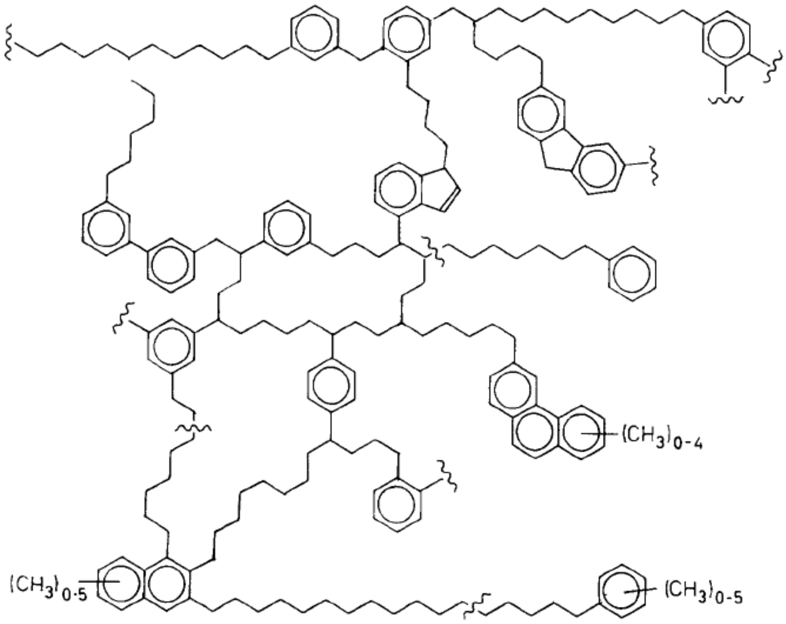

Figure 14: Chemical network structure of humic acid from soil[192]

The mechanism involved in the sodium hydroxide extraction of brown coal has been explained as a combination of (i) neutralisation of acidic functional groups and (ii) formation of an electrical double layer by sodium ions and water molecules, leading to (iii) mutual repulsion of the double layers and overcoming the van der Waals forces and hydrogen bonding between particles[193].

The exact amount of material extracted from brown coal with alkali depends upon the pH value of the solution. At relatively low pH values, only carboxyl groups dissociate, whereas both carboxyl and phenol groups dissociate at relatively high pH values. Increasing the extent of dissociation of acidic functional groups allows a greater degree of disruption of the coal structure.

To date, a structural model for humic acid from Victorian brown coal has not been published. However, Figure 15 below shows a structural model for Morwell brown coal. It is not surprising that the structure of brown coal, which is the ancient remains of humified plant biomass, is very similar to the structure of humic acid from soil.

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[191] Schulten *et al*. 1991

[192] *Ibid*.

[193] Camier and Siemon 1978

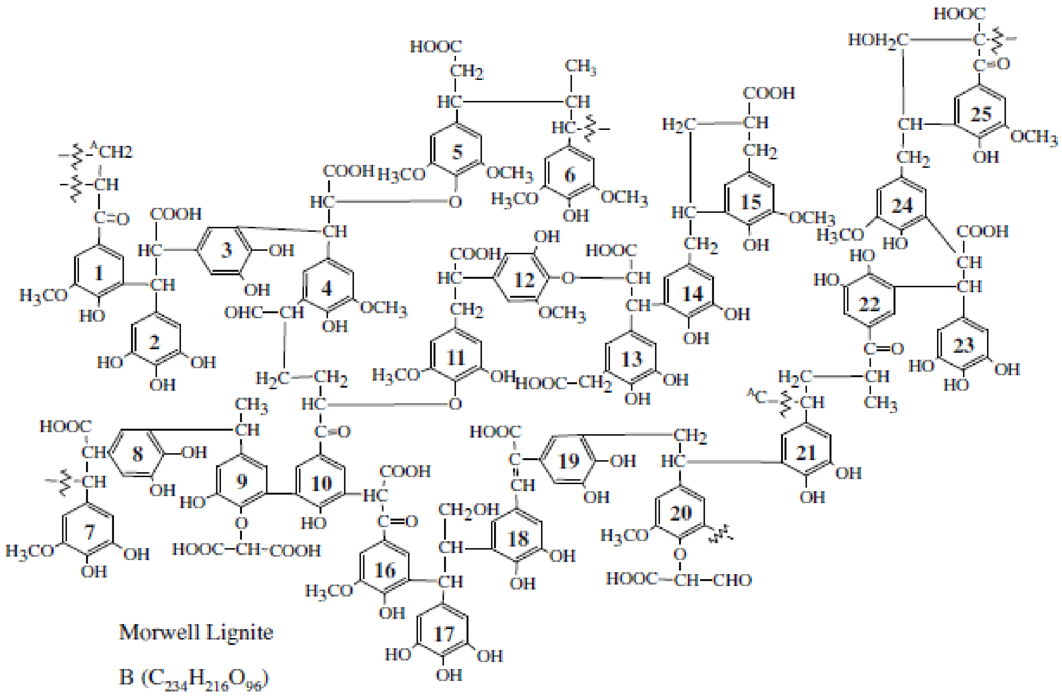

Figure 15: Structural model of Morwell brown coal[194]

6.2. Commercial extraction of humic substances from brown coal

The international patent literature reveals that processes for the economical extraction of humic substances from lignite have been developed since the 1960s, through to the present day. A summary of processes for extraction of both humic acid and fulvic acid is provided below.

6.2.1. Humic acid

The first humic product from leonardite (oxidised brown coal) was produced by extracting lignite with ammonium hydroxide, potassium hydroxide or sodium hydroxide. The resulting liquid solution was used to promote seed germination[195].

A compound humate-fertiliser powder was produced by reacting a slurry of leonardite with phosphoric acid and then anhydrous ammonia, followed by clarification, addition of supplementary fertiliser ingredients, and then spray drying[196].

A more energy-efficient variant of this process was subsequently developed, which involved blending pulverised leonardite with fertiliser ingredients and feeding the mixture into a rotary drum pelletiser. Phosphoric acid was fed into the inlet of the drum pelletiser to form humic acid and anhydrous ammonia gas was fed into the discharge end to form colloidal ammonium humates. The damp pellets were then dried in a rotary dryer against a counterflow of hot air[197].

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[194] Salmon *et al.* 2009

[195] Gardner 1963

[196] Karcher and Canfield 1963

[197] Cooley 1968

A further development of this concept involved reacting a slurry of leonardite with phosphoric acid, then blending the resulting humic acid slurry with fertiliser ingredients and anhydrous ammonia simultaneously in a rotary drum pelletiser. The damp pellets were then dried in a rotary dryer against a co-current flow of hot air. The dried pellets were screened to achieve a uniform particle size distribution, and undersized particles were returned to the rotary pelletiser to improve the granulation process[198].

An unusual liquid humic acid solution was produced by extracting leonardite in the presence of sodium sulphite at pH 8 or above. It was found that the humic acid extracted by this process remained in solution at pH values above about 4.5, making it more suitable for blending with fertiliser solutions. This unusual property was thought to be caused by the sulphite reducing the molecular weight of the humic acid[199].

A liquid plant growth stimulant was produced by reacting an aqueous slurry of leonardite with ammonia, then neutralising the pH of the humic acid solution with phosphoric acid, and then supplementing the mixture with fish emulsion or yeast strains[200].

A liquid humic acid concentrate was prepared by reacting an aqueous slurry of leonardite with caustic soda at a pH of 6.5 to 8.0 (optimally pH 7) at ambient temperature for a minimum of 40 hours. This process was claimed to produce a solution containing 23% humic acid, whereas conventional extraction under strongly alkaline conditions reduced the maximum concentration to 8%[201].

A liquid humic acid-fertiliser product has been developed in Romania that involves extraction of lignite using potassium carbonate, and then blending with fertiliser ingredients[202].

The Coal Corporation of Victoria (CCV) developed a process for extracting humic acid from Victorian brown coal. While the details of the process have not been disclosed, it is assumed that KOH is the alkali used in the extraction. The process was licensed to HRL Agriculture, which was subsequently purchased by the Omnia group of South Africa. Omnia Specialties (Australia) Pty Ltd currently sells both liquid and dried forms of humic acid to the local and international markets.

The CCV also investigated the production of ammoniated nitrohumic acid (ANH) from Loy Yang coal. The process involved oxidation of coal with nitric acid, then adjusting the slurry to pH 7 with ammonia solution. The recovered powder contained 8.0% N. The effects of ANH on urea-N uptake and dry matter production by wheat plants were studied in pot experiments. Results indicated that when pellets made by incorporating ANH with urea were applied to plants grown on a fertile soil, no significant benefits occurred that could not be attributed to urea alone. When similar pellets were applied to plants growing on a nutrient-poor soil, some increases in N uptake and dry weight of plants occurred due to the presence of nitrohumic acid[203]. No further development work with ANH appears to have been done.

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[198] Karcher 1970

[199] Schwartz 1968

[200] Chambers and Kimbro 1973

[201] Goff 1982

[202] Pârvan *et al*. 2013

[203] Wang *et al*. 1995

6.2.2. Fulvic acid

Fulvic acid is the fraction of the humic substances that is soluble at acidic and neutral pH. Fulvic acid is not a specific macromolecule, but can be visualised as a hydrophilic polymeric structure than can adsorb hydrophobic compounds. It forms a sponge-like structure made up of hydrogen-bonded phenolic and benzenecarboxylic acids, upon which alkanes and fatty acids are adsorbed. Fatty acids also form esters with phenolic humic “building blocks”. Through this mechanism, fulvic acid can fix, stabilise and preserve relatively large amounts of hydrophobic organic compounds[204].

Fulvic acid can be recovered from an aqueous suspension of leonardite, although the yield is low. For example, a process was patented in which a water slurry of leonardite was digested with compost microorganisms for 3 days. After this time, fulvic acid was recovered by filtration and two ultrafiltration steps, with a yield of 7.5% of the original leonardite. Although the yield was low, the absence of chemical extractants was claimed to be advantageous for gaining organic certification of the fulvic acid[205].

The yield of fulvic acid can be increased by controlled oxidation of the coal. In Section 4.3 it was noted that oxidation of lignite with hydrogen peroxide leads to a large loss of recoverable solids. Taking this a step further, reaction of lignite in an excess of aqueous H_2O_2 leads to almost complete conversion of carbon to water-soluble organics. For example, oxidation of Morwell brown coal in 20 volumes of 30% H_2O_2 solution for 24 hours at 60 °C converted 81% of the coal mass to water-soluble compounds, including phenolic acids, benzenecarboxylic acids, methanol and short-chain fatty acids (SCFA) such as formic acid, acetic acid, glycolic acid and malonic acid. In this case, it was proposed that these products arose through decomposition of the coal structure and introduction of oxygen by the H_2O_2 treatment, as illustrated in Figure 16 below[206].

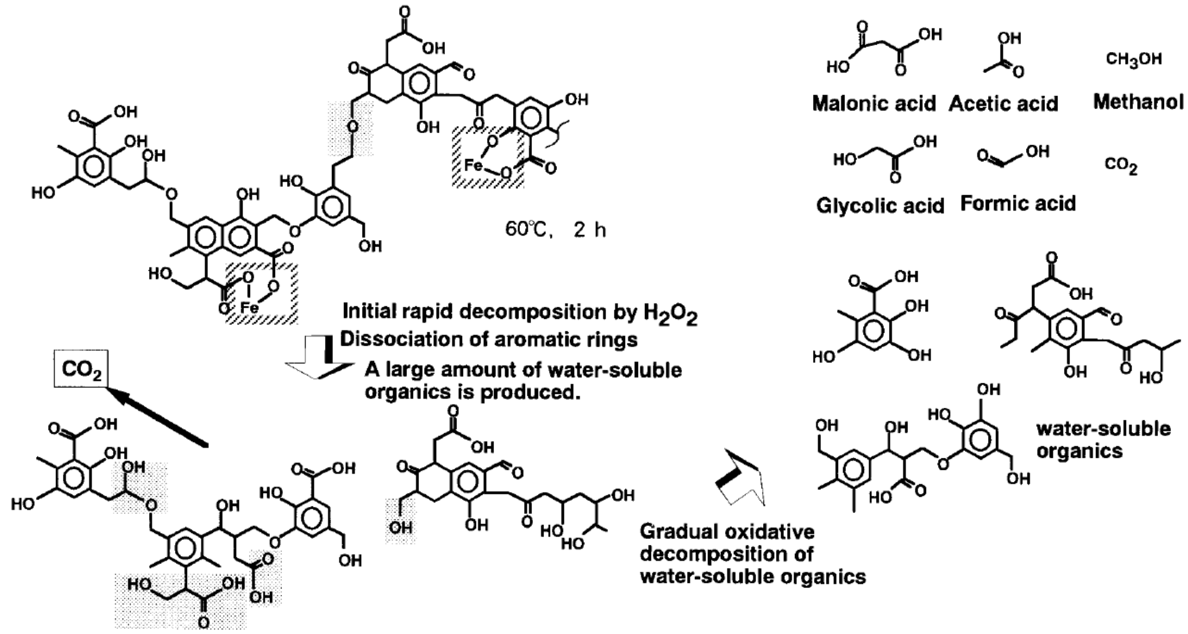

Figure 16: Presumed mechanism for the H_2O_2 oxidation of Morwell brown coal[207]

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[204] Ogner and Schnitzer 1971; Khan and Schnitzer 1971; Schnitzer and Neyroud 1975

[205] Karr 2011

[206] Miura *et al*. 1996

[207] Miura *et al*. 1996

The first stage of the reaction involved cleavage of – C – O – linkages, producing a large amount of water-soluble large molecules. The large molecules were then decomposed to produce short-chain fatty acids. Rupture of aromatic rings also produced SCFA. Visually, the colour of the aqueous solution changed progressively from dark brown, to brown, to light brown to yellow.

Although it was not stated specifically in this reference, it seems evident that oxidation of brown coal with hydrogen peroxide resulted in the production of fulvic acid, which was subsequently degraded to methanol and SCFA.

A disadvantage of producing fulvic acid by hydrogen peroxide treatment of brown coal is the long reaction time involved (e.g. 24 hours at 60 ^{o}C for 81% conversion). The process can be accelerated dramatically by carrying out the reaction in supercritical water, i.e. at temperatures greater than 374.0 ^{o}C and pressures greater than 22.1 MPa. For example, more than 80% of a Chinese black coal was solubilised within 20 minutes using H_2O_2 in supercritical water at 420 ^{o}C and 25.0 MPa[208]. At 600 oC and 25.0 MPa, 80% of a Changzhi bituminous coal was solubilised in 90 seconds[209].

The solubilisation of coal using hydrogen peroxide in supercritical water was explained through a free radical mechanism. The hydrogen peroxide is easily decomposed to hydroxyl radical, which can react with almost all hydrogen-containing compounds to fragment the coal structure. Under hydrothermal conditions, the larger fragments (i.e. fulvic acid) were decomposed to SCFA (acetic acid and formic acid), and ultimately to CO_2 and H_2O. The extent of oxidation was found to increase with increasing temperature, H_2O_2 concentration, and flow rate of H_2O_2 solution[210].

A similar result has been achieved by using oxygen as an oxidant instead of hydrogen peroxide. This patented process[211], known as oxidative hydrothermal dissolution (OHD), also converts coal into a clear solution of dissolved organic products, as shown in Figure 17 below.

Figure 17: Diluted OHD product derived from Victorian brown coal[212]

It has been found that the reaction rate is dependent on particle size, reaction temperature, oxidant loading and flow/contact time, as well as varying with initial substrate. The liquor obtained from

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[208] Wang and Zhu 2004

[209] Wang *et al*. 2011

[210] *Ibid*.

[211] Anderson *et al*. 2013

[212] Anderson *et al*. 2015

Victorian brown coal contains a mixture of phenolic acids, benzenecarboxylic acids and short-chain fatty acids (SCFA), as would be expected in a typical fulvic acid[213].

Greenpower Energy Ltd is currently supporting the development of the OHD process for producing value-added products from Victorian brown coal, and is investigating the agricultural potential of the OHD liquor. While further process fine-tuning may be required to optimise the liquor composition, the advantage of the OHD process is that it produces an aqueous extract from brown coal using only oxygen as a chemical input. This is likely to be an advantage for applications in the organic farming market.

6.3. Manufacture of humic substances from brown coal

The global market for humic substances was valued at US$325.6 million in 2014, and it is expected to grow with a combined average growth rate of 12.9% during 2015 - 2020. On the basis of crop type, the global market is segmented into row crops, fruits and vegetables, turf and ornamentals, and others. The market was dominated by the row crop segment in 2014[214]. Humic substances are being used in a variety of concentrations and physical forms for usage in these applications, either directly by spraying, or by adding them to soil.

Products containing leonardite, humic acid and fulvic acid are currently produced by many companies around the world. Table 6 below provides an (incomplete) overview of the range of products available, demonstrating that extracts from brown coal are universally regarded as being beneficial for agriculture.

Company	Country	Products/Trademarks
Actagro	USA	Actagro Liquid Humus
Adler Agro	Spain	Humic acid
Agrofill	Italy	Humic acid
Agxplore International	USA	HA12
Apg Tarim	Turkey	Leonardite, humic acid, fulvic acid, K-humate
Arvensis	Spain	Humipower
Biolchim	Italy	Take Up, Humidrip, Humic Up
Borregard Lignotech	USA	Borregro line
Brandt Consolidated	USA	Uptake, Leonardite Plus
Canadian Humalite International	Canada	Liquid and power extracts from oxidised sub-bituminous coal
CIFO	Italy	Biotron line, Cifoumic
Cosmocel	Mexico	Humical, Humicrop, H-85
Double Dragons Humic Acid Co	China	Humic acid, K-humate, P-humate, B-humate, Nitro humic acid, Poultry Mate
Fine Humate Industry Co	China	Humic acid, Na-humate, K-humate, NH_4-humate
GOFAR Agro Specialities	China	Fulvic acid, humic acid, Na-humate, K-humate
Greenworks Technology	China	Huminova – Leonardite, humus, K-humate, B-humate, fulvic acid

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[213] Thermaquatica and Greenpower Energy Ltd. "*Conversion of Australian Coals*"

[214] http://www.prnewswire.com/news-releases/global-humic-acid-market-is-expected-to-grow-with-13-cagr-during-2015---2020-551351851.html

Hazem Kimya	Turkey	Flash-OTD (Leonardite)
Hefe Fertilizer	Spain	Hefe Humus
Helena Chemicals	USA	Hydra-Hume, Trafix
Humic Growth Solutions	USA	Humi-K line, Ful-Gro
Humintech	Germany	Liqhumus, Powhumus, Perlhumus
Jiloca Industrial	Spain	Humilig, Fulvin
Liaoyang County Decavem Import and Export	China	Decavem line (humic acid, fulvic acid, Na-humate, K-humate, nitro humic acid)
Live Earth	USA	Granular humate range, Great-8, Liquid-6
Loadstar Unimars	Latvia	Na-humate
Mapon Humic Acid Development	China	Humistrong
Numerator Technologies	USA	NuHumic WDG Verge
Omnia Specialities	Australia/ South Africa	K-humate, K-fulvate, fulvic acid
Quimica Foliar	Mexico	Acidos Fulvicos, Fulvigran, QF Activator
Shandong Chuangxin Humic Acid Technology	China	Humic acid, fulvic acid, K-humate, fulvic + urea
Shenyan Humate Technology	China	Huminrich
SNLO	Romania	Ferthum, Folhum (K-humate organomineral fertilisers)
SPA-Ret	Russia	Lignohumate
Timac Agro	Spain	Fertiactyl GZ (sulfonated humates)
Tradecorp International	Spain	Humical, Humistar
Valagro	Italy	Fulvic 100, Humic 80, AU15%
Vellsam Materias Bioactivas	Spain	Humivel line
VM Crop Care	India	Biostar, Humic Acid, Leonardite soil conditoner
Xi'an Tbio Crop Science	China	Humic acid, fulvic acid, K-humate

Table 6: Commercially available humic substances from brown coal

The products shown in Table 6 include both wholesale generic products (e.g. humates, fulvates) and branded specialty products from lignite processors. The generic products on-sold either as on-farm supplements or for use as ingredients in manufactured biological farming products.

The purported advantages of using humic substances rather than bulk brown coal or leonardite are (i) suitability for inclusion in liquid products and (ii) reduced bulk and correspondingly reduced freight costs. However, the total global market for humic substances (US$325.6 million) is not huge, which may in part be attributed to the high costs involved with extraction of humic substances from brown coal, as well as the freight costs associated with transporting dilute liquid preparations, or the added cost of producing a dry powder.

It does not appear to be a forgone conclusion that extraction of humic substances is the most cost-effective way to deliver the benefits of brown coal for agriculture. A commercial evaluation is required to establish the most cost-effective product format(s) for distribution and use in Australia.

6.4. Applications for humic substances in agriculture

Humic acids derived from brown coal have a wide range of potential applications in agriculture, including solubilisation of essential plant trace elements, stimulation of plant growth, amelioration of acidic soils, improvement of fertiliser use efficiency and as animal feed supplements. Each of these applications is reviewed below.

6.4.1. Chelation of metal ions

Humic substances are valued for their ability to chelate (i.e. form stable complexes) with metal ions, particularly essential plant trace elements (e.g. Fe, Mn, Zn and Cu), which would otherwise be poorly soluble. Humic substances are considered to be both a source of trace elements and a carrier to transport trace elements through the soil to plant roots. As such, they are highly valued and widely used in biological farming systems[215].

The chelation property of humic substances is attributed to their high content of oxygen-containing functional groups. The two most important reactions involve phenolic OH and COOH groups, as shown in Figure 18 below:

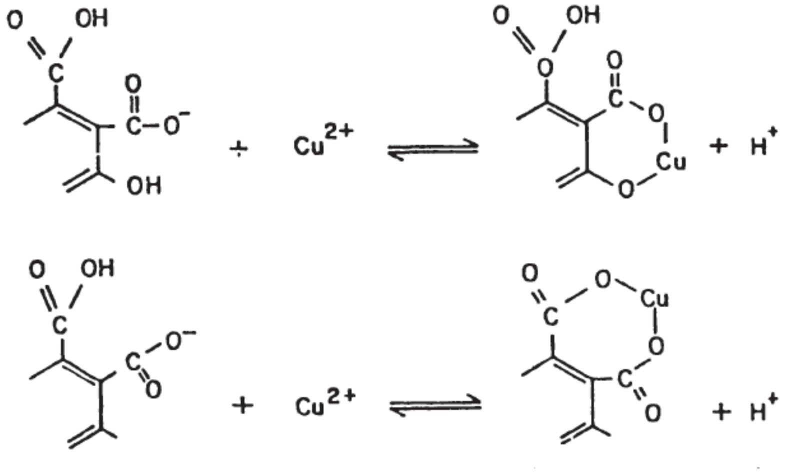

Figure 18: Mechanisms for chelation of metal ions by humic substances[216]

Humic substances form both soluble and insoluble complexes with polyvalent cations, depending upon the degree of saturation. Factors influencing the quantity of metal ions bound by humic substances include pH, ionic strength, molecular weight and functional group content. For any given pH and ionic strength, the strength of complex formed is in the order: $Al^{3+} > Fe^{3+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$. Fulvic acid has a lower molecular weight and a higher proportion of acidic functional groups than humic acid, so fulvic acid-metal complexes are more soluble[217].

Under the right pH conditions, trivalent cations and, to some extent, divalent cations, are effective in precipitating humic substances from very dilute solutions. This property is utilised in wastewater

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[215] See, for example: http://npk-industries.com/plant_nutrition_humic_acid_fulvic.html

[216] Chen and Stevenson 1986

[217] Chen and Stevenson 1986

treatment systems, where aluminium sulphate or iron nitrate are used to coagulate dissolved organic matter in contaminated water[218].

Humic substances can increase the availability of essential plant micronutrients by competitively desorbing them from insoluble complexes in the soil. For sensitive crops growing on deficient soils, the application of complexes of trace elements and humic substances can be beneficial.

Skill is required for preparation of shelf-stable complexes of trace elements with humic substances, particularly for foliar spray applications. Fulvic acid is generally preferred in this application, because it forms complexes that are more soluble. Even then, flocculation may still occur over extended periods. It has been found that the shelf stability can be improved by adding secondary chelating substances, such as organic acids[219] or pyrophosphates[220]. Some of the commercial products mentioned in Table 6 include such ingredients as proprietary know-how.

6.4.2. Plant growth promotion

Humic acids are widely acknowledged as having plant growth-promoting effects, although the mechanism(s) involved are not clear. It is likely that one or more of the following factors is involved[221]:

- Formation of chelates and improved uptake of essential micronutrients
- Decreased toxicity of aluminium and heavy metals
- Improved soil aggregation and structure
- Increased pH buffering and cation exchange capacity
- Plant hormone-like effects.

Internationally, there has been an enormous research effort to elucidate the benefits of humic substances in agriculture. It is understood that humic substances can help to reduce fertiliser application rates, enhance efficiency of nutrient use, replace synthetic plant regulators, increase water stress tolerance, decrease disease incidence, enhance early growth and flowering, while their chemical composition may be suitable for use as a carrier for beneficial microorganisms[222]. However, the results are not uniformly predictable, and further information is needed to understand how humic substances can be employed most effectively.

Brown Coal Innovation Australia (BCIA) provided funding for researchers at Monash University to investigate the potential benefits of humic acids in agriculture. Part of this work involved a meta-analysis of the plant growth-promoting effects reported in the literature. The goal was to determine the magnitude and likelihood of plant-growth response to humic substances and to rank the factors contributing to positive growth promotion. These factors included the source of the humic substances, the environmental growing conditions, the type of plant being treated, and the manner of application.

One of the outcomes of this project was a review of the literature on exogenously applied humic substance-plant interactions. In total, 390 research papers were evaluated, of which 81 were quantitatively analysed using meta-analytic and regression tree techniques. Overall, the analysis estimated that humic substance application led to shoot dry weight increases of 22±4% and root dry

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[218] Schmitt *et al*. 1996

[219] Marihart 1988; Freire *et al*. 2011

[220] Sequi *et al*. 2000

[221] Rose *et al*. 2014

[222] Canellas *et al*. 2015

weight increases of 21±6%. However, actual responses varied considerably and were mainly influenced by the source of humic substance applied, the rate of application, and to a lesser extent, plant type and growing conditions[223].

Consistent with this analysis of the literature, experimental trials at Monash University have yielded generally encouraging but inconsistent results. A commercial preparation of K-humate was found to be an effective soil conditioner for both acidic and sodic soils, improving aggregate stability and increasing soil pH and CEC[224]. A greenhouse pot trial showed that applications of commercial K-humate and K-fulvate on tomatoes resulted in increased fresh/dry biomass of shoot and fruits and increased NPK nutrient uptake[225]. On the other hand, glasshouse and field experiments with a variety of crops (pasture, leeks, wheat) did not give any significant yield increases. The researchers concluded that there is good evidence that HS can improve certain soil properties and plant growth, but more research is needed to identify the primary variables that lead to maximum efficacy[226].

6.4.3. Amelioration of acidic soils

Acidic soils can be ameliorated using surface applications of lime, but the effectiveness of the treatment is limited by poor solubility and limited diffusion through the soil. In 1991, researchers in South Africa reported that a coal-derived Ca-fulvate was much more effective as a carrier of calcium in the soil profile. The subsoil pH was considerably higher when Ca-fulvate was applied to the surface than when gypsum, Ca-EDTA, $Ca(OH)_2$ or $CaCO_3$ were applied[227].

CSIRO subsequently obtained samples of similar products from South Africa for testing in Australia. The two organic amendments were manufactured by Council for Scientific and Industrial Research (CSIR) and described as 'calcium-oxiproduct' (OXPR) and 'calcium-oxifulvate' (OXFU). The OXFU was a Ca derivative of water-soluble oxifulvic acid. The OXFU contained 90% Ca-oxihumate and 10% Ca-oxifulvate. The amendments were tested on an acid red podsol (pH 4), with $CaCO_3$ as a control. The effects of $CaCO_3$ on exchangeable Al and pH were limited to the surface 2 cm. In contrast, the two coal-derived amendments were effective in decreasing exchangeable Al and increasing pH and exchangeable Ca to depth. At an application rate of 0.8 t/ha, both OXPR and OXFU were effective to a depth of 20 cm[228].

Researchers at Monash University prepared Ca-humic acid and Ca-fulvic acid-rich (about half fulvic acid) samples from Loy Yang brown coal. The coal was oxidised with hydrogen peroxide, dissolved in NaOH, fractionated and then reacted with calcium chloride at pH 5. Leaching experiments were carried out in a typical acidic Australian soil with high levels of soluble aluminium. Each treatment was applied at an application rate of 1.6 t C/ha. The fulvic-rich preparation was the most effective, removing virtually all of the aluminium to a depth of 8-10 cm. The pH increased over the top 15 cm of the column from 3.8 to 4.5-5.4. The humic acid preparation was less effective, but it increased soil pH (to 4.0-4.7) and exchangeable Ca in the top 6 cm of the column and decr3ased exchangeable Al in the

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[223] Rose *et al*. 2014

[224] Imbufe *et al*. 2004, Imbufe *et al*. 2005

[225] Patti *et al*. 2013

[226] Little *et al*. 2014

[227] Van der Watt *et al*. 1991

[228] Noble *et al*. 1995

top 12 cm. Both preparations were superior to lime, which only gave significant improvement near the soil surface[229].

No further work with calcium humates as soil conditioners has been reported subsequently. Given the large areas of acidic soils in Australia, and the poor apparent efficiency of lime as a surface amendment, further investigation of the potential of calcium humates seems warranted.

6.4.4. Organomineral fertilisers

In China, it is well accepted that humic acid applied along with urea can increase crop yields relative to urea-only treatments. It has been reported that 350,000 tonnes of humic acid are used in Chinese agriculture each year[230].

In South Africa, humic acid has been combined with urea and sold as 'Black Urea'. In pot trials and field trials the yield of maize increased by 20-46% when Black Urea was applied and compared to standard urea. It has also been found that 10-20% and 30-50% less Black Urea was required than normal urea when applied as topdressing on an alkaline and acid soil respectively[231]. In Australia, Black Urea is produced by Advanced Nutrients Pty Ltd in Brendale Qld[232].

Similarly, the co-application of humic acid and phosphorus fertilisers can lead to increased P availability and crop yields, especially on alkaline soils. It has been demonstrated that humic acid can slow or prevent the precipitation of poorly soluble phosphates as insoluble calcium phosphates, increasing the availability of P to plants[233].

In Australia, Omnia Specialities produces a humic acid fertiliser coating called 'FertiCoat', which can be used with either N or P fertilisers[234]. Extensive field trial testing has established that FertiCoat can deliver higher yields and improved fertiliser use efficiency.

The BCIA-funded research at Monash University has verified that humic acids can improve the utilisation efficiency of N and P fertilisers, and is helping to identify the composition ratios needed for optimum performance.

6.4.5. Animal feed supplements

In Germany, HuminTech manufactures a product called 'HuminFeed', which is sold as an animal feed supplement. 'HuminFeed' is a water soluble sodium humate that can be applied to livestock (swine, poultry and cattle) as feed or drink water additive to stimulate the immune system and to stabilise the intestinal flora. It is said to increase the animal's appetite and feed intake, improve the feed conversion and thereby promote the growth rate[235].

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[229] Peiris *et al*. 2002

[230] Dong *et al*. 2009

[231] Van Vuuren and Claassens 2009

[232] www.advancednutrients.com.au

[233] Delgado *et al*. 2002; Alvarez *et al*. 2004

[234] http://www.australianhumates.com.au/product/ferticoat/

[235] http://www.humintech.com/livestock-breeding/products/water-soluble-products/huminfeed.html

Research supports the benefits of humic acid for poultry growth and egg production[236]. Humic acids are also known to be beneficial for the growth of pigs[237] and calves[238].

The potential market for humic substances as animal feed supplements in the Australian market is potentially huge, but little seems to have been done to develop this opportunity. Currently, only one product is available on the Australian market, from LawrieCo in South Australia. 'BioMAX Animal Humic Fulvic Powder' is sold as an animal-grade mixture of humic and fulvic acids which is suitable for use with dairy, pig, poultry, cattle, sheep, horse and fish. It is said to improve feed and supplement digestion, faster animal weight gains, reduce odour in animal waste, increase dairy feed efficiency and reduce mastitis, animal stress and healing time[239].

Further research is required to understand the regulatory issues concerning this potential application, and to assess the potential for producing value-added products targeted to the needs of the local market.

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[236] Yörük *et al*. 2004; Ozturk *et al*. 2010

[237] Ji *et al*. 2006; Wang *et al*. 2008

[238] Cusack 2008

[239] http://www.lawrieco.com.au/item_details.php?item_id=33&item_type=photo_gallery&content_list_id=12

7. Agricultural uses for brown coal fly ash

Fly ash is a major by-product of electricity generation using pulverised fuel coal combustion. Fly ash is captured from the flue gas stream by electrostatic precipitation and transported as a water suspension to holding dams where it is stored. Australian production of fly ash is currently around 14,000 tonnes/year, of which only 30% is used for value-added products (geopolymers, glass, zeolites, catalysts and molecular sieves) or in concrete manufacture[240]. The remaining 70% accumulates in onsite ponds, where it must be prevented from contaminating the surrounding environment.

Victorian brown coals are rich in alkaline and alkaline earth metal salts, so the fly ash is enriched in Na, Ca and Mg. Morwell fly ash is particularly rich in Ca and Mg, while Yallourn fly ash is rich in Fe[241]. Early results from a pot experiment with perennial ryegrass suggested that Latrobe Valley fly ash may serve as a good source of Mg, comparable to commercial fertilisers[242]. However, subsequent investigations established that Latrobe Valley fly ashes are extremely saline, are strongly alkaline (pH 10-13) and contain excessive levels of B[243].

Boron is one of the eight essential micronutrients for healthy crop growth, but has a very narrow threshold between deficiency and toxicity. Boron is mobile in the soil and readily leached, so boron deficiency is a widespread problem in relatively humid areas of the world[244]. However, in the dry, alkaline-soil cropping regions of southern Australia, high concentrations of soil B have been identified as a limitation to crop growth and grain yield. The highest concentrations of B in this region have been found at depths between 40 and 100 cm in the soil profile[245]. It is apparent that in dry areas the limited precipitation does not leach the B down beyond the root zone and, as alkaline soils absorb more B than acid soils, only a small fraction of the free B is leached out of the root zone[246]. The amelioration of B toxicity through soil modification is not an economic or practical solution in this region, so the breeding of more tolerant crop varieties is the focus of research efforts[247].

Glasshouse experiments to assess the phytotoxicity of Latrobe Valley fly ash with French bean and Rhodes grass demonstrated that the plant growth was inhibited by B toxicity[248]. Further pot trials with canola established that the toxicity effects could be avoided by applying the ash to the soil surface at rates of no more than 36 t/ha[249]. At application rates of >36 t/ha in alkaline soil the ash increased the pH in the top soil layer, as well as the salinity, and caused higher uptake of the toxic elements Mo and Se by the plants[250].

Based on some of the experiences overseas, included in the discussions earlier in this report, it may have been anticipated that Victorian brown coal fly ash could serve a useful role in admixture with brown coal preparations, either to neutralise the acidic pH of the coal or as a source of beneficial plant nutrients. However, despite the fact that Latrobe Valley fly ash does contain useful nutrients,

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[240] Ukwattage *et al*. 2013

[241] Aitken *et al*. 1984

[242] Hill and Lamp 1980

[243] Aitken *et al*. 1984

[244] Yau and Ryan 2008

[245] Hobson *et al*. 2006

[246] Yau and Ryan 2008

[247] Hobson *et al*. 2006

[248] Aitken and Bell 1985

[249] Manoharan *et al*. 2010a

[250] Manoharan *et al*. 2010b

particularly Ca and Mg, the potential benefits are outweighed by the potentially harmful characteristics of the ash: i.e. its high salinity and high levels of B. Even the very high pH of the ash may not be very useful, since it has a low pH buffering capacity[251] and a large proportion of ash would be needed to adjust the acidity of the coal.

There is certainly a strong motive to find a useful application for the large quantities of fly ash that have been accumulated in the Latrobe Valley, and there is reason to believe that the risks to crops associated with the use of fly ash in agriculture could potentially be managed. However, there is also a legitimate concern about the longer term, cumulative effects of repeated applications of B-rich amendments in regions that do not have sufficient rainfall to leach the excess B out of the root zone.

This suggests that efforts to find potential agricultural uses for Latrobe Valley fly ash should be directed to applications in areas of high rainfall and/or acidic soils, where B deficiency is likely to be a problem. In these areas, the high B content of fly ash would be an advantage. Further research is required to investigate the potential for applications in such areas.

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[251] Aitken *et al*. 1984

8. Conclusions and recommendations

The use of brown coal and humic substances is not new in Australian agricultural, and has been supported by over 40 years of research. To date, though, the market for such products has been quite small and there have been only a small number of companies involved. This is consistent with the situation in other countries, with the global market for humic substances estimated as only US$325.6 million in 2014. The most likely explanation for this is that coal-derived substances are included in the category of ‘biological farming’ products, which tend to be complex materials with poorly defined performance characteristics. They are regarded by agronomists as ‘fringe’ or ‘alternative’ products, and are largely ignored by the majority of farmers.

This view ignores the fact that brown coal is very similar in composition to the organic matter in soil, and has been proven to be a valuable soil amendment. Australian soils are generally poor in organic carbon, which is a limitation on soil health and productivity, so it makes sense to think that amending agricultural soils with brown coal products will improve the productivity and profitability of farming.

The fundamental problem with realising this vision is that there is currently no well-defined way to quantify the financial benefits of increased soil organic carbon (SOC). This is exemplified by the wide range of estimated cost benefits from previous studies, which were summarised in Table 1. The estimates have been based on easily quantifiable measures, such as the equivalent fertiliser value associated with SOC, or improved productivity, or the resulting environmental benefits. To date, there has been no analysis that has attempted to quantify the full range of benefits that accrue from increased SOC. This is a real and significant problem, because farmers need to clearly understand the benefits that can be expected from their investment in soil amendments.

This review has taken the view that the Australian Government endorsement of the ‘4/1000 Initiative’ provides the motivation raise the profile of the importance of SOC to Australian agriculture. As a starting point, it is recommended that a modelling tool be developed to use the best available information to quantify the value to farmers of increasing SOC on their properties.

This report has shown that, even with the most determined efforts, it will not be possible meet the ‘4/1000 Initiative’ target in actively managed agricultural soils by using the recommended management practices alone. At best, there will be a shortfall of 29 million tonnes of carbon each year, which will have to be provided through supplementary soil amendments. Victorian brown coal is the only carbon-rich source available in the quantities needed to meet this requirement. The challenge is to transform the coal into commercial products and deliver them to farmers at an acceptable price.

This review has demonstrated that there is a range of potential uses for brown coal in Australian agriculture. Coal or extracted humic substances can be used as soil amendments and in organomineral fertilisers. Coal itself can be used as a carrier for microbial biofertilisers and to reduce ammonia and N_2O emissions from beef cattle feedlots and other intensive animal-rearing systems. Humic acids can be used as animal feed supplements to improve animal health and growth rates.

The conceptually simplest way to increase SOC with brown coal is to apply it in bulk (i.e. in the order of tonnes per hectare), either alone or in combination with other soil amendments, e.g. gypsum, lime, mineral-rich rock dusts. Bulky products are relatively expensive to transport and apply, so the farmer will need to be convinced of the value proposition. The challenge is that the value of higher SOC is poorly quantified, and the effects of brown coal amendments may take several years to become fully apparent. Bulk brown coal products may be the most useful for building SOC on a large scale, but there is insufficient performance and cost data to quantify the value of the carbon content of the coal.

This review has shown that there are a number of strategies that can be employed to increase the rate at which brown coal is converted to SOC. These include chemical processes, such as oxidation with nitric acid or gaseous ozone, as well as biological processes such as composting or inoculation with specific coal-solubilising microorganisms. The viability of these processes will depend upon whether they can deliver a demonstrable benefit in the field to justify the extra costs involved.

In the first instance, it may be more effective to focus on coal-based products that address the needs of specific problem soils, e.g. coal + lime for acidic soils, coal + gypsum for saline/sodic soils, coal + rock dust for sandy soils, etc. This approach would simplify the marketing message. Even so, it will be important to conduct high quality field trials, with the active cooperation of 'alpha-farmers', to generate the quantitative data needed to establish the full value proposition for these products.

From a marketing perspective, it would also be relatively easy to promote organomineral fertiliser products, based on blends of brown coal and/or humic substances and proven fertiliser ingredients (either chemical or biological). Such products would be more appealing to farmers who want to maintain profitability while doing something to help rebuild the soil. There is a good body of evidence to show that brown coal and/or humic substances can increase the efficiency of N and P fertilisers, which makes for a simple value proposition. The inclusion of known fertiliser ingredients will give short-term evidence of value for money, buying time for the coal to be properly incorporated into the soil.

Development of organomineral fertiliser products should be led by industry, since it will be important to develop proprietary formulations at a viable price point. This has to be done in a commercially focussed fashion, using equipment that is beyond the scale of academic researchers. However, effective marketing of such products will rely on supporting data from reputable field trials. It is recommended that these commercial trials be undertaken with the support of academic expertise, such as that of Tony Patti's team at Monash University, to ensure that they are correctly designed and monitored.

Brown coal can be used as a carrier for microbial biofertilisers, and are used in this manner at large scale in India. However, this is in the context of low-productivity subsistence agriculture, where the farmers cannot afford to buy chemical fertilisers. In Australia, the market for biofertilisers is very small, and is dominated by the inoculants needed for all legume crops. This will remain a niche market for the foreseeable future, and does not represent a market for large quantities of brown coal.

At the present time, humic substances represent the main agricultural market for coal-derived products, both in Australia and elsewhere. Humic substances represent the 'active ingredient' in brown coal and, in dry form, are much cheaper to transport. Even so, their total market size is relatively small, which is probably because they are expensive to produce, expensive to transport in liquid solution, and give unreliable responses in the field. These factors suggest that humic substances will continue be regarded as premium, high-performance ingredients in specific applications, e.g. foliar sprays, fertigation. It is recommended that applications for humic substances should be supported by peer-reviewed scientific research, to create a premium image to match the premium price.

In particular, humic substances show great potential for use as animal feed supplements, where they are reported to improve stock health, growth rates and feed conversion efficiency. This is a premium application with great potential significance for Australian agriculture. Further research is needed to understand the regulatory issues that relate to using humic substances in this manner, and to produce the additional supporting performance data that is sure to be required.

Less expensive, bulk brown coal products also have potential applications in animal husbandry. Researchers at the University of Melbourne have demonstrated that brown coal can reduce emissions of ammonia and greenhouse gases from beef cattle feedlots. The mixture of coal and manure scraped out of the pens is enriched in nitrogen, and can be composted for use as fertiliser. Most Australian beef cattle feedlots are in NSW and Queensland, so transport costs will be a major issue for this application.

In the first instance, it may be more profitable to determine whether similar benefits can be achieved in other intensive animal husbandry industries, e.g. poultry and pork, with a focus on those in Victoria. There is potential for a ‘virtuous circle’ to be established, with bulk coal being sent to an animal-raising facility and returned in the form of nutrient-rich coal and manure, which could then be composted for inclusion in an organomineral fertiliser blend and sold into other markets. It is recommended that further research be undertaken to identify suitable animal-raising facilities and generate trial data to support a business case for this process.

This review also included potential agricultural uses of Latrobe Valley fly ash, a by-product of electricity production from brown coal. Applications for the fly ash are generally limited because of its strong alkalinity and high concentration of boron (B). It is suggested that there may be potential agricultural applications in areas of high rainfall and/or acidic soils, where B deficiency is likely to be a problem. In these areas, the high B content of fly ash would be an advantage. Further research is required to investigate the potential for applications in such areas.

The production of value-added agricultural inputs represents the ‘low-hanging fruit’ of the potential range of products that can be derived from Victorian brown coal. The capital and processing costs are relatively low, and there is a large potential market. There is definitely a role for the use of brown coal in boosting the organic carbon content (hence productivity and profitability) of Australian agricultural soils. Innovative, cost-effective new products are needed to achieve this, along with performance data that establishes a clear value proposition for the farmer. Industry needs to take the lead in developing these opportunities, supported by the academic expertise that is already in place.

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