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HOMBRE

"Holistic Management of Brownfield Regeneration"

D 5.4: Operating Windows of Two Important Low Input Technologies for Greening Urban Brownfield

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Disclaimer

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Executive Summary

Introduction

The HOMBRE (Holistic Management of Brownfield Regeneration) project seeks to aid both the prevention of sites from becoming brownfields (BFs) and the regeneration of existing BFs into usable sites. Work Package 5 of the HOMBRE project aims to improve solutions for long term land use of current and potential future BFs. To achieve this, WP5 looks to both the development of new, and improvement of existing, technologies for the regeneration of BFs into green end uses. The objective of this report is to fulfil HOMBRE deliverable 5.4, which has the aim of investigating and providing guidance on the operating windows of:

1. Biochar and other *in situ* stabilisation agents
2. Organic matter recycling

These are examples of two important low input technology groups for regenerating BF, supporting specific soil functionality and risk management on site, as well as providing wider environmental benefits (e.g. carbon sequestration). This report provides an overview of existing literature regarding these technologies and their potential uses, as well as their advantages and disadvantages for utilisation in greening urban BF. It also discusses the outcomes of several experimental studies undertaken as joint initiatives between HOMBRE and the Greenland project (FP7-KBBE-266124) involving the investigation of biochar and recycled organic wastes as potential methods for remediating soil contaminated with copper.

Biochar

Biochar is the carbon-rich end product of the pyrolysis of biomass. Amongst other uses, it has been suggested that biochar can be used for carbon sequestration, pollution remediation and recycling of agricultural wastes. It has even been proposed that biochar could be used in bio-energy production. There are strong suggestions that biochar may be applied as an amendment to soil. In this application, biochar may provide both cultivation improvements (through nutrient provision, improved water retention and pH control) and immobilisation of soil contaminants.

Biochar can be produced from a range of biomass types. The feedstock utilised in production is a key factor in determining the physico-chemical properties of biochar. Some biochar properties are less dependent on feedstock and may be controllable by altering the production process conditions. However, general properties of biochar include a high carbon content and high porosity. The heterogeneity resulting from variations in the feedstock and production of biochar is a key positive attribute and contributes to its versatility, as biochar can be tailored to suit the use for which it is required.

Biochar is increasingly being investigated for its potential as an *in situ* remediation agent to immobilise contaminants in the soil matrix. Several characteristics of biochar contribute to its ability to remediate contaminated soils:

- Porosity and large surface area.
- Large cation exchange capacity.
- Typically high pH.

Studies suggest that both organic contaminants and trace elements may be successfully immobilised using biochar. A review of literature reporting the numerous different contaminants to have been treated using biochar is provided as an annex. Biochar may prove more durable than alternative soil amendments. Studies have reported biochar to have a residence time of between 8 and 4000 years.

Despite the positive effects of biochar on the immobilisation of contaminants in soil; there are some concerns that biochar itself may be a source of contamination. The feedstock used to produce the biochar may contain metals that could be transferred to the final product. Additionally, some contaminants can be formed during the conversion (pyrolysis) process. These include polycyclic aromatic hydrocarbons (PAH) and in some cases, dioxins. Studies have shown that organic contaminant concentrations in biochar depend on multiple parameters of the pyrolysis process, i.e. pyrolysis temperature, pyrolysis time, and feedstock properties. Potentially then, the risk of biochar as a source of contamination can be reduced by utilising appropriate feedstocks and production processes.

Biochar may be argued to be more advantageous than other methods of *in situ* stabilisation as it may offer soil and environmental benefits additional to the immobilisation of contaminants, potentially including the provision of a means for carbon sequestration. It has been proposed that biochar could be employed for this purpose, due to its extremely high carbon content. Additionally, the unique attributes of biochar suggest it can contribute beneficially to soil characteristics, resulting in improvements for the cultivation of biomass. Soil structure, nutrient availability, pH and water retention may all be improved through biochar addition to soil.

Recycled Organic Matter

Recycled organic matter (ROM) can be derived from multiple organic waste sources and can be tailored to suit a specific purpose. Organic waste can be defined as waste which is biodegradable and may include household and commercial sources, such as food; garden wastes; paper; cardboard and wood, alongside agricultural wastes, sewage sludge, such as manure and crop residues. Organic waste can be processed in a variety of manners, including composting or anaerobic digestion. Organic wastes may be recycled and utilised in various ways; the two major end-uses being as a soil amendment and for fuel/energy production.

As a soil amendment, input of ROM can improve biomass growth on BF sites, through the improvement of soil conditions and can also be utilised in soil forming. ROM increases nutrient availability, improves soil structure and can increase soil functioning through stimulation of microbial activity. Further, applying ROM to land could increase the amount of carbon stored in soils and so contribute to the reduction of greenhouse gas emissions (therefore helping to mitigate climate change).

Trials have investigated the use of ROM to reduce the amount of available contaminants in soil, as a result of increased sorption sites and amelioration of acidic conditions. However, trace element mobilisation and increased availability has also been noted with ROM application to soil, as a result of dissolved organic carbon (DOC) competing with metals for sorption sites; or due to DOC forming soluble complexes with metals, preventing sorption onto soil particles. Similar to biochar, ROM may also be a source of trace elements. Certain types of ROM may be considered "high" risk, for example sewage sludge or compost-like-outputs derived from mechanical biological treatment of non-source-segregated municipal solid waste. To reduce risks, ROM should be tested prior to soil application and ROM amendment should be site specific.

Experimental Studies

Trace element contamination is an important environmental issue, as unlike organic contaminants, trace elements do not degrade over time. As trace elements are very persistent in the environment and traditional methods of remediation (e.g. involving soil removal and replacement) are often costly, it is important that innovative methods of remediation for trace element contaminated soils are developed. As discussed earlier in this report, soil amendments such as biochar and recycled organic matter may be suitable for *in situ* immobilisation of trace element contaminants in soil. Experimental studies were carried out on the promising combination of biochar and ROM to immobilise trace elements and facilitate revegetation. Several biochars and green waste composts as single and combined amendments were tested for the treatment of a copper contaminated soil.

Experimental work was undertaken as a collaboration between the Greenland project (FP7-KBBE-266124)[1] and HOMBRE and was initiated by a scoping study in 2013. The results from this experiment helped facilitate the development of a longer term study and supporting Master of Science project, which were conducted in 2014. Copper contaminated soil used in the three projects was obtained from a former wood preservation site in the Gironde County of South-West France.

The scoping study examined the effects of compost and biochar, applied both exclusively and combined, on the leachability of copper in the soil and the soil's phytotoxicity. A series of progressively more detailed leach tests was carried out, alongside a plant trial to establish a "ball park" effective range for the amendments.

[1] The Greenland project was established to investigate, improve and increase usage of gentle remediation options (GRO) including phytoremediation and *in situ* stabilisation using amendments (www.greenland-project.eu).

The detailed study and supporting MSc study investigated the use of three different biochars as single amendments and in combination with green waste compost. One biochar was commercially produced, developed and patented by C-Cure Solutions™ Ltd for the remediation of metal contaminated substrates. The other two biochars were produced by the Greenland project, using poplar grown at the site from which the contaminated soil was obtained. The detailed study examined the effect of biochar and compost on the leachability and phytotoxicity of copper in soil. Leach tests were carried out before and after a two-week incubation period and following a seven week growth period in the soil. A plant trial using *Helianthus annuus* L. was undertaken, with biomass and copper concentration in biomass recorded post-growth to determine phytotoxic effects. The supporting MSc study used sequential extraction to determine the effects of biochar and compost on mobility and fractionation of copper in soil. Sequential extractions were carried out before and after a two week incubation period and following a six week plant trial (again using *H. annuus*).

The results of the experimental studies demonstrated that mobility and phytotoxicity of copper was reduced in amended soils, with both biochar as a single amendment and in combination with compost proving successful in this capacity. These results were attributed to various factors associated with biochar and compost amendments, including increased sorption sites for soil contaminants, increased pH (decreasing copper availability, and in turn phytotoxicity) and increased nutrient provision (aiding plant growth). It could therefore be concluded that biochar and compost can be used successfully to aid remediation of a copper contaminated site. The amendments can also be used in combination with phytoremediation to further decrease pollution risks and potentially provide a saleable energy crop.

Operating Windows

To help stakeholders establish if ROM and biochar as soil amendments are suitable for risk management and the provision of sought-after additional services, “high level” and “detailed” operating windows have been developed. The detailed operating windows follow the traditional operating window rationale where the function is to identify the optimal conditions for applying a GRO in terms of its process parameters. HLOWs act as instruments to provide relevant information to stakeholders and support them in taking decisions for the selection of appropriate interventions in BF redevelopment / regeneration projects to deliver particular services. Operating windows can be used to establish if a particular remediation option may be suitable for use on a site, however further expert advice must be sought to develop a detailed remediation plan ensuring sufficient risk management can be provided by the selected remediation option(s). These are explained in detail in the report and also HOMBRE Deliverable D5.2.

Recommendations

Based on the outcomes of this report, it is clear that there is scope for biochar and compost to be successfully used in BF regeneration to soft end-uses. However, more research is required to further establish the detailed operating windows of these amendments and to more clearly define the influence of different feedstock materials on biochar and ROM properties. Future research could include trials to determine the effect of feedstock material on effective application rates for ROM and biochar. Additionally, the amendments successfully trialled in our research require field trials to determine their efficacy on a larger scale and confirm their potential for deployment on a full-scale remediation site.

1. Introduction

1.1 HOMBRE Project Overview

The HOMBRE (Holistic Management of Brownfield Regeneration) project seeks to aid both the prevention of sites from becoming Brownfields (BFs) and the regeneration of existing BFs into usable sites. BF sites can be described as derelict or underused sites which:

- Have been affected by previous land use of the site or surrounding land;
- Are mainly in partly or fully developed urban areas;
- Require intervention to bring them back to beneficial use;
- May have real or perceived contamination problems[2].

BF sites occur when previously developed land (potentially with a history of industrial use) falls out of use, following the cessation of its previous use. Negative perception of the land and reluctance on the part of potential investors to take on possible liabilities prevents redevelopment of the land, leading to the land becoming unused and derelict. BFs can have wider ranging impacts on the local and regional environment and economy.

BF regeneration can help reduce the effects of urban sprawl, by both reducing the demand on Greenfield sites and returning BF to green uses. In turn, re-use of BF land allows for a more sustainable built environment. The HOMBRE project has a focus on moving BF management practices towards greater sustainability. HOMBRE attempts to achieve this through strategies integrating BF re-use with local and regional (re)development, resource efficiency and effective stakeholder engagement. As areas affected by the presence of BFs often have concomitant socio-economic problems, including low employment, high crime figures, and poor infrastructure and housing (Tang & Nathanail, 2012), significant socio-economic gains can be obtained through the improvement of BFs. BF redevelopment may therefore contribute to all three elements of sustainable development (social, economic and environmental sustainability).

1.2 Report Objectives and Aims

This report is HOMBRE Deliverable 5.4, which has the aim of providing guidance on operating windows of two important low input technologies for greening (i.e. soft re-use of) urban BF:

[2] CABERNET (The Concerted Action on BF and Economic Regeneration Network). http://www.cabernet.org.uk/

1. Biochar and other *in situ* stabilisation agents
2. Organic matter recycling [to BF land]

The purpose of using these low input GROs for redeveloping/regenerating BF for soft re-use is to support soil improvement and risk management on site. However, they also provide wider environmental benefits (e.g. carbon sequestration). This report provides an overview of existing literature regarding these technologies and their potential uses, as well as their advantages and disadvantages for utilisation in greening urban BF. It also includes the outcomes of several experimental studies undertaken as joint initiatives between HOMBRE Project and the Greenland Project[3] (FP7-KBBE-266124) investigating biochar and composts as potential methods for remediating soil contaminated with trace metals. The hypotheses to be tested are:

H_1 – "Biochar application to soil is an opportunity to combine soil improvement, carbon sequestration and risk management (via *in situ* stabilisation)."

H_2 – "Organic matter addition to soil provides a durable immobilisation of trace elements and a carbon sequestration opportunity."

A combination of both experimental outcomes and conclusions from literature are used in an attempt to establish viable operating windows for these techniques. These are used as part of a series of operating windows in decision support guidance developed in HOMBRE Deliverable 5.2, the "Brownfield Opportunity Matrix" (see Section 5.3).

1.3 *In Situ* Remediation, Gentle Remediation and Risk Management

Biochar and recycled organic matter application to soil is one of several *in situ* stabilisation methods that may be employed for the management of BFs. *In situ* remediation describes treatment-based remediation processes that are carried out without the excavation of contaminated soils to the surface prior to treatment (*ex situ* treatment). Soils are treated "in place" as part of a risk management strategy with the aim of reducing the movement of a contaminant through the subsurface.

Two broad concepts have emerged in contaminated land management over the past 30 years: the use of risk assessment to determine the seriousness of problems, and the use of risk management to mitigate problems found by risk assessment to be significant. For a risk to be present (see Fig. 1) there needs to be a ***source*** (of hazardous contamination), one or more ***receptors*** (which could be adversely affected by the contamination) and one or more exposure ***pathways*** (linking the source to the receptors). Receptors might be human health, water resources, a built construction, or the wider environment. Requirements for land and groundwater remediation strictly depend on risk management needs. Risk management focuses on breaking the contaminant linkage, either by controlling the source; managing the

[3] www.greenland-project.eu

pathway(s); protecting the receptor(s), or some combination of these components (Nathanail *et al.*, 2007; Vegter *et al.*, 2002).

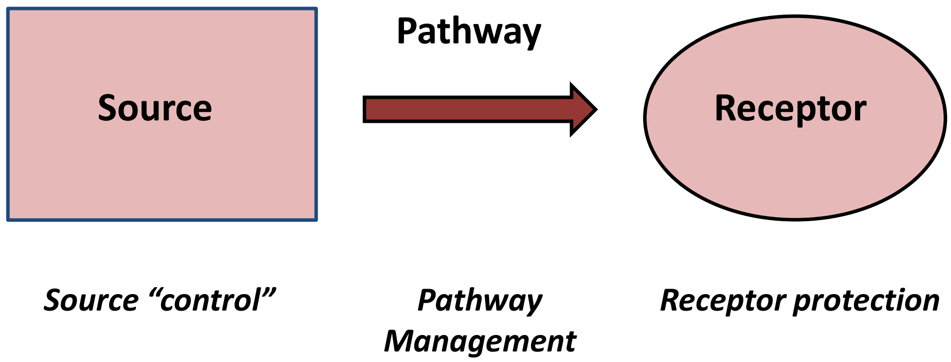

Figure 1: Contaminant Linkage and Risk Management Options (after Cundy *et al.*, 2013).

Conventional approaches to contaminated land risk management have focussed on containment, cover and removal to landfill (or "dig and dump"). However, since the late 1990s there has been a move towards treatment-based remediation strategies using *in situ* and *ex situ* treatment technologies. Treatment based remediation depends upon the destruction, degradation, extraction or stabilisation of contaminants, mediated by one or more of the following broad classes of processes: biological, chemical, physical, solidification/stabilisation or thermal (Nathanail *et al.* 2007).

In situ remediation is now a significant remediation market segment (Nathanail *et al.* 2013), although it is still only employed on a minority of projects. *In situ* remediation has a number of broad benefits, over *ex situ* processes where soil/water is excavated/pumped and treated on the surface (Harbottle *et al.*, 2008; Harbottle *et al.*, 2007). It enables remediation to be undertaken with minimal disruption to site operations and with minimal exposure of site workers and others to the contaminants (e.g. in dust, gas or vapours). The "footprint" of an *in situ* remediation project tends to be much smaller than for an *ex situ* scheme, meaning that treatment can usually be carried out where access and available space are restricted, and off site waste generation is reduced. *In situ* techniques can also provide a treatment option at sites where removal to the surface is likely to be problematic; e.g. where the contaminated material is at an impracticable depth or underneath infrastructure. Additionally, risks to site workers associated with exposure to contamination (e.g. toxic vapours) are reduced. Other environmental impacts of removing contamination to the surface may also be avoided; including dust and gas emissions.

Gentle remediation options (GRO) are risk management strategies/techniques that result in no gross reduction (or a net gain) in soil functionality as well as risk management. Hence they have particular usefulness for maintaining biologically productive soils (Cundy *et al.*, 2013). This concept is based on an older concept of "extensive" (i.e. low input, long term) treatment technologies developed in the Netherlands over the 1990s (Bardos & van Veen, 1996). The rationale is to both to minimize any negative effects of the remediation treatment process on soil systems, but also to reduce overall economic costs and management requirements (Menger *et al.,* 2013).

GROs encompass a number of technologies which include the use of plant (phyto-), fungal (myco-) or microbiologically-based methods, with or without chemical additives, for reducing contaminant transfer to local receptors by *in situ* stabilisation (using biological or chemical processes) or extraction of contaminants (e.g. Mench *et al*., 2010; Onwubuya *et al*., 2009; Vangronsveld *et al*., 2009; Chaney *et al.*, 2007; Grispen *et al*., 2006; Ruttens *et al*., 2006), such as phytovolatilisation, phytodegradation, phytoextraction, rhizofiltration, phytostabilisation and mycoremediation.

Intelligently applied GROs can provide: (a) rapid risk management via pathway control, through containment and stabilisation, coupled with a longer term removal or immobilisation/isolation of the contaminant source term; and (b) a range of additional economic (e.g. biomass generation), social (e.g. leisure and recreation) and environmental (e.g. CO_2 sequestration) benefits. In order for these benefits to be optimised or indeed realised, effective decision support and stakeholder engagement is required.

1.4 Gentle Remediation Options for Brownfield Soft Re-use

The overarching aim of HOMBRE Work Package 5 (WP5) has been to improve solutions for long term soft re-use of current and potential future BFs. The umbrella concept of “soft re-use” describes intended end uses of sites which are not based on built constructions or infrastructure (“hard” re-use). Instead, soft re-use describes BF redevelopment or regeneration where the soil remains unsealed and biologically functional. Examples include provision of public open space, parkland, cultivation and forestry. Soft and hard re-use scenarios may be integrated on one site. For example, a café may be built on a site that has been redeveloped into a public park (Menger *et al.,* 2013).

Soft end-uses of regenerated BF sites can lower the social, environmental and economic burden of a site; risk management strategies employed during regeneration are likely to lower environmental and public health risks, while provision of green-space, or public open space may improve all three elements of sustainable development. There are a range of circumstances in which soft re-use may offer economically viable and sustainable remedies for BF land that is otherwise undevelopable, improve the economic value of land, including adjacent land, through improved public perception of the land and surrounding area following the soft regeneration of a site. There may be important urban renewal arguments for developing amenity land, particularly in areas of urban deprivation (Menger *et al*., 2013).

Gentle remediation options (GRO) are low input risk management strategies/techniques that result in no gross reduction (or a net gain) in soil functionality as well as risk management. Hence they have particular usefulness for maintaining biologically productive soils and so are highly compatible with soft re-use of BFs (Cundy *et al.,* 2013, Menger *et al.,* 2013). GROs are more likely to be lower cost than their high-intensity counterparts and therefore more feasible for sites intended for soft-end use, as these sites are commonly economically limited.

For example, the use of GROs can be highly compatible with biomass end use (e.g. Van Slycken *et al*., 2013a, b; Bardos *et al.*, 2011a; Bardos *et al.*, 2010; Puschenreiter *et al.*, 2009)

GROs could be attractive alternatives to conventional clean-up methods in these situations owing to their relatively low capital costs and the inherent aesthetic value of planted or "green" sites. In addition, "greening" of contaminated or marginal land may have additional wider benefits in terms of educational and amenity value, CO_2 sequestration, resource deployment (as a compost re-use) and providing a range of ecosystem services (Menger *et al.*, 2013; Witters *et al.*, 2012; Bardos *et al*., 2011b).

Application of recycled organic wastes and biochars for the purpose of *in situ* immobilisation is a GRO strategy which may have a wide range of benefits that may be employed to help improve the viability of regenerating BFs to soft end uses.

2. Biochar use in Brownfield Redevelopment/Regeneration to Soft Re-uses

2.1 Biochar Background

Biochar is the carbon-rich end product of the pyrolysis of biomass. It is currently the focus of much scientific research, in part due to the diverse nature of its potential environmental applications. Amongst other uses, it has been suggested that biochar can be used for carbon sequestration, pollution remediation and recycling of agricultural wastes (Ahmad *et al*., 2014). It has even been proposed that biochar could be used in bio-energy production (Laird, 2008). There are strong suggestions that biochar may be applied as an amendment to soil. In this application, biochar may provide both cultivation improvements (through nutrient provision, improved water retention and pH control) and immobilisation of soil contaminants.

Biochar can be produced from a range of biomass types (or "feedstocks") including wood and plants (Singh *et al.* 2010a), manure (Cao & Harris, 2010; Ro *et al.*, 2010; Singh *et al.* 2010a; Cao *et al.* 2009) and wastes from the food and paper industries (Özçimen, & Ersoy-Meriçboyu, 2010; Singh *et al.* 2010a). The feedstock utilised in production is a key factor in determining the physico-chemical properties of biochar. Indeed, these properties may vary relatively widely depending on both the initial feedstock material and the method of production. As a result of this variability, it is difficult to give a definitive overview of physical and chemical characteristics that can be used to define biochar. However, general properties of biochar include a high C content and high porosity. Both these features result from the biomass origin of biochars; a high C content derived from the organic C in the production biomass and porosity resulting from the cellular morphology of the biomass (Downie *et al*., 2009).

Certain biochar properties are more strongly affected by variability in feedstock than others (e.g. amount of contaminants in biochar) (Shackley *et al.*, 2010). Some biochar properties are less dependent on feedstock and may be controllable by altering the production process conditions. Novak *et al.* (2009) found that various biochar characteristics could be altered using different pyrolysis temperatures. For example, higher pyrolysis temperatures created biochars with greater surface areas and a higher pH.

The heterogeneity resulting from variations in the production of biochar is a key positive attribute and contributes to its versatility, as biochar can be tailored to suit the use for which it is required. Nonetheless, as a result of the diversity of production and corresponding diversity in the physico-chemical attributes of biochars, conclusions drawn from experimental studies on the effects of biochar on soil and other environmental media must remain specific to the biochar types studied.

Alternative soil amendments to biochar for remediating contaminated soil have been studied in recent years, and indeed are still under investigation, with the aim of increasing the understanding of key performance factors and efficiency. Examples of such amendments are haematite, zero-valent iron, zeolites etc. In the frame of FP7 Greenland project[4], a set of amendments were tested (either as pure amendments or mixtures of them) in order to estimate their efficiency towards supporting gentle remediation techniques like phytostabilisation and/or phytoexclusion on soils contaminated with trace elements. Examples of tested amendments are: $CaCO_3$, drinking water residue, Ca-phosphate, green waste compost, slags, gravel sludges, siderite, cyclonic ashes and iron grit (equivalent to zero-valent iron). These amendments may originate from industrial activities (i.e. slags, sludges), municipal waste streams (green waste) or from primary resources (i.e. siderite).

The cost of biochar production and application in remediation is highly dependent on many variables including the feedstock and production process (Mohan *et al.*, 2014). Shackley *et al.* (2011) estimate the cost of production, transportation and application in the UK to be between £148-389 t^{-1}. Mohan *et al.* (2014) conclude that the cost of biochar production can be decreased if produced as part of a pre-existing process, where value-added co-products are generated, e.g. bioenergy.

2.2 *In Situ* Stabilisation using Biochar

Biochar is increasingly being investigated as an *in situ* stabilisation agent, i.e. for its potential to immobilise contaminants in the soil matrix. Several characteristics of biochar contribute to its ability to immobilise contaminants:

- **Porosity and large surface area.** Biochar has a large surface area as a result of its highly porous nature. It has been suggested that the pore space of biochar is several thousand times greater than that of the pre-pyrolysed biomass (Thies and Rillig, 2009). This large surface area provides an increased ability to adsorb contaminants.

[4] http://www.greenland-project.eu/

- **Large cation exchange capacity.** Addition of biochar to soil can improve the availability of cation exchange sites in the soil, giving increased potential for contaminant adsorption.
- **pH.** Biochar is usually alkaline, meaning biochar additions to soil have the potential to increase soil pH, therefore reducing availability of some trace metal contaminants (Zhang *et al.*, 2013).

Biochar also has a range of wider benefits as a GRO, and in particular, for BF soft re-use projects (described in more detail in the sections below):

- Ease of application to soils
- Persistence: biochars may remain in soils for many hundreds, if not thousands, of years
- Carbon sequestration
- Improvement of soil function.

A possible concern over biochar application to soil is the possibility that it may contain entrained contaminants, in particular products of incomplete combustion such as PAHs (see Section 2.2.6). However, these were not found to be at problematic levels in the charcoals tested by HOMBRE (see Chapter 4).

2.2.1 Biochar's Performance as an *In Situ* Stabilisation Agent

Studies suggest that both organic contaminants and trace elements may be successfully immobilised using biochar (Ahmad *et al.*, 2014; Tang *et al*., 2013). Annex 1 gives an overview of the numerous contaminants that have been treated by biochar, both as a single amendment and in combination with other treatments. Soil amendment with biochar may also work synergistically with several forms of phytoremediation for example by improving biomass yield, or complementing phytostabilisation.

A range of soil treatment studies have been carried out, including those detailed in this section. For example, Uchimiya *et al.* (2011) demonstrated that biochars derived from cottonseed hull effectively stabilised trace elements including lead and copper and used positive matrix factorisation to determine the processes responsible for the binding of metal ions. The authors showed that the amount of metal sorption occurring was directly linked to the number of oxygen-containing surface functional groups (carboxyl, hydroxyl, and phenolic) found in soil organic and mineral components; biochar was found to increase the number of these functional groups. Tong *et al.* (2011) found comparable results, concluding that biochar adsorption of copper (II) was specifically through surface complex formation with phenolic hydroxyl and -COOH groups. Biochar amendment of soil can increase the number of these surface functional groups in the soil, thereby immobilising contaminants.

The unique properties and versatility of biochar mean that it may offer advantages over alternative *in situ* stabilisation agents. For example, biochars can be tailored to suit the specific demands of a remediation site. Any of a large number of feedstocks and production processes can be used to alter the physico-chemical properties of biochar, allowing the production of “designer” biochars (Novak *et al.*, 2009). Cao *et al.* (2009) demonstrated that dairy manure derived biochar was more effective at sorption of lead and atrazine compared to a commercially purchased activated carbon product. Additionally, the authors found that where lead and atrazine coexisted, less competition for sorption was observed on the biochar compared to the activated carbon. Additional benefits of biochar may include its longevity, as some studies have suggested it may require fewer reapplications than other organic amendments (see Section 2.3.4). Further, whilst working as an immobilisation agent, biochar may concurrently improve key characteristics associated with soil quality on the treated contaminated land (see Section 2.2.5). This is an important benefit of biochar application, as soils on contaminated sites are often degraded.

Biochar can increase soil pH, reducing the availability of some contaminants (Zhang *et al.*, 2013), consequently reducing phytotoxicity and improving soil conditions for cultivation. Khan *et al.* (2013) showed that sewage sludge biochar increased the pH of an acidic paddy soil, decreasing bioavailable arsenic, chromium, cobalt, nickel, and lead and increasing *Oryza sativa* L. yields.

Similar to all remediation options, biochar application has some negative aspects. Some papers have concluded that under certain conditions, biochar may in fact have an adverse effect on soil contaminant availability. For example, Beesley *et al.* (2010) found copper was mobilised in soil when biochar was added as a result of increased dissolved organic carbon (DOC) associated with organic amendment addition. Lucchini *et al.* (2014a) also found that biochar application increased the water soluble proportion of lead. However, this was attributed to the feedstock and production process of the biochar, in combination with the specific soil conditions of the site.

In summary, biochar has great promise as an *in situ* stabilisation agent, with the potential to immobilise both organic and trace element contaminants in soil. It may provide a low cost and multi-purpose soil improving agent for the further improvement of BF sites. However, in common with all *in situ* remediation agents, biochar application should be approached on a site specific basis to reduce environmental and health risks.

2.2.2 Biochar Application to Soil

Conventional techniques for fertiliser applications could also be used for biochar applications, providing a readily available and widely held pool of expertise and capability. The options generally considered are: *uniform top soil mixing*, incorporation with other mediums (manure, compost, liquid manures and slurries), *deep banded in rows*, and *topdressing*. Techniques like top soil mixing and topdressing might be enhanced with mitigation measures against wind and water erosion to improve efficiency (Verheijen *et al.*, 2010).

Practices from biochar applications into soil have revealed that the particle size could have a direct impact on cost, efficiency and the wider side effects on surrounding areas. Particle size is a key consideration in determining the machinery suitable for application to soil and to control the potential for exposure to dust (Shackley *et al.*, 2010).

Coarse products from slow pyrolysis may need to be reduced to finer sizes. It is to be expected that if commercial biochars are to be provided with some uniformity of particle size, this would certainly impact on the costs of its production due to agglomeration or grinding processes needed, even though necessary technologies are well established as the above author reports.

Very fine sized particles, essentially those produced from fast pyrolysis, may need to undergo agglomeration, to avoid dispersion via wind and therefore posing a hazard (Laird, 2008). A two-year field trial set up by BlueLeaf Inc. in Canada found 30% of biochar applied was wind-blown as dust, or lost during handling and transport (Husk & Major, 2010).

In addition to loss by wind during/after application, biochar can also be lost by water erosion. As for soil erosion itself, sloping terrain may aggravate this problem. Authors have reported significant losses of biochar incorporated into very flat topographies in areas where intense rainfall events occur (Major *et al*., 2010). Best management practices may consist in rapidly incorporating biochar into soil, especially on land with pronounced slopes or where intense rainfalls occur.

Hence there are human health and wider environmental hazards to consider when applying biochar to land. It is thought that the greatest risks for health and the environment from the use of biochars as soil amendments occur during application itself and the period directly following this. However, health and environmental risks posed by biochar are overall small relative to other remediation technologies. To reduce any environmental or health risks, biochars should be selected to suit the remediation site and reduction of risks should be built into the remediation design. Mitigation measures may also include waiting for optimal weather conditions for applying biochars, i.e. low wind and mild rain conditions. Applying moisture to biochar or moist manure may be alternative options (International Biochar Initiative[5]).

2.2.3 Persistence of Biochar in Soil

The durability of an *in situ* stabilisation agent is important in several ways. Firstly, if the agent is labile it will eventually degrade and the stabilised contaminant may be remobilised. Secondly, if the agent is very durable, the need for repeat applications is obviated reducing the cost, effort and impacts of repeat applications on site.

The observation of *terra preta* (black earth) in the Amazon Basin (Kleiner, 2009) illustrates the potential longevity of biochar in soil. However, this longevity also poses problems in determining the persistence of biochar on an experimental basis.

[5] www.biochar-international.org

It has been suggested that the stability/durability of biochar in soil could be estimated on the basis of its elemental composition and in particular monitoring its molar oxygen/carbon (O/C) ratio (Spokas, 2010; Abdel Fattah, 2014). O/C ratios lower than 0.2 indicate a biochar's half-life to be over 1000 years. However, O/C ratios above 0.2 would indicate a shorter half-life, ranging from 100 to 1000 years. Spokas (2010) observed that higher pyrolysis temperatures gave rise to combustion products with a low O/C ratio, i.e. high fixed carbon and reduced oxygen content in biochars. Figure 2, below shows how O/C ratios and type of combustion products are organised on a scale of O/C ratios. O/C ratio is a function of pyrolysis temperature and feedstock material.

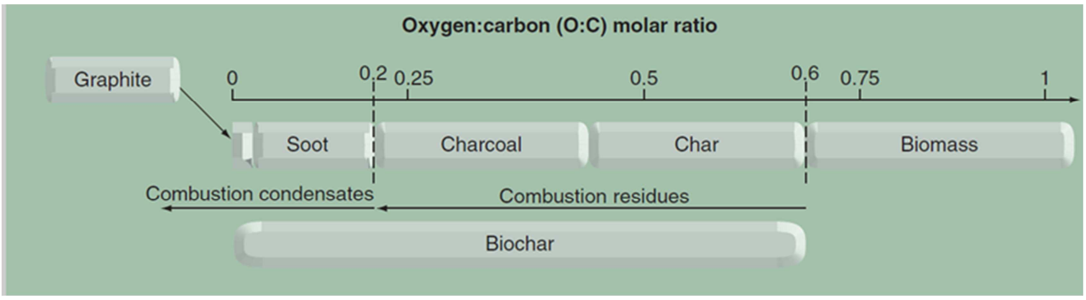

Figure 2: the combustion product spectrum as a result of the chemical-thermal conversion of biomass (Spokas, 2010).

In the absence of validation for this method, some authors/organisations, for example the UK Biochar Research Centre (UKBRC), have proposed alternative approaches for estimating biochar stability. The method developed by the UKBRC consists of an accelerated ageing process in which biochars are submitted to oxidative treatments (i.e. thermal and chemical oxidation) aimed at replicating ageing processes that would naturally occur in the environment (Mašek *et al.*, 2013) over longer periods of time. After the simulated ageing process, the stable C fraction contained in the biochar is estimated. These experiments also showed that with increasing pyrolysis temperatures, the recalcitrant carbon fraction (i.e. stable carbon) in biochar increased. Hence, the concentration of stable C in biochar increases with increasing pyrolysis temperature. However, increasing the temperature of diminishes biochar yield.

Several other studies have also shown biochar to be very long lasting in soil (e.g. Haefele *et al.*, 2011), particularly as a carbon store (Quilliam *et al.*, 2012). Gurwick *et al.* (2013) reviewed literature estimating biochar stability and found that *in situ* studies of biochar decomposition rates reported residence times of between 8 and 4000 years.

Overall, biochar has been demonstrated to potentially provide stable and long-lasting effects on soil. Biochar's durability means it does not require numerous applications, therefore reducing the likelihood of trace element accumulation which might be associated with alternative amendments, such as sewage sludge, which are relatively rapidly degraded in the soil (Beesley *et al.*, 2010).

2.2.4 Carbon Sequestration using Biochar

One of the most important additional benefits of biochar use for BF regeneration is the potential provision of a means of carbon sequestration. Through the sequestration of CO_2, biochar may constitute a useful tool to help combat climate change (Kauffman *et al.*, 2014; Oleszczuk *et al.*, 2013; Hammond *et al.*, 2011; Shackley *et al.*, 2009; Yin Chan & Xu, 2009). Indeed, carbon sequestration in soil has been recognized as one of the possible measures through which greenhouse gas emissions can be mitigated (IPCC, 2014).

Carbon sequestration is the process of capturing atmospheric carbon dioxide and retaining it in some form of storage[6]. This process is intended to help mitigate climate change resulting from anthropogenic CO_2 emissions. Biomass is a natural carbon store, as carbon dioxide is taken up by plants during photosynthesis and stored as organic carbon. However, this store is only temporary as carbon is released when biomass decomposes (Lehmann & Joseph, 2009). Biochar may provide longer term storage for carbon, as it is persistent in soil. The process of biochar production itself, may also be carbon negative, if it is part of a biomass to energy process.

Biochar addition may affect the emission and generation of greenhouse gases by soil processes. For example, Zhang *et al.* (2010) found that wheat straw biochar addition at 40t ha^{-1} increased methane emissions by 34-41% in a rice paddy in China relative to non biochar amended soils. However, the same paper showed nitrous oxide emissions were reduced by 40-51% with biochar addition combined with N fertilisation, or 21-28% with biochar addition alone. N_2O is a potent greenhouse gas. Hence biochar addition may reduce soil greenhouse gas emissions resulting from nitrogen fertilisation of crops.

Ding *et al.* (2010) found biochar application to soil reduced NH_4^+ losses overall. It has also been suggested that inorganic N losses associated with biochar addition to soil may be as a result of reduced conversion to N_2O. Several studies have shown reduced N_2O emissions associated with biochar addition to soils (Khan *et al.*, 2013; Jia *et al.*, 2012; Taghizadeh-Toosi *et al.*, 2011).

2.2.5 Biochar Effects on Soil Functioning and Cultivation

Biochar addition can be strongly beneficial for soil structure and function, facilitating revegetation, for example, for the cultivation of biomass. Several papers have demonstrated an increase in plant biomass associated with biochar addition to soil (Akhtar *et al.*, 2014; Carter *et al.*, 2013; Khan *et al.*, 2013; Kammann *et al.*, 2011). Soil nutrient availability, pH and water retention may all be improved through biochar addition to soil (McLaughlin *et al.*, 2009; Steiner *et al.*, 2007). These potential benefits may be highly useful in the remediation of BF sites, which commonly have poor soil quality (Mallik & Karim, 2008; Nixon *et al.*,

[6] http://www.undeerc.org/pcor/sequestration/whatissequestration.aspx

2001) or where contamination often co-exists with other characteristics indicative of poor soil fertility. Biederman and Jarpole (2013) carried out a meta-analysis of 371 independent studies (collected from 114 published manuscripts) and showed that despite variability introduced by soil and climate, the addition of biochar to soils generally resulted in increased above ground productivity, crop yield, soil microbial biomass, rhizobia nodulation, plant potassium tissue concentration, soil phosphorus, soil potassium, total soil nitrogen, and total soil carbon compared with control conditions. Soil pH also tended to increase, becoming less acidic, following the addition of biochar.

Several papers have demonstrated an increased availability of plant nutrients as a result of biochar application to soil. For example, Gaskin *et al.* (2010) found that biochar produced using a peanut hull feedstock increased available potassium, calcium and magnesium in the surface soil. Similarly, Haefele *et al.* (2011) found in field-applications of rice husk biochar to a rice production site increased total soil nitrogen and available phosphorus and potassium. Biochar may contribute to plant nutrition both directly, through increased provision of nutrients; and indirectly, through improvement of soil structure to aid retention of nutrients, or the improvement of soil biological functions (Prendergast-Miller *et al.* 2014; Xu *et al.* 2013; Yin Chan & Xu, 2009). Direct release is important for cations including potassium, calcium, sodium and magnesium. There is also potential for biochar to be used as a carrier matrix for nitrogen fertilisation (Spokas *et al.* 2012).

Indirectly, biochar may prevent losses of nutrients through: reduced leaching, as a result of altering soil pH; and increasing sorption of nutrients, as a result of improved cation exchange capacity (Carter *et al.*, 2013; Liang *et al.*, 2006). This adsorption of nutrients may be improved through steam activation of biochar. Borchard *et al.* (2012) found that biochar that underwent a technical steam activation had an improved positive effect on nutrient retention in soil relative to a non-activated biochar. Other types of “activation” of biochar that have been successfully trialled include chemical activation with potassium hydroxide (Trakal *et al.*, 2014).

Additionally, pH increases associated with biochar may improve the general chemical characteristics of the soil, making them more favourable to plant growth, as acidic conditions are phytotoxic for some species. Soil pH changes induced by biochar may also have a further bearing on nutrient availability, as each key plant nutrient will be optimally available at a particular range, usually close to neutral.

Some research has suggested that biochars may have the potential to improve water retention in soils (Streubel *et al.*, 2011). This is likely to be as a result of the sorbency of charcoal, improved soil structure and organic matter content associated with biochar additions to soil. Kammann *et al.* (2011) demonstrated that biochar application to soil can improve drought tolerance in *Chenopodium quinoa* Willd in a sandy soil. Similarly, Laird (2008) suggested biochar could provide long term improvement to soil quality and the provision of bioavailable water. Bruun *et al.* (2014) also demonstrated that biochar can improve water retention in poor quality sandy soils. The authors saw a 2.65% (v/v) increase in plant available water per% (m/m) of char. Char additions at 1% increased plant yield; however, the authors also found biochar additions at 4% had a negative effect on plant growth, attributed to excessive water retention. Biochar application should therefore be optimised through further experimental trials to determine the effective limits. Akhtar *et al.* (2014) found that biochar could increase soil water retention and improve the yield of *Solanum lycopersicum* L. under reduced irrigation conditions.

The improvement in soil characteristics associated with biochar addition may improve the biological functioning of soil. Soil organisms are crucial in the functioning and fertility of a soil and play a key role in many nutrient cycles (Sparling, 1997). Biochar has been suggested to provide improved habitat for soil organisms and micro-organisms (Lehmann *et al.*, 2011, Lehmann & Rodon, 2006). McLaughlin *et al.* (2009) suggest microbes may have a synergistic relationship with biochar. Biological nitrogen fixation could be beneficially supported by biochar in soil (Lehmann & Rodon, 2006). Lehmann *et al.* (2011) reviewed the effects of biochar on soil biota.

There are, however, reports that biochars may have an adverse impact on cultivation and soil quality in some circumstances (Mukherjee & Lal, 2014). For example, Gajić and Koch (2012) found growth of *Beta vulgaris* L. was reduced with the addition of a hydrochar (produced through hydrothermal carbonisation), attributed to nitrogen immobilisation associated with high carbon inputs to soil. A review by Ippolito *et al.* (2012) presents previous reports of nitrogen immobilisation and a concurrent decrease in plant available nitrogen associated with large carbon inputs into soil (e.g. Leifield *et al.*, 2002).

2.2.6 Potential Contamination of Biochar by Trace Elements and Organic Contaminants

Despite the positive effects of biochars on soil, plant growth and climate change mitigation, there is increasing debate about their innocuousness with regards to human health and the environment, due to their possible contaminant content (Oleszczuk *et al*., 2013). There are two main potential factors that influence contaminant content in biochar: feedstock (source material), and the conversion process. Depending on the feedstock, produced biochar may contain trace elements and organic compounds. Some of these compounds will be altered or destroyed during pyrolysis; others will remain unchanged or give rise to potentially harmful substances (Shackley *et al.*, 2010). The significance of any risks posed depends on the biochar application and the likelihood of exposure of receptors. However, in general, if biochars contain levels of trace elements and organic compounds that substantially exceed typical soil background levels, the likelihood is that their practical use as an *in situ* stabilisation agent will be constrained by regulatory concerns that the material is a “waste” under the terms of the Waste Framework Directive (2008/98/EC).

The content of trace elements in biochar depends largely on feedstocks used (Qian *et al.*, 2013). In turn, trace element contents of the feedstock will depend on its origin and/or level of contamination; e.g. agricultural residues, biomass crops, municipal waste, sewage sludge etc. During pyrolysis, the fate of trace elements contained in the feedstock depends on pyrolysis technique (i.e. flash or slow pyrolysis, hence heating rate) and temperature. At low temperatures, i.e. ≤ 450ºC, the main product of pyrolysis is biochar. As a consequence, trace elements remain in the biochar, whereas their concentrations in oils tend to be below detection limits (Al Chami *et al.,* 2014). At very high temperatures though (700ºC – 800ºC and higher), metal transfer to volatile pyrolysis products has been observed. Trace elements contained in this fraction end up in condensation products of pyrolysis, i.e. bio-oils (Stals *et al.,* 2010).

In the context of ecosystems, especially agro-ecosystems, a key factor for estimating possible risks due to the presence of contaminants in soil is their leachability (capacity of contaminants to be washed out from the solid phase to the pore water) and bioavailability, (the proportion of contaminants available for uptake by biota). These factors are in turn very dependent on site/environmental specific conditions such as pH; soil mineralogy; presence and concentration of organic and inorganic ligands, including humic and fulvic acid; root exudates; microbial metabolites; and nutrients (Violante *et al.*, 2010). Total concentrations of contaminants in soils are not an appropriate indicator for estimating biological effects (Harmsen, 2007; Alexander, 2000). The water soluble fraction is the most biologically active and has the highest potential for contamination of the food chain, surface water and ground water (Singh, 2013 & Kalamdhad, 2013).

In other words, if contaminants contained in biochars cannot be mobilised or leached from the biochar matrix they will not be able to migrate to other environmental compartments and will not cause harm to any receptors (plants, animals, micro-organisms etc.). In recent years, much effort has been deployed investigating leaching behaviour of different biochars and gaining a better knowledge of their potential harm to health and the environment when used as soil amendments.

To a great extent, leachability of trace elements contained in biochar after pyrolysis is dependent on temperature (Agrafioti *et al*., 2013), where increasing pyrolysis temperatures tend to enhance stability of trace elements in biochar (He *et al*., 2010; Stals *et al.*, 2010). Deviations from these tendencies have been observed, and may be attributed to feedstock, pyrolysis process and alkalinity of biochars. Under identical pyrolysis parameters, differences in leachability tendencies could be observed from one specific metal to another, however, overall, leachability has been reported as far below those of the feedstock material and below guideline values for hazardous waste (Chen *et al*., 2014).

In experiments carried out using sewage sludge - a feedstock containing higher metal concentrations - pyrolysis has been shown to reduce the leachability of trace elements (Song *et al.*, 2014). This has been attributed to the capacity of pyrolysis in binding and stabilising trace elements in the biochar matrix (Jin *et al.,* 2014; Hwang *et al.,* 2007). It has been observed that the bioavailability and eco-toxicity of trace elements in biochar could be reduced as the mobile and bioavailable metal fractions are transformed into relatively stable fractions through the pyrolysis process (Devi & Saroha, 2014).

In addition to trace elements, products of incomplete combustion (PICs) may give cause for concern. PICs can be formed in the conversion (pyrolysis) process. These include polycyclic aromatic hydrocarbons (PAH) and potentially, in some cases, dioxins. PAHs are produced as a consequence of incomplete combustion of organic components. Most PAHs are known carcinogens and/or mutagens. These contaminants can possibly be present in the biochar matrix and even bioavailable to exposed organisms.

Studies carried out to date have found that PAH contents in biochar depend on multiple parameters, i.e. pyrolysis temperature, pyrolysis time but also feedstock properties (Brown *et al.,* 2006). It has been observed that with increasing time and temperature in slow pyrolysis processes, PAH concentrations generally decreased, giving rise to concentrations below existing environmental quality standards for PAH concentrations in soils. For example, concentrations of bioavailable PAHs produced during slow pyrolysis have been shown to be lower than concentrations reported for relatively clean urban sediments (Hale *et al.,* 2012). The same authors report low dioxin concentrations in biochars (below 100 $\mu g\ t^{-1}$) and concentrations below analytical detection limits for bioavailable dioxins. Other authors have observed the influence of pyrolysis temperature on extractable PAH in biochars. Results obtained show a temperature range (i.e. approx. between 400ºC and 500ºC) where PAH concentrations in extractable fractions exceeds those observed at both higher and lower temperatures (Keiluweit *et al.,* 2012; Kloss *et al.,* 2011). These findings are in line with observations made by Hale *et al.* (above). Potentially then, the risk of biochar as a source of contamination can be reduced by utilising appropriate feedstocks and production processes.

Hence, there are some possible risks associated with biochar application to land from trace elements or organic compounds. Biochar composition should be tested before any decision for use. Typically biochar should be tested in both pot and field plot trials prior to full scale deployment to land to ensure any potential contaminants are below levels considered problematic.

3. Recycled Organic Matter for Brownfield Regeneration to Soft-End Uses

3.1 Recycled Organic Matter Background

Recycled organic matter (ROM) can be derived from multiple organic waste sources and can be tailored to suit a specific purpose. Organic waste can be defined as waste which is biodegradable and may include household and commercial sources, such as food; garden wastes; paper; cardboard and wood, alongside agricultural wastes, such as manure and crop residues (Bardos *et al.,* 2010; Bardos *et al.,* 2001). Other forms of organic waste include sewage sludge, produced as a result of waste water treatment. Organic wastes may be recycled and utilised in various ways; the two major end-uses being as a soil amendment and for fuel/energy production.

Organic wastes may be utilised directly as ROM on BF, but more commonly undergo some form of processing prior to re-use, typically via composting or anaerobic digestion[7] (Bardos *et al*., 2010). As a result of the variability in feedstocks and processing methods, the end products of organic waste recycling are highly varied. However, the typical organic matter and nutrient rich nature of these end products makes them highly beneficial for application as soil amendments, as discussed in the following chapters.

The cost of organic matter for redevelopment/regeneration is highly dependent on the proximity of the site to sources of supply and the quality of the organic matter being used. In some situations (for example, compost like outputs "CLOs" produced from mixed wastes) the waste producer may bear all the costs of supply, transport and application as the material is hard to place. Sewage sludges and anaerobic digestates may also be available at no or low costs, and sometime even green waste composts if there is a local over-supply of material. However, typically higher grade materials will cost more to use both in terms of their cost per tonne and absence of cross-subsidies, such as the supplier paying for application (Bardos *et al.*, 2010).

There are three broad interventions (reviewed below) where organic matter might be applied to land for BF redevelopment/regeneration for soft re-uses:

- Soil forming (for example, where sites are denuded of top soil or are on made ground);
- Improvement of soil function where the fertility and/or structure of an existing soil needs to be upgraded;
- Potentially as a means of contaminant immobilisation (although mobilisation may also be possible).

Organic matter applications may fulfil more than one purpose simultaneously.

Organic matter application to soils may also provide a series of wider benefits, including: re-use of organic matter and plant nutrients (which would otherwise have to be supplied from mineral fertiliser sources); a beneficial re-use for wastes that would otherwise be landfilled or incinerated; relative ease of use; and potential carbon sequestration. Importantly, through improvement of plant growth, the re-use of organic matter may enhance the performance of a range of vegetation-based soft re-use services, including, but not limited to: phytoremediation, biomass production (for energy or feedstock), landscaping, and habitat creation. The re-use of organic matter avoids the re-use of imported primary resources such as peat, mineral fertilisers, soil or aggregate and so contributes to resource efficiency and the circular economy.

[7] Organic wastes and residues are also a feedstock for biochar production as described in Chapter 2

However care needs to be taken over several factors: the possibility of contaminants in the ROM; the possibility that organic matter may mobilise trace elements already present in the site's soil; and the possibility that they may deliver excessive levels of nitrogen and phosphorous (leading to unacceptable impacts on air, water and/or cause local nuisances such as odour and bio-aerosols).

3.2 Recycled Organic Matter for Soil Forming

Soil-forming describes the use of non-soil materials used in land reclamation to support vegetation growth. These are usually derived from mineral wastes, such as: overburden materials (i.e. soils lying above minerals of interest for mining), uneconomic geological materials encountered during quarrying or mining (spoils), various industrial by-products such as pulverised fuel ash, dredged materials, remediation treatment residues (e.g. treated outputs from soil washing), and made ground. Soil-forming materials must also have the propensity to turn into soils over time. This process can be encouraged by treatment to relieve compaction; the incorporation of organic matter such as green waste compost; and the choice of appropriate vegetation types that will endure and improve the quality of the substrate. These materials may have chemical or physical properties that are hostile to plants. They may also contain contaminants. In general the importation to site of materials with entrained contamination should be prevented. The use of on-site materials containing contaminants will need to be subject to risk assessment and, if necessary, remediation measures (including gentle remediation options). Soil forming materials need to be improved by the addition of ROM and require cultivational measures to encourage soil formation. The soil forming and soil improvement processes need to be designed with the envisaged revegetation in mind, for example, as a very simple instance tree and grassland establishment have very different requirements, for example, as a very simple instance tree and grassland establishment have very different requirements (CL:AIRE, 2009; Defra, 2009; Forest Research, 2009; DCLG, 2008; Nason *et al.*, 2007; Foot & Sinnett, 2006).

3.3 Recycled Organic Matter for Soil Improvement

ROM has the potential to be utilised beneficially in BF management in a number of ways, not least through improving the condition of the soil. ROM can effectively stabilise soil structure, improve oxygen diffusion and water availability, and optimise nutrient conditions to sustain biota or phytoremediation practices (Gandolfi *et al.*, 2010; Bes & Mench, 2008). This is important for both contaminated and non-contaminated BF sites.

ROM in certain forms (e.g. compost) is well established as a beneficial soil amendment (EC, 2003), which can improve various soil characteristics including nutrient supply, nutrient cycle functioning and soil structure (Ohsowski *et al.*, 2012; Hargreaves *et al.*, 2008). The beneficial role of ROM products is largely a function of their provision of organic matter to soils. Table 1, below, outlines the key roles of organic matter in soil. Improvements achieved through the addition of organic matter to soil can increase the quality and yield of crops grown on the land.

Table 1: An overview of the role of organic matter in soil (Bardos *et al.,* 2001; Based on Stevenson, 1994).

Property	**Remarks**	**Effects on Soil**
Colour	The typical dark colour of many soils is often caused by organic matter	May facilitate warming in spring
Soil Biodiversity	The organic fraction in soils provides a source of food for a diverse range of organisms. The diversity of the organic materials will generally be reflected in the diversity of the organisms	Many of the functions associated with soil organic matter are related to the activities of soil flora and fauna
Water Retention	Organic Matter can hold up to 20 times its weight in water	Helps prevent drying and shrinking. May significantly improve the moisture retaining properties of sandy soils. The total quantity of water may increase but not necessarily the AWC except in sandy soils
Combination with clay minerals	Cements soil particles into structural units called aggregates	Permits the exchange of gases. Stabilises structure. Increases permeability
Reduction in the Bulk Density of Mineral Soils	Organic materials normally have a low density, hence the addition of these materials 'dilutes' the mineral soil	The lower bulk density is normally associated with an increase in porosity because of the interactions between organic and inorganic fractions.
Solubility in water	Insolubility of organic matter because of its association with clays. Also salts of divalent and trivalent cations with organic matter are insoluble. Isolated organic matter is partly water-soluble.	Little organic matter is lost through leaching
Buffer action	Organic matter buffers in slightly acid, neutral and alkaline ranges	Helps to maintain uniform reaction in the soil.
Cation exchange	Total acidities of isolated fractions of organic matter range from 300 to 1400 $cmol_c\ kg^{-1}$	May increase the CEC of the soil. 20 to 70% of the CEC of many soils is associated with organic matter.
Mineralisation	Decomposition of organic matter yields CO_2, NH_4^-, NO_3^- PO_3^{4-} and SO_4^{2-}	A source of nutrients for plant growth
Stabilisation of	Stabilisation of organic materials in	Stability may depend on the

Property	Remarks	Effects on Soil
contaminants	humic substances including volatile organic compounds	persistence of the soil humus and the maintenance or increase of the carbon pools in the soil
Chelation of metals	Forms stable complexes with Cu^{2+}, Mn^{2+}, Zn^{2+} and other polyvalent cations	May enhance the availability of micronutrients to higher plants

ROM can provide both an initial increase in nutrients to enhance crop establishment, as well as a pool of slow-release nutrients to maintain crops. Indeed, ROM has been shown to increase the yield of some crops (Montemurro *et al.,* 2006). Further, Allievi *et al.* (1993) found soil fertility and crop quality improvements derived from compost treatment were apparent even after several years. Weber *et al.* (2007) found compost amendment of soil improved bioavailability of nutrients, specifically phosphorus, potassium and magnesium in a sandy soil. Likewise, Busby *et al.* (2007) found total inorganic N to be increased in municipal waste compost amended soils. The beneficial effects of organic amendments can also be seen on contaminated sites. For example, Hartley *et al.* (2009) found green waste compost improved yields of *Miscanthus* in an arsenic contaminated soil. Many organic amendments also have a liming effect leading to increased soil pH (Mkhabela & Warman, 2005; Walker *et al.,* 2004; Whalen *et al.,* 2000).

ROM tends to have a positive impact on microbial populations in the soil. Many studies have reported increases in soil microbial populations and functioning as a result of ROM additions to soil (e.g. Gandolfi *et al.,* 2010; Albiach *et al.,* 2000). Tejada *et al.* (2006) showed poultry manure and compost addition to saline soil improved microbially driven nitrogen cycle processes, including stimulation of urease and BAA protease activity. This could have positive implications for soil nutrition.

Addition of ROM increases biological activity in the soil, which results in the formation of stable aggregations of soil mineral and organic particles improving soil structure, condition and resilience (Bardos *et al.,* 2001). Pagliai *et al.* (2004) demonstrated that livestock manure and compost both had positive effects on the structure of soil on an arable agricultural site. Troeh and Thompson (2005) suggested that organic matter inputs can increase water content in a sandy soil and alleviate waterlogging in clay soil.

Soil structure and organic matter content is integral to water retention in soil. Indeed, several papers have demonstrated that ROM additions can improve the water holding capacity of soil. For example, Aggelides and Londra (2000) found compost produced from a mixture of town wastes, saw dust and sewage sludge improved several soil physical properties when applied to clay and loamy sands, including water retention. pH and CEC were also found to be increased as application rates increased. Evanylo *et al.* (2008) similarly found increased water holding capacity in field trial soils treated with compost, although the effects of compost treatment were not apparent until the 3rd year of treatment.

3.4 Recycled Organic Matter for Management of Organic Contaminants

ROM can also be used for the immobilisation of organic contaminants. For example, García-Jaramillo *et al.* (2014) trialled three types of ROM: olive oil production residue, compost from organic wastes and an organic waste biochar. They applied the amendments to paddy soils spiked with the pesticides bentazone and tricyclazone and found that compost and biochar reduced the mobility of tricyclazone in the soil as a function of increased adsorption from dissolved organic matter. Beesley *et al.* (2010) found a reduction in total and bioavailable PAH concentrations with compost addition which was attributed to improved soil texture and enhanced microbial degradation. Gandolfi *et al.* (2010) demonstrated that compost amendment of contaminated soil can enhance biodegradation of some hydrocarbons.

The addition of organic matter and rooting habit of some crops may assist the generation of a new "clean" soil horizon and provide further containment and rooting zones may support enhanced microbial activity leading to contaminant degradation and immobilisation. An example is the immobilisation of PAHs in humus (Banach-Szott *et al.*, 2014; Eschenbach *et al.,* 2001; Stegmann *et al.,* 1991). Phytostabilisation (see Section 1.3) is an engineered approach to achieving degradation and immobilisation of contaminants in the soil.

3.5 Recycled Organic Matter and Trace Element Mobilisation / Immobilisation

In many cases, addition of ROM to soils reduces the mobility of trace elements, facilitating revegetation and water resource protection. However, in some cases mobilisation has been found to occur as a result of complexation of trace elements with dissolved organic carbon (DOC) compounds. Where immobilisation occurs, there can be concern that the effect is limited in time, with remobilisation taking place as the organic matter is degraded. The durability of added organic matter in soil is discussed in Section 3.6.2. However, ongoing repeat applications of ROM may support durable immobilisation of contaminants in the same way it maintains carbon sequestration.

3.5.1 Mobilisation

There are concerns that ROM may increase the availability of trace elements in the soil (Defra, 2007). Organic amendments may increase bioavailable metal concentrations in soils in two ways. Firstly, the high organic matter inputs associated with ROM applications to soil may cause increased mobility for some metals, as a result of DOC competing with metals for sorption sites (Redman *et al*., 2002) or forming soluble complexes with metals, preventing the sorption of metals onto soil particles. It has been hypothesised that this effect increases over time, as organic matter in applied amendments begins to degrade, increasing DOC (Antoniadis *et al.,* 2008). Secondly, some types of ROM may contain levels of metals which would be considered a risk if applied to soil. This risk could also increase over time as a result of the breakdown in organic matter releasing metal ions.

Several studies support the notion that trace elements may be mobilised with the addition of organic amendments to contaminated soil. Hartley *et al*. (2009) found mobilisation of arsenic in soil with the addition of compost. Similarly, Beesley *et al.* (2010) reported increased concentrations of water-extractable copper and arsenic as a result of compost addition. Compost also increased lead levels found in soil pore water. Compost amendment induced considerable solubilisation of arsenic to pore water in a heavily contaminated mine-soil (Beesley *et al.*, 2014).

3.5.2 Immobilisation

Higher pH resulting from ROM addition can reduce the amount of exchangeable metals for a number of trace elements, due to increased cation exchange capacity and the strong affinity of metals for organic complexation sites (Bes and Mench, 2008; Fleming *et al.*, 2013). ROM amendments can therefore be used directly for *in situ* immobilisation of metals. Numerous different ROM amendments can be used for this practice. Song and Greenaway (2004) demonstrated that compost has the potential to successfully bind metals, and therefore could be successfully applied in the remediation of contaminated land. Similarly, Farrell and Jones (2010) significantly reduced trace element concentrations over two months in soil from a former copper mine, using several types of compost. Compost was also shown to enhance above and below ground biomass in grass (*Agrostis capillaris*). However the amendment mix ratio was very high at 60% compost, 40% contaminated soil. Alvarenga *et al.* (2009) showed that composts derived from green waste and municipal solid waste reduced mobile concentrations of copper, lead and zinc as a consequence of improved soil chemical characteristics, including pH and organic matter content.

Sewage sludge and manure have also been shown to decrease the availability of metals in soil. For example, Kacprzak *et al.* (2014) investigated plant growth and uptake of zinc, cadmium and lead in five grass species following the addition of industrial sewage sludge to contaminated sandy soil from a zinc smelter site. Their results showed reduced plant uptake, attributed to stabilisation of soil metals; and enhanced plant growth. The increase in plant biomass was attributed to increased nutrition and soil characteristics with sewage sludge addition, as the soil was initially nutrient and OM poor, and slightly acidic. Similarly, Walker *et al.* (2004) found that cow manure significantly decreased the exchangeable concentrations of copper, zinc, manganese and lead in mining-waste contaminated soil, as well as improving plant growth and decreasing plant uptake of metals. Metal availability reductions were attributed to an increase in soil pH with manure addition.

Conversely incorporation of some forms of ROM such as wood chips and composted sewage sludge to *alkaline* soils (technosols) were found to decrease soil pH and limit the labile pool of arsenic, chromium, and Mo (Oustrière *et al.*, 2014).

ROM amendments may also be useable in combination with inorganic amendments to increase the level of contaminant immobilisation and soil improvement achieved. Pardo *et al.* (2014) combined organic (pig slurry and compost) and inorganic (hydrated lime) soil amendments to remediate metal contaminated mine soil. Compost gave the most significant results due to more abundant essential nutrients, which lead to improved soil health, plant growth and decrease in metal mobility. Faz *et al.* (2008) also found combined treatments to be a suitable remediation agent for polluted soils; the authors studied the effects of pig manure and lime application in a mine soil field trial. The results of the trial suggested pig manure in combination with lime decreased DTPA- and water-extractable zinc, lead and cadmium and increased plant growth at the site. Combined use of organic amendments with zeolite has also been demonstrated to be an effective method of *in situ* immobilisation and enhancing plant growth in mine wastes (Leggo *et al.,* 2013; Hwang *et al.,* 2012).

ROM can also support the establishment or improvement of vegetative cover on a BF site through improvement of soil quality and reduction of available metals, which may be important from a risk management point of view, as well as improving the visual appearance of the site. If a BF site is contaminated, vegetation can act as a barrier to reduce migration of the pollutant(s) via wind or water, therefore reducing the likelihood of the contamination reaching a receptor (phytocontainment). Vegetative cover may also be an active component of a treatment based remediation strategy, i.e. phytoremediation (see Section 1.3).

The combined use of *in situ* stabilisation agents, ROM and revegetation (or improved vegetative cover) may have an immobilisation effect that is greater than any one component alone (in terms of reducing the mobility of trace elements). The system would also be self-sustaining over time. An example combination of great interest is combined applications of composts and biochars to support vegetative growth, which has been investigated in detail by HOMBRE (see Chapter 4).

3.6 Wider Benefits of Recycled Organic Matter Re-use

3.6.1 Ease of Re-use

Agricultural equipment and skills are widely available for the application of ROM to land making this an easily deployable operation. Conventional techniques for fertiliser applications could also be used for biochar applications, providing a readily available and widely held pool of expertise and capability (SNIFFER, 2010; Forest Research, 2009; Nason *et al.,* 2007; US EPA, 2007).

Consideration should be given to the mobilisation of nitrogen and phosphorus into surface water or groundwater from organic amendments or inorganic fertilisers, and for some amendments gaseous emissions of ammonia may be problematic where the application is in the vicinity of a low nitrogen habitat. Some amendments (e.g. composts, digestates or sewage sludge) may be associated with nuisances from odour or bio-aerosols. Others may cause nuisance from dust emissions off site. It can be particularly important to find organic amendments of high stability and low odour, and to use application methods that minimise emissions of odour, bio-aerosol and/or dust. Care needs also to be taken that amendments do not contain viable seeds or root fragments, particularly for invasive species such as bracken or Japanese Knotweed. Extensive guidance is available, (e.g. WRAP, 2012).

3.6.2 Carbon Sequestration

Applying ROM to land could increase the amount of carbon stored in soils and so contribute to the reduction of greenhouse gas emissions (Chen *et al.* 2013; Bustamante *et al.*, 2010). Adding organic matter to degraded soils with an already low carbon content has much greater potential to increase carbon storage than the amendment of more developed soils which are closer to their carbon storage limits (Brown *et al.*, 2010; Stewart *et al.*, 2008). Repeat applications of ROM to soil appear more likely to have a durable carbon sequestration effect compared with single large applications (Beesley, 2014; Beesley, 2012; Farbizio *et al.* 2008) especially when combined with the establishment of vegetative cover.

Soil type has also been listed as key parameter influencing amendment decomposition rate, e.g. clay content which would be linked to microbial activity. Hence, amending a clay soil with ROM may accumulate more organic matter than if the same amount of ROM is added to a sandy soil. It has been observed that in sandy soils, microorganisms have more access to organic matter than in clay soils (where sorption of organic carbon to soil minerals limits its microbial decomposition (Sissoko & Kpomblekou, 2010; Khalil *et al.*, 2005).

Estimates of carbon sequestration on three contaminated sites remediated with soil amendments (i.e. biosolids, composts, pellets) showed clear evidence on all three sites of enhanced carbon storage performances after completion of remediation measures (US EPA, 2011).

There is some uncertainty about the overall benefits of ROM to soil for carbon sequestration and some authors believe more detailed information on the dynamics of carbon and how carbon storage may be built or lost in these soils is needed (Beesley & Dickinson, 2010). For example, disturbance to soils could favour contacts between degrader organisms and substrate and so provoke depletion of carbon stocks (Fontaine *et al.*, 2007). It has been argued that adding organic materials such as crop residues or animal manure to soil, whilst increasing soil organic carbon, generally does not constitute an additional transfer of carbon from the atmosphere to land, depending on the alternative fate of the residue (Powlson *et al*., 2011). This suggests carbon storage potential resulting from sustainable organic waste management by means of soil amendments should consider a wider life cycle approach, where all impacts and benefits would be balanced. In this respect, it is worth noting that the contribution of ROM soil amendments to climate change mitigation is provided as a function of the wider benefits resulting from good practices in organic waste management, i.e. it indirectly reduces GHG emissions through:

- Reducing methane emissions from landfilling.
- Reducing GHG emissions through improved manure management.
- Sequestering biogenic, compost derived carbon in the soil.

- Replacing or decreasing the use of mineral fertilisers.
- Reducing methane emissions from soil, or increasing soil methane absorption.
- Reducing nitrous oxide emissions from soil.
- Improving plant biomass production, resulting in increased sequestration of plant carbon.
- Supplying auxiliary GHG emission savings (e.g. reduced need for irrigation, reduced erosion, reduced need for liming, reduced nitrate leaching).

It has been suggested that subsoil is an important carbon sink to store stable carbon (Rumpel *et al*., 2012; Sanaullah *et al.*, 2011; Lorenz *et al*., 2006). Based on findings of Rumpel *et al*. (2012) it seems that temperature, moisture conditions and nutrient availability in subsoils may favour reduced organic matter mineralisation in comparison to surface horizons. Observations made by Lorenz *et al*. (2011) concluded that the production of carbon in stable pools is higher in deeper soils. Chen *et al.* (2012, 2013) observed changes in soil carbon pools from urban land development and subsequent post development soil rehabilitation. This may suggest that the soil rehabilitation practices of subsoiling (deep tillage) and organic matter incorporation can be used to enhance urban soil carbon reserves. This is particularly important for BF where soil has been removed or does not exist (spoil heaps, landfill caps) or which are made ground. Some forms of revegetation require significant depths of soil cover, encompassing subsoil and topsoil systems, for example a metre of more for tree planting in some cases (DCLG, 2008; Foot & Sinnett, 2006; Forest Research 2009).

Compared with biochars, ROM degrades relatively quickly in soil (Bolan *et al.,* 2012). More stable forms of ROM, such as mature composts, will have a longer half-life in soil (Fabrizio *et al*., 2009; Flavel & Murphy, 2006; Bernai *et al*., 1998) On the other hand, less stable forms of ROM have a greater stimulatory effect on soil microbial biomass which also builds soil organic matter. In addition, where more stable ROM is added to soil, this has been accompanied by a release of CO_2 during its production through a composting and/or digestion process.

It has been suggested ROM used together with biochar could have synergetic effects on carbon sequestration and soil amelioration. Based on previous studies that highlighted both suppression and stimulation of native soil organic carbon decomposition by biochar (Cross *et al*., 2011; Fischer *et al.,* 2012; Luo *et al.*, 2011; Zimmerman *et al*., 2011), Shin *et al*. (2014) investigated carbon sequestration in soil amended with organic compost and biochar. Results obtained using amendments of different composts (i.e. cow compost, pig compost, anaerobic digestate) alone and in combination with biochar (produced from rice hull), indicated increased capacity for carbon sequestration when composts were amended with biochars. The strongest effect was observed when biochar was combined with cow compost. Crop growth (crop height and biomass) measured during the experiment indicated there were no significant differences in plant growth with the co-amendment of compost and biochar (compared to compost alone), giving the author reason to conclude that the use of the combined treatment had the potential to enhancing carbon storage without harming agricultural productivity.

A slower rate of organic matter decay in soils amended with compost may be achieved by addition of stabilising agents such as clay and mineral residues (e.g. water treatment residues). Such effects have been attributed to the immobilisation of carbon with metal oxides (iron, aluminium oxides) provided by stabilising agents and reduced DOC bioavailability after induced precipitation (Scheel *et al.*, 2008).

Compost blends incorporating minerals rich in calcium and magnesium silicates may promote improved carbon sequestration benefits. On degraded BF land, related silicate compounds are often present in waste materials such as concrete and steel slags. These materials are also often present in made ground or fill materials on BF sites. Carbon is sequestered as a result of mineral carbonation, where CO_2 reacts with calcium and/or magnesium containing minerals to form stable carbonate materials (Manning *et al*., 2013; Olajire *et al*., 2013). Manning *et al.* (2013) investigated carbonate precipitation in artificial soils produced from basaltic quarry fines mixed with compost. The formation of an artificial of pedogenic carbonate minerals was observed, representing a long lived sink for atmospheric CO_2.

3.6.3 Resource Efficiency

Resource efficiency is supported by ROM use on BF sites (Gandolfi *et al.*, 2010). In most EU countries, 60-70% of municipal waste is made up of biodegradable substances (EEA, 2009), this totalled 87.9 million tonnes across the EU in 2004 (Prognos, 2008). Where organic wastes are recycled and put to beneficial use, the amount of waste that requires disposal through traditional waste streams (landfill, incineration) is reduced with concurring economic and environmental benefits (e.g. reduction in methane production associated with biodegradation of organic materials in landfill). In May 2010 the European Commission (EC) *Communication on Future Steps in Biowaste Management in the EU* (EC, 2010) described the broad sustainability benefits of greater re-use of these urban biowastes (including reducing greenhouse gas emissions, organic matter return to soil and reusing nitrogen and phosphorus). These benefits would also apply to reusing biowastes from farm sources. However, the materials available for recycling to soil vary in their quality.

In many European countries lower grades of ROM, such as CLOs, or even in some countries sewage sludge, are not permitted to be used on agricultural land because of concerns over the potential content of toxic elements and organics (see Section 3.7).

3.7 Potential Negative Impacts of Recycled Organic Matter Use

Some types of ROM may have significant contents of trace elements and /or toxic organic compounds. This is a particular concern for sewage sludge and CLOs.

In terms of the organic amendment itself being contaminated, certain ROM feedstocks may be considered more of a risk than others. For example, compost-like-outputs (CLO) derived from biodegradable fractions of municipal solid waste (MSW) may have high metal concentrations. Levels of many potentially toxic elements, in particular arsenic, cadmium, copper, lead, and especially zinc, tend to be elevated in CLO and sewage compared with soils (Defra, 2007; Bardos, 2005.). There are also concerns that CLOs and sewage sludge may contain persistent organic pollutants (POPs) at unacceptable levels, although not all authors agree that this is a cause for concern (Smith, 2009; Amlinger *et al*., 2004). A recent review of the potential risks of the use of CLO on land has been published by the Environment Agency (2009) which raised concerns about impacts from cadmium, chromium, zinc and several organic pollutants.

Sewage sludge has also been well established in literature to potentially contain high levels of trace elements (Defra, 2007). Antoniadis *et al*. (2008) investigated sewage sludge application to soil at various rates. At the highest rate of application (50t ha^{-1}), DTPA-extractable cadmium, nickel and zinc were significantly increased after 16 weeks. Increases in availability to ryegrass were also observed, although these were temporally variable. This work mirrors the findings of Antoniadis and Alloway (2001) who found increases in $CaCl_2$ leachable nickel and cadmium and plant uptake with sewage sludge addition. Additionally, Kızılkaya (2004) found sewage sludge increased the mobility of copper and zinc and their availability to earthworms.

The risk of metal contamination as a result of the composition of organic amendments added could be significantly reduced if materials are analysed for metal content prior to application to soil. Whilst it has been indicated that there is also some risk from added organic matter mobilising metals already present in soil, this could be decreased through repeated applications of soil organic matter which can maintain the levels of sorption sites.

Other negative impacts of ROM use include the possibility of nuisance and/or risks from odour, dust and bio-aerosols and impacts of nitrogen or phosphorous on water (see Section 3.6.1). Table 2 summarises the various strengths and weaknesses of several types of ROM for soil formation or improvement on marginal land.

Table 2: Strengths and Weaknesses of Different forms of Organic Matter for Soil Formation or Improvement on BF (taken from Bardos *et al.,* 2010)

Type	Description	Strengths	Weaknesses
Source segregated – "green waste" compost	Material produced by composting or anaerobic digestion from separately collected materials from private and public gardens and parks (including leisure facilities such as golf courses).	Material contains useful amounts of stabilised organic matter and plant nutrients. Properly treated materials should be sanitised of animal pathogens and most plant pathogens. Materials may have a protective effect by: liming (increasing pH, immobilising toxic substances and reducing the effects of some plant pathogens). Some jurisdictions may have quality standards for these	Materials may command a price per m^3, unless processed on-site from green wastes (in which case revenue generation may be possible). These materials may contain hazardous materials, albeit at lower levels than for most mixed waste composts. Unstabilised material is highly odorous and may also carry wider public health / nuisance risks. Stored materials may pose

Type	Description	Strengths	Weaknesses
		composts which offer element of quality assurance, and these materials may be seen as "recycled" and hence no longer under waste regulations. Generally source segregated materials are well perceived.	risks from some micro-organisms such as *Aspergillus fumigatus*.
Source segregated – food waste compost	Material produced by composting or anaerobic digestion from separately collected materials from private kitchens and/or catering operations or commercial food producers / processors.	Properly treated materials should be sanitised of animal pathogens and most plant pathogens. Materials may have a protective effect by: liming (increasing pH, immobilising toxic substances and reducing the effects of some plant pathogens). Note: under European law all such material has to have a minimum treatment to sanitise animal pathogens (Regulation EC 1774/2002). Some jurisdictions may have quality standards for these composts which offer element of quality assurance, and these materials may be seen as "recycled" and hence no longer under waste regulations. Generally source segregated materials are well perceived.	Materials may command a price per m^3, unless processed on-site (in which case revenue generation may be possible). These materials may contain hazardous materials, albeit at lower levels than for most mixed waste composts. Unstabilised material is highly odorous and may also carry wider public health / nuisance risks. Stored materials may pose risks from some micro-organisms such as *Aspergillus fumigatus*.
CLO	Material produced by composting or anaerobic digestion from mechanically processed fractions of mixed municipal (household) waste; or other similar collected wastes from commercial sources (Cameron *et al.* 2008).	Material contains useful amounts of stabilised organic matter and plant nutrients The material may be available at low or zero cost, or potentially in some regulatory jurisdictions its use could command a gate fee. Properly treated materials should be sanitised of animal pathogens and most plant pathogens. Note: under European law all such material has to have a minimum treatment to sanitise animal pathogens (Regulation EC 1774/2002). Materials may have a protective effect by: liming	Mixed waste composts tend to contain higher levels of inert materials (e.g. plastic traces) and hazardous materials than some other forms of organic matter: for example, PTEs, POPs and sharps such as glass fragments. The best mixed waste composts are likely to have PTE levels similar to poorer source segregated materials. Mixed waste composts may suffer from a poor perception by some stakeholders and a more stringent regulatory regime than some other forms of organic matter.

Type	Description	Strengths	Weaknesses
		(increasing pH, immobilising toxic substances and reducing the effects of some plant pathogens). Some jurisdictions may have quality standards for mixed waste composts which offer an element of quality assurance. Stabilised material is generally free from odour.	Unstabilised material is highly odorous and may also carry wider public health / nuisance risks. Stored materials may pose risks from some micro-organisms such as *Aspergillus fumigatus*.
Sewage sludge "biosolids"	Residues remaining after treatment of human effluents at a municipal scale. Untreated dilute sewage fractions have been used to irrigate energy forestry.	Very high levels of usable organic matter and plant nutrients. Potentially available at low or zero cost	Untreated materials will pose materials handling difficulties as well as problems of odour and potential microbial risks. They are likely to require special handling. Sewage materials tend to contain higher levels of inert materials (e.g. plastic traces) and hazardous materials than some other forms of organic matter: e.g. PTEs, POPs.

4 Experimental Studies

4.1 Experimental Background

Trace element contamination is an important environmental issue, as unlike organic contaminants, trace elements do not degrade over time (Megharaj *et al.*, 2011). As trace elements are very persistent in the environment and traditional methods of remediation (e.g. involving soil removal and replacement) are often costly (Bolan *et al.*, 2014), it is integral that innovative methods of remediation for trace element contaminated soils are developed. As discussed earlier in this report, soil amendments such as biochar and ROM may be suitable for *in situ* immobilisation of trace element contaminants in soil. The studies detailed herein examined the use of different biochars and green waste composts as single and combined amendments for the treatment of a copper contaminated soil.

Although copper is an essential micronutrient required for plant growth, it is phytotoxic in excess (Burkhead *et al.*, 2009; Lepp, 1981). Phytotoxicity of copper has been demonstrated for numerous plant species, with roots being most greatly affected. Copper toxicity to plant roots has negative implications for photosynthesis, respiratory processes and protein synthesis (Yruela, 2009; Ali *et al.*, 2004). Metalloids such as copper, lead, chromium and zinc are known to bioaccumulate in plant roots or on the root exodermis, inhibiting growth and nutrient uptake (McBride, 1994). Phytotoxicity is highest in soils where copper concentrations in soil pore waters are higher. This is due to increased metal bioavailability. Bioavailability is influenced by various processes including pH, soil texture and ionic composition of the soil solution (Ali *et al.,* 2004).

Biochar properties vary depending on the production process and accordingly, its effect on soil characteristics will vary (Novak *et al.*, 2009). Biochar application affects various soil characteristics that may influence copper distribution and availability in soil. There is scope therefore for biochar use for the purpose of reducing phytotoxicity of copper in contaminated soils. Similarly, compost has the potential to increase the copper sorption capacity of the soil (Beesley *et al.*, 2010; Vaca-Paulin *et al.*, 2006).

4.2 Overview of Studies

Experimental work was carried out as a collaboration between the Greenland project (FP7-KBBE-266124)[8] and HOMBRE. To help determine the remediation capabilities and operational windows of a range of biochars and composts as single and combined amendments, experimental studies were undertaken on copper contaminated soil obtained from a Greenland project remediation site. Research was initiated by a scoping study undertaken in 2013. The scoping study examined the effects of compost and biochar, applied both exclusively and combined, on the leachability of copper in the soil and the soil's phytotoxicity. The results from this experiment helped facilitate the development of further laboratory studies. A more detailed study was conducted in 2014 on the leachability and phytotoxicity of copper in soil following the application of three different biochars with and without compost. Simultaneously, a supporting Master of Science project was carried out, using sequential extraction to determine the effects of biochar and compost on mobility and distribution of copper in soil. Table 3, below, gives an overview of the three studies, outlining key participants and aims.

Table 3: HOMBRE/Greenland collaborative research studies. Project links are shown – links to the HOMBRE project are highlighted in blue; Greenland project in green.

	Scoping study	**Detailed study**	**Supporting MSc**
Aim(s)	- To establish if biochar and compost could be effective soil amendments for treatment of the Cu contaminated soil at the remediation site. - To establish a rough	- To gain further insight into the optimal modes of use for biochar and compost amendments. - To establish is biomass for energy	- To determine if biochar, compost and/or plant growth have an effect on the fractionation of Cu in the soil.

[8] The Greenland project was established to investigate, improve and increase usage of gentle remediation options (GRO) including phytoremediation and *in situ* stabilisation using amendments (www.greenland-project.eu).

<table>
<tr><th></th><th>Scoping study</th><th>Detailed study</th><th>Supporting MSc</th></tr>
<tr><td></td><td>effective application range.</td><td>generation can be produced on marginal land.

-To determine if biomass produced on a remediation site can be used for further soil improvement.</td><td></td></tr>
<tr><td>Location of work</td><td>University of Reading(UoR), Reading, UK</td><td>IIAG-CSIC, Santiago de Compostela, Spain</td><td>University of Reading (UoR), Reading, UK</td></tr>
<tr><td rowspan="3">Participants, organisations and roles</td><td rowspan="2">-Fredrick Siemers, UoR, UK. Experimental work carried out as MSc dissertation.

-Steve Robinson, UoR, UK. MSc project advisor, arrangement of UoR technician support.

-Anne Dudley, Karen Gutteridge, Martin Heaps, UoR, UK. Technician support.</td><td>-Sarah Jones, r3, UK. Experimental work carried out.

-Petra Kidd, IIAG-CSIC, Santiago de Compostela, Spain. Experimental advice, provision of laboratory facilities, arrangement of CSIC technician support.</td><td>- Joshua Giulianotti, UoR, UK. Experimental work carried out as MSc dissertation.

- Denise Lambkin, UoR, UK. MSc project advisor, arrangement of UoR technician support.

-Anne Dudley, Karen Gutteridge, UoR, UK. Technician support.</td></tr>
<tr><td colspan="2">-Wolfganag Friesl-Hanl and Gerhard Soja, AIT Austrian Institute for Technology, Vienna, Austria. Manufacture of biochar and technical advice.

-Rolf Herzig, Phytotech, Bern, Switzerland. Supply of sunflower seeds.</td></tr>
<tr><td colspan="3">-Michel Mench, INRA, University of Bordeaux, France. Provision of soil.

-Tony Hutchings and Frans de Leij, C-Cure Solutions™Ltd, Farnham, UK. Provision of biochars and technical advice.

-Pierre Menger, Tecnalia Research and Innovation, San Sebastian, Spain. Analysis of soil and amendment characteristics; technical advice.

-Paul Bardos and Sarah Jones, r3 environmental technology ltd.,</td></tr>
</table>

	Scoping study	Detailed study	Supporting MSc
	(r3), Reading, UK. *Provision of technical advice, supervision.* -**Andy Cundy**, Univiersity of Brighton, Brighton, UK. *Provision of technical advice across D5.4.* -**Petra Kidd**, IIAG-CSIC, Santiago de Compostela, Spain. *Provision of technical advice across D5.4.*		

4.3 Site Context

Copper contaminated soil was obtained from a former wood preservation site in the Gironde County Saint Médard d'Eyrans, France (N 44^0 43.353, W 000^{0}30.938). This site has been used for over a century to preserve and store timbers, posts, and utility poles. Creosote and/or various copper salts were successively used (Mench and Bes, 2009). Topsoils of this site are contaminated by either copper (e.g. sub-site P1-3) or copper and PAHs (e.g. sub-site P7). There is spatial variability of contamination across the site, stemming from different treatment processes and activities. (Bes *et al.*, 2010; Bes, 2008). Two different soils (P1-3 & P7, fluvisols) were obtained from different areas of the site; both are characterised by their high levels of phytotoxicity. The soils are largely classified as a sandy loam. (Lagomarsino *et al.*, 2011). Further information about each soil can be obtained from Bes and Mench (2008) and Lagomarsino *et al.* (2011) respectively.

P7 soil has been previously tested in terms of effectiveness of different remediation techniques (Bes and Mench, 2008) and has been characterised as slightly acidic (pH 6.25), having a low organic matter (OM) content (27.2g kg^{-1}) and high levels of copper contamination (2600 mg Cu kg^{-1}). At the part of the site where P7 was obtained, wood was dipped in creosote and copper sulphate for treatment. This soil has been characterised as one of the most ecotoxic soils on the site (Mench & Bes, 2009). Bes and Mench (2008) recorded the effects of amendments on P7 soil phytotoxicity to dwarf bean plants. It was noted that amendments that reduced copper concentrations in solution had a limited effect on plant growth improvement. Amendments adding Ca to the soil system demonstrated the greatest reduction in phytotoxicity; however copper was still mobile in pore water. (Bes & Mench, 2008).

The second soil (P1-3) is from a copper-contaminated area due to washing of treated wood by rainfall. The P1-3 soil is reported as having lower levels of copper contamination (up to 1000 mg kg^{-1}). A combined 66% of the copper in the P1-3 soil is recorded as being in the acid soluble (e.g. hydroxides, carbonates) and reducible fractions (e.g. iron and manganese oxides), with low quantities in the exchangeable and soluble fractions. Consequently there are lower copper concentrations in soil pore water compared to soils from the rest of the site. The soil has a low cation exchange capacity (3 cmol kg^{-1}) (Lagomarsino *et al.*, 2011). The authors of the papers above state that phytotoxicity in both of these soils is attributable to copper.

4.4 Scoping Study

4.4.1 Introduction and Aims

The scoping study was developed to examine the effects of two different biochars, alongside compost application, on copper stabilisation in the heavily copper contaminated soils outlined in 4.2. Both P 1-3 and P 7 soils were investigated. Mobility of copper after treatment with biochar and compost was assessed through a series of $CaCl_2$ leaching tests and bioavailability was analysed via a bioassay using *Lepidium sativum.* Biochar was applied as both a single factor and combined with compost, following on from findings that combined amendments are most effective in reducing phytotoxicity (Bes & Mench, 2008).

4.4.2 Methods

4.4.2.1 Soils and Amendments

Soil samples of the two sub-sites "P1-3" and "P7" were extracted using an unpainted steel spade in April 2013 and transported to the University of Reading. Samples were air dried (36ºC) for one week, before being sieved (<2mm) to remove coarse debris and homogenised. pH measurements were taken, to examine if this changed with amendments and significantly influenced results. pH was determined by mixing three replicate soil samples with deionised water at a 1:2.5 ratio and analysed using a pH probe. Water content (from air dried) and loss on ignition were calculated by measuring weight lost after heating at 105ºC and 500ºC respectively for a 24 hour period. (Rowell, 1994). A Beckman Coulter LS 230 laser granulometer was used to determine particle size distribution. (Buurman *et al.*, 1997).

Based on the soil characteristics reported (see Section 4.3.3.1), C-Cure Solutions™ Ltd (Farnham, UK) [9]suggested testing two patented biochars "NC" and "FC". (Patent numbers: WO2009016381A2 and 61372PCT1, respectively). NC was formulated to immobilise cations; FC was formulated to immobilise arsenate. Two types of compost were trialled (aged garden compost [GC] and commercially produced retail compost based on wood fibre [WF]) in initial testing. In final leach tests and pot trials, an alternative green waste compost (VE-GWC) obtained from Vital Earth Ltd (Derbyshire, UK)[10] was applied. Vital Earth compost was obtained for the final tests as this product is more representative of what might be available for use on a BF site (compared to garden or retail compost). Additionally this compost complied with PAS:100 standards (Vital Earth Ltd, 2009).

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[9] www.ccuresolutions.com
[10] www.vitalearth.tv

The soils and amendments were analysed by Tecnalia Research & Innovation (Álava, Spain) for metal and organic contaminant content, as well as copper partitioning in order to assess the factors controlling phytotoxicity. A summary of the analyses used is shown in Table 4 below:

Table 4: Soil and Amendment Analyses Methods

Analysis	Method
TOC	Sulphocromic oxidation; Standard: UNE EN 13137:2002
pH	Potentiometry; Standard: UNE EN ISO 10390:2012
Total Kjeldahl Nitrogen	UV/VIS spectrophotometry
Exchangeable cations (Na, K, Ca, Mg)	UV/VIS spectrophotometry
Metals	ICP-AES following aqua regia digestion
Chromium VI	Plasma emission spectrometry (ICP-AES) and molecular absorption spectrophotometry (UV) following alkaline digestion of samples.
PAHs/PCBs	Gas Chromatography Mass Spectrometry (GC/MS). Standard: EPA 8270: 1996
Total hydrocarbons	Gas Chromatography with Flame Ionization Detector (GC/FID). Standard: EN ISO 77307:2000
Phenols	Gas Chromatography Mass Spectrometry (GC/MS). Standard: EPA 8270: 1996
BTEXs, volatile organic compounds, vinyl chloride	Gas Chromatography Mass Spectrometry (HS/GC/MS) and a headspace sampler as sample introduction system. Standard: EPA 5021:1996 and EPA 8260:1996
Total halogens	TOX Analyzer microcoulometry; Standard: EPA 9076:1994
Sequential extraction of Cu	BCR

4.4.2.2 Leaching Tests

Leaching tests were conducted in accordance with the methodology in waste acceptance criteria guidelines. (Environment Agency, 2005). Unamended and amended soil samples (2.5g) were placed in centrifuge tubes and mixed with 25ml of 0.01M $CaCl_2$, before being placed on a spinner for 24 hours in a controlled temperature room (10ºC). Samples were centrifuged (3600rpm, 15 minutes; MSE Mistral 3000i centrifuge, MSE, London, UK), then filtered (Whatman no. 540), before metal concentrations were determined using ICP-OES. For each treatment type, three replicate subsamples were prepared.

Three sets of leach tests were carried out. Firstly, a preliminary trial was carried out with both soils and biochar only. Both biochars (NC and FC) were trialled at various amendment rates (unamended, 1%, 2% and 5% w/w) following the advice of the producer. By utilising multiple amendment rates, the concentration at which biochar was most effective could be determined and subsequently applied to further tests.

Following results from the preliminary tests, further leach tests were completed in the P7 soil, as this soil saw the greatest results in initial tests. The biochars were most effective at 1% so this amendment rate was trialled in combination with compost. Two different composts were tested (aged garden compost from home composting and commercially produced wood fibre compost). Composts were applied at 2% w/w. This amendment rate was selected on the basis of likely allowable nitrogen addition in the UK (Defra, 2013b). As NC biochar was effective at 1%, lower rates (0.5% and 0.25% w/w) of this biochar were also trialled (as biochar only amendments). To help determine reasons for differences in leaching tests, pH and DOC were analysed in the leachate. DOC was analysed using a Shimadzu Total Organic Carbon Analyser (Shimadzu Corporation, Kyoto, Japan).

Finally, detailed leaching tests mirroring plant trials were carried out with the most effective biochar: NC. Amendment rates of 0.25%, 0.5% and 1% w/w were once again used as higher amendment rates did not offer any substantial improvement in copper immobilisation. Again, these leach tests were carried out in the P7 soil only. Biochar was applied alongside a green waste compost (2% w/w) produced from botanic residues, obtained from Vital Earth Ltd, that complied with PAS:100 standards (Vital Earth Ltd). Again, pH and DOC were analysed in the leachate.

4.4.2.3 Plant Trials

Following on from the leaching tests, it was clear that the NC biochar was particularly effective in reducing copper mobility and consequently had the potential to reduce phytotoxicity. Plant trials therefore only utilised NC biochar. Whilst biochar amendments were generally not as effective when combined with compost, combined amendments have been shown previously to be more effective at reducing phytotoxicity (compared to single amendments) as a result of decreased copper mobility and increased soil Ca concentrations. (Bes & Mench, 2008). VE-GWC was therefore also trialled alongside the biochar.

Pots with a 6cm diameter were filled with P7 soil both unamended and treated with NC biochar (0.25%, 0.5% and 1% w/w) and VE-GWC (2% w/w) as both single and combined amendments. Mixtures were rehydrated and left in pots for one week prior to planting to equilibrate. Four replicates were created of each pot. Cress (*Lepidium sativum*) (25 seeds per pot) was planted in June 2013 in a glass house in the University of Reading (temperature range 10-35ºC). Pots were watered using deionised water on a daily basis (100-150ml) over a two week period. Plant height, leaf and germination information was collected and above soil biomass harvested. Wet and dry biomass weights were recorded, and a nitric acid digestion carried out on dry plant biomass. Plants were left for 24 hours in 10ml nitric acid (analytic reagent grade, 70%), then digested for 9 hours at 110ºC. Samples were filtered (Whatman no.540), diluted to 100ml using ultra-pure water and then analysed using ICP-OES. pH of soil in pots was analysed by mixing soil and deionised water at a 1:2.5 ratio. (Rowell, 1994). Cress weight was too low to separate different parts (e.g. stem and leaves) and analyse these individually. Similarly there was too little root growth to analyse elemental concentrations in root matter.

4.4.2.4 Statistical Analysis

To determine statistical differences between different amendment types, one way ANOVAs were performed alongside Tukey's comparison tests to formally establish any significant differences found. In many cases, data had to be transformed to represent normal distributions. In one case (initial leaching test, P7 soil) data could not be transformed, so a non-parametric Kruskal-Wallis test was performed to review statistical differences between samples. To analyse the link between pH, DOC and copper concentrations in leachate and plant biomass, correlation tests were performed (Pearson coefficient reported to show strength of correlation, along with P value). Statistical analyses were carried out using *Minitab 16* (Minitab, State College, PA, USA).

4.4.3 Results

4.4.3.1 Soil and Amendment Characteristics and Metal Composition

Table 5 lists the basic soil characteristics found for the investigated soils. Both soils were similar in terms of texture (loamy sands) and had low OM content. Conversely, pH values were different between soils, values in the P1-3 are close to neutral (7.34) and those in soil P7 are slightly acidic (6.02). Results of compositional analysis can be seen in Tables 6 and 7.

Table 5: Average values for pH, texture and loss on ignition

	Soil P7	**Soil P1-3**
pH	6.0	7.3
Texture (% clay, silt, sand)	3.4%, 16.9%, 79.6%	2.9%, 16.9%, 80.3%
Loss on ignition %	2.8%	1.9%

Previous studies carried out on these soils have demonstrated that copper is a major contaminant and whilst there are elevated levels of some PAHs, these are not at concentrations that might cause phytotoxicity. (Kumpiene *et al.*, 2011; Lagomarsino *et al*., 2011; Bes, 2008; Bes & Mench, 2008). The biochars and compost tested were determined to have relatively low levels of BTEX, PAHs, phenols and trace elements.

Table 6: Soil and amendment organic content

Contaminant (mg kg^{-1} dry matter)	P 1-3 Soil	P 7 Soil	Biochar NC	Biochar FC	Vital Earth Compost
BTEX					
Benzene	<0.01	<0.01	1.67	<0.01	<0.01
Toluene	<0.02	<0.02	0.79	<0.02	<0.02
Ethylbenzene	<0.02	<0.02	0.08	<0.02	<0.02
Total Xylenes	<0.05	<0.05	0.11	<0.05	<0.05
Total BTEX	<0.10	<0.10	2.70	<0.10	<0.10
PAHs					
Napthalene	0.04	0.46	0.17	<0.01	0.02
Acenaphthylene	0.33	1.70	0.03	<0.02	0.03
Acenaphthene	0.02	0.16	0.03	<0.03	0.13
Fluorene	0.05	0.32	0.02	<0.04	0.13
Phenanthrene	0.68	3.00	0.22	0.01	0.95
Anthracene	0.57	6.40	0.04	0.01	0.17
Fluoranthene	2.90	7.90	0.10	<0.01	1.40
Pyrene	2.80	7.50	0.14	0.02	1.00
Benzo (a) anthracene	1.60	5.30	0.06	<0.01	0.011
Chrysene	1.40	4.50	0.05	<0.01	0.35
Benzo (b) fluoranthene	3.40	13.00	0.07	0.03	0.66
Benzo (k) fluoranthene	1.10	3.90	0.02	<0.01	0.15
Benzo (a) pyrene	2.00	4.10	0.04	<0.01	0.37
Indeno (1,2,3-cd) pyrene	2.30	4.4	0.03	<0.01	<0.01
Dibenzo (a,h) anthracene	0.32	1.00	<0.01	<0.01	<0.01
Benzo (g, h, i) perylene	1.40	2.2	0.02	<0.01	<0.01
Total PAHs	21.00	66.00	1.00	0.07	5.40
PCBs					
2,2,5 Trichlorobiphenyl	<0.0005	0.002	<0.0005	<0.0005	<0.0005
2,4´,5 y 2,4,4´ Trichlorobiphenyl	<0.005	0.002	<0.0005	<0.0005	<0.0005
2,2´,5,5´ Tetrachlorobiphenyl	0.001	0.037	0.003	0.002	<0.0005
2,2´,3,5´- Tetrachlorobiphenyl	<0.005	0.007	<0.0005	<0.0005	<0.0005
2,2´,4,5,5´ Pentachlorobiphenyl	0.001	0.700	0.006	0.005	0.004
2,2´,3,4´,5´,6- Hexachlorobiphenyl	0.002	1.900	0.010	0.010	<0.0005
2,3´,4,4´,5 - Pentachlorobiphenyl	0.001	0.280	0.020	0.003	<0.0005
2,2´,4,4´,5,5´- Hexachlorobiphenyl	0.003	4.100	0.018	0.021	<0.0005
2,2´,3,4,4´,5´- Hexachlorobiphenyl	0.002	3.000	0.011	0.015	<0.0005
2,2´,3,4,4´,5,5´ heptachlorobiphenyl	0.001	3.800	0.011	0.015	0.005
´2,2´,3,3´,4,4´,5 heptachlorobiphenyl	<0.005	0.590	0.001	0.002	<0.0005
Total PCBs	0.012	14.000	0.063	0.074	0.009
Total Hydrocarbons (C10.C40)	45.00	210.00	80.00	51.00	360.00
Phenols	0.20	0.17	0.14	<0.25	0.31

Contaminant (mg kg^{-1} dry matter)	P 1-3 Soil	P 7 Soil	Biochar NC	Biochar FC	Vital Earth Compost
Total organic carbon (%)	1.40	2.20	n/a	n/a	n/a

Table 7: Soil and amendment potentially toxic element (PTE) content

PTE (mg kg^{-1} dry matter)	P 1-3 Soil	P 7 Soil	Biochar NC	Biochar FC	Vital Earth Compost
As	<5	13	<5	<5	11.3
Cd	<1	<1	<1	**3.89**	<1
Pb	15.1	26	8.56	6.4	**148**
Ni	6.02	<5	<5	105	**20.6**
Hg	<0.1	13	<0.1	<0.1	<0.1
Cr	10.7	15	21.3	**69.3**	38
Mn	131	126	165	1460	416
Cu	**860**	**892**	20.4	<5	59
Mo	<1	<1	8.04	5.57	2.28
Zn	29.7	**75**	**51.4**	8.67	**243**
B	<5	<5	108	<5	22.3
Fe % of dry matter	0.45	0.6	0.13	23.5	1.71
K	835	959	11.6 (% of dry matter)	0.1(% of dry matter)	0.87 (% of dry matter)
P	175	183	13.2	104	0.31 (% of dry matter)
Co	n/a	n/a	<5	<5	6.36
Ba	n/a	n/a	37	5.3	358
Sn	n/a	n/a	<5	<5	7.86
Se	n/a	n/a	<0.1	<0.1	<0.1
Cr (VI)	<5	<5	<5	<5	<5
Total Halogens	35	32	8834	588	4765
Kjeldahl Nitrogen	480	440	2.1 (% of dry matter)	450	1.6 % of dry matter)

Values in bold exceed background values for French sandy soils (Mench & Bes, 2009).

4.4.3.2 Leaching Tests

4.4.3.2.1 Preliminary Leach Tests – Biochar Only

Figures 3 and 4 (below) show the average copper concentrations in soil leachate obtained using a $CaCl_2$ extraction. The leaching tests revealed interesting patterns with the application of both biochars to the soils.

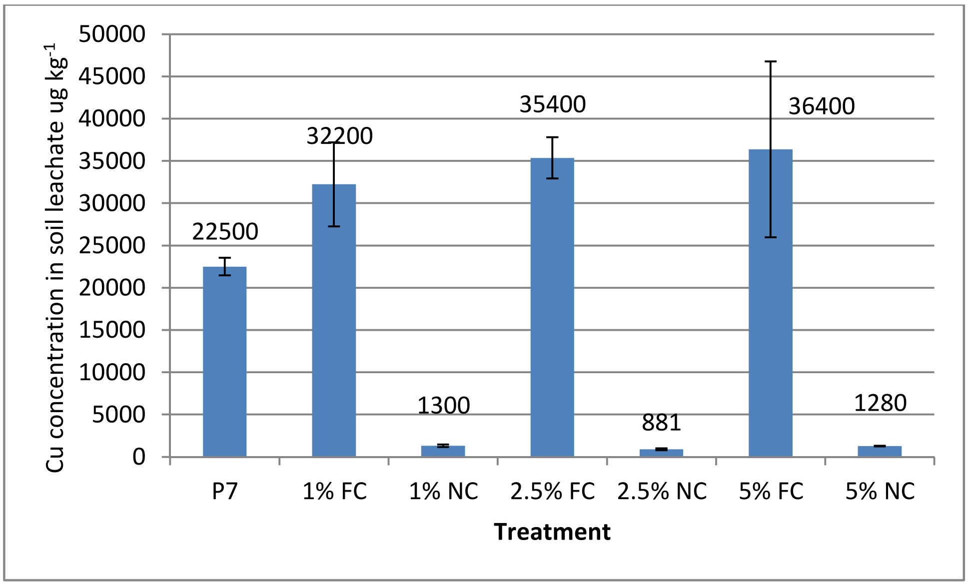

Figure 3: Mean concentration of leachable Cu µg kg^{-1} in P7 soil treated with different amendments (n=3). Data not normally distributed, Kruskal-Wallis non-parametric tests (P= 0.003).

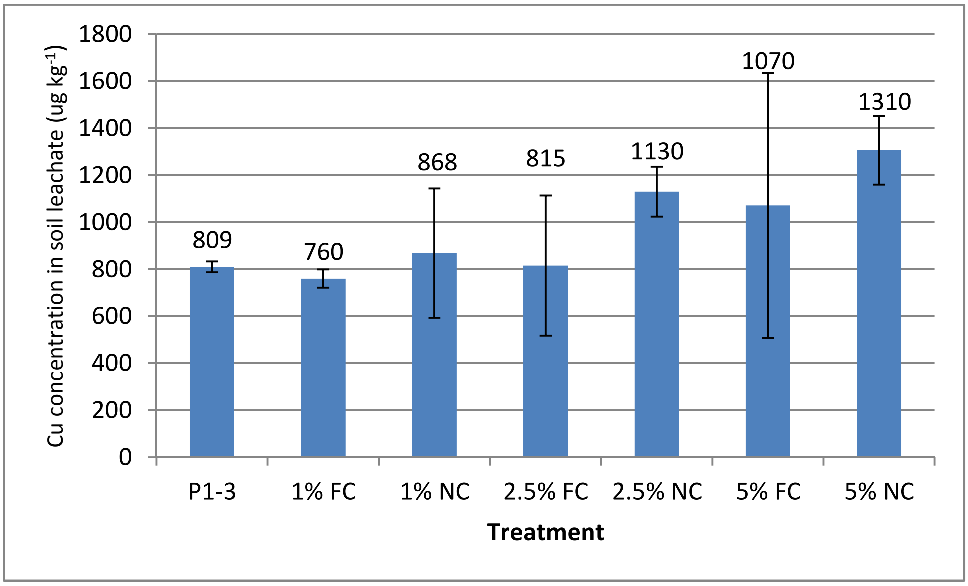

Figure 4: Mean concentration of leachable Cu µg kg^{-1} in P1-3 and soil treated with different amendments (n=3). No statistical significance determined between treatments.

The only effective biochar amendment was the NC biochar in soil P7 at all amendment rates (fig 1). In soil P7, leachable copper concentration was high (22.5 mg kg^{-1}) (fig 3). The addition of 1% FC biochar increased leachable copper concentrations to >32.0 mg kg^{-1}. Conversely 1% NC biochar reduced copper concentrations to <1.30 mg kg^{-1}. With an increase in amendment rate of both biochars, there was little change in copper mobility. As data were not normally distributed, a Kruskal-Wallis test was performed, confirming a statistical difference between samples.

Leachable copper concentrations in the unamended P1-3 soil was 0.80 mg kg^{-1} (fig 4), much less than in the P7 soil. In most cases biochar addition marginally increased copper concentration in solution, except for 1% FC. No significance in the data was recorded to support these patterns. For other metalloids (arsenic, cobalt, chromium, nickel, lead and zinc) tested in both soils, no significant differences in concentrations were recorded and in many cases values were be ICP-OES detection limits.

4.4.3.2.2 Combined Biochar and Compost Leach Tests

Similar to results seen in the preliminary leaching tests (Fig 1), the secondary leach tests showed that single NC biochar amendments in the P7 soil decreased copper mobility. However, 1% FC biochar as a single amendment increased copper mobility (Fig 5).

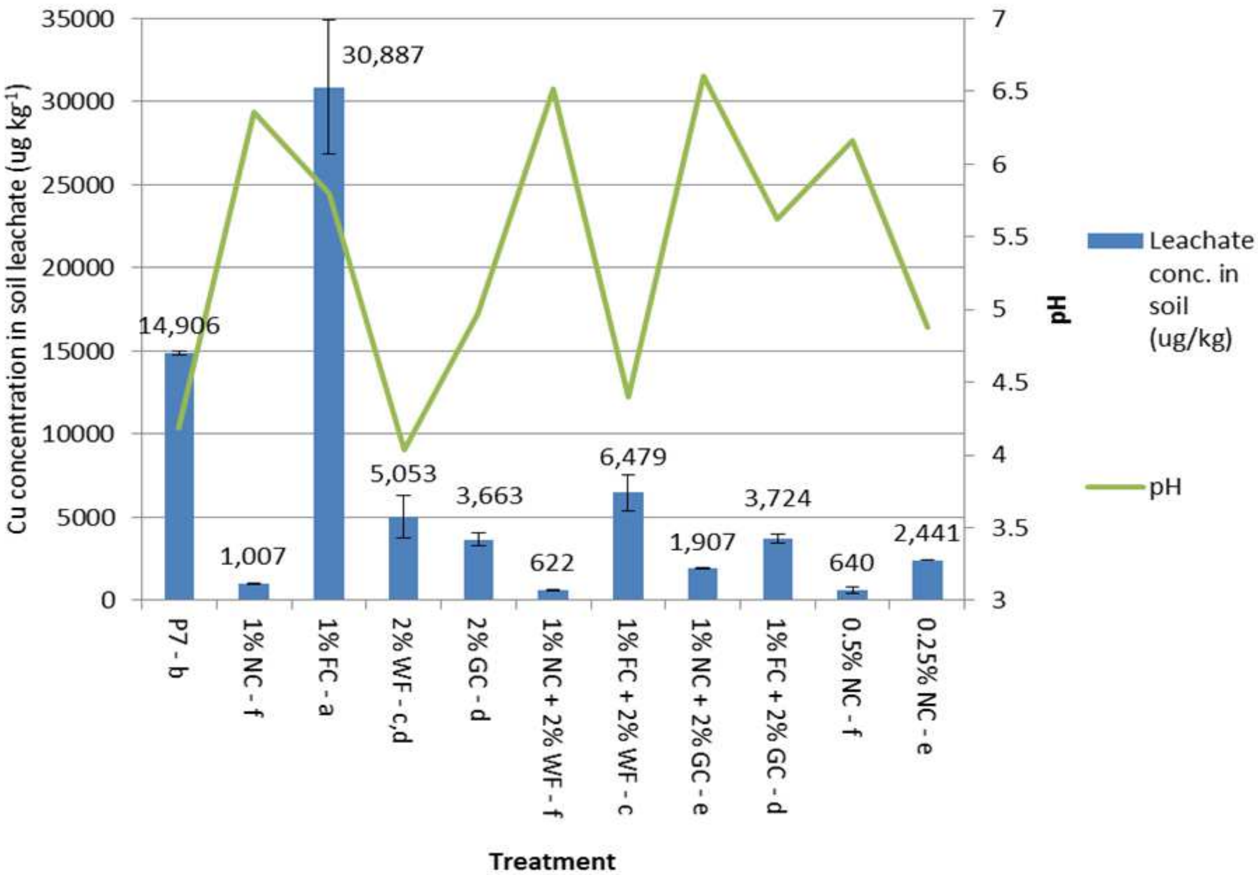

Figure 5: Mean concentration of leachable Cu µg kg^{-1} (bar graph) and pH in leachate (line graph) for soil P7 treated with different amendments (n=3). Different letters after each treatment indicate statistical difference of Cu concentration in solution based on the Tukey Method (ANOVA: P<0.01).

Both composts as single amendments decreased copper mobility compared to unamended soil, but not as effectively as 1% NC biochar as a single amendment. FC biochar applied with compost increased the efficacy of the biochar, as well as the WF compost improving NC biochar. GC reduced effectiveness of NC biochar. NC biochar (0.5%) was statistically the same as 1%; however, 0.25% was not as effective.

A negative correlation was found between pH and copper concentration (P>0.03; Pearson correlation value = -0.62). This indicates that with a less acidic solution there is less copper in leachate.

A significant difference was determined between DOC values of different treatments; samples amended with compost and biochar (>1%) had leachate DOC values significantly greater than the unamended soil. No correlation was found between DOC and copper concentration in leachate.

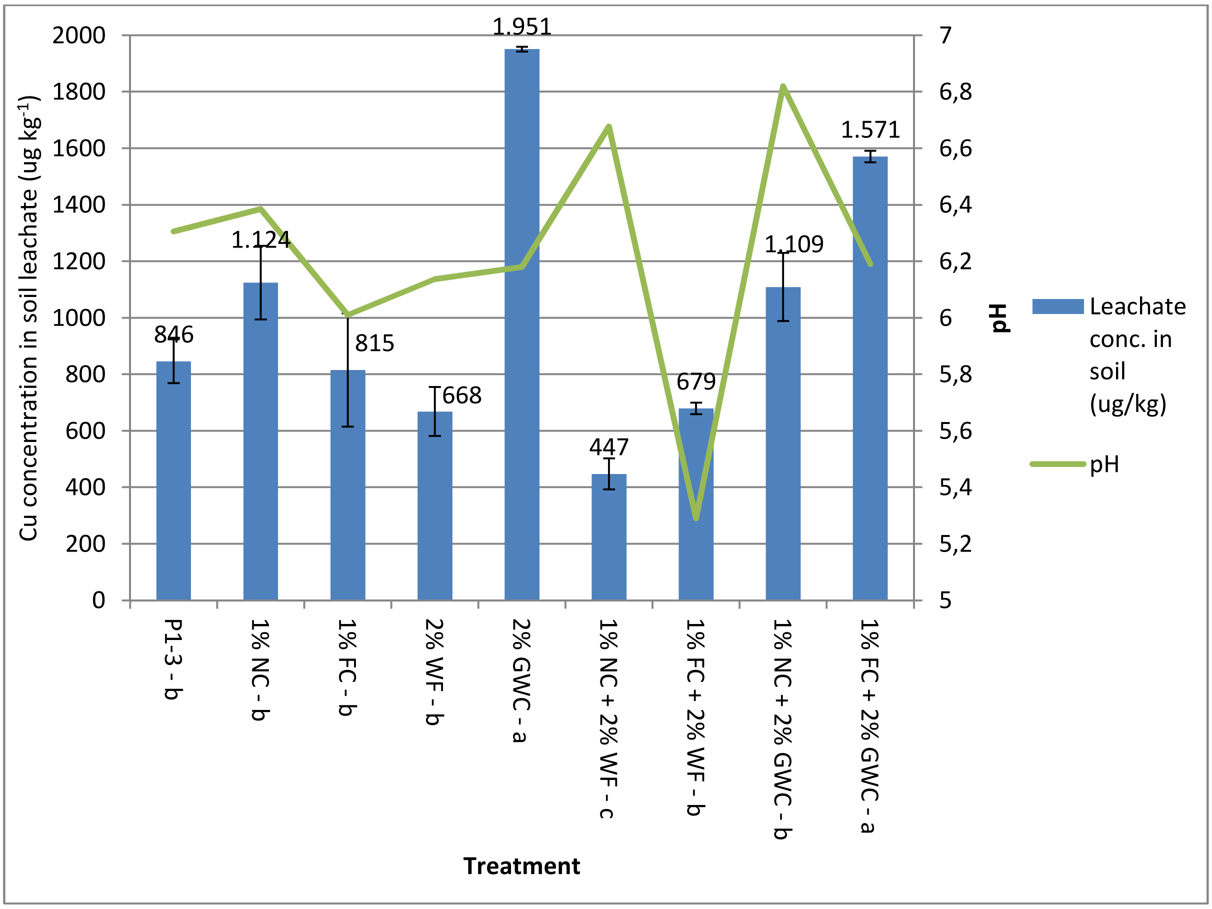

Figure 6: Mean concentration of leachable Cu µg kg^{-1} (bar graph) and pH in leachate (line graph) for P1-3 soil treated with different amendments (n=3). Different letters after each treatment indicate statistical differences based on the Tukey Method (ANOVA P<0.001).

Only one combination, 1% NC biochar with wood fibre compost, was found to reduce copper concentrations in leachate for P1-3 soil. GC both singularly and combined with 1% FC increased copper mobility (fig 6). No statistical difference was determined in pH between the treatments, but DOC of samples increased with compost and biochar addition. No correlation was found between either of these factors and copper mobility. pH in the unamended P7 leachate was much lower (4.20) than the unamended P1-3 (6.30).

4.4.3.2.3 Leach Tests Mirroring Pot Trials

Compost and biochar combinations drastically reduced leachate levels of copper. Similar to composts applied in the second set of leach tests (fig 5), the VE-GWC compost decreased copper mobility in soil P7 (fig 7). Furthermore, VE-GWC reduced the effectiveness of the NC biochar at all biochar amendment rates, a trend that was also observed with GC in the second set of leach tests (fig 5).

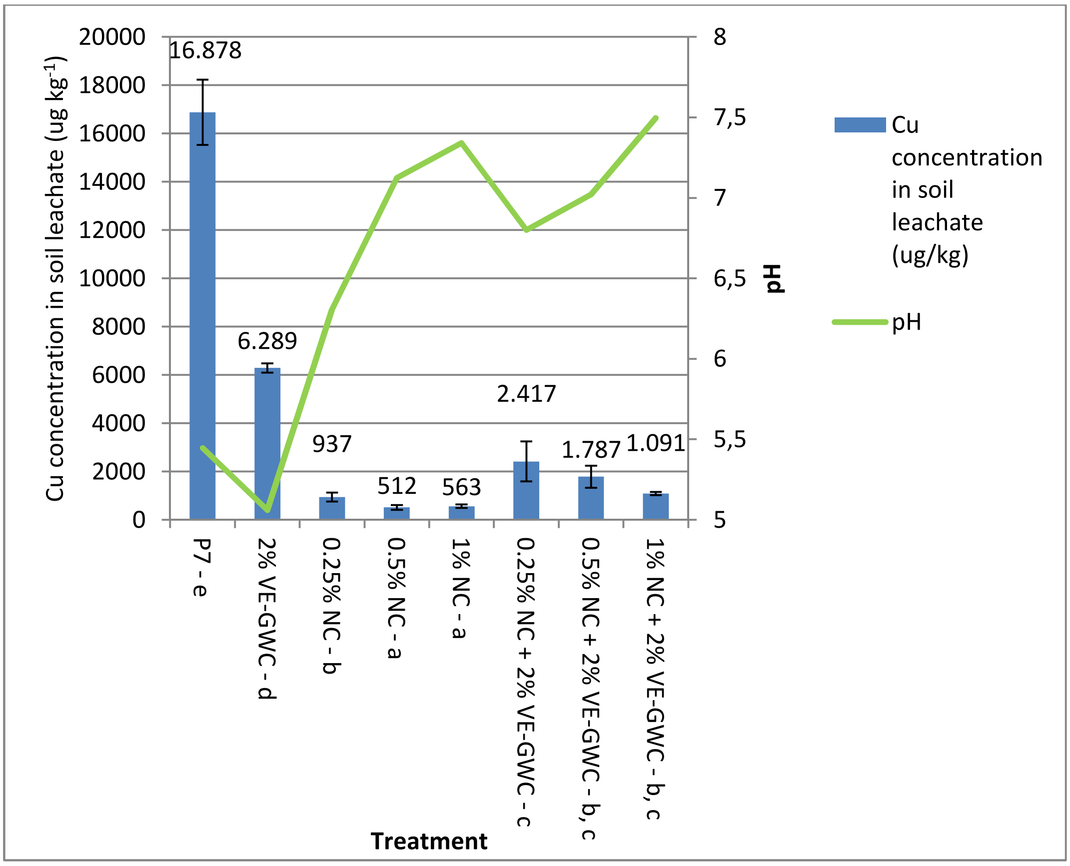

Figure 7: Mean concentration of leachable Cu µg kg^{-1} (bar graph) and pH in leachate (line graph) for P7 soil treated with different amendments (n=3). Different letters after each treatment indicate statistical differences based on the Tukey Method (ANOVA P<0.001).

A correlation was found between pH values and copper concentrations in leachate displayed in fig 7 (Pearson correlation value = -0.73, P<0.01). With a decrease in acidity, there were reduced copper concentrations in solution.

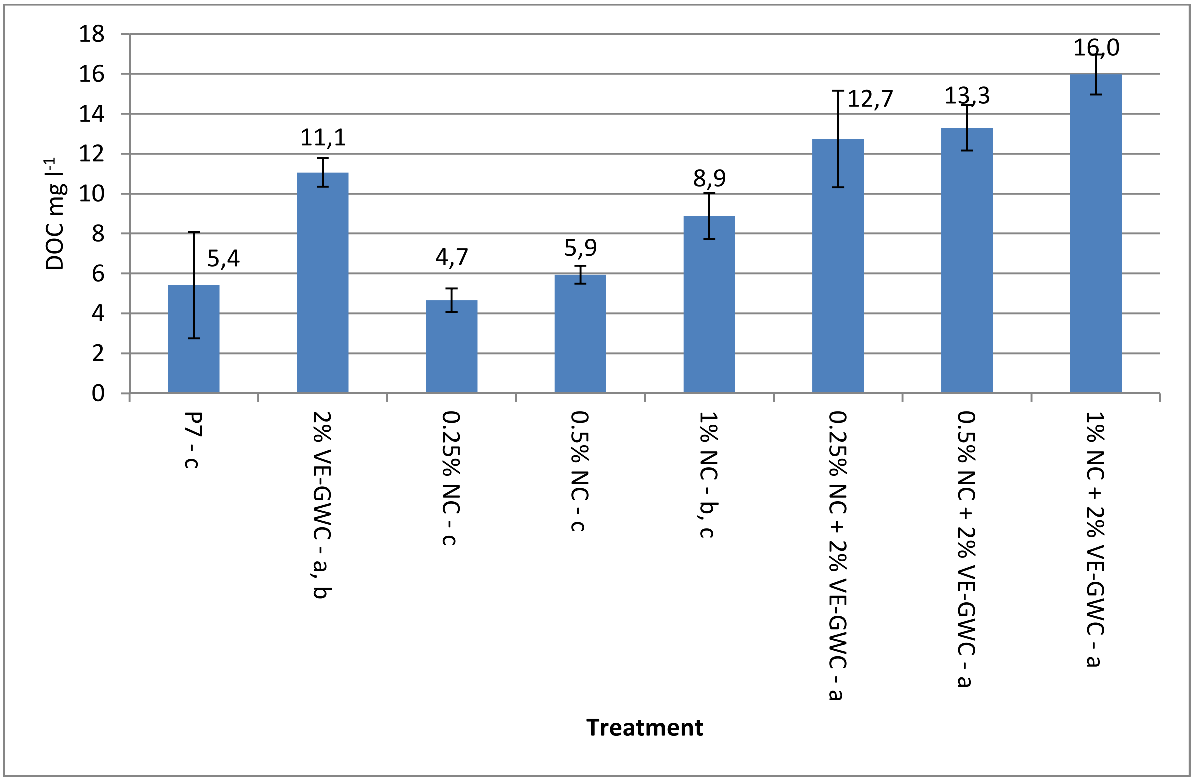

Figure 8: Mean DOC values of P7 soil leachate samples (n=3). Different letters after each treatment indicate statistical difference in DOC values based on the Tukey Method (ANOVA $P<0.001$.)

Leachate DOC concentrations increased significantly with all compost amendments; however, biochar amendments did not significantly increase DOC in leachate. No correlation was determined between DOC concentration and copper concentration in leachate. This follows patterns found throughout the study, where DOC increases significantly with compost amendments, but there is no significant link to copper mobilisation.

4.4.3.3 Pot Trials

Table 8 shows data recorded on growth and germination as well as biomass on harvest. Across all treatments there was a general pattern of improvement in plant characteristics associated with both increasing biochar amendment rate and with compost addition (Table 8). Figure 9 (a) and (b) shows plant growth in unamended and 1% biochar addition respectively. Statistical tests indicated that combined amendments and greater biochar amendments rates were most effective in improving plant physical characteristics.

Table 8: Mean plant growth data from cress (*Lepidium sativum*) grown in (P7) with different amendments (n=4). Letters after values indicate statistical difference based on the Tukey Method, (ANOVA P<0.003 - all columns).

Pot	Number germinated	Height (cm)	Leaf size (cm)	Dry biomass weight in pot (g)
P7	11.00(a)	1.20(a)	0.20(a)	0.03(a)
2% VE-GWC	21.80(b)	2.80(a)(b)	0.40(b)	0.07(b)
0.25% NC	22.80(b)	3.90(b)	0.40(b)	0.06(b)
0.5% NC	24.50(b)	6.30(c)	0.80(b)(c)	0.11(c)
1% NC	24.30(b)	7.80(c)	1.00(c)	0.09(c)
0.25% NC + 2% VE-GWC	24.30(b)	5.50(b)(c)	0.5(b)	0.11(c)
0.5% NC + 2% VE-GWC	21.00(b)	7.50(c)	1.00(c)	0.10(c)
1% NC + 2% VE-GWC	23.30(b)	8.30(c)	1.10(c)	0.10(c)

Figure 9: Cress growth at two weeks in unamended (a) and NC 1% biochar amended (b) soils.

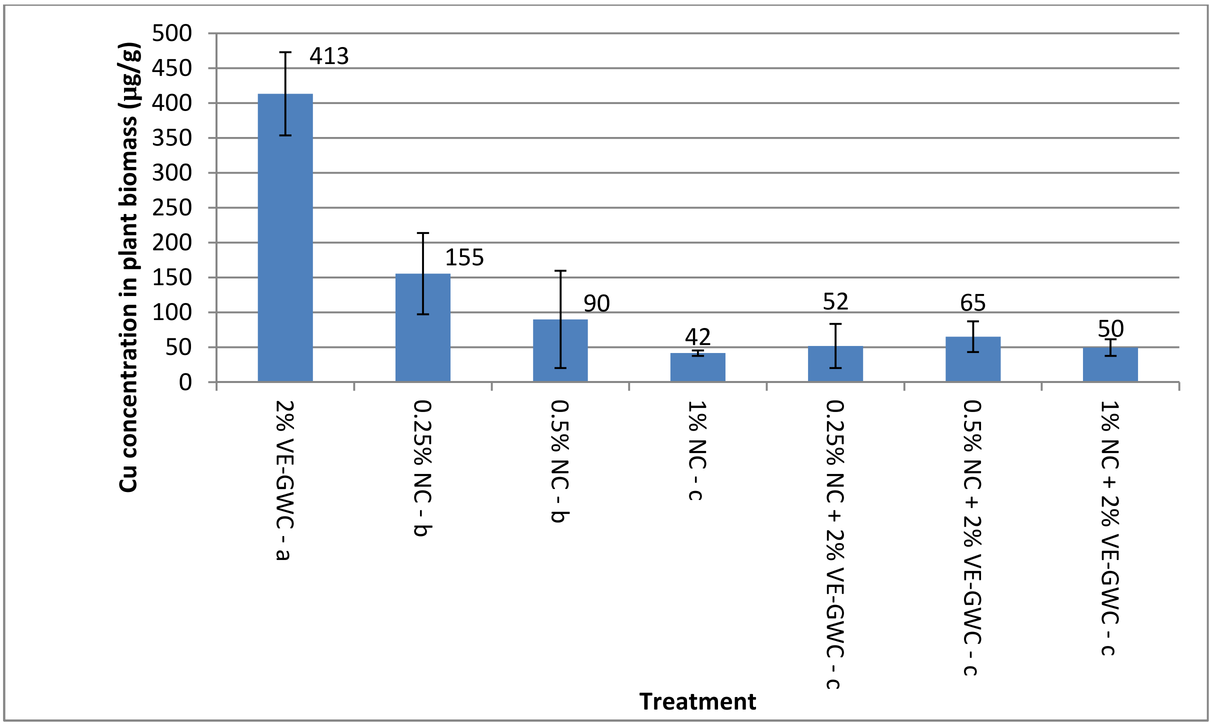

Figure 10: Mean shoot concentration of Cu µg g^{-1} in Cress (*Lepidium sativum*) grown in P7 soil with different amendments (n=4). Different letters after each treatment indicate statistical difference of Cu concentrations in plant biomass based on the Tukey Method (ANOVA P<0.01).

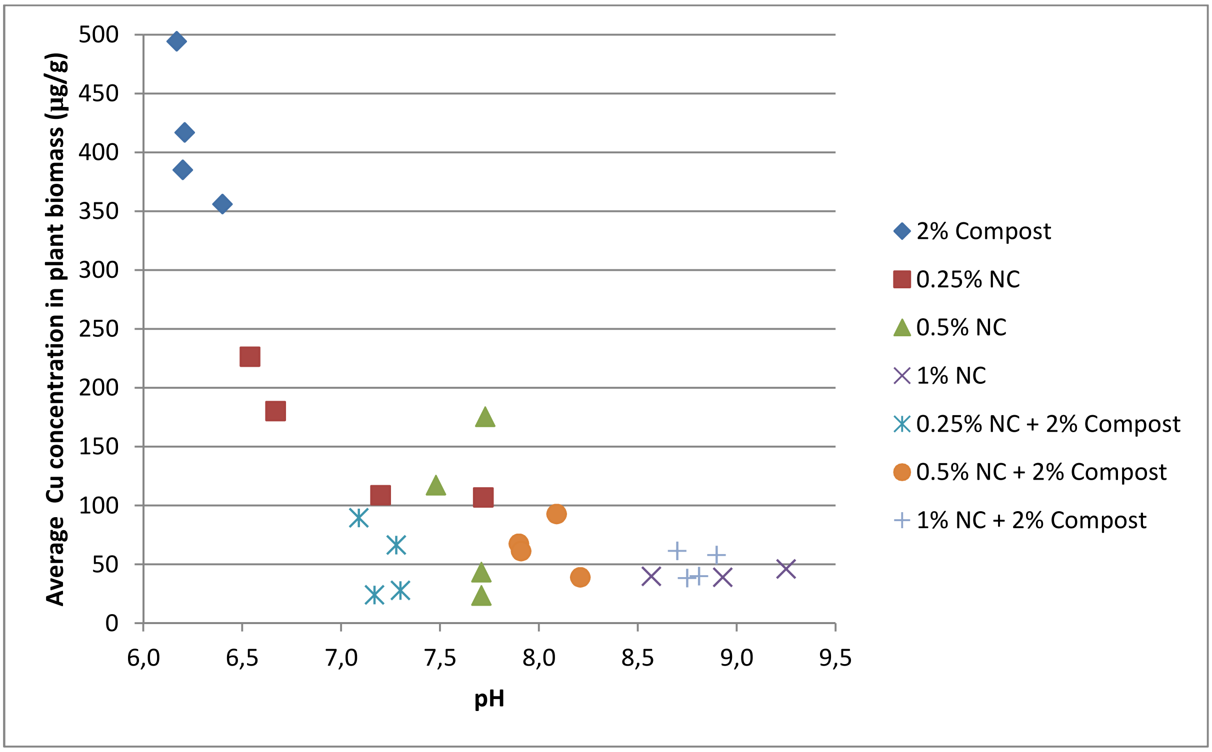

Figure 11: Scatterplot of shoot Cu concentration in cress against pH of pots (n=4). P<0.001. Pearson correlation values = -0.76.

Elemental composition could not be obtained from cress grown in the unamended soil. This was because of the lack of plant biomass in these pots. The most effective amendments for reducing copper concentrations in plant biomass included 1% NC biochar and all combined compost and biochar amendments (Fig 10). All other amended pots reduced phytotoxicity of the unamended soil, however not as effectively as combined and 1% NC biochar amendments. Interestingly the most successful amendments for reducing copper concentrations in soil leachate were NC biochar added as a single factor (Fig 5, 7), whereas in plant trials 0.25% and 0.5% biochar was much more effective when combined with VE-GWC compost (Fig 10). This agrees with previous findings reporting that phytotoxicity is reduced most greatly when amendments that reduce copper mobility and increase soil calcium concentration are applied together (Bes & Mench, 2008). Green waste composts have reliably high available calcium.

There was a strong negative correlation between soil pH and copper concentrations in cress biomass (Fig 11). This is in line with leach test results which indicated that increasing pH reduces copper availability in soil.

Significant correlations were found between copper concentrations and other elemental concentrations in plant shoots. Strong, significant and positive correlations (Pearson >0.9, P<0.05) were found between copper and aluminium, cobalt, chromium, iron, manganese and lead. With an increase in shoot copper concentration, there was also an increase in these elements. Moderate, significant and a negative correlation (Pearson >-0.7, P<0.05) was found between copper and calcium and potassium. With decreasing copper uptake in plants, there was increasing uptake of calcium and potassium.

4.4.4 Scoping Study Discussion

4.4.4.1 Copper Toxicity in Tested Soils

Concentrations of copper in soil pore water above 1 mg kg^{-1} are likely to be phytotoxic (McBride, 1994). Values of leachable copper in the P1-3 soil did not exceed this (approximately 0.8 mg kg^{-1}) however, values obtained in the P7 soil were at least 15 times this value (>15 mg kg^{-1}). In all leaching tests, many of the other elements considered phytotoxic were beneath detection limits. This matches the low total element concentrations seen in Table 7 for these metals. Leachable copper concentrations in soil P1-3 are high, however not exceptionally. This can be linked back to the findings of Lagomarsino *et al.* (2011), who noted that 66% of the copper in this soil was located in the acid soluble and reduced fractions, consequently having reduced availability.

4.4.4.2 Amendment Impact on Copper Mobility

No major immobilisation benefit from amendment use was found in the P1-3 soil. In the P1-3 soil, the leachable copper concentration is <1 mg kg^{-1}, which is lower than the 'phytotoxic limit' suggested by McBride (1994). Low leachable levels of copper were expected based on the findings of Lagomarsino *et al.* (2011), where the authors recorded in the same soil that the copper was locked in acid soluble forms and in reducible fractions.

The leaching tests demonstrated that the FC biochar increased copper mobility in the P7 soil. Conversely, the NC biochar caused a significant decrease in copper concentrations in leachate. In the case of 1% NC biochar addition in the second set of leach tests, copper concentrations in the P7 soil leachate decreased from 14.9 mg kg^{-1} to approximately 1.01 mg kg^{-1}. WF compost increased the effectiveness of the NC biochar in this set of leach tests, however, GC compost decreased the effectiveness of NC biochar.

In the final set of leach tests, NC biochar at 1% and 0.5% additions reduced copper in leachate from 16.9 mg kg^{-1} to 0.563 and 0.512 mg kg^{-1}, respectively. GWC as a single amendment decreased concentrations of copper relative to the unamended soil. However, GWC decreased the effectiveness of NC biochar.

Whilst no correlation was determined between DOC and copper concentration in samples, there were still significantly higher levels of DOC in samples with the application of compost. Even though no correlation was found, there is a possibility that increased DOC concentrations could have influenced metal mobility. The various effects of DOC from remediation amendments have been well reported, with biochar possibly forming soluble organo-metallic complexes and compost increasing sorption to humic and fulvic acids. (Karami *et al.*, 2011; Lagomarsino *et al.*, 2011; Beesley & Dickinson, 2010; Bradl, 2004).

In all of the P7 soil leaching tests, there was a strong correlation between pH and copper concentration in solution. pH modification is known to be a major factor in determining copper and other metal availability in the soil. Copper has a ‘u’ shaped solubility curve in the soil at different pH values; solubility is lowest at a soil pH of around 8-9, and increases either side of this, but at a much greater rate in acidic soils. (Ross, 1996; McBride, 1994). This is clearly shown in our results, with an increasing pH value (to approximately 7), the copper concentration in solution is 15 times less than that of the unamended P7 soil (pH 5.5).

Although this scoping study found a clear link between pH and copper mobility, it cannot be stated that this was the sole reason for reducing copper concentration in solution.The two biochars FC and NC both applied at 1% have opposite effects on copper concentrations in soil P7 leachate; however, pH of these two biochars are both greater than that of the unamended soil and are not statistically different. This could be attributed to the differences in sorption capabilities of each biochar. As previously mentioned, upon addition to the soil, biochar can improve characteristics such as the cation exchange capacity of the soil, the extent of this changing with various feedstocks and production processes. (Novak *et al.*, 2009). Furthermore, the chemical composition of a biochar can further aid in the reduction in availability of contaminants; Karami *et al.* (2011) demonstrated increased lead sorption to biochar, attributed to high concentrations of phosphorus in the biochar. The two C-Cure Solutions™ amendments (NC and FC) were applied based on the soil characteristics and the types of contaminants in the soil. Both amendments had similar effects on pH in the P7 soil;

however, concentrations of leachable copper were very different. These differences can be attributed to the differing characteristics and chemical composition of each biochar.

4.4.4.3 Amendment Impact on Phytotoxicity

The lowest shoot concentrations (42.0 $\mu g\ g^{-1}$) were found in soils treated with 1% NC biochar as a single factor. This value is within the range of acceptable concentrations (5-50 $\mu g\ g^{-1}$) suggested by Epstein and Bloom (2005). The second most efficient treatment was 1% NC biochar + 2% compost (50.0 $\mu g\ g^{-1}$). This treatment was just within the aforementioned acceptable range, whereas all other treatments were above this range. Nonetheless, all biochar only and combined treatments significantly reduced copper concentrations in plants relative to the compost only samples which had a mean concentration of 413 $\mu g\ g^{-1}$.

Insufficient plant growth occurred in the unamended soil to assess copper concentrations in biomass. This can be linked to the leaching tests which showed that unamended soil had high levels of bioavailable copper. Comparably, Sheldon and Menzies (2005), demonstrated an increasing copper concentration in solution increased copper concentrations in Rhodes grass (*Chloris gayana*), as well as plant physical deficiencies such as reduced number and length of root hairs.

Amendments with combined biochar and compost resulted in significantly reduced shoot copper concentrations compared to biochar alone for the lower rates of biochar addition. It has been previously shown that in the P7 soil, amendments may act in different manners; zero-valent iron grit has been shown to be effective in reducing copper in solution, whereas composts were much more effective for improving plant growth (Bes & Mench, 2008). In our study, biochar amendments were successful in reducing copper concentrations in soil pore waters; however, compost may have improved both the nutrient and microbial status of the soil, thus aiding plant growth. In cress biomass, a correlation was found: decreasing copper concentrations resulted in increased calcium uptake by plants. Calcium has been shown to compete with copper for plant uptake (Burkhead *et al*., 2009). Biochar reduced copper concentrations in solution; however, compost would have increased soil Ca:Cu ratio, thus increasing calcium uptake by plants (Vital Earth Ltd, 2009).

A strong negative correlation was determined between pH and copper concentration in cress, strengthening the findings from the leaching tests that pH is a major factor in reducing copper concentrations in solution. pH values generated by amendments were much closer to pH 8-9, at which copper solubility is at its lowest (Ross, 1996; McBride, 1994). These pH values are closer to those determined in table 5 and by Bes & Mench (2008), who previously tested on this soil; this is possibly due to pot trials being more representative of a soil system and the acid washing of equipment prior to carrying out leaching tests.

4.4.5 Scoping Study Outcomes

The results of the scoping study were used to frame further work. As the results showed that leachable copper was notably higher in the P7 soil than in the P1-3 soil, and that little benefit was gained in the P1-3 soil through the addition of amendments, the detailed study and supporting MSc project used only the P7 soil. As copper phytotoxicity was high in the P7 soil, it was determined that future trials should also include plant trials to determine the efficacy of applied amendments. It was decided that biochar and compost treatments would be utilised in further research, as biochar was shown to reduce leachability of copper in the P7 soil and improve plant growth and combined applications of biochar and compost were beneficial when biochar was applied at lower application rates.

4.5 Detailed Study and Supporting MSc project

4.5.1 Introduction and Aims

This detailed study and the supporting MSc study aimed to more comprehensively investigate some of the findings from the scoping study. These projects, like scoping study, were a collaborative effort between the HOMBRE and Greenland projects. The studies again focussed on the ability of biochars and green waste compost to immobilise copper in contaminated soil. The results of the studies helped to gain insight into the optimal mode of use of biochars and compost as gentle remediation options for copper contaminated soils.

An additional aim was to provide an indication of the potential for the growth of biomass usable for energy production on marginal land, by establishing if there was an improvement in yield when green amendments were applied. Bioenergy production on marginal land has previously been discussed (e.g. Gelfand *et al.*, 2013; Fahd *et al.*, 2012; Kolbas *et al.*, 2011; Zhuang *et al.*, 2011; Bardos *et al.*, 2001). Bardos *et al.* (2011a) outline a decision support framework for determining the suitability of energy crop production on a marginal site and for establishing site-specific practical and sustainability issues. Other studies have shown that the idea of growing bioenergy crops on marginal or contaminated land is a feasible one. Hartley *et al.* (2009) evaluated the potential of growing *Miscanthus* for energy generation on an arsenic contaminated site and found that whilst biomass was reduced, crop growth was possible on the site. Studies have also suggested that soil amendments can improve the growth of energy crops on marginal land. For example, Houben *et al.* (2013) found that biochar addition improved the yield of *Brassica napus* L. on cadmium, lead and zinc contaminated soil and concluded that plant uptake of metals was low enough to be useable as a feedstock for bioenergy production.

As the biomass used for biochar production was grown on the site from which the contaminated soils were obtained, the projects also investigated the possibility of recycling biomass produced on contaminated sites for further site improvement.

The research explored the effectiveness of different treatments for the reduction of copper leaching to water bodies and phytotoxicity as summarised in figure 12. Copper leaching and phytotoxicity were driven by the availability of copper in the contaminated soil. The different treatment regimens of plant growth and amendments were explored which altered interacting influencing factors such as pH and DOC. The impact of the treatments on these influencing factors was studied to help understand the mechanisms driving copper availability in soil.

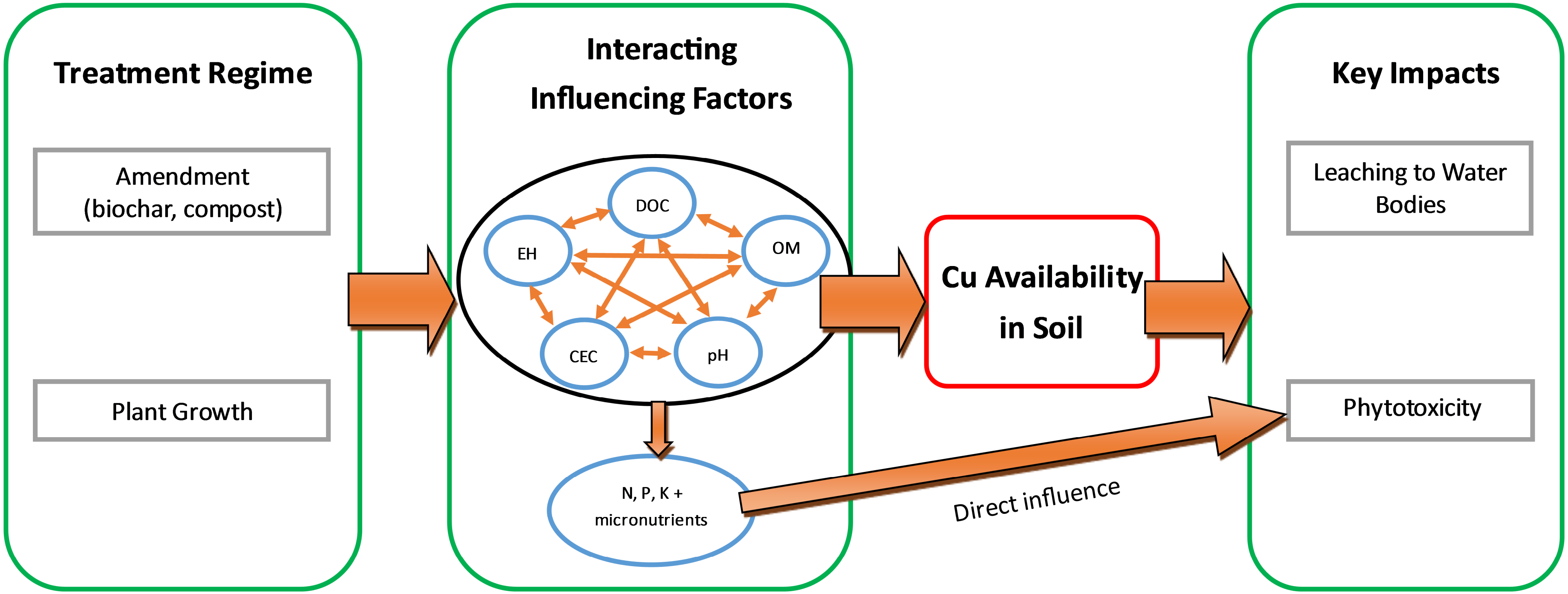

Figure 12: Project conceptual diagram

The supporting MSc project examined the fractionation of copper in the soil, at three different stages, including following a period of plant growth. The distribution of metals in soil is important to determine bioavailability, mobility and toxicity (Long *et al.*, 2009; Samsoe-Petersen *et al.*, 2002). Based on sequential extraction, the operational bioavailability of a metal is split into the following fractions; acid soluble (exchangeable), reducible, oxidisable and residual. Exchangeable is the most bioavailable, with the reducible and oxidisable fractions still relatively active with a greater dependency on soil properties such as pH. Residually bound copper is considered the most inactive (Lu *et al.*, 2009). The management of copper distribution is an important objective for land restoration; a reduction in leaching throughout the soil profile can be achieved through the formation of insoluble, bound or sorbed chemical species, reducing the fraction of bioavailable copper (Boisson *et al.*, 1999).

4.5.2 Methods

4.5.2.1 Soil and Amendments

For this research, a fresh sample of the “P7” soil from the remediation site (see Section 4.3) was obtained in February 2014. This sample was manually homogenised and sieved to 4mm. Three biochars were trialled, identified as BC1, BC2 and BC3. BC1 was a specialised biochar called C-Cure Metal, developed and patented for the remediation of metal contaminated substrates (C-Cure Solutions™ Ltd, Farnham, UK)[11](patent number: WO2009016381A2). BC1 was obtained from C-Cure Solutions™ as opposed to the “NC” successfully used in the scoping study as BC1 was available in larger volumes and therefore represented a product that could be used commercially in remediation. BC2 + BC3 - two biochars (unamended and iron-amended), produced by the AIT Austrian Institute of Technology GmbH using poplar grown at the remediation site where the contaminated soil was obtained. BC2 + BC3 were produced via pyrolysis at 525°C in a Pyreg reactor (Pyreg GmbH, Dörth, Germany) with a residence time of approximately 15-20 minutes. Following this, BC3 was mixed with 20% Fe_2O_3 purchased from VWR (VWR International GmbH, Darmstadt, Germany). Fe_2O_3 was trialled in an attempt to improve the number of sorption sites on the biochar. Iron oxides have known sorption capabilities and have been applied on their own as intended “sinks” for certain trace elements (Gomez-Eyles *et al.*, 2013). Compost was commercially purchased in France. Compost was made from Green waste and sandy soils/sand. Compost was stored at the remediation site for one year under tarpaulin. Soil and amendments were split and transported to IIAG-CSIC[12], Spain; and the University of Reading, UK.

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[11] www.ccuresolutions.com
[12] www.iiag.csic.es

4.5.2.2 Experimental Methods for the Detailed Study

(i) Experimental Design

Soils were amended with 20 different treatments alongside unamended soil (see table 9 below). Each of the biochars was trialled as a single amendment at rates of 1% and 3% w/w. Green waste compost (C) was also trialled as a single amendment at application rates of 1% and 2% w/w. Additionally, each of the three biochars was trialled in combination with compost, at the aforementioned application rates.

Table 9: Amendments and rates

Amendment ID		
Unamended	Compost (1%)	BC3 (3%) + C (1%)
BC1 (1%)	Compost (2%)	BC1 (1%) + C (2%)
BC2 (1%)	BC1 (1%) + C (1%)	BC2 (1%) + C (2%)
BC3 (1%)	BC2 (1%) + C (1%)	BC3 (1%) + C (2%)
BC1 (3%)	BC3 (1%) + C (1%)	BC1 (3%) + C (2%)
BC2 (3%)	BC1 (3%) + C (1%)	BC2 (3%) + C (2%)
BC3 (3%)	BC2 (3%) + C (1%)	BC3 (3%) + C (2%)

Prior to soil amendment, all biochars were air dried for three days then ground to <2mm. Compost was sieved to <2mm before addition and rates were amended to allow for moisture content. For each amendment type, 150g of soil was amended for pre-plant trial tests. For plant testing, soil was sieved to 4mm and amended in batches of 3kg. To determine the effect of the soil amendments on copper mobility and phytotoxicity, leach tests and plant trials were carried out. pH, DOC and Eh were measured in parallel to leach tests to determine the reasons behind differences between treatments.

(ii) Soil and Amendment Characteristics and Composition

General physico-chemical characteristic tests were carried out on the soil and amendments. Soil and amendment moisture content and loss on ignition were determined as described in 4.3.2.1. Available inorganic nitrogen was measured using a KCl extraction. Briefly, three replicates (7g) of soil and amendments were mixed well with 35ml of KCl 2 N. Samples were placed on a rotary shaker for 30 minutes before centrifugation for 5 minutes at 3000 rpm (J2-MI, Beckman Coulter, Inc., Brea, CA, USA) and filtration using CHMLAB F2040 filter paper (CHMLAB Group, Barcelona, Spain). Total inorganic nitrogen in filtrates was determined via Kjeldahl distillation (Keeney and Nelson, 1982).

Further background characteristic tests, metal and PAH content of soils and amendments were carried out by Tecnalia Research & Innovation (Álava, Spain). A summary of these analyses is shown in Table 10 below.

Table 10: Soil and amendment analyses

Analysis	Method
Texture	Laser diffraction particle size (Malvern)
Organic matter %	Loss on ignition at $500^{0}C$
TOC	Sulphochromic oxidation; Standard: UNE EN 13137:2002
pH	Potentiometry; Standard: UNE EN ISO 10390:2012
Exchangeable cations (Na, K, Ca, Mg)	UV/VIS spectrophotometry
CEC	Rowell (1994)
Metals	ICP-AES
PAHs	Gas Chromatography Mass Spectrometry (GC/MS). Standard: EPA 8270: 1996

Metal and PAH testing was also repeated on all amended soils post growth.

(iii) Leaching Tests

Leaching tests were carried out to determine the effect of amendment application on the mobility of copper in soil. Aliquots of 2.5g (4 replicates) were removed to 50ml centrifuge tubes and mixed with 25ml of 0.01M $CaCl_2$. Samples were then placed on a shaker for 24 hours prior to centrifugation at 5000 rpm for ten minutes (J2-MI, Beckman Coulter, Inc., Brea, CA, USA). Samples were then filtered (F2040 - CHMLAB Group, Barcelona, Spain) and analysed for concentration of copper and other metals using ICP-OES.

From each 150g amended soil sample, an 80g sub-sample was removed, moistened with 20ml of water and then stored at $20^{0}C$ for two weeks. Throughout the two week incubation, a repeated wet/dry cycle (two days wetting, followed by two days drying) was implemented to replicate conditions that may occur in the environment. Leaching tests as outlined above were repeated following the incubation stage. Soils collected after plant growth were also tested in this manner; post growth soils were sieved to and analysed at both <4mm and <2mm.

(iv) pH, Eh, DOC

To determine pH and Eh, four replicate samples (10g) of each amended soil were weighed into 50ml centrifuge tubes. To each tube, 25ml of Milli-Q water was added. pH and Eh were then measured using a Metrohm 632 pH meter (Metrohm AG, Herisau, Switzerland). Samples were centrifuged at 5000rpm for ten minutes (J2-MI, Beckman Coulter, Inc., Brea, CA, USA) before filtration (F2040 - CHMLAB Group, Barcelona, Spain). Centrifugation and filtering steps were repeated due to turbidity of samples. Following this, samples were membrane filtered at 0.22µm, then acidified with one drop of reagent grade nitric acid. After 24 hours, the supernatant of each sample was removed to a clean glass vial before analysis using a Vario TOC Cube (Elementar Analysensysteme GmbH, Hanau, Germany). This method was repeated with soil samples post-incubation (4 replicates) and after plant growth (5 replicates).

(v) Plant Trials

Following on from leach testing, plant trials were conducted using the same series of amendments to determine the effect of biochar and compost addition on phytotoxicity in soil. For each amendment type, five replicate pots were prepared with 750g of soil. To each pot, two sunflower seeds (*Helianthus annuus* L.; IBL04 Mother clone, Phytotech, Bern, Switzerland) were added. Plants were watered from below, with water being placed in the saucer underneath pots for uptake. After germination, seedlings were thinned to one plant per pot. After seven weeks, plants were harvested, washed and separated into roots, stems and leaves. Wet and dry biomass was recorded.

Sunflower was selected for this trial as one of the key aims of this project was to establish if biomass usable for energy generation could be produced on marginal land with the aid of soil amendments. Sunflower has been investigated numerous times as a potential crop for energy and fuel production (Zhao *et al*., 2014; Mench *et al*., 2010; Amon *et al.*, 2002; Gerçel, 2002). Sunflower is well suited to biofuel production due to its high lignocellulosic biomass. It also facilitates a move away from simple sugar based biofuel production, essential for protecting the global food supply (Ziebell *et al.*, 2013). Sunflower is a desirable plant for a combined deployment of phytoremediation and biofuel production, as it accumulates low levels of metals, and has high adaptability and aesthetic appeal.

(vi) Analysis of Plant Material

Dried plant material was manually ground and 0.3-0.8g of material was weighed into glass test tubes. To this, 2ml of nitric acid (analytic reagent grade, 70%) was added and left overnight. Hydrochloric acid (1ml, 37%) was then added to each tube. Samples were digested at 120^0C for 9 hours. Samples were transferred to 10ml volumetric flasks and made up to the mark with deionised water. Samples were then analysed via ICP-OES (Varian Vista-Pro, Varian Inc., Palo Alto, CA).

4.5.2.3 Experimental Methods for the Supporting MSc study

(i) Experimental Design

Biochar (air dried, <2mm sieved) and compost (wet, <2mm sieved) amendments were first mixed with the prepared contaminated soil (air dried, <2mm sieved). Fractionation of copper was determined using a sequential extraction carried out at three time points: pre-incubation (two days after amendment), post-incubation (following a two week incubation) and post-growth (following a five week growth period). There were eight treatments in total (T1-8). Table 11 shows the biochar and compost amendments rates (T1-T8). Unplanted pre- and post-incubation samples were kept under the same conditions as samples containing plants. Samples were destructively sampled and homogenised prior to analysis.

Table 11: Treatment (T) amendment percentages: biochar (oven dry) and compost (wet)

Amendment	T1	T2	T3	T4	T5	T6	T7	T8
Biochar: 3%	BC1	BC1	BC2	BC2	BC3	BC3	N/A	N/A
Compost: 1%	N	Y	N	Y	N	Y	N	Y
Replicates	3	3	3	3	3	3	3	3

(ii) Leaching Test and Water Holding Capacity

Leaching tests were carried out in using the same method outlined in 4.4.2.3 Pre-incubation. Water holding capacity was determined by mass loss at 105^{0}C, following 16hr saturation and 16hr draining, (Rowell, 1994).

(iii) Fractionation study

The modified Community Bureau of Reference (BCR) sequential extraction (Lui *et al.*, 2013; Fernandez *et al.*, 2004) was used to determine fractionation of copper in the soil. Briefly, amended soil samples (0.5g) were weighed out and the following reagents prepared: Solution, A, (20ml Acetic acid, (0.1M), Solution B, (20ml Hydroxylamine hydrochloride, 0.5M), Solution C, (10 ml Hydrogen Peroxide, 8.8M, stabilised to pH 2-3), and Solution D, (25ml Ammonium acetate, 1.0 M, (HNO3 stabilised to pH 2.0 ±0.1). Each reagent was added sequentially. After each addition, samples were shaken over-end at 30±10rmp for 16hrs and centrifuged (3300rmp, 20 minutes; MSE Mistral 3000i centrifuge, MSE, London, UK). The residue was washed (10m UP water), shaken, centrifuged and the waste supernatant discarded. Residual material was digested via modified aqua regia (3.5ml AnalaR grade HCl and 1.2ml AnalaR grade HNO3, 140oC, 2.5h).

(iv) Plant Trials

Sunflower seeds (*Helianthus annuus* L.; IBL04 Mother clone, Phytotech, Bern, Switzerland) were graded by diameter < 4mm (Small) ≤ 4.75mm (Large), one of each was planted per pot (10cm diameter, 500g dry soil). Seeds were soaked for 24 hours prior to planting. Soil was moistened (70% field capacity) and allowed to equilibrate overnight, pots were given 25ml of deionised water daily for a growth period of 40 days. Plant and incubation trials were conducted in the University of Reading Soil Science greenhouse (04/06/14 – 13/07/14).

(iv) Analysis of Plant Material

Above ground biomass was harvested and dried at 70^{0}C before being weighed. Shoot copper was determined by digesting 0.25g (or total biomass if <0.25g) ground shoot material with 5ml nitric acid at 60^{0}C for 3hours, then raised gradually to 110^{0}C for a further 6h. The residue was filtered (Whatman 540) and diluted with ultrapure water prior to ICP-OES analysis.

4.5.2.4 Statistical Analysis

Statistical Analysis of the detailed study and supporting MSc study was performed using *Minitab 17* (Minitab, State College, PA, USA). All datasets were assessed using Anderson-Darling tests. All datasets showed non-normal distributions and were largely not transformable to represent normal distributions. Resultantly, non-parametric statistical analyses were used. Kruskal-Wallis tests were used to determine if there were differences between the soil amendments for the variables measured. Differences between amendments pre- and post-incubation, pre- and post-growth and between 2mm and 4mm post-growth soil were established using Mann-Whitney U tests. Correlations between different variables were established using Rank Spearman correlation. For all tests, a confidence level of 95% was used. Therefore, where $p>0.05$, results were considered "not significant".

4.5.3 Results

4.5.3.1 Soil and Amendment Characteristics and Metal Composition

The sample of P-7 soil was found to be very mildly acidic, while the compost had a neutral pH and the biochars were found to be alkaline. Table 12 shows general physico-chemical properties of the soil and the amendments. Notably, BC1 was found to have double the cation exchange capacity (CEC) compared to the other biochars; however, compost had the greatest CEC of all the amendments. The texture of the soil collected for the detailed study and supporting MSc was determined to be a sand (1.5% clay, 89.5% sand, 9% silt); slightly sandier than the soil sample collected for the scoping study. Table 12 also shows that compost had low organic matter at 18.1 %; comparably, >25% is recommended for general landscaping/establishment and maintenance of grass/plants (WRAP, n.d.), potentially as a result of sand additions during compost processing.

Table 12: Mean values of the general physico-chemical characteristics for soil and amendments[13]

Parameter		P 7 Soil	BC1 (C-Cure)	BC2 (AIT)	BC3 (AIT+Fe)	Compost
pH		6.9	10.4	10.2	10.0	7.6
Moisture % at 105^0C		0.8	91.6	42.0	15.8	22.6
Organic Matter % at 500^0C		2.8	49.0	41.5	40.4	18.1
Total organic carbon %		1.0	7.5	3.8	3.5	8.5
Available N		4.2	33.6	8.0	5.8	25.0
CEC ($cmol_c$ kg^{-1} dry soil)		4.0	17.8	8.7	10.3	31.7
Exchangeable cations ($cmol_c$ kg^{-1} dry soil)	Ca	2.6	34.3	30.0	21.3	57.2
	Mg	0.4	7.3	7.0	5.0	7.4
	K	0.2	76.0	41.2	32.6	2.8
	Na	0.3	1.0	0.7	0.7	0.9

Compositional analysis showed total PAHs in the soil to be below levels generally considered as a risk. Nonetheless, certain individual PAHs were detected, e.g. benzo (a) pyrene is present at 0.830 mg kg^{-1}. Copper in the soil was found to be slightly lower than in previous studies at this site (e.g. Kolbas *et al.*, 2013; Kumpiene *et al.*, 2011), although still high at 1010 mg kg^{-1}. The site has been noted for its heterogeneity, with spatial variability of pollution seen across the site (Bes, 2008). Other trace metals in the soil were not found to be present at significant concentrations, although some do exceed background levels found in French sandy soils (results exceeding these levels are shown in bold). Total PAHs were higher in BC1 compared to the other biochars or compost, however they are present at just 7% of the concentrations found in the soil. Copper concentrations are comparable in all the amendments, ranging between 32-43 mg kg^{-1}. Lead, zinc and barium are notably higher in the biochars compared to the soil, particularly in BC1. For example, barium is 750% higher in BC1 than in the soil. Post growth analysis of PAHs and metals in amended soils are listed in Annex 2.

[13] The estimated value of CEC was determined separately to exchangeable cations. The level of CEC recorded is improbably low, as the sum of the cations exceeds the CEC value. The results for CEC should therefore be viewed as indicative of the differences between the soil and amendments only.

Table 13: Soil and Amendment Compositional Analysis

Contaminant (mg kg^{-1} dry matter)	P 7 Soil	BC1 (C-Cure)	BC2 (AIT)	BC3 (AIT+Fe)	Compost
PAHs					
Napthalene	0.38	1.17	0.07	0.08	<0.010
Acenaphthylene	0.92	0.34	<0.010	<0.010	0.02
Acenaphthene	0.13	0.07	<0.010	<0.010	<0.010
Fluorene	0.62	0.10	<0.010	0.01	<0.010
Phenanthrene	2.83	0.37	0.05	0.04	0.03
Anthracene	9.07	0.07	<0.010	0.02	0.02
Fluoranthene	4.30	0.16	0.01	0.01	0.05
Pyrene	4.83	0.15	0.02	0.01	0.05
Benzo (a) anthracene	1.67	0.02	<0.010	<0.010	0.04
Chrysene	2.40	0.02	<0.010	<0.010	0.04
Benzo (b) fluoranthene	3.83	<0.010	<0.010	<0.010	0.08
Benzo (k) fluoranthene	1.17	<0.010	<0.010	<0.010	0.02
Benzo (a) pyrene	0.83	<0.010	<0.010	<0.010	0.04
Indeno (1,2,3-cd) pyrene	0.93	<0.010	<0.010	<0.010	0.05
Dibenzo (a,h) anthracene	0.16	<0.010	<0.010	<0.010	<0.010
Benzo (g, h, i) perylene	0.44	<0.010	<0.010	<0.010	0.03
Total PAHs	34.60	2.57	0.15	0.19	0.45
Metals					
As	13.63	< 5.0	< 5.0	< 5.0	Not analysed
Ba	28.70	244.33	41.80	36.33	Not analysed
Cd	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Cr	20.43	17.47	10.73	28.67	7.09
Cu	**1096.67**	**32.30**	**32.87**	**34.33**	**42.80**
Mo	< 1.0	3.26	2.19	1.97	Not analysed
Ni	10.93	13.47	14.32	**25.37**	< 5.0
Pb	29.70	54.07	5.17	8.40	< 5.0
Sb	< 1.0	< 1.0	< 1.0	< 1.0	Not analysed
Se	<0.4	<0.1	< 0.1	< 0.1	Not analysed
Zn	**47.17**	**247.00**	**143.67**	**111.33**	< 5.0
Hg	8.26	<0.1	< 0.1	< 0.1	0.39

Results in bold exceed background concentrations for French sandy soils (Mench and Bes, 2009)

4.5.3.2 Leaching Tests

The results of pre-incubation $CaCl_2$ leaching tests showed a significant reduction in leachable copper across all treatments relative to the unamended soil (see Fig 13). As data was not normally distributed, non-parametric tests were used. Kruskal-Wallis testing determined a significant difference between treatments (P<0.01). For biochar only treatments, leachable copper was reduced in the order: BC1>BC2>BC3 for both the lower and higher rate of application. This trend was repeated in the combined treatments at 1% compost addition. Combined compost and biochar treatments improved the performance of the 1% biochar application rate. The greatest overall reduction in leachable copper was found to be BC1 (3%). This treatment led to a 91% reduction in leachable copper relative to the unamended samples. Compost alone (1%) proved the least effective treatment; although leachable copper was still reduced by 47%.

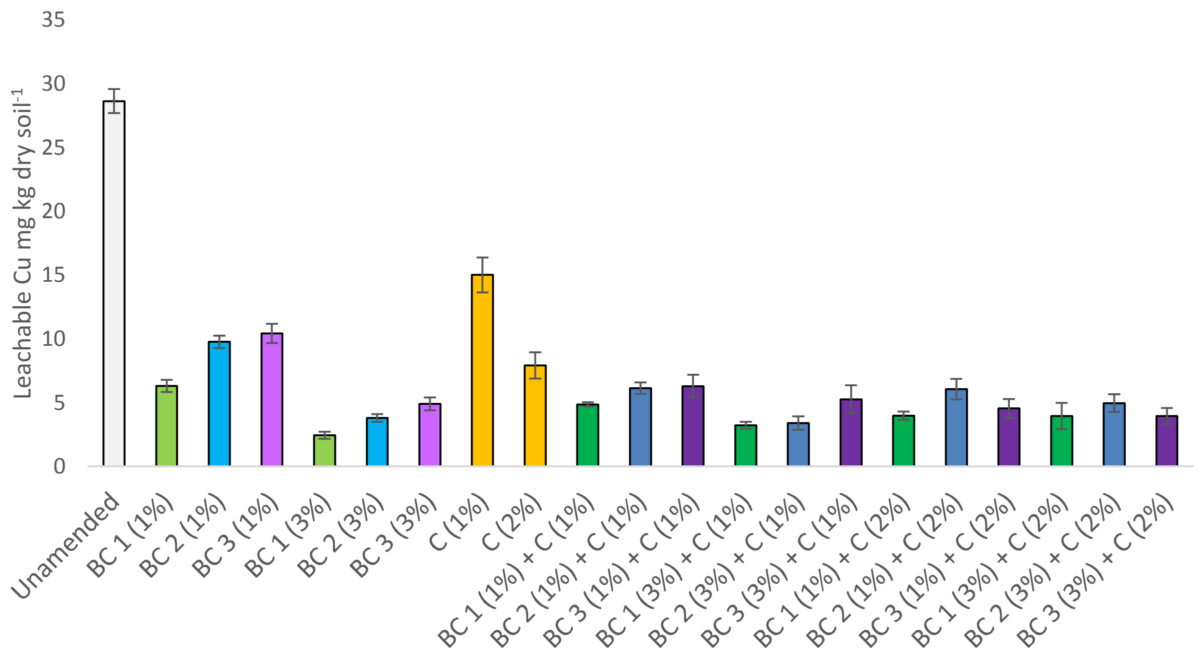


Figure 13: Mean concentration of leachable Cu mg kg^{-1} in pre-incubation soils (± standard error, n=4).

The results for leach testing following a two week incubation period mirrored the pre-incubation leaching tests to some extent. However, the differences between biochars in terms of copper immobilisation were less discernible post-incubation (see Fig 14). Similar to the pre-incubation leach tests, significant differences were found between the treatments (P<0.01) and all treatments reduced the leachable copper compared with the unamended. It is also notable that the leachable copper in the unamended samples decreased by 25% compared to pre-incubation. Mann-Whitney U tests suggested that there were significant differences between pre- and post-incubation datasets (medians: 5.09 mg kg^{-1} and 4.13 mg kg^{-1} respectively, p=0.01).

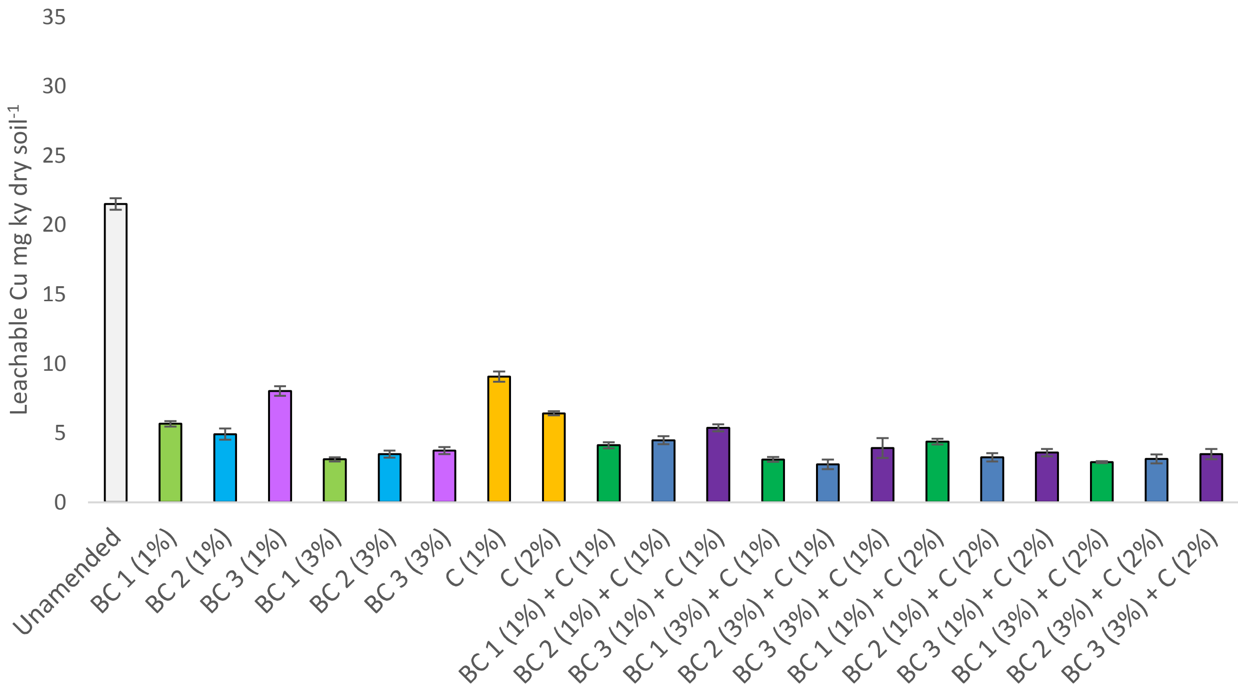


Figure 14: Mean concentration of leachable Cu mg kg^{-1} in post-incubation soils (± standard error, n=4).

The leaching tests performed on soils taken from pots after a seven week growth period again showed a significant reduction in leachable copper across all treatments compared to the unamended samples (see Fig 15)($P<0.01$). Mann-Whitney U testing suggested there were no significant differences between leach tests carried out in soils sieved to 2mm compared to those sieved to 4mm. However, pre- and post-growth leach tests were found to be significantly different from one another (medians: 5.09 mg kg^{-1} and 0.91 mg kg^{-1} respectively, $p<0.01$).

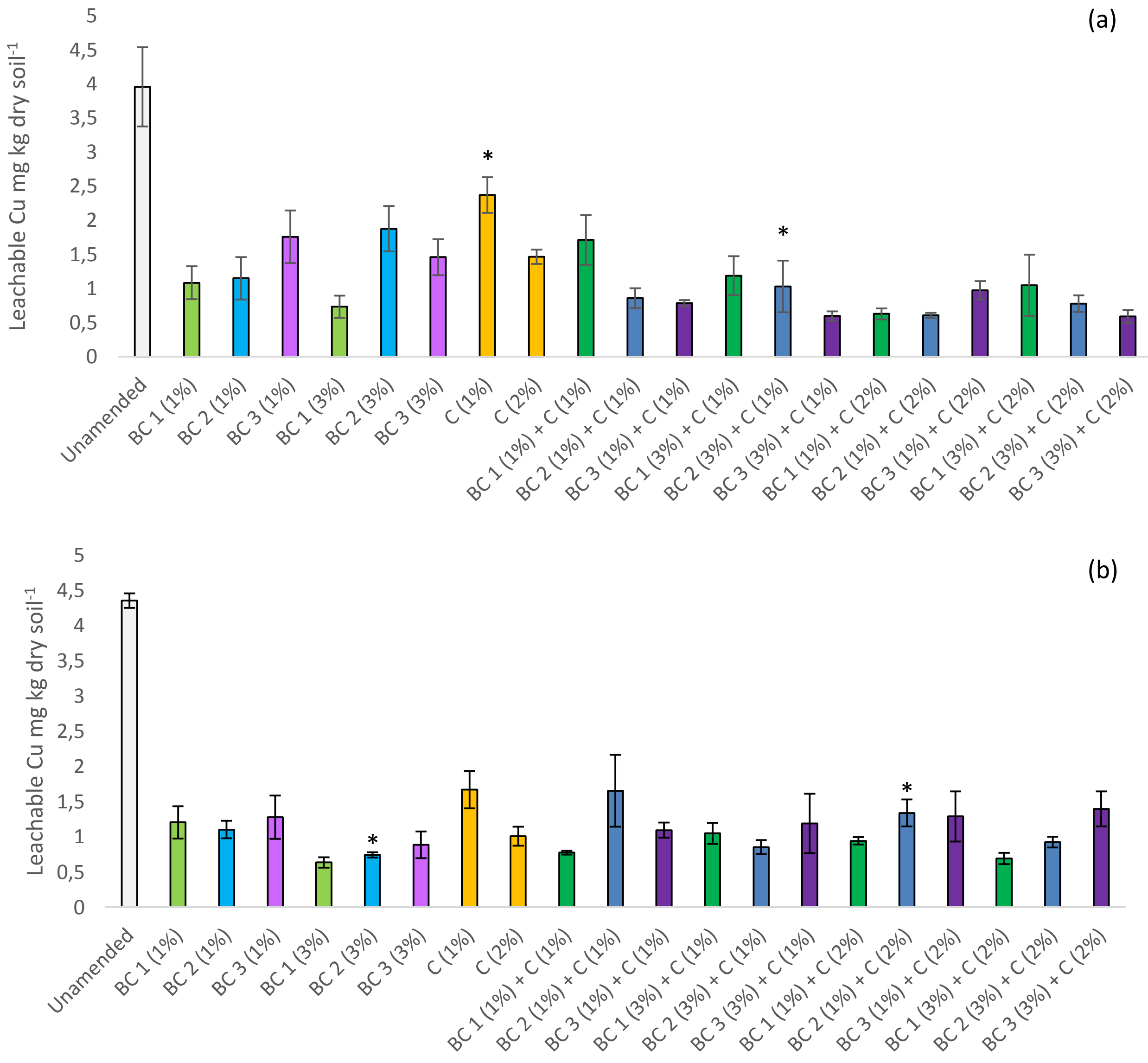


Figure 15: Mean concentration of leachable Cu mg kg^{-1} in post-growth soils, sieved to 2mm (a) and 4mm (b) (± standard error, n=5). *outlier (determined using Grubbs outlier test) has been removed: n=4. Note - change in y-axis scale.

A dramatic drop in leachable copper was seen in the post-growth samples across all treatments and the unamended samples; a mean reduction of 75% was observed compared to pre-incubation leachable copper. Leachable copper in the unamended samples decreased by 85% between the two leach tests.

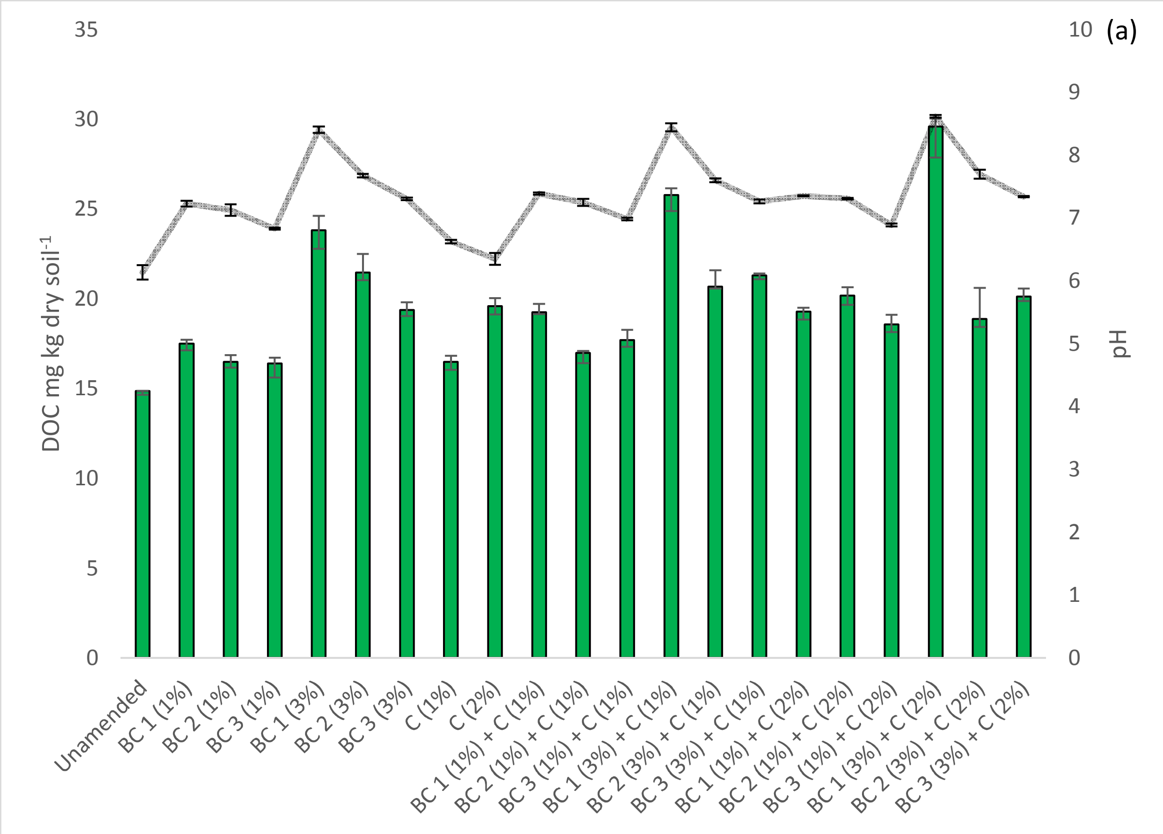
4.5.3.3 pH, DOC, Eh

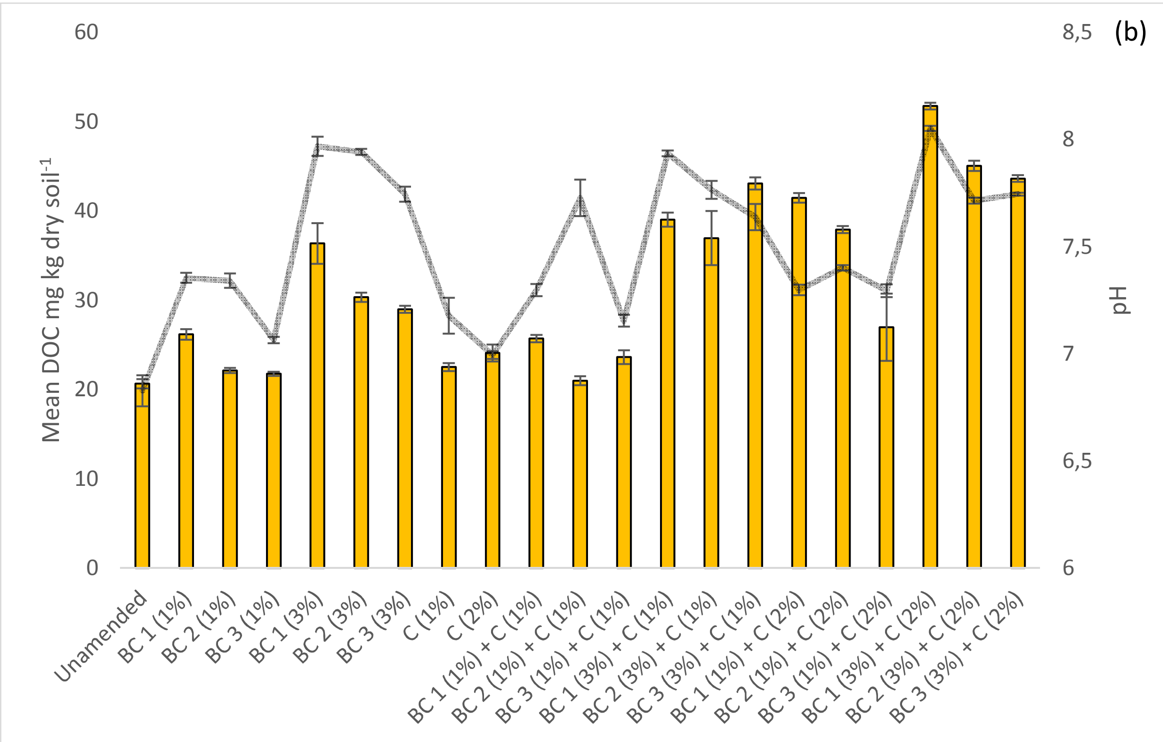
Significant differences were found between the treatments in terms of pH in solution at each of the three time points ($p<0.01$). At all time points, pH was increased in all treatments compared to the unamended soil (see fig 16, below). However, less variation in pH was seen between treatments post-growth compared to the pre- and post-incubation tests.

Pre-incubation pH showed a similar trend to pre-incubation leach tests; BC1 (3%) with and without compost was found to increase pH most greatly (inversely comparable to leachable copper, where BC1 (3%) with and without compost decreased leachable copper most greatly). Data was not normally distributed, so non-parametric Rank Spearman correlation tests were used. Rank Spearman testing found a strong negative correlation between these two variables pre-incubation; as pH increased, leachable copper decreased. This was determined to be significant ($r= -0.85$, $p<0.01$). Post-incubation pH also displayed a weak negative correlation with leachable copper, which was determined to be significant ($r= -0.84$, $p<0.01$). No significant relationship was found between pH and leachable copper post-growth. However, again comparable to leachable copper, Mann-Whitney U testing determined a significant difference between pre- and post-growth pH (Medians: 7.33 and 7.64 respectively, $p<0.01$) as well as pre- and post-incubation (Medians: 7.33 and 7.41 respectively, $p=0.01$).

Significant differences were found between treatments for DOC in solution across all time points (see fig 16, $p<0.01$). Pre-incubation DOC follows a comparable trend to pH (and inversely to leachable Cu), with BC1 (3%) with and without compost increasing DOC most greatly. A weak significant correlation was determined between DOC and pH pre-incubation (positive; $r= 0.78$, $p<0.01$) and leachable copper pre-incubation (negative; $r= -0.80$, $p<0.01$).

A significant overall increase was found in DOC between pre-incubation and post-incubation (medians: 19.3 mg kg^{-1} and 29.0 mg kg^{-1}, $p<0.01$). A weak negative correlation was determined between post-incubation DOC and leachable copper ($r= -0.79$, $p<0.01$). No significant relationship could be established between post-growth DOC and leachable copper. However, a significant increase in DOC was observed post-growth compared to pre-growth (medians: 19.3 mg kg^{-1} and 78.5 mg kg^{-1}, $p<0.01$). This shows a comparable but inverse trend to leachable copper, which overall significantly decreased post-growth.


(a)
DOC mg kg dry soil-1
pH
0
5
10
15
20
25
30
35
0
1
2
3
4
5
6
7
8
9
10
Unamended
BC 1 (1%)
BC 2 (1%)
BC 3 (1%)
BC 1 (3%)
BC 2 (3%)
BC 3 (3%)
C (1%)
C (2%)
BC 1 (1%) + C (1%)
BC 2 (1%) + C (1%)
BC 3 (1%) + C (1%)
BC 1 (3%) + C (1%)
BC 2 (3%) + C (1%)
BC 3 (3%) + C (1%)
BC 1 (1%) + C (2%)
BC 2 (1%) + C (2%)
BC 3 (1%) + C (2%)
BC 1 (3%) + C (2%)
BC 2 (3%) + C (2%)
BC 3 (3%) + C (2%)


(b)
Mean DOC mg kg dry soil-1
pH
0
10
20
30
40
50
60
6
6,5
7
7,5
8
8,5
Unamended
BC 1 (1%)
BC 2 (1%)
BC 3 (1%)
BC 1 (3%)
BC 2 (3%)
BC 3 (3%)
C (1%)
C (2%)
BC 1 (1%) + C (1%)
BC 2 (1%) + C (1%)
BC 3 (1%) + C (1%)
BC 1 (3%) + C (1%)
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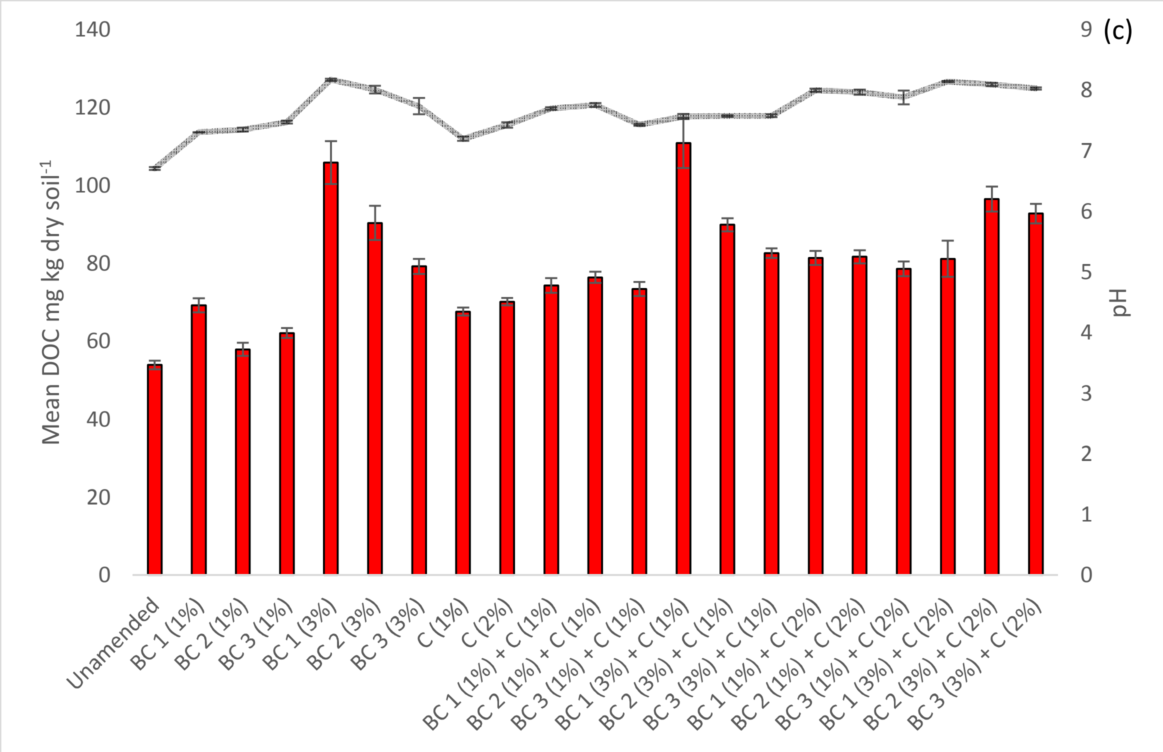

Figure 16: Mean DOC (bar chart) and pH (line graph) in solution ± standard error: pre-incubation (a), post-incubation (b) and post-growth (c), n=3, 3, 5. Note - change in y-axis scales.

Significant differences were determined between the treatments at all three time points for redox potential (Eh) in solution. However, the trends are not analogous across all the time points; pre-incubation and post-growth, Eh was reduced in all treatments relative to the unamended samples (see fig. 17, below). Conversely, post-incubation Eh was increased or similar to the unamended samples in the majority of the treatments.

No statistical relationship was found between leachable copper and Eh at any time point, although Eh post-growth was found to be weakly correlated to both DOC ($r= -0.67$, $p<0.01$) and pH; ($r=-0.83$, $p<0.01$).

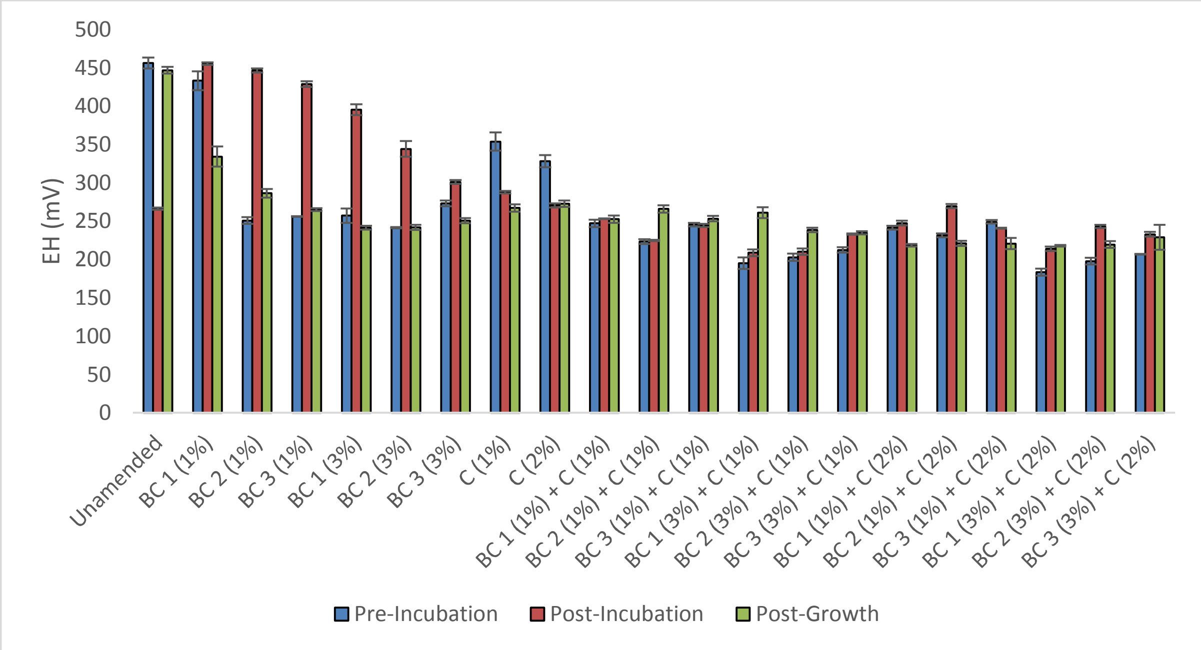

Figure 17: X Mean Eh (± standard error): pre-incubation, post-incubation (b) and post-growth (c) in solution, n=3, 3, 5.

4.5.3.4 Plant Trials

(i) Plant Height

Plant height in *H. annuus* over the seven week growth period was most greatly increased by soil amendment with BC1 (3%) in combination with compost at both application rates (See table 14). At the lower rate of biochar application (1%), compost addition had a greater impact on the plant height of the BC2 and BC3 plants compared to the BC1 samples, with compost addition at (2%) doubling plant height for these two biochars. However, it should be noted that BC1 (1%) as a single amendment in all cases achieved greater plant heights than the other biochars. It achieved almost double the height of the BC2 (1%) treatment and more than double the BC3 (1%) value. Plant height and root length were severely reduced in the unamended plants compared to all of the treated samples; the most effective treatment (BC1 (3%) + C (1%)) improved plant height by 89% and root length by 81%.

Table 14: Mean values of plant height and root length in the different treatments (± standard error).

Treatment	Mean Plant height (cm) ± standard error	Mean Root length (cm) ± standard error
Unamended	4.62 ±0.93	2 ±0.34
BC 1 (1%)	22.7 ±1.39	4.1 ±0.48
BC 2 (1%)	13.84 ±0.80	7.6 ±2.74
BC 3 (1%)	9.86 ±0.70	3.2 ±0.71
BC 1 (3%)	31.48 ±3.27	11.2 ±2.18
BC 2 (3%)	18.42 ±4.63	6.18 ±1.23
BC 3 (3%)	22.86 ±2.34	6.66 ±1.48
C (1%)	11.42 ±0.90	2.82 ±0.09
C (2%)	24.54 ±2.19	4.7 ±1.09
BC 1 (1%) + C (1%)	24.92 ±3.59	4.7 ±1.10
BC 2 (1%) + C (1%)	26.34 ±3.61	7.48 ±1.47
BC 3 (1%) + C (1%)	13.34 ±1.18	2.88 ±0.35
BC 1 (3%) + C (1%)	43.12 ±1.46	11.02 ±1.53
BC 2 (3%) + C (1%)	27.5 ±2.36	12.24 ±2.49
BC 3 (3%) + C (1%)	32.58 ±4.63	5.7 ±0.94
BC 1 (1%) + C (2%)	26.72 ±2.02	5.42 ±1.30
BC 2 (1%) + C (2%)	30.16 ±1.74	5.64 ±1.27
BC 3 (1%) + C (2%)	26.46 ±2.12	7.52 ±1.49
BC 1 (3%) + C (2%)	40.04 ±2.33	14.9 ±2.81
BC 2 (3%) + C (2%)	29.4 ±2.09	9.3 ±1.07
BC 3 (3%) + C (2%)	33.64 ±3.59	8.4 ±1.86
P	<0.01	<0.01

(ii) Plant Biomass

Kruskal-Wallis testing showed significant differences between treatments for both above ground and root dry biomass (see fig 18, below) ($P<0.01$). Mirroring plant height data, the most notable increases in above ground biomass were achieved in BC1 (3%), with and without compost. BC3 treated soils generally resulted in the lowest biomass increases, however, BC3 achieved a greater biomass yield than BC2 at 3% both as a single amendment, and with 2% compost. For the root dry biomass, there was less variation between amended and unamended samples and between the different amendments. Nonetheless, the general trend showed combined treatments and higher application rates improved biomass yields. Unlike the leach tests, the compost only treatment, even at 1% increased yields comparably to the lower rate of biochar application. Rank Spearman testing determined that there was a strong, positive correlation between plant biomass and plant height ($r= 0.89$, $p<0.01$). No significant relationship was found between plant biomass and post-growth leachable copper in soil.

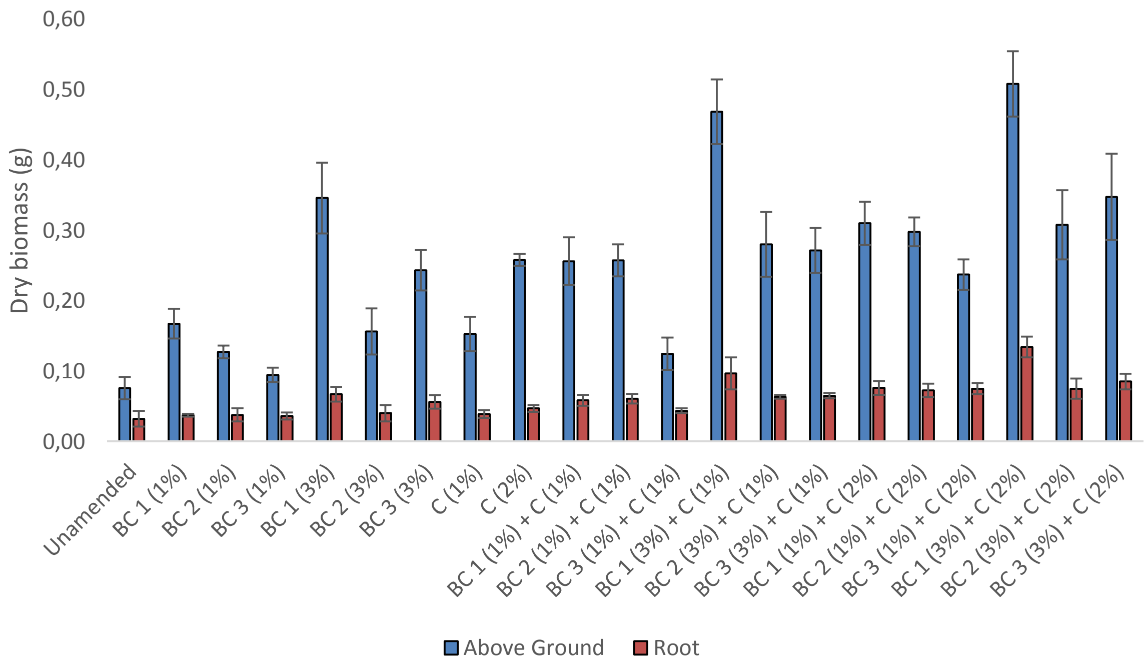

Figure 18: Mean Dry Biomass (g), above ground and roots (± standard error, n=5).

(iii) Plant Accumulation of Copper

Kruskal-Wallis tests suggested there were significant differences between treatments for copper concentration in both the above ground biomass ($p<0.01$) and root biomass ($p<0.01$). There was less of a clear trend in the data compared to previous data sets (see fig 19); however, higher application rates and combined amendments overall reduced the uptake of copper in the plants. Copper uptake is multi-fold higher in the root samples compared to the above ground plant parts.

A weak, significant correlation was determined between plant copper concentration and plant biomass for both leaf ($r= -0.72$, $p<0.01$) and stem data ($r= -0.84$, $p<0.01$). No relationship was determined between these two variables for the root samples.

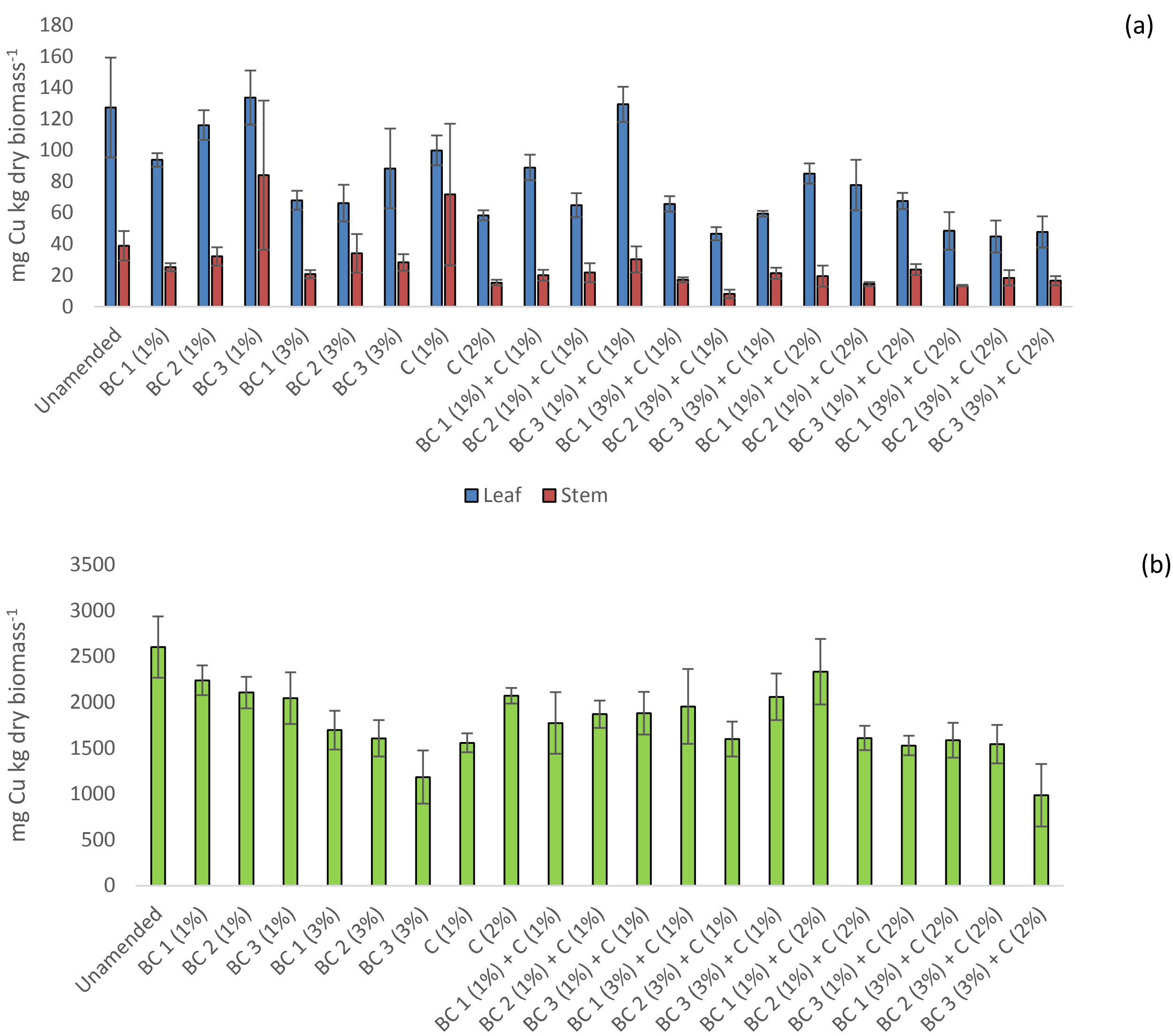

Figure 19: Mean Cu concentrations mg kg^{-1} in plant dry biomass: above ground (a) + roots (b) (± standard error, n=5).

(iv) Plant Nutrient Accumulation

Nutrient concentrations were generally higher in treated samples than in the unamended (see table 15, below). Significant differences were found between treatments for plant nutrient accumulation. Of the 3 biochars, BC1 treated plants had the highest concentration of Ca, Mg, K and Na. Compost only treatments generally had higher plant nutrient levels than the lower application rate of biochar, however the higher rate of biochar was largely comparable or better in terms of enhancing plant nutrient levels.

Table 15: Mean nutrient concentrations mg kg^{-1} in above ground dry biomass (± standard error, n=5)

Amendment	**Ca (mg/kg)**		**Fe (mg/kg)**		**K (mg/kg)**		**Mg (mg/kg)**		**P (mg/kg)**	
Unamended	6640	±1745	293	±60.3	7145.44	±1361	4516.39	±834	5112.30	±1008
BC1 (1%)	10800	±1830	122	±14.8	42800	±5050	2690	±222	1920	±179
BC2 (1%)	9320	±1070	155	±21.4	27400	±2400	2970	±664	2320	±207
BC3 (1%)	11800	±2910	437	±93.2	24600	±4400	4280	±480	2870	±185
BC1 (3%)	25800	±1540	102	±10.7	92600	±7410	5000	±201	4800	±374
BC2 (3%)	21300	±4350	256	±126	57700	±7740	4030	±549	3030	±301
BC3 (3%)	28500	±11150	217	±76.8	70100	±20900	5360	±1260	3200	±818
Compost (1%)	12600	±1980	258	±108	9570	±1390	3390	±777	2480	±245
Compost (2%)	16500	±2450	165	±10.9	18400	±2610	4210	±767	1630	±80.0
BC1 (1%) + C (1%)	14400	±1310	145	±20.7	42400	±5820	3000	±401	1990	±221
BC2 (1%) + C (1%)	17700	±4330	145	±14.1	35100	±2540	2990	±433	1690	±95.5
BC3 (1%) + C (1%)	8350	±469	305	±42.3	23400	±2300	2690	±70.3	1940	±130
BC1 (3%) + C (1%)	26500	±1340	106	±18.9	88500	±9860	4500	±209	4320	±547
BC2 (3%) + C (1%)	24200	±4680	97.7	±13.7	48300	±3420	3800	±310	2500	±220
BC3 (3%) + C (1%	30000	±3600	120	±23.9	51100	±5270	4090	±406	2750	±266
BC1 (1%) + C (2%)	21100	±3120	130.	±20.4	45500	±8030	338	±567	1790	±219
BC2 (1%) + C (2%)	25100	±4090	174	±50.5	45900	±4840	3900	±703	2290	±292
BC3 (1%) + C (2%)	18300	±2350	163	±15.9	43900	±853	2990	±202	2000	±45.6
BC1 (3%) + C (2%)	27400	±5170	59.6	±10.7	69300	±7400	4140	±748	3460	±505
BC2 (3%) + C (2%)	22000	±4790	95.8	±12.2	53100	±6750	3780	±641	2780	±351
BC3 (3%) + C (2%)	24400	±5580	109	±0.6	51300	±5480	3890	±533	2520	±356
	P<0.01		P<0.01		P<0.01		P=0.02		P<0.01	

4.5.3.5 Supporting MSc Study – Leaching test and Water Holding Capacity

The incorporation of biochar into the soil enhanced water holding capacity and retention. BC1 retained the largest mass by percentage at 31.4%, followed by BC2 at 24.9% and BC3 at 24.3%, in comparison to unamended at 16.1%. The addition of compost further enhanced water retention of BC1 (3%) + C (1%) to 36.8% (+5.4%), BC2 (3%) + C (1%) to 25.7% (+0.82%), BC1 (3%) + C (1%) to 25.6% (+1.29%) and C (1%) to 18.55% (+2.46%).

The leachability of copper for all treatments and compost is shown in figure 20. All treatments significantly reduced leachable copper compared to unamended. Data was non-

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normally distributed so Kruskal-Wallis testing was used ($p<0.01$). However, combined biochar and compost treatments did not significantly decrease copper compared to the biochar alone.

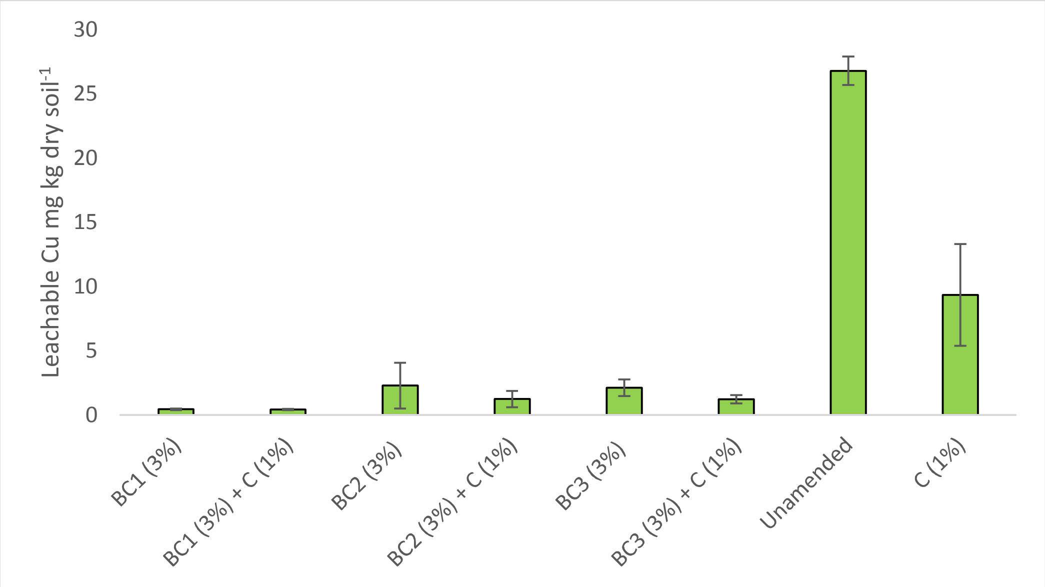

Figure 20: Mean leachable copper mg kg^{-1} in pre-incubation soils (± standard error, n=3).

4.5.3.6 Supporting MSc Study - Sequential Extraction

Data was not normally distributed so non-parametric Kruskal-Wallis testing and Mann-Whitney U tests were used for sequential extraction results. No significant differences were found in the amount of exchangeable copper between pre-incubation and post-incubation. However, differences were found between treatments pre-incubation. ($P=0.04$), but not at post incubation. The treatment that reduced copper most greatly pre-incubation was BC2 (3%) + C (1%), reducing exchangeable copper from 670 mg kg^{-1} in the unamended to 518 mg kg^{-1}. Reducible copper also did not show a significant reduction between pre-incubation and post-incubation, nor between treatments at either pre- or post-incubation. The oxidisable fraction showed a significant difference pre- and post-incubation, with all values for biochar treatments lower post-incubation (medians: 125 mg kg^{-1}, 106 mg kg^{-1} respectively; $p<0.01$). However, again no differences were found between treatments at either time. No significant differences were found between residually bound copper at pre- and post-incubation. However, residually bound copper was significantly different post-incubation between treatments. Unamended soil had a value of 80.6 mg kg^{-1} and decreased to 53.5 mg kg^{-1} in residually bound copper with BC1 treatment ($p<0.01$) post-incubation. Figure 21 shows how copper fractionation changes in amended soils between pre- and post-incubation.

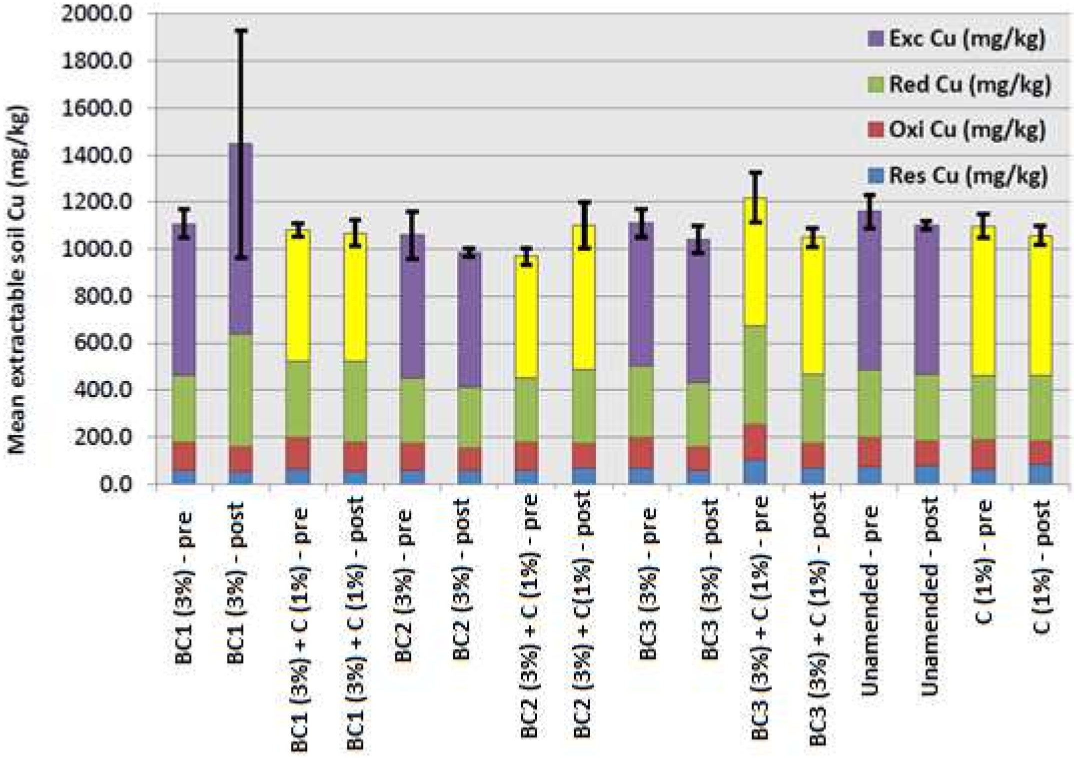

Figure 21: Distribution of exchangeable, reducible, oxidisable and residual Cu extracted from each treatment pre-incubation (pre) and post-incubation (post) ±standard error. Yellow denotes compost amendment.

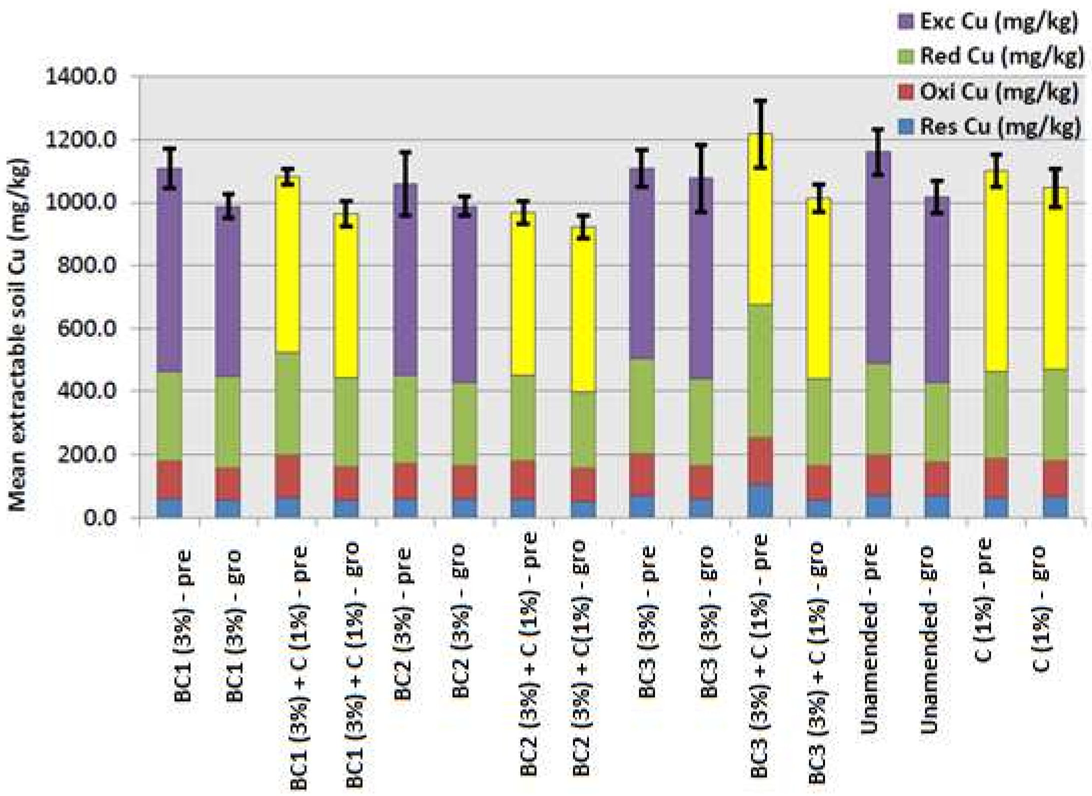

Figure 22: Distribution of exchangeable, reducible, oxidisable and residual Cu extracted from each treatment pre-incubation (pre) and post-growth (gro), ±standard error. Yellow denotes compost amendment.

Mann-Whitney U tests showed there was no significant difference in exchangeable copper concentration between pre- and post-growth samples. However, reducible copper was significantly different pre-incubation compared to post-growth (medians: 295 mg kg^{-1}, 265 mg kg^{-1} respectively; P=0.03). Oxidisable copper, compared to pre-incubation, was also significantly lower post-growth (medians: 125 mg kg^{-1}, 106 mg kg^{-1} respectively; p<0.01). Residual copper was again, compared to pre-incubation, significantly lower post-growth (medians: 65.6 mg kg^{-1}, 55.8 mg kg^{-1} respectively; p=0.02). There were no significant differences observed between treatments for any of the fractions of copper post-growth. Table 16, below, gives mean post-growth copper fraction concentrations.

Table 16: Differences in exchangeable, reducible, oxidisable and residual copper between amendments post-growth.

Treatment	**Exchangeable Cu**		**Reducible Cu**		**Oxidisable Cu**		**Residual Cu**	
BC1 (3%)	541	±12	286	±15	106	±8.0	54.9	±1.6
BC1 (3%) +C (1%)	518	±26	282	±12	107	±0.18	56.7	±3.1
BC2 (3%)	561	±18	262	±5.2	104	±2.2	60.7	±6.1
BC2 (3%) +C (1%)	522	±15	240	±19	105	±0.87	54.6	±1.1
BC3 (3%)	634	±67	274	±27	107	±3.1	60.8	±8.7
BC3 (3%) +C (1%)	570.	±24	275	±11	109	±5.9	57.7	±2.2
Unamended	590	±16	250	±6.0	105	±2.7	73.4	±3.3
C (1%)	575	±25	291	±31	112	±4.3	68.5	±0.88
P	>0.05		>0.05		>0.05		>0.05	

4.5.3.7 Supporting MSc Study - Plant Trial

Data was not normally distributed so non-parametric Kruskal-Wallis testing and Mann-Whitney U tests were used for plant trial results. There was a strong significant difference ($p<0.01$) between mean plant height and treatment, see figure 23. The three most effective treatments were BC1 (3%) at 194.0mm, BC1 (3%) + C (1%) at 191.5mm and BC2 (3%) at 167.0mm. Plants heights in the unamended soil were 18.4mm and 19.5mm in C (1%); significantly different from the other treatments. The addition of compost increased the mean height of all treatments to 124.8mm compared to no compost at 108.0 mm, this was not statistically significant. Seeds did not germinate in one replicate of BC3 (3%) + C (1%) and one replicate of the unamended. BC3 treated soil had greater leaf discoloration.

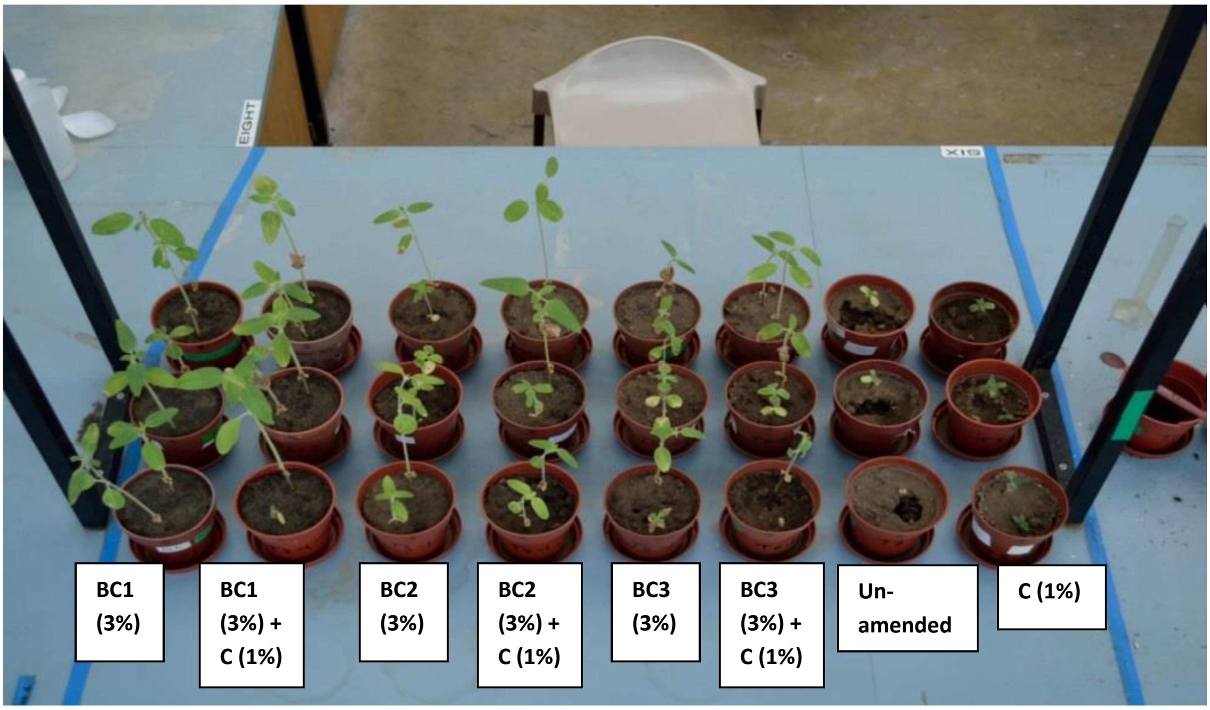

Figure 23: Plant growth comparison between treatments at five weeks. Note obvious significant differences between biochar and no biochar amendments.

Mean dry mass yield (Fig. 24), showed a strong significant difference between treatment types, ($p<0.01$), BC1 (3%) + C (1%) at 0.212g; BC1 (3%) at 0.174g; and BC2 (3%) + C (1%) at 0.127g produced the greatest mean mass. BC1 was again the most effective treatment. Plants from unamended samples had a mean biomass of 0.0323g, whilst C (1%) had a mean biomass of 0.027g. Both unamended and compost only were significantly smaller than all other treatments. The addition of compost did not significantly increase biomass in biochar amended samples.

Figure 24 also shows the strong relationship between plant mass and plant copper concentration in above ground biomass, BC1 and BC1 (3%) + C (1%) not only produced the largest average above ground dry biomass, but also had the lowest copper concentration, Rank Spearman showed a strong significant relationship ($p<0.01$). BC1 (3%) + C (1%) most greatly reduced plant copper concentration to 40.8 mg $kg^{-1,}$ followed by BC2 (3%) + C (1%) at 39.8 mg kg^{-1}. Kruskal-Wallis testing of plant copper concentrations showed a strongly significant difference between treatments ($p<0.01$). Plants grown in unamended soil had the highest copper concentration at 258 mg kg^{-1}, followed by C (1%) at 170 mg kg^{-1}. Despite the reduction in copper, plant growth in compost only samples was still severely inhibited. BC1 (3%) and BC1 (3%) + C (1%) produced the largest mean above ground biomass, but above ground copper concentrations were not significantly less than any other combined amendments. Compost reduced plant copper concentrations in above ground biomass for every treatment except BC3 where copper was increased by 15.1 mg kg^{-1} compared to without compost.

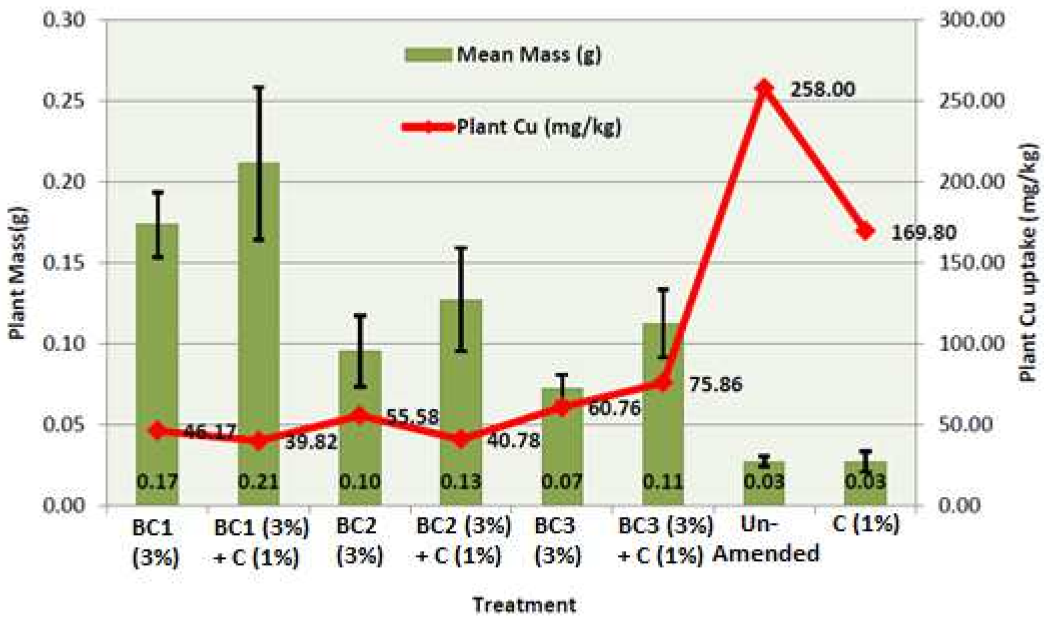

Figure 24: Combined chart of mean above ground dry biomass (g) and Cu concentration in biomass (mg kg^{-1} dry mass), after plant growth period at five weeks (P3), standard error bars.

4.5.4 Discussion

4.5.4.1 Effects of Amendments on Copper leachability

Previous studies have shown biochar can immobilise trace elements in soils, including copper (see Annex 1 for an overview studies). Our results confirmed this, with a significant decrease in leachable copper associated with application of all three biochars relative to the unamended samples. BC1 was the most effective biochar in terms of copper immobilisation; however after incubation and plant growth, there were less discernible differences between BC1, BC2 & BC3. This suggests the effects of time and soil equilibrium are important factors to consider when measuring the effectiveness of soil amendments on trace element concentrations. Alternately, the results could suggest that BC1 was a faster acting biochar compared to BC2 and BC3.

BC3 was found to be the least effective biochar with regards to immobilisation of copper in the soil. This biochar was produced in the same manner as BC2, but post-production was mixed with haematite. Iron oxides are a known sorbent for some trace elements (Gomez-Eyles *et al.*, 2013) and have been demonstrated as successful soil amendments for the immobilisation of metals in various studies (Tighe *et al.*, 2005; Hartley *et al.*, 2004; Warren *et al.*, 2003). However, as iron-oxide reduced the effectiveness of the biochar in this instance, it is possible that iron-oxide decreased sorption sites for copper, as opposed to increasing the number. The reasons for this effect are not clear. Further research is required on the mineralogy and crystallinity of the iron oxides, which are known to influence active surface area (e.g. Cundy *et al.*, 2008).

Compost was shown to significantly reduce leachable copper compared to the unamended samples; however as a single amendment, it did not perform as effectively as biochar in this capacity. Leachable copper is likely to have decreased in the presence of compost as a result of the high organic matter content of compost. Copper is well-documented as having a strong affinity for organic matter (Kumpiene *et al.*, 2008). Further, compost could have increased copper sorption as a result of increased CEC associated with compost additions to soil. Literature confirms the idea that compost can be utilised for the immobilisation of copper. For example, Song & Greenway (2004) demonstrated that compost has the ability to bind metals. Further, Kiikkilä *et al.* (2002) found contaminated soil incubation with compost decreased exchangeable copper in polluted forest soil. Similarly, Farrell & Jones (2010) found reduced levels of soil solution contaminants, including copper, with the addition of various composts. Nonetheless, compost addition has been shown in some literature to increase copper mobility in soils (Beesley & Dickinson, 2011; Beesley *et al.*, 2010), as a result of increased dissolved organic matter forming Cu-complexes via humic and fluvic acids (Clemente & Bernal, 2006; Hsu & Lo, 2000). These findings are contrary to the results of this study, suggesting mobilisation/immobilisation dynamics of copper as a result of compost addition may be dependent on the specific chemical characteristics of the compost used and the soil that is amended.

In contrast to the results of the scoping study, there was a general trend shown that application of biochar and compost as combined amendments led to enhanced copper immobilisation. Combined application with compost was especially effective at the lower rate of biochar addition. This is in contrast to the results found in the scoping study, which found that compost decreased the effectiveness of biochar in terms of leachable copper. However, some literature suggests compost can improve the immobilisation of metals in combination with biochar. For example, Karami *et al.* (2011) found increased reduction of lead in pore water when biochar was applied in combination with green waste compost. However, the same study showed that whilst copper was successfully reduced by compost and biochar in combination, biochar alone brought about the greatest reduction in copper. Overall, in the current study the application rates of both biochar and compost showed an inverse relationship with copper leachability, with the higher rate of both compost (2%) and biochar (3%) increasing immobilisation of copper. However, the scoping study showed that at applications rates of 1% biochar was not more effective than at 0.5%, suggesting that each individual biochar has a maximum application rate at which additional gains can be achieved.

Notable differences were seen across the time points in terms of leachable copper, with a dramatic drop seen in all the samples post-growth in the detailed study. It is possible for plant growth to decrease the solubility of copper in soils (Römkens *et al.,* 1999), particularly when a relatively small volume of soil is used (e.g. in pot trials). Further, plants may take up copper into their biomass, therefore reducing the available pool in the soil (Kolbas *et al.,* 2011). However, there was a large reduction in leachable copper in the unamended samples, in which plant growth, especially root growth, was very stunted. It is unlikely therefore that the reduction in copper is attributable solely to plant growth effects on soil characteristics. Additionally, the amount of copper found to have been taken up by the plant biomass was an order of magnitude less than the leachable copper found in soil and therefore not great enough in any of the treatments to account for such a significant drop in Cu. It is also unlikely that the copper was washed out of the soil, as plants were watered from below, with water being placed in the saucer underneath pots for uptake. Saucers were tested following harvest to ensure no copper build-up, and concentrations found were comparable to the post-growth leachate.

Differences were found between treatments in terms of redox potential at all three time points. Pre- and post-growth, all amendments reduced redox potential relative to the unamended samples. Whilst some papers suggest a decrease in redox potential can lead to decreased metal solubility (Kashem & Singh, 2001; Charlatchka & Cambier, 2000), the magnitude of the decrease between treated and unamended samples was not great enough to suggest it was causal in the reduction of copper in the amended samples relative to the unamended samples. Kacprzak *et al.* (2014) considered Eh values of +100mV to +350mV to represent moderately reduced soils. Indeed, the values remained largely consistent with this range throughout the experiment, although some of the results for the unamended samples and lower application rate treatments were closer to 450mV.

For both pre- and post-incubation leach tests, pH was found to be negatively correlated with copper leachability. pH is well documented as a driver of metal availability in soil (Kong *et al.,* 2014), including copper availability (Kumpiene *et al.,* 2008). It is possible then that pH was one of the driving factors effecting a decrease in copper associated with amendment application. Although significant differences were found in pH pre- and post-growth, there was a median difference of less than one pH point between the two datasets. It is therefore unlikely that the difference in pH could account for the aforementioned decrease in leachable copper post-growth.

Organic amendments are known to increase DOC in soils (Cao *et al.,* 2003; Antoniadis & Alloway, 2002). DOC increases associated with biochar and compost applications in this study therefore follow trends found in other papers. Indeed, Beesley *et al.* (2010) found increased DOC associated with the application of biochar and green waste compost amendments to soil. Further, our study showed DOC was significantly increased post-growth compared to pre-growth. Plant growth is known to increase DOC in soils (Römkens *et al.,* 1999), as a result of root exudates. However, in this study, an increase was seen across all treatments and the unamended samples. As previously discussed, plant growth was very limited in the unamended samples, making it unlikely that plant-growth derived DOC was causal in the reduction of copper seen post growth. Indeed, the significant difference in DOC post-growth combined with a notable decrease in leachable copper contrasts with the established nature of DOC-metal interactions. DOC is generally regarded as having a negative effect on soil copper immobilisation, as a result of DOC competing with metals for sorption sites or by forming complexes with the metal ions, preventing sorption of metals onto sequestering surfaces (Chirenje *et al.,* 2002; Redman *et al.,* 2002; Weng *et al.,* 2002; Giusquiani *et al.,* 1998).

However, the observed trend was somewhat repeated in earlier tests; in both pre- and post-incubation leach tests, increased DOC resulting from amendment application was associated with a decline in leachable copper. It is possible then, that a more strongly influential tertiary factor was affecting both DOC and copper immobilisation in the soil; increasing both factors. The soils used in this experiment were initially air-dry and subjected to dry-wet cycles during both the two-week incubation period and during growth. It has been demonstrated that DOC can increase as a result of drying and rewetting, potentially as a result of releases of OM trapped in small pores, or associated with the death of soil organisms during drying (Merckx *et al.,* 2001). Moreover, Amery *et al.* (2007) found soils that had been stored as air-dry or subjected to wet-dry cycles had elevated DOC concentrations, but soil dissolved organic matter had low copper mobilising potential. The authors hypothesised that the poor quality dissolved organic matter consisted of non-humified organic compounds and was as a result of lysis of biomass. Potentially then, this could in part explain the results of this experiment; DOC may have been increased as a result of rewetting, but the DOC had a low affinity for copper (so the expected subsequent increase in leachable copper was not seen).

The drop in copper post-incubation and post-growth could also be explained by the rewetting process. Wenzel and Blum (1999) highlight that air-drying soils prior to analysis of mobile metal content can result in the overestimation of metal concentrations, including copper. Haynes and Swift (1991) demonstrated that air drying soils increased the extractability of copper, but that this effect was reversible; after a two week incubation period following rewetting, copper extractability had decreased to a level comparable to pre-drying. This trend was attributed to metal-retaining organo-mineral associations being disrupted and then reformed by drying and subsequent rewetting. It is possible then, that the initial leach test results showed unrealistically high copper concentrations as a result of this process. The decrease in copper seen in the post-growth leach tests could accordingly be attributed to an extended period following rewetting allowing the establishment of a stable equilibrium.

Nonetheless, even if the unamended samples soil in the post-growth leach tests is accepted as the “true” representation of leachable copper in the soil, the effects of biochar and compost are not negligible. Indeed, as discussed in the following section, the post-growth soils prior to amendment are above levels considered phytotoxic. Further, a clear reduction is seen in leachable copper in the amended soils, even post-growth, compared to unamended samples.

4.5.4.2 Effects of Amendments on Phytotoxicity

The initial status of the soil (prior to amendment) was shown to have characteristics associated with phytotoxicity, including a very high total copper concentration. Total soil copper concentrations commonly range from 25-60mg kg^{-1} (Baker & Senft, 1995). Previous research carried out on these soils shows copper to be a major cause of phytotoxicity, due to concentrations of approximately 2,600 mg $kg^{-1}$and 1000 mg kg^{-1} in the P7 soil (Lagomarsino *et al.*, 2011; Bes & Mench, 2008). However, the results of analysis described herein suggest copper concentrations in the P7 soil to be lower (although still significant), at 1096 mg kg^{-1}. Nonetheless, the soil is notable for spatial variation of contaminants, with other studies finding lower copper values for the soil. For example Mench *et al.* (2013) found copper values of 706 ±99 mg kg^{-1}.

High copper soil concentrations will generally only exhibit a phytotoxic effect when copper is exchangeable and available to plants, e.g. in soil pore waters. (Du Laing, 2010; Lock & Janssen, 2003). In the detailed study, the results of the pre-incubation leach tests on unamended soil suggested leachable copper in the soil was 28.8 mg kg^{-1}. As detailed in section 4.3.4.1, phytotoxic effects occur when soil pore water copper is greater than 1 mg kg^{-1}. Additionally, the texture of the soil (sand) and initial nutrient status were poorly suited to plant growth. For example, exchangeable Ca in the soil was determined to be 2.61 mg kg^{-1}; exchangeable Ca levels below 10 mg kg^{-1} have been associated with calcium deficiency in plants. Calcium levels this low typically occur concomitant with sandy soil textures and low organic matter (Fenton & Conyers, 2002).

All biochar and compost amendments improved plant growth in *H. annuus* relative to the unamended samples, with the exception of the compost only treatment in the supporting MSc study. This mirrors the findings of Beesley *et al.* (2010) who found that compost, biochar and combined application reduced phytotoxicity in a multi-element polluted soil. Similarly, Buss *et al.* (2012) found copper uptake was significantly reduced and biomass increased in *Chenopodium quinoa* Willd grown in copper spiked soils amended with biochar.

Improved plant growth in copper contaminated soils with biochar and compost addition may be the result of several factors including decreased bioavailability of copper in the soil (at each time point, all amendments decreased leachable copper in soil) and improved soil nutrient and water provision resulting from amendment incorporation into the soil. Indeed, Bruun *et al.* (2014) demonstrated that biochar addition to a poor quality sandy subsoil improved plant available water retention and reported a concomitant increase in plant yields. The water holding capacity and availability of water in soil is an important factor for plant growth. Basso *et al.* (2013), suggested that biochar is an important amendment to sandy soils for plant growth and increased water holding capacity (WHC). Our results show the addition of all biochars enhanced WHC. The best results were achieved by the BC1 biochar: BC1 (3%) increased WHC by 95.2% and BC1 (3%) + C (1%) increased WHC by 128%.

Similar to soil characteristics in our studies, Alburquerque *et al.* (2014) trialled different biochars to examine the effect of biochar on growth of *H. annuus* L. in OM poor, low nutrient, slightly acidic, loamy sand. The authors found biochar increased conditions pertinent to crop growth, especially at the higher application rates. Yields were improved, but the extent of this improvement was a function of biochar type (in terms of nutrient content) and application rate. Our study showed that the greatest increases in yield were observed in the BC1 treatments at the higher application rate; BC1 amended soil had notably improved growth compared to the other biochars or compost as a single amendment. As the leach tests suggested that over time differences between biochars became less significant, it is probable that an alternate factor caused the disparity between BC1 and the other two biochars in terms of plant growth. It is possible that differences in nutrient provision between the three biochars was a driving factor in plant yields. Certainly, some available nutrients were increased in BC1 compared to the other biochars. For example, BC1 had the highest concentration of the three biochars of exchangeable cations including calcium, magnesium, potassium and sodium. As discussed in Section 4.3.4.3, calcium competes with copper for plant uptake; essentially decreasing copper uptake when increases in the soil (Burkhead *et al.*, 2009). Comparably, Major *et al.* (2010) found enhanced crop yields associated with the application of biochar in savannah oxisols, attributed to enhanced available magnesium and calcium in biochar amended soils. Additionally, plant biomass concentrations of certain nutrients were greater in soils treated with BC1. For example, plants grown in soils treated with BC1 (3%) had an average of 93 g kg^{-1} potassium in above ground dry biomass, compared to 70 g kg^{-1} in BC3 (3%) plants, or 58 g kg^{-1} in BC2 (3%).

In the detailed study, compost addition as a single amendment improved yields comparably to biochar only treatments (in contrast to leach test results). Additionally, compost further improved the effectiveness of the biochar when applied in parallel. Therefore, the notion is furthered that nutrient provision may have contributed to the reduction in phytotoxicity. Indeed, the nutrient provision effects of compost are well established and compost has been shown to improve characteristics including soil structure and water retention which in combination with other soil improvements from compost additions can lead to improved yields (see Section 3.3). Liu *et al.* (2009) showed chicken manure compost to have a positive effect on plant growth of *Triticum aestivum* L. in a cadmium contaminated soil. Phytotoxicity decreases were attributed to an increase in pH and complexing of cadmium by organic matter, both resulting from compost addition to the soil. It should be noted, however, that the compost utilised in the detailed study and supporting MSc had a relatively low level of organic matter. Potentially then, increased benefits may be seen if a higher-quality compost was used.

When compost and biochar were applied as singular amendments, higher application rates decreased plant concentrations of copper in above ground plant parts. This trend was largely repeated when the amendments were applied in combination, with combinations mostly improving on the results of the single amendments. The uptake of metals ions by plant roots is, in part, dependent on the concentration in the soil and at the root surface (Wild, 1993). As amendments increase copper adsorption and reduce the free cation concentration in soil solution, phytoavailability and therefore plant uptake is reduced (Batley *et al.*, 2004). Kolbas *et al.* (2013) state that copper availability to plants may be influenced by a range of factors including soil type and DOC, redox potential and pH of soil pore waters. Results of our study have shown that all of these factors were altered by biochar and compost additions to soil.

Epstein and Bloom (2005) state that shoot copper concentration is generally between 5-50µg g^{-1} dry weight, with deficiency often seen when concentrations fall beneath this range and phytotoxic effects when concentrations exceed this. This is supported by data from MacNicol and Beckettt (1985), who state that phytotoxic effects are observed with leaf concentrations exceeding 20-25 µg g^{-1}. Unamended samples in our study had a multi-fold higher level of copper in plant leaves than this (127 mg kg^{-1}). Most treatments significantly reduced the copper concentration in plants. Numerous studies have shown biochar to decrease the availability of contaminants to plants; Kloss *et al.* (2014) found four different types of biochar all decreased concentrations of copper in plant tissue. Park *et al.* (2011) observed increases in plant growth and a decrease in plant uptake of metals with biochar addition to soil spiked with cadmium, copper and lead. Namgay *et al.* (2010) demonstrated that biochar application reduced the concentration of copper, arsenic and cadmium in shoots of *Zea mays* L. in trace-element spiked soil. Khan *et al.* (2013) found sewage sludge biochar application to paddy soils decreased the bioaccumulation of multiple metals, including copper in rice biomass. Similarly, Cui *et al.* (2011) reported reductions in cadmium concentrations in rice following the application of biochar to contaminated paddy soils. Comparable results have been found for compost application to soil. For example, Ruttens *et al.* (2006) found domestic and garden waste derived commercial compost to reduce uptake of zinc, cadmium and lead in grass species at a former zinc smelter site in Belgium. Karami *et al.* (2011) showed that the addition of both biochar and compost significantly reduced the levels of shoot copper in ryegrass in comparison to unamended treatments.

This research looked to determine whether soil amendments could aid the production of biomass for use as fuel on contaminated sites. This idea is already well established in literature (see Section 4.5.1). Here, the results of the detailed study and the supporting MSc study showed that both biochar and compost as single and combined amendments significantly improved the yield of sunflower (*Helianthus annuus*) in soils obtained from a copper contaminated site. The results also confirm that copper uptake by sunflower is relatively low. This is an important consideration when establishing the suitability of a contaminated site for bioenergy crop production, as contaminant concentration in the crop determines the suitability of the plant for energy retrieval. Crops which contain too high quantities of contaminants may be considered a human health or environmental risk on combustion.

4.5.4.3 Effects of Amendments and Plant Growth on Fractionation of Copper in Soil

The results of the fractionation experiment showed few significant and clear trends in exchangeable and more recalcitrant fractions. Overall the implication of these studies seems to be that any major differences in leachability (in 0.01M CaCl2) between treatments is between pore water and exchangeable forms, as the fractionation studies showed no clear patterns. This is consistent with the known behaviour of the charcoals tested for cations, which offer exchange sites. Cations can be desorbed from these exchange sites at reduced pH (see Sections 2.2.6 and 3.5.1). The biochar does not therefore "lock up" copper in non-exchangeable fractions to any detectable degree.

However, pre-incubation, significant differences were found between treatments for exchangeable copper, with BC2 in combination with compost reducing exchangeable copper from 670 mg kg^{-1} (in the unamended samples) to 518 mg kg^{-1}. This potentially indicates that biochar and compost can successfully reduce the most available fraction of copper in soil. The concentration of metal ions in the soil solution is determined by many complex interactions with soil particles, organic matter (humus), manganese, iron, and aluminium oxides. Metals such as copper occur in the solution as cations and are adsorbed by negatively charged soil particles especially humus (Wild, 1993). Nonetheless, no differences between treatments were found post-incubation, indicating that the effects caused by amendments may not be stable. Oxidisible copper in biochar only amended soils showed an overall decrease between pre- and post-incubation. Incubation, therefore may cause a reduction in some forms of copper. Significant differences were found between treatments for residually bound copper post-incubation, with BC1 causing a decrease from 80.6 mg kg^{-1} (in unamended samples) to 52.9 mg kg^{-1}. Reducible, oxidisable and residual copper were overall significantly lower post growth.

4.5.4.4 Implications for the Use of Biomass Produced on a Contaminated site for Further Site Improvement

Two of the biochars tested were produced using poplar grown on the contaminated site; an additional aim of this project was to determine whether biomass grown on a remediation site could be used for further soil improvements. The results of this experiment demonstrated that this may be possible, as BC2 and BC3, the two biochars manufactured from biomass grown on the contaminated site, significantly improved soils in terms of both phytotoxicity and leachable copper, although not to the same extent as the commercially produced biochar. However, care should be taken when preparing chars from biomass grown on a contaminated site. If the feedstock contains high levels of contaminants, the resulting biochar is likely to also contain high levels of contaminants which may be transferred to land and further pollute the remediation site (Lucchini *et al.*, 2014b). However, the biochars used in this study did not have elevated levels of contaminants. If biochar feedstocks are derived from biomass grown on contaminated land, contaminant excluding cultivars should be considered for growth and biochar should be compositionally analysed before application to land to reduce risk.

5 Operating Windows for Low Input Technologies (Gentle Remediation Options)

5.1 Operating Windows

Operating window methods are primarily used in engineering to improve reliability (Scott & Nathanail, 2004). In this context, operating windows are defined as limits for a critical factor, above or below which failure of a machine or process occurs.

The FP7 projects HOMBRE and Greenland have developed the concept of operating windows and adapted it to fit in the frame of decision support guidance for BF soft re-use and GRO applications respectively. In relation to BF soft re-use, the two project aims are synergetic and complement each other. HOMBRE and Greenland have distinguished two levels of detail:

i) “High level operating windows”
ii) “Detailed operating windows”

The detailed operating windows follow the traditional operating window rationale where the function is to identify the optimal conditions for applying a GRO in terms of its process parameters (such as effective soil pH, soil texture etc.)

However, the operating windows idea was also seen as having great value in providing a unifying concept for more general decision making for helping stakeholders understand when a particular technique or intervention might be most applicable to deliver a particular outcome (i.e. service) in a BF redevelopment / regeneration project. These services and interventions are far wider in scope than risk management (see Section 5.3).

HOMBRE has therefore developed “high level operating windows” (HLOWs), primarily for soft re-use scenarios, as instruments to provide relevant information to stakeholders and support them in taking decisions for the selection of appropriate interventions in BF redevelopment / regeneration projects to deliver particular services. The reason behind this is that on many BF sites a range of interventions may be considered, depending on the soft re-use envisaged and the services required. In some cases, a particular technique may provide more than one service: for instance, charcoal amendment may assist contaminant immobilisation, facilitate plant growth by managing soil pH (Verheijen *et al*., 2010; Sneath *et al.*, 2009), and provide carbon sequestration.

The data available in HLOWs are intended to provide stakeholders with key information about intervention groups which stakeholders might be interested in considering as a means for providing the services they have themselves identified as possible project objectives or preferences. For this purpose, the content of HLOWs should respond to the broadest possible interests that could arise in early stages of regeneration project design. Hence, the information provided through the HLOW is intended to be of a wide spectrum, i.e. addressing technical, environmental, and eventually social and economic, issues that might drive stakeholders to opt for one type of intervention (or group of interventions) rather than another from a qualitative perspective. Also, the width of information provided may support the overall process of stakeholder engagement as very diverse categories of stakeholders (Cundy *et al.*, 2013) might find information matching their specific interests and level of expertise at the different stages of decision making. The types of information provided in the HLOWs are listed in Table 17.

Table 17: Information available in High Level Opportunity Windows

Information	Description	Link with project development stage
Definition	A brief summary of what the group of interventions entails. This is important as users will have varying levels of expertise in different areas. This section explains what the HLOW and the associated row in the matrix relates to.	1, 2
Technical Applicability	Brief summary of the technical information regarding the level 2 intervention grouping. Brief description of each of the example interventions that fall under the level 2 category. The information provided at this point may be different depending on the intervention grouping. For example, in the HLOW for ex situ remediation, a section is included for what types of contaminants can be treated by each example remediation intervention – whilst this is not applicable to other interventions outside of the remediation HLOWs where other specific information may be supplied.	2, 3
Pros and Cons (advantages and disadvantages)	A technical list of the pros and cons associated with each example intervention where relevant and some generic pros and cons associated with the overall group of interventions. This section does not appear in HLOWs where this information is not applicable.	2, 3
Compatibility with other interventions	A checklist indicating the potential synergy with other level 2 interventions groups through a simple positive (+) or negative (–) symbols. Synergy opportunities are critical to the matrix as application of interventions in synergy with more services and value as outputs is fundamental to the purpose of the matrix.	2, 3
Potential sustainability benefits and disbenefits	A list of potential key sustainability indicators (both positive and negative) associated with application of the interventions. The sustainability indicators are derived from SuRF-UK "Annex 1" categories, and are not exhaustive; indicative only.	1, 2
Further information	Includes detailed information on the intervention via signposting; relevant technical references and case studies demonstrating deployment of the specific example interventions in the field.	1, 2, 3

5.2 Use of Operating Windows in the HOMBRE Brownfields Opportunity Matrix

HOMBRE's "Brownfield Opportunity Matrix" (BOM) is a design aid to help developers and others involved in BFs to identify what services they can get from soft re-use interventions for their site, how these interact, and what the initial default design considerations might be. It is a simple *Excel* based screening tool that essentially maps the services that might add value to a redevelopment project against the interventions that can deliver those services, as shown in broad terms in Table 18 below.

Table 18: Main services and interventions within the Brownfield Opportunity Matrix

Services	**Interventions**
• Soil Improvement • Water Resource Improvement • Provision of Green Infrastructure • Risk Mitigation of Contaminated Soil and Groundwater • Mitigation of Human Induced Climate Change (global warming) • Socio-Economic Benefits	• Soil Management • Water Management • Implementing Green Infrastructure • Gentle Remediation Options • Other Remediation Options • Renewables (energy, materials, biomass) • Sustainable Land Planning and Development

Operatively, access to the HLOW is gained by clicking on the appropriate cell (see fig 25 below).

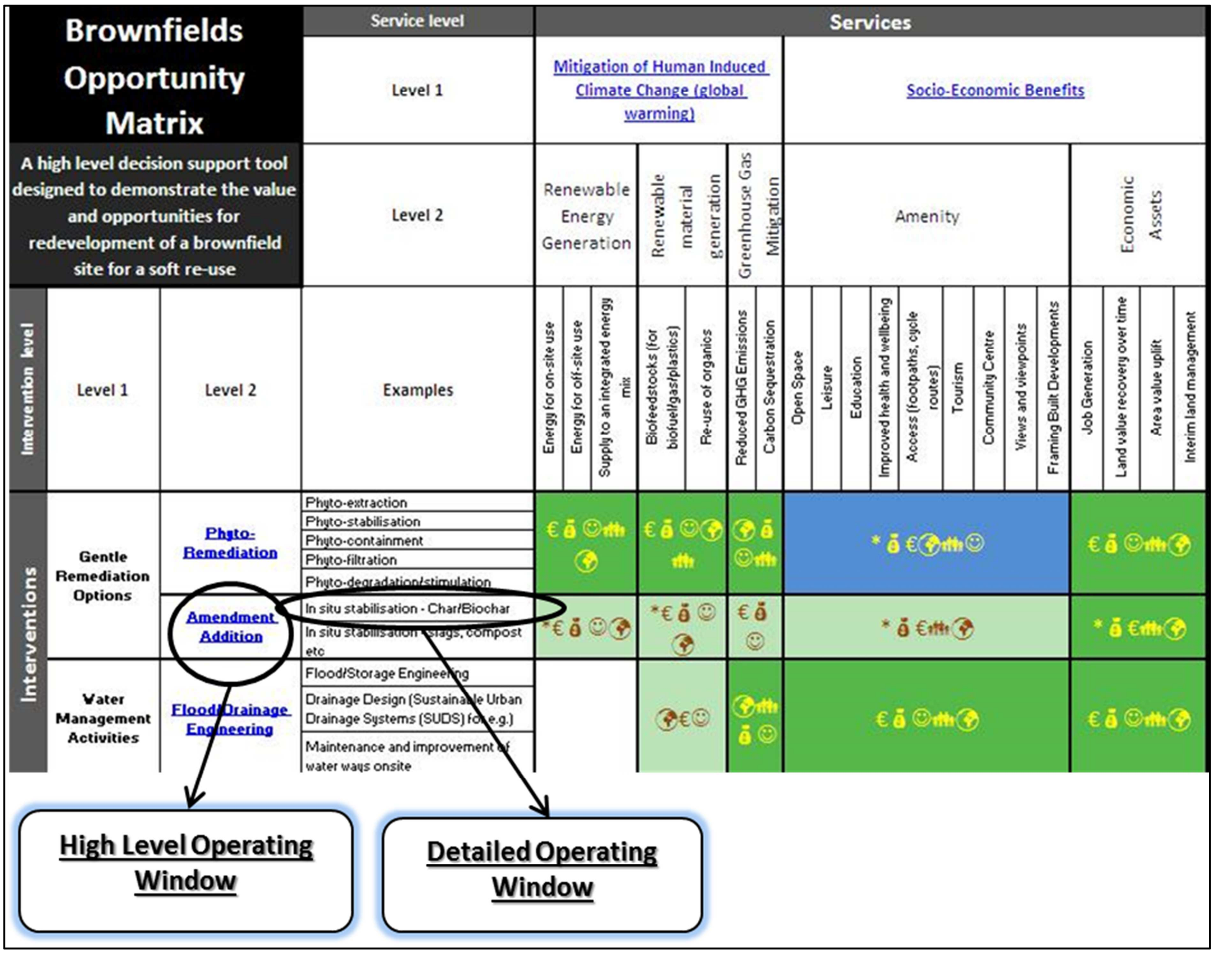

Figure 25: Mapping of operating windows in the Brownfield Opportunity Matrix: for illustrative purposes only

More insight on the BOM is provided in HOMBRE deliverable D5.2 "Decision support system on soft uses" (2014). The HLOWs are key elements of this matrix (Beumer *et al.*, 2014).

5.3 High level Operating Windows for Gentle Remediation Techniques

HLOWs provide qualitative and exhaustive information about regeneration interventions for soft re-use of BFs. There are three gentle remediation HLOWs provided by the BOM:

1. Phytoremediation
2. Amendment addition for *in situ* stabilisation
3. Natural attenuation of groundwater.

Each of these HLOWs covers a group of more specific techniques. For example the phytoremediation HLOW encompasses phytoextraction, phytostabilisation, phytocontainment, phytofiltration, and phyto-degradation/stimulation. The HLOWs for phytoremediation and use of amendments are shown in Table 19 and 20 below, along with a HLOW for the use of amendments for soil management (in terms of structure and fertility, Table 21.

Table 19: HLOW for Phytoremediation

HLOW: Phytoremediation (GRO)	
Definition:	Phytoremediation is the direct use of plants and their associated microorganisms to stabilize or reduce contamination in soils, sludges, sediments, surface water, or ground water (USEPA, 2012 - see link in further information). Phytoremediation is thus a gentle remediation option (GRO) which can provide rapid risk management of organic, inorganic and radioactive contaminants via pathway control, through containment and stabilisation, coupled with a longer term removal or immobilisation of the contaminant source term. In North America, application of GRO is arguably more developed than in Europe with the US Interstate Technology & Regulatory Council listing 48 sites, largely within the USA, as hosting "full-scale" phytoremediation trials (as of 2007). GRO application generally in North America ranges from relatively small-scale phytoremediation projects that are driven and implemented by the local community to larger "green-technology"-based remediation programmes at Superfund sites which involve tree planting, soft cover etc. Intelligently applied GRO can provide: (a) rapid risk management via pathway control, through containment and stabilisation, coupled with a longer term removal or immobilisation/isolation of contaminants; and (b) a range of additional economic (e.g. biomass generation), social (e.g. leisure and recreation) and environmental (e.g. CO2 sequestration, water filtration and drainage management, restoration of plant and animal communities) benefits. Phytoremediation techniques involving in situ stabilisation of contaminants or gradual removal of the labile (i.e. bioavailable or easily-extractable) fraction of contaminants present at a site can be durable solutions as long as land use and land management practice does not undergo substantive change causing shifts in pH, Eh, plant cover etc., suggesting that some form of institutional or planning control may be required. The use of institutional controls over land use however is a key element of urban remediation using conventional technologies (e.g. limitation of use for food production), so any requirement for institutional control and management with phytoremediation continues a long established precedent.

Technical Applicability:	Phytoremediation is primarily deployed to gradually remove the labile (or bioavailable) pool of inorganic contaminants from a site (phytoextraction), remove or degrade organic contaminants (e.g. phytodegradation), protect water resources (e.g. rhizofiltration), or stabilise or immobilise contaminants in the subsurface (e.g. phytostabilisation, in situ immobilisation). Phyto-based treatment technologies include, but are not limited to: • Phytoextraction: The removal of bioavailable metals or organics from soils by accumulating them in the biomass of plants. When aided by use of soil amendments, this is termed aided phytoextraction. • Phytodegradation / phytotransformation: The use of plants (and associated microorganisms such as root-zone bacteria) to uptake, store and degrade organic pollutants. • Rhizodegradation: The use of plant roots and associated root-zone microorganisms to degrade organic pollutants. • Rhizofiltration: The removal of pollutants from aqueous sources by plant roots and associated microorganisms. • Phytostabilisation: Reduction in the bioavailability of pollutants by immobilizing or binding them to the soil matrix and / or living or dead biomass in the soil. When aided by use of soil amendments, this is termed aided phytostabilisation. • Phytovolatilisation: Use of plants to take pollutants from the growth matrix, transform them and release them into the atmosphere. • “Phytocontainment”: Use of plants to facilitate the isolation of contaminants, particularly surface contamination, under new soil • In situ immobilisation / phytoexclusion: Reduction in the bioavailability of pollutants by immobilizing or binding them to the soil matrix through the incorporation into the soil of organic or inorganic compounds, singly or in combination. Phytoexclusion, the implementation of a stable vegetation cover using plants which do not extract contaminants, can be combined with in situ immobilisation.	
Pros and Cons:	**Advantages**	**Disadvantages**
	May provide an opportunity for the recovery of usable biomass (e.g. as feedstock or for energy), as well as a range of other services related to for example water management and soil improvement. Phytoextraction can provides rapid removal of dissolved forms of metals limiting the capacity of metals to spread and therefore valuable as a pathway management application to protect water resources and ecological receptors.	May require cultivation measures, re-grading or decompaction, or other soil improvement measures to support adequate plant growth Usually requires ongoing management and monitoring, e.g. fertilisation (which may be via recyclates), to prevent pest damage, and/or recover biomass Benefits, both as a remediation technique and for providing other beneficial services may be seasonally limited, e.g.

	Phytoextraction has the potential to remove metals from contaminated soil, and furthermore these metals may be recoverable in ash from harvested biomass, in particular if “hyper-accumulators” are used. Phytodegradation, phytotransformation, and rhizodegradation can provide a long term solution for a range of organic contaminants, including some recalcitrant forms such as PAHs. Processes of phytocontainment, rhizofiltration and phytostabilisation can provide pathway management solutions for a broad range of organic and inorganic contaminants in parallel. Phytovolatilisation may be an effective means of removing some volatile organic compounds from shallow groundwater.	diminishing during periods of plant dormancy Remediation effectiveness may also be limited to rooting depth. Harvested biomass may not be readily usable as its content of metals may require special permitting from regulators. Harvested biomass needs to be evaluated (and potentially monitored) to show that contaminants have not migrated to it Phytoextraction processes may take many years (decades), and some metals may be inaccessible or unavailable to the phyto-extraction process. Hence phytoextraction is limited in its suitability as a source management tool for removing bulk metals from soil. Very few types of hyper-accumulator are suitable for practical remediation use. Phytovolatilisation is the transfer of contaminants from matrix (groundwater) to another (air) and as such may raise regulatory objections.
Compatibility with other interventions*:*	Amendment Addition	+++
	Natural attenuation	+++
	In situ techniques	+++
	Ex situ techniques	++
	Re-naturalisation of soils	++
	Amendment addition	+++
	Attenuation of contaminated surface water	+++
	Flood/drainage engineering	O
	Ecological engineering	+/-
	Biodiversity and environmental management	+/-
	Conservation	+/-
	Producing renewable feedstocks	+++
	Energy generation	+++
	Development of amenities	++
	Strategic planning of land use over time	+++
	+++ Strongly likely ++ Likely + Possible +/- May be a positive or negative impact on this service / intervention depending on the specific conditions 0 No relationship likely	
Potential	**Benefit**	**Disbenefits**

sustainability benefits and disbenefits	ENV 1: Net removal of greenhouse gases ENV2: Improved soil functionality ENV3: Source term removal for some approaches and elimination of mobile forms ENV 4: may provide biodiversity benefits depending on plant species used ENV5: destruction of contaminants or their removal (depending on remedial approach); generation of recyclate(s); energy recovery SOC1: Risk mitigation in terms of both chronic and acute risks to human health. SOC2: Intergenerational equality – pollution and associated risks not passed to future generations. (depending on remedial approach) SOC3: improvement of locality and improved sense of place SOC4: Long term compliance with local policies and spatial planning objectives. ECON1: Liability discharge; site value uplift, low cost approach with potential long term revenues from use of biomass ECON2: Value uplift in the surrounding area, potential for creation of local business opportunities connected with site re-use and biomass ECON 3: Potential to support local job creation, education linkages and skills development over the project period from the long-term management of sites and biomass valorisation ECON 5: Agricultural based approaches are adaptable and can be revised to reflect changing circumstances, treatment effect is long term	ENV1 Process emissions ENV2: Degraded soil functionality ENV3: Process emissions ENV4: Use of non-native species may not support biodiversity, on site ecologies will be changed (which may be a positive or negative effect) ENV5: use of energy and resources / generation of wastes from biomass SOC1: Potential risks to site workers and public from agricultural equipment and road traffic, especially if site not managed appropriately, including: from accident, exhaust emissions, and emissions from thermal conversion of biomass, especially PM10 emissions from smaller scale units SOC3:Process impacts such as noise, odour, traffic and other forms of nuisance from operations SOC4: some stakeholders may require reassurance that effectiveness of site management can be assured into the long term SOC5: validation of process outcomes requires long term monitoring and may be technically challenging ECON1: May limit range of possible land uses over a long period, management input required over a long period ECON2: Impacts of disruption during initial remediation works ECON 5: ongoing management input required
	Notes on benefits / disbenefits: • All are strongly dependent on site specific factors, the considerations above are indicative only of possible general trends for the intervention. • Where provided benefits and disbenefits are grouped according to the SuRF-UK "Annex 1" categories, and are not exhaustive and are indicative only. • Where no indicator class is mentioned, factors are likely to be dominated by site specific factors • Additional factors may occur in categories depending on the site specific context. Absence of an Annex 1 category from the list above does not mean it may not apply at a particular site.	
Further Information:	Phytoremediation for trace element contaminated sites: the Greenland project www.greenland-project.eu ITRC Phytotechnologies guidance, www.itrcweb.org/Guidance/GetDocument?documentID=64 Application at US Superfund sites (USEPA, 2014), www.epa.gov/superfund/accomp/news/phyto.htm CLU-IN phytotechnologies overview, www.clu-in.org/techfocus/default.focus/sec/Phytotechnologies/cat/Overview	

Table 20: HLOW for Amendment Addition (GRO)

HLOW: Amendment Addition (GRO)	
Definition:	One form of "gentle remediation" is the use of amendments which can be incorporated into the soil surface to achieve remediation by *in situ* stabilisation. The processes of stabilisation are a form of pathway management as the contaminants remain *in situ* but their mobility and bioavailability are reduced, thus also reducing leaching through the soil profile. Processes of immobilisation include sorption to biomass, sorption to soil organic matter (for example PAHs to humic matter), and sorption to surfaces of introduced materials such as charcoal. For trace metals, the most important processes involved in this immobilisation involve the transformation of metals in soils, through precipitation–dissolution, adsorption–desorption, complexation processes and ion exchange. Amendments may be materials designed for specific functions, such as modified chars; or bulk materials, such as composts and slags. Immobilisation may also follow amendment of soil pH, for example by lime addition. However, this is usually considered reversible and not suitable as a long term measure. Nonetheless, in some cases amendments can generate soil pH decrease due to mineralisation processes, and are therefore recommended to be combined with liming agents. Many BF sites that are contaminated are complex by nature and may be polluted by a wide ranging mixture of contaminants. As a result, it may be necessary to apply more than one remediation technique across a site, and/or combine processes in a treatment train to reduce the concentrations of pollutants to acceptable levels (risk assessed levels that will not cause harm). The selection of the treatment approach is heavily dependent on site specific conditions and contaminants.
Technical Applicability:	Primarily deployed to mitigate risk of harm from contamination to acceptable levels for revegetation and groundwater resources. Example amendments and the contaminants treated include: Modified charcoals / specific chars: A range of products have been developed, or are in development. These may be based on specific feedstocks, such as bone biochar or chars including modifying agents such as zerovalent iron. An emerging application may be the use of charcoals as a carrier for microbial inocula to promote in situ biodegradation (bioaugmentation). Other proprietary amendments: DaramendTM: DaramendTM is a mixed organic material with zerovalent iron and is used to treat organic contaminants which are susceptible to reductive degradation. Liming agents: calcite, burnt lime, slaked lime, dolomitic limestone. Phosphates and apatites: metal immobilisation, and in particular Pb immobilisation, has been successful when using a range of high phosphate materials, such as synthetic and natural apatites and hydroxyapatites, phosphate rock, phosphate-based salts, diammonium phosphate, phosphoric acid and their combinations. Composts and other organic recyclates: composts and organic amendments such as sewage sludge have been found to reduce mobility of inorganic and organic species. However, the effect is highly specific to material and site, and dissolved organic matter has been found to mobilise metals in some tests. Slags: some types of slags, in particular blast furnace slags, have been used to immobilise metals in situ. Zeolites: there is strong research interest in the use of naturally occurring zeolite materials for the immobilisation of metals in situ to facilitate revegetation. Biochars: there is extensive research on the use of biochars for the immobilisation of metals and organic compounds Iron / iron products: iron oxidises in soil and mobile species may be sorbed to the oxides / hydroxides produced and the oxidation process. Amendments rich in metal oxides combined with compost, fertilisers, beringite, cyclonic ashes or lime have been found to effectively

<table>
<tr><td></td><td colspan="3">immobilise trace metals and enhance plant growth.</td></tr>
<tr><td>Pros and Cons:</td><td>Advantages</td><td colspan="2">Disadvantages</td></tr>
<tr><td></td><td>Rapid immobilisation of mobile species facilitating revegetation and protection of water receptors affected by contamination spreading from the site.

Combinations such as compost and char can be used to achieve risk management and soil improvement services in parallel.

The use of chars / biochars may achieve (temporary) carbon sequestration in soils.

Amendments can restore soil quality by balancing pH, adding organic matter, increasing water holding capacity, re-establishing microbial communities, and alleviating compaction.

Compatible with many other interventions, including measures to achieve improved conservation, biodiversity (depending on the amendment selected).

Amendments can usually be deployed using readily available agricultural equipment.

Use of some amendments represents a means of sustainable re-use of waste products (agricultural and industrial).</td><td colspan="2">Care is needed when several amendments are combined as they may interfere with each other.

Validation and verification may be relatively complex, in particular to make the case of a long term protective effect to regulators.

Unlikely to be protective of human health where direct contact is a major exposure pathway.

Some amendments (e.g. composts and digestates or sewage sludge may be associated with nuisances from odour or bioaerosols. Others may cause nuisance from dust emissions off site. It is particularly important to find organic amendments of high stability and low odour, and to apply application methods that minimise emissions of odour bioaerosol and/or dust</td></tr>
<tr><td>Compatibility with other interventions:</td><td colspan="2">Phyto-remediation
Natural attenuation
In situ
Ex situ
Re-naturalisation of soils
Amendment addition
Attenuation of contaminated surface water
Flood/drainage engineering
Ecological engineering
Biodiversity and environmental management
Conservation
Producing renewable feedstocks
Energy generation
Development of amenities
Strategic planning of land use over time</td><td>+++
+++
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O
+/-
+/-
+/-
+++
+++
++
+++</td></tr>
<tr><td></td><td colspan="3">+++ Strongly likely
++   Likely
+   Possible
+/-   May be a positive or negative impact on this service / intervention depending on the specific conditions
0   No relationship likely</td></tr>
<tr><td>Potential</td><td>Benefit</td><td colspan="2">Disbenefits</td></tr>
</table>

sustainability benefits and disbenefits	ENV1: Carbon sequestration ENV2: Improved soil functionality ENV3: Pathway management ENV5: Beneficial application of a recyclate SOC1: Risk mitigation in terms of both chronic and acute risks to human health from water SOC3: improvement of locality and improved sense of place SOC4: Long term compliance with local policies and spatial planning objectives ECON1: Liability Discharge; site value uplift ECON2: Value uplift, surrounding area	ENV1 Process emissions ENV3: Process emissions ENV5: use of energy and resources / generation of wastes SOC1: Potential short term risks to site workers and public from remediation works, especially if site not managed appropriately, including: from accidents, dust and allergens. SOC3: Process impacts such as noise, odour, vibration and other forms of nuisance. Traffic impacts from materials transportation. SOC5: validation of process outcomes may be more difficult than for ex situ approaches ECON1: Process costs, impacts of process duration ECON5 long term maintenance and monitoring of risk management performance
	Notes on benefits / disbenefits: • All are strongly dependent on site specific factors, the considerations above are indicative only of possible general trends for the intervention. • Where provided, benefits and disbenefits are grouped according to the SuRF-UK "Annex 1" categories, and are not exhaustive and are indicative only. • Where no indicator class is mentioned, factors are likely to be dominated by site specific factors • Additional factors may occur in categories depending on the site specific context. Absence of an Annex 1 category from the list above does not mean it may not apply at a particular site.	
Further Information:	*In situ* stabilisation using amendments	Kumpiene, J., Lagerkvist, A., & Maurice, C. (2008). Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments–a review. *Waste management*, **28**(1), 215-225
	Iron Products	Cundy, A. B., Hopkinson, L., & Whitby, R. L. (2008). Use of iron-based technologies in contaminated land and groundwater remediation: A review. *Science of the total environment*, *400*(1), 42-51.
	Zeolites	Shi, W. Y., Shao, H. B., Li, H., Shao, M. A., & Du, S. (2009). Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite. *Journal of hazardous materials*, *170*(1), 1-6. Leggo, P. J. (2013). Enhancing the Growth of Plants on Coal Waste Using a Biological Fertilizer. *International Journal of Environment and Resource*, **2**(3), 59-66.
	ROM	Park, J. H., Lamb, D., Paneerselvam, P., Choppala, G., Bolan, N., & Chung, J. W. (2011). Role of organic amendments on enhanced bioremediation of heavy metal (loid) contaminated soils. *Journal of Hazardous Materials*, *185*(2), 549-574. Nason, M., Williamson, J.,Tandy, S., Christou, M., Jones, D. & Healey, J. (2007). Using

		organic wastes and composts to remediate and restore land: best practice manual. School of the Environment and Natural Resources, Bangor University. ISBN: 978-1-84220-101-5. http://ies.bangor.ac.uk/TWIRLS/Web%20version%20Manual.pdf
	Biochars	Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D. Vithanage, M., Lee, S. S. & Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere*, **99**, 19-33. Lehmann, J. & Joseph, S. (Eds.) (2009). *Biochar for Environmental Management: Science and Technology*. London, UK: Earthscan.

Table 21: HLOW for Amendment Addition (Soil Management)

HLOW: Amendment Addition (Soil Management)	
Definition:	The addition of soil improvers is a major part of soil management at many sites. Typically these are added to increase soil fertility and improve soil condition and structure. Very often organic materials make excellent soil improvers as they enhance soil organic matter levels, which are strongly associated with good soil structure, and biological activity which is associated with good fertility. There are also inorganic soil amendments which may be used for specific purposes, such as liming to manage pH. Typically soil improvers can be incorporated into soil using a range of well-established agricultural techniques. Many soil improvers may also have a risk management benefit - see HLOW on Soil Management Activities à Amendment Additions (GRO). Note: in some conservation applications it is necessary to maintain a low fertility in soil. Soil improvers vary greatly in their properties and therefore need to be carefully matched to their applications. Key concerns are likely to be their impact on soil properties of interest, plant nutrient supply, along with their stability, hygiene and odour, potential contaminants, ease of deployment and potential risks of impacts to water resources from mobile N and P. Restoration may need to consider soil "engineering" to quite deep levels, for example for tree planting over a landfill cap. Different amendment rates (or materials) may be required at different depths, for example in subsoil vs. topsoil. There are quality standards available in many countries for composts and digestates, although mixed waste origin materials may be excluded from these. Recommended levels of use for agricultural applications may be limited by the Nitrates Directive (and increasingly the Water Framework Directive) to levels that provide only limited soil improvement benefit. Usually a special case is allowable for BF restoration and regeneration, although concerns of nitrogen leaching to groundwater and N&P runoff to surface water will need to be addresses.
Technical Applicability:	Primarily deployed to optimise / improve soil fertility and function for a particular type of vegetation. In general this HLOW describes a context where the soil amendment is being applied to improve soil functionality because an existing surface has low fertility or a poor soil condition. However, in some habitat and green infrastructure applications it may be necessary to reduce soil fertility (as mentioned above) Example amendments and their applications include: **Composts**: a wide variety of composts are produced from different feedstocks from urban, processing and agricultural sources. There is also a range of processing approaches. Composts

are produced by the aerobic processing of organic materials with a characteristic period of elevated temperature processing. There are two broad strategies to management of compost (and digestate) feedstocks. In some jurisdiction: source segregation where the waste producer separates out, for example garden wastes, for separate collection; and mixed waste inputs (for example from "grey bin" collections from households or sewage sludge). Composts (and digestates) produced from either mixed waste or source segregated may be suitable for use for soil improvement on BFs depending on their quality. However, in some jurisdictions there is reluctance by regulators (and land owners) to accept materials of a mixed waste origin, particularly "compost like outputs" from mixed bin wastes.

Functional applications of compost include:

- Improvement of soil structure and functionality (such as buffering) from improved soil organic matter levels
- Supply of major and minor plant nutrients (N typically in slow release form)
- Liming (increasing soil pH)
- Improvement of soil biological processes

Digestates: a wide variety of digestates are produced from different feedstocks from urban, processing and agricultural sources. There is also a range of processing approaches. Digestates are produced by the anaerobic processing of organic materials with accompanying production of methane, typically used for renewable energy. There are two broad strategies to management of compost (and digestate) feedstocks. In some jurisdiction: source segregation and mixed waste inputs (see above). Digestates as produced have very low solids content, limiting the radius of cost effective transportation. Dewatering may increase solids content to ~40%. Digestates may be post-processed by composting, in which case the output becomes a compost.

Functional applications of digestates include:

- Improvement of soil structure and functionality (such as buffering) from improved soil organic matter levels
- Supply of major and minor plant nutrients (N typically in more mobile form than in composts)
- Liming (increasing soil pH)
- Improvement of soil biological processes
- Irrigation (for under watered digestates)

Sewage sludge: a wide variety of sewage sludges are produced from different stages of sewage processing, and these may be treated in different ways at the water treatment plant, most frequently by anaerobic digestion. In some cases untreated sewage effluents have been used in forestry and reclamation, but that is not recommended for reasons of odour and pathogen control. It is the sludges resulting from anaerobic digestion treatments that is most commonly used as a soil amendment in agriculture (for many countries) and for reclamation. These AD sludges may be further treated primarily by dewatering and in some cases by lime stabilisation or composting.

Functional applications of sewage sludges include:

- Improvement of soil structure and functionality (such as buffering) from improved soil organic matter levels
- Supply of major and minor plant nutrients (N typically in more mobile form than in composts)
- Liming (increasing soil pH)
- Improvement of soil biological processes

Biochars: biochars are produced as a result of pyrolysis of plant residues, often of woody wastes, but increasingly other plant residues as well. Biochars provide useful amounts of potassium and potentially phosphate to soils. They increase soil buffering and cation exchange capacity and may also increase its water holding capacity. They also tend to have a liming effect on soil. Wider properties of biochars, depending on type may be the immobilisation of mobile inorganic contaminants and organic contaminants (in particular if these are polar in nature). See Gentle Remediation – amendment addition

Functional applications of biochars include:

- Improvement of soil structure and functionality (such as buffering, cation exchange capacity, water holding)
- Supply of major (K and P) and minor plant nutrients
- Liming (increasing soil pH)

Mineral amendments: a range of mineral amendments may be used to improve soil condition

	including fertilisers, lime, gypsum, slags, and zeolites, but possibly also bulk amendments such as gravel or sand. Typically there are four broad aims as set out below. Functional applications of mineral amendments include: • Improvement of functionality (such as buffering / cation exchange) using zeolites • Improvement of soil structure in particular circumstances (e.g. heavy clay soils): gypsum, slags • Supply of plant nutrients from mineral fertilisers • Liming (increasing soil pH).	
Pros and Cons:	**Advantages**	**Disadvantages**
	Amendments can usually be deployed using readily available agricultural equipment. Many soil amendments are recyclates, and therefore relatively cheap (excluding transportation costs). As recyclates they also avoid the use of virgin materials and bring other sustainability advantages. Soil amendment application (combined with appropriate cultivation) can be used to create new topsoils in situ from relatively poor existing substrates. A complete engineered soil approach can be considered across a full rooting depth, from subsoil to topsoil, for example to facilitate tree growth over a landfill cap. Soil improvement with amendments may be an outcome of some forms of remediation (e.g. ex situ bioremediation of soil). It may be a necessary aftercare for other types of ex situ treatment such as soil washing or thermal treatments. Addition of organic amendments may be a part of some forms of managed wetlands, and composts may be used in swales in flood management. The use of organics amendments and chars / biochars may achieve (temporary) carbon sequestration in soils. Organic amendments can be carefully blended to provide a mixture of rapid and slow release forms of plant nutrients. Rapid immobilisation of mobile species facilitating revegetation and protection of water receptors affected by contamination spreading from the site. Combinations such as compost and char can be used to achieve risk management and soil improvement services in parallel. Compatible with many other interventions, including measures to achieve improved conservation, biodiversity (depending on the amendment selected).	Care is needed when several amendments stored, applied and incorporated into soil, as machinery may inadvertently cause soil compaction. Additional regulatory permissions may be required for the re-use of recyclates. Performance standards for soil amendments may be available. These may be a prerequisite or simply facilitate decision making but they can also reduce the range of possible recyclates that can be considered. Consideration should be given to the mobilisation of nitrogen and phosphorus into surface water or groundwater from organic amendments or inorganic fertilisers, and for some amendments gaseous emissions of ammonia may be problematic where the application is in the vicinity of a low nitrogen habitat. Some amendments (e.g. composts and digestates or sewage sludge) may be associated with nuisances from odour or bioaerosols. Others may cause nuisance from dust emissions off site. It is particularly important to find organic amendments of high stability and low odour, and to apply application methods that minimise emissions of odour bioaerosol and/or dust. Care needs also to be taken that amendments do not contain viable seeds of root fragments, particularly for invasive species such as bracken or Japanese Knotweed. Mineral fertilisers carry high embedded carbon costs and mineral phosphate is a limited primary resource
Compatibility with other interventions:	Phyto-remediation	+++
	Amendment addition (as a GRO)	+++
	Natural attenuation	+++
	In situ remediation	+++
	Ex situ remediation	++
	Re-naturalisation of soils	++
	Attenuation of contaminated surface water	+++
	Flood/drainage engineering	O

	Ecological engineering Biodiversity and environmental management Conservation Producing renewable feedstocks Energy generation Development of amenities Strategic planning of land use over time	+/- +/- +/- +++ +++ ++ +++
	+++ Strongly likely ++ Likely + Possible +/- May be a positive or negative impact on this service / intervention depending on the specific conditions 0 No relationship likely	
Potential sustainability benefits and disbenefits	**Benefit**	**Disbenefits**
	ENV1: Carbon sequestration ENV2: Improved soil functionality ENV3: Potential compatibility with remediation ENV5: Beneficial application of a recyclate SOC2: Supports recycling (depending on amendment used) SOC3: improvement of locality and improved sense of place SOC4: Long term compliance with local policies and spatial planning objectives ECON1: Facilitation of revegetation / productive use of the site ECON2: Value uplift, surrounding area	ENV1 Process emissions ENV3: Process emissions ENV5: use of energy; use of resources for amendments which are not recyclates SOC1: Potential short term risks to site workers and public from remediation works, especially if site not managed appropriately, including: from accident dust and allergens.. SOC3::Process impacts such as noise, odour, vibration and other forms of nuisance. Traffic impacts from materials transportation. ECON1: Process costs, impacts of process duration
	Notes on benefits / disbenefits: • All are strongly dependent on site specific factors, the considerations above are indicative only of possible general trends for the intervention. • Where provided benefits and disbenefits are grouped according to the SuRF-UK "Annex 1" categories, and are not exhaustive and are indicative only. • Where no indicator class is mentioned, factors are likely to be dominated by site specific factors • Additional factors may occur in categories depending on the site specific context. Absence of an Annex 1 category from the list above does not mean it may not apply at a particular site.	
Further Information:	Organic amendments	Rejuvenate: http://www.snowman-era.net/downloads/REJUVENATE_final_report.pdf Scotland and Northern Ireland Forum For Environmental Research - SNIFFER (2010) Code of Practice for the use of sludge, compost and other organic materials for land reclamation Code ER11, also supporting Technical Document; www.sniffer.org.uk/files/7413/4183/7993/ER11_Code_of_Practice.pdf US Environmental Protection Agency (2007) The Use of Soil Amendments for Remediation, Revitalization, and Re-use EPA 542-R-07-013 http://nepis.epa.gov/Exe/ZyNET.exe/60000LQ7.TXT?ZyActionD=ZyDocument&Client=EPA&Index=2006+Thru+2010&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5Czyfiles%5CIndex%2

		0Data%5C06thru10%5CTxt%5C00000001%5C60000LQ7.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=p%7Cf&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyPURL
	Biochar	Verheijen, F.G.A., Jeffery, S., Bastos, A.C., van der Velde, M., and Diafas, I. (2009). Biochar Application to Soils - A Critical Scientific Review of Effects on Soil Properties, Processes and Functions. EUR 24099 EN, http://www.biochar-international.org/sites/default/files/Verheijen%20et%20al%202010%20JRC_Biochar_Soils_Review.pdf
	Mineral amendments	US Environmental Protection Agency (2007) The Use of Soil Amendments for Remediation, Revitalization, and Reuse EPA 542-R-07-013 G.M. Tordo , A.J.M. Baker *, A.J. Willis (2000) Current approaches to the revegetation and reclamation of metalliferous mine wastes. Chemosphere 41 (2000) 219-228. http://www.researchgate.net/profile/Alan_Baker2/publication/12499193_Current_approaches_to_the_revegetation_and_reclamation_of_metalliferous_mine_wastes/links/00b4953b850afdc679000000

5.4 Detailed Operating Window

GRO can be effectively used as part of a wider risk management strategy at contaminated sites, while promoting additional economic, environmental and social benefits. GRO can be implemented in a range of soil types and climates, across a range of site and contaminant types. Similar to other remediation strategies, however, they are not a simple "off-the-shelf" solution that can be applied to every site situation and type, and a site specific assessment is required prior to implementation. The Greenland Project has developed a Detailed Operating Window structure for a range of specific GROs (primarily specific phytoremediation techniques) (Cundy *et al.*, 2014). In the Greenland system, these link from a quick reference table on GRO applicability (shown in Table 22 below), and include an outline applicability check, a contaminant treatability table and a cost tool.

Table 22: Quick reference: Are GRO applicable to your site? (Cundy *et al.*, 2014)

Key questions:	If YES, are GRO potentially applicable?
Does the site require immediate redevelopment?	**Unlikely** (except immobilisation / phytoexclusion which can show immediate positive effects)
Are your local regulatory guidelines based on total soil concentration values?	**Unlikely** for phytoextraction but **possibly** for some other GRO
Is the site under hard-standing, or has buildings under active use?	**Unlikely** (there is a need to remove the hard-standing or buildings and to establish a soil layer enabling plant growth).
Do you require biological functionality of the soil during and after site treatment?	**YES**
Is the treatment area large, and contaminants are present but not at strongly elevated levels?	**YES** (even where soil ecotoxicity is high, use of soil pretreatments and amendments may enable GRO application)
Are the contaminants of concern present at depths within 5 – 10m of the soil surface?	**YES** (depending on soil porosity, if contamination is present within 1m of the soil surface then treatment is possible by most plants. Deeper contamination may be addressed using trees, with interventions where necessary to promote deeper rooting).
Is the economic case for intervention and use of "hard" remediation strategies marginal?	**YES**
Are you redeveloping the site for soft end-use (biomass generation, urban parkland etc)?	**YES**

A user can check the outline applicability of GRO (grouped as phytoextraction, phytostabilisation, and immobilisation/phytoexclusion) to a specific site, in terms of local soil pH, site plant toxicity, climate, soil type, and depth of contamination. The purpose of a detailed operating window is to highlight the potential applicability of GRO at a site, NOT to confirm that GRO will be a successful risk management tool at that site. Further input and expertise will be required to design and implement a GRO strategy that effectively manages contaminant risk, and delivers wider benefits.

In essence, the Detailed Operating Window consists of a check-list with focused items corresponding to site specific parameters. The focused items are meant to address key parameters that may hinder or influence the effectiveness of an intervention to such extend that it could compromise its viability on a specific site. Each parameter is split in three value categories (depending on the parameter, these can be qualitative or quantitative), see Figure 26. The Detailed Operating Window provides the users with a default valuation of the technique's likeliness to be efficient under the circumstances defined with the parameter's value. These default valuations are based on state of the art knowledge available in literature.

Key parameter #	**Valuation**
Range 1 of key parameter #	
Range 2 of key parameter #	
Range 3 of key parameter #	

Figure 26: Detailed operating window entries

The valuation cells contain default qualitative valuation indicating how the specific technique would perform under the circumstances described by the range of the key parameter. As default answers, Greenland uses the following system:

- [YES +] = feasible without further enhancement/corrective measures to provide effect
- [YES +/-] = feasible but probably some enhancement/corrective measures would be necessary to provide effect – Useful indications might be available in HLOW.
- [*?*] = on site feasibility study is recommended/required to confirm effect can be provided

5.5 Detailed Operating Window for use of Compost and Biochar Amendments

Figure 27 shows an outline applicability Detailed Operating Window for use of compost and biochar amendments, based on the findings of this report, using the Greenland structure. Table 23 shows an indicative treatability matrix based on the findings of this report, following the structure used in Nathanail *et al.* (2007). The quick reference table (Table 22 is also considered applicable to the use of compost and biochar amendments).

soil pH	Valuation
5 - 8	YES +
4 – 5 / 8 – 9	YES +
2 – 4 / 9 - 11	*?*

Vegetation type	Valuation[14]
Diversity and density of plant species are similar to surrounding areas (on non-contaminated soil)	YES +
Diversity and density of plant species is visibly less / different to surroundings (non-contaminated soil)	YES +
No plant species are growing on the contaminated site	? +

Climatic conditions	Valuation
Arid	YES +
Semi-arid	YES +
Humid - Temperate	YES +

Soil type – composition of soil on the site	Valuation
Clay	YES +
Loam	YES +
Sand	YES +

Soil depth contamination	Valuation
Top soil (0 – 30 cm)	YES +
Subsoil (30 – 90cm)	YES +
Deep soil (> 90cm)	*?*

Figure 27: Detailed OW Immobilisation Using Biochar and Compost

[14] Note: caution is needed for specific ecosystems of interest, especially if these are dependent on strict conditions of soil nutrient status and/or pH

Table 23: Outline contaminant treatability matrix for Immobilisation Using Biochar and Compost

APPLICABLE CONTAMINANTS								
Organic	Halogenated volatile	□✓	Organic	PCBs	✓	Inorganic	Cyanides	?
	Halogenated semivolatile	✓		Pesticides/herbicides	✓		Corrosives	?
	Non-halogenated volatile	✓		Dioxins/furans	?	Misc.	Asbestos	X
	Non-halogenated semivolatile	✓	Inorganic	Volatile metals	✓		Oxidisers	?
	Organic corrosives	?		Non-volatile metals	✓		Reducers	?
	Organic cyanides	?						

Applicability		
Indicative suggestions only; each table includes a list of detailed technical references for further information; if there is any doubt a treatability study should be carried out.	✓✓	Usually applicable
	✓	Potentially applicable
	?	May be applicable
	□	Not treatable
	□□	May worsen situation

6 Conclusions

This report provides an overview of existing literature discussing the use of biochar and recycled organic matter (ROM) in the redevelopment / regeneration of BF sites, in particular focusing on their use in contaminant risk management. A promising combination is the combined use of composts and biochar to promote revegetation. Experimental studies were carried out to investigate this possibility, considering two hypotheses:

H_1 – "Biochar is an opportunity to combine soil improvement, carbon sequestration and risk management (via *in situ* stabilisation)."

H_2 – "Organic matter addition to soil provides a durable immobilisation of trace elements and a carbon sequestration opportunity."

Following the results of this report, both null hypothesis can be largely rejected. Both experimental and literature review work provide evidence that ROM and biochar have the potential to simultaneously stabilise soil contaminants, improve soil quality and offer carbon sequestration benefits.

The literature review demonstrated that biochar as a soil amendment may offer multiple benefits including: carbon sequestration, soil conditioning and a means of waste re-use. Use of biochar in BF management allows the utilisation of contaminant immobilisation for a wide range of contaminants, whilst concurrently reaping the aforementioned soil and environmental benefits. Biochar has been shown to have significant longevity and therefore may be economically attractive, as it may provide a long-term effect without repeat applications. It is highly versatile and can be tailored to suit a specific site, widening further its application potential. Due to the versatility of biochar, it can also be applied on a BF site with multiple problems or spatial disparity of issues. For example, if a BF site is contaminated with metals in some areas, but low soil quality alone in others, biochar can still be utilised across the site to improve both problems. However, the suitability of biochar as a remediation option is dependent on site specific circumstances. The effectiveness of biochar application to land for any purpose is determined by its specific properties, in turn a result of feedstock and the production process. Certain biochar production processes and feedstock may also cause biochar to be source of contaminants. Similar to all remediation options, it is important that care is taken in designing an intervention strategy incorporating biochar use.

ROM can be derived from multiple sources and can be tailored to suit a specific purpose. Depending on the feedstock, biochar may be regarded as a type of ROM. As a soil amendment, ROM may provide numerous benefits, for the improvement of BF sites. ROM is well established as a conditioner for soil, improving many qualities associated with cultivation benefits, such as enhanced soil structure and nutrient supply. The use of ROM contributes to resource efficiency, as it both decreases the volume of waste that requires disposal through traditional routes and provides a low-cost amendment for soil conditioning and potentially remediation. However, there may be risks associated with the application of ROM to land, as metal concentrations may be increased or mobilised. Nonetheless, ROM amendments have also been demonstrated to decrease metal availability in contaminated soils. Care should be taken in selecting a ROM product for use to ensure it is suitably matched to the receiving site and its composition is satisfactorily low in metals.

The experimental studies demonstrated that biochar and compost can be used successfully to aid remediation of a copper contaminated site. The amendments can also be used in combination with phytoremediation to further decrease pollution risks and potentially provide a saleable energy crop. It can be established that the aims of the HOMBRE/Greenland joint experimental projects were largely positively achieved:

1. **To determine if biochar and green waste compost can be successfully used to immobilise copper in a contaminated soil:** in the supporting MSc study, very few significant differences between treatments were observed in terms of changes in copper fractionation. Nonetheless, in all the studies, biochar and compost were shown to reduce leachable copper in contaminated soil.

2. **To improve optimal modes of use:** see operating windows below. Biochars and composts were shown to increasingly immobilise copper with increased application rate. Combined application of the two amendments was shown to be effective for immobilisation and plant growth.

3. **Explore production of biomass on marginal land:** plants were successfully grown in the contaminated soil in every study, with significant yield gains brought about by the soil amendments. It was determined that amendments do not effect a reduction in copper bioavailability alone, but rather initiate multiple concomitant changes to soil which contribute to reduced phytotoxicity.

4. **The use of amendments produced using biomass produced on a contaminated site for further soil improvement:** biochars produced using poplar biomass grown on the contaminated site immobilised soil copper and improved plant growth, however these effects were not as great as those resulting from the commercially produced biochar.

Both ROM and biochar as GRO can be implemented for soft end-use of regenerated BF sites. Soft-end uses can lower the social, environmental and economic burden of a site; risk management strategies employed during regeneration are likely to lower environmental and public health risks, while provision of green-space, or public open space may improve all three elements of sustainable development.

To help stakeholders establish if ROM and biochar as soil amendments are suitable for risk management and the provision of sought-after additional services, “high level” and “detailed” operating windows have been developed. The detailed operating windows follow the traditional operating window rationale where the function is to identify the optimal conditions for applying a GRO in terms of its process parameters. HLOWs act as instruments to provide relevant information to stakeholders and support them in taking decisions for the selection of appropriate interventions in BF redevelopment / regeneration projects to deliver particular services. Operating windows can be used to establish if a particular remediation option may be suitable for use on a site, however further expert advice must be sought to develop a detailed remediation plan ensuring sufficient risk management can be provided by the selected remediation option(s).

Based on the outcomes of this report, it is clear that there is scope for biochar and compost to be successfully used in BF regeneration to soft end-uses. However, more research is required to further establish the detailed operating windows of these amendments and to more clearly define the influence of different feedstock materials on biochar and ROM properties. Future research could include trials to determine the effect of feedstock material on effective application rates for ROM and biochar. Additionally, the amendments successfully trialled in our research require field trials to determine their efficacy on a larger scale and confirm their potential for deployment on a full-scale remediation site.

References

Abdel-Fattah, T. M., Mahmoud, M. E., Ahmed, S. B., Huff, M. D., Lee, J. W., & Kumar, S. (2014). Biochar from woody biomass for removing metal contaminants and carbon sequestration. *Journal of Industrial and Engineering Chemistry*, In Press.

Aggelides, S. M., & Londra, P. A. (2000). Effects of compost produced from town wastes and sewage sludge on the physical properties of a loamy and a clay soil. *Bioresource Technology*, **71**(3), 253-259.

Agrafioti, E., Bouras, G., Kalderis, D., & Diamadopoulos, E. (2013). Biochar production by sewage sludge pyrolysis. *Journal of Analytical and Applied Pyrolysis*, **101**, 72-78.

Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D. Vithanage, M., Lee, S. S. & Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere*, **99**, 19-33.

Akhtar, S. S., Li, G., Andersen, M. N., & Liu, F. (2014). Biochar enhances yield and quality of tomato under reduced irrigation. *Agricultural Water Management*, **138**, 37-44.

Albiach, R., Canet, R., Pomares, F., & Ingelmo, F. (2000). Microbial biomass content and enzymatic activities after the application of organic amendments to a horticultural soil. *Bioresource Technology*, **75**(1), 43-48.

Alburquerque, J. A., Calero, J. M., Barrón, V., Torrent, J., del Campillo, M. C., Gallardo, A., & Villar, R. (2014). Effects of biochars produced from different feedstocks on soil properties and sunflower growth. *Journal of Plant Nutrition and Soil Science*, **177**(1), 16-25.

Alburquerque, J. A., de La Fuente, C., Bernal, M. P. (2011). Improvements of soil quality after "alperujo" compost application to two contaminated soils characterised by differing heavy metal solubility, *Journal of Environmental Management*, **92,** 733-741.

Al Chami, Z., Amer, N., Smets, K., Yperman, J., Carleer, R., Dumontet, S., & Vangronsveld, J. (2014). Evaluation of flash and slow pyrolysis applied on heavy metal contaminated *Sorghum bicolor* shoots resulting from phytoremediation. *Biomass and Bioenergy*, **63**, 268-279.

Alexander, M. (2000). Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environmental Science & Technology*, **34**(20), 4259-4265.

Ali, N. A., Ater, M., Sunahara, G. I., Robidoux, P. Y., (2004). Phytotoxicity and bioaccumulation of copper and chromium using barley (*Hordeum vulgare* L.) in spiked artificial and natural forest soils. *Ecotoxicology and Environmental Safety*, **57,** 363-374.

Allievi, L., Marchesini, A., Salardi, C., Piano, V., & Ferrari, A. (1993). Plant quality and soil residual fertility six years after a compost treatment. *Bioresource Technology*, **43**(1), 85-89.

Alvarenga, P., Gonçalves, A. P., Fernandes, R. M., De Varennes, A., Vallini, G., Duarte, E., & Cunha-Queda, A. C. (2009). Organic residues as immobilizing agents in aided phytostabilization: (I) Effects on soil chemical characteristics. *Chemosphere*, **74**(10), 1292-1300.

Amery, F., Degryse, F., Degeling, W., Smolders, E., & Merckx, R. (2007). The copper-mobilizing-potential of dissolved organic matter in soils varies 10-fold depending on soil incubation and extraction procedures. *Environmental Science & Technology*, **41**(7), 2277-2281.

Amlinger, F., Pollak, M. & Favoino, E. (2004) Heavy metals and organic compounds from wastes used as organic fertilisers. Report ENV.A2/ETU/2001/024, July 2004, European Commission, Rue de la Loi, Brussels, Belgium. <Online, available at: http://europa.eu.int/comm/environment/waste/compost/pdf/hm_finalreport.pdf >.

Amon, T., Amon, B., Kryvoruchko, V., Machmüller, A., Hopfner-Sixt, K., Bodiroza, V., Hrbek, R., Friedel, J., Pötsch, E., Wagentristl, H., Schreiner, M. & Zollitsch, W. (2007). Methane production through anaerobic digestion of various energy crops grown in sustainable crop rotations. *Bioresource Technology*, **98**(17), 3204-3212.

Antoniadis, V., & Alloway, B. J. (2002). The role of dissolved organic carbon in the mobility of Cd, Ni and Zn in sewage sludge-amended soils. *Environmental Pollution*, **117**(3), 515-521.

Antoniadis, V., & Alloway, B. J. (2001). Availability of Cd, Ni and Zn to ryegrass in sewage sludge-treated soils at different temperatures. *Water, Air, and Soil Pollution*, **132**(3-4), 201-214.

Antoniadis, V., Robinson, J. S., & Alloway, B. J. (2008). Effects of short-term pH fluctuations on cadmium, nickel, lead, and zinc availability to ryegrass in a sewage sludge-amended field. *Chemosphere*, **71**(4), 759-764.

Arnon, D. I., Stout, P. R. (1939). The essentiality of certain elements in a minute quantity for plants with special reference to copper, *Plant Physiology*, **14,** 371-375.

Baker, D. E., & Senft, J. P. (1995). Copper. In: Alloway, B. J. (ed.) *Heavy Metals in Soils*. London, UK: Blackie Academic and Professional, 179-205.

Banach-Szott, M., Debska, B., & Rosa, E. (2014). Effect of soil pollution with polycyclic aromatic hydrocarbons on the properties of humic acids. *Journal of Soils and Sediments*, **14**(6), 1169-1178.

Bardos, R.P. (2005). Composting of Mechanically Segregated Fractions of Municipal Solid Waste – A Review. Project Carried out for SITA Environmental Trust, The Barn, Brinkmarsh Lane, Falfield, GL12 8PT. <www.compostinfo.info>.

Bardos, P., Andersson-Sköld, Y., Keuning, S., Polland, M., Suer, P., & Track, T. (2010). Crop Based Systems for Sustainable Risk Based Land Management for Economically Marginal Degraded Land. Final Research Report. (Rejuvenate Project) Report for the

European Commission's 6th Framework Programme project SNOWMAN (contract no ERAC-CT-2003-003219). <Online, available at: http://www.snowman-era.net/downloads/REJUVENATE_final_report.pdf>.

Bardos, P., Bakker, L., Slenders, H., & Nathanail, P., (2011b). Sustainable Remediation, in: Swartjes, F.A. (Ed.), *Dealing with Contaminated Sites: From Theory towards Practical Application.* Dordrecht: Springer Publishers, pp. 889-948, ISBN: 978-90-481-9756-9.

Bardos, R. P., Bone, B., Andersson-Sköld, Y., Suer, P., Track, T., & Wagelmans, M. (2011a). Crop-based systems for sustainable risk-based land management for economically marginal damaged land. *Remediation Journal*, **21**(4), 11-33.

Bardos, R. P., & Van Veen, H. J. (1996). Review of longer-term or 'extensive' treatment technologies. *Land Contamination & Reclamation*, **4**(1), 19-36.

Bardos, R.P., French, C., Lewis, A., Moffat, A. and Nortcliff, S. (2001). Marginal Land Restoration Scoping Study: Information Review and Feasibility Study. *exSite Research Project Report 1*. ISBN 0953309029. LQM Press (Nottingham) http://www.lqm.co.uk/lqmpress/ DOI: 10.13140/2.1.4495.1680.

Barriuso, E., Andrades, M.-S., Benoit, P., & Houot, S. (2011). Pesticide desportion from soils facilitated by dissolved organic matter coming from composts: experimental data and modelling approach. *Biogeochemistry*, **106**(1), 117-133.

Basso, A. S., Miguez, F. E., Laird, D., Horton, R., Westgate, M. (2013). Assessing the potential of biochar for increasing water-holding capacity of sandy soil, *Global Change Biology Bioenergy*, **5,** 132-143.

Batley, G. E., Apte, S. C., Stauber, J. L. (2004). Speciation and bioavailability of trace metals in water: progress since 1982, *Australian Journal of Chemistry*, **57,** 903-919.

Beesley, L., Inneh, O. S., Norton, G. J., Moreno-Jimenez, E., Pardo, T., Clemente, R., & Dawson, J. J. (2014). Assessing the influence of compost and biochar amendments on the mobility and toxicity of metals and arsenic in a naturally contaminated mine soil. *Environmental Pollution*, **186**, 195-202.

Beesley, L. (2012). Carbon storage and fluxes in existing and newly created urban soils. *Journal of Environmental Management*, **104**, 158-165.

Beesley, L., & Dickinson, N. (2011). Carbon and trace element fluxes in the pore water of an urban soil following greenwaste compost, woody and biochar amendments, inoculated with the earthworm *Lumbricus terrestris*. *Soil Biology and Biochemistry*, **43**(1), 188-196.

Beesley, L., & Marmiroli, M. (2011). The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environmental Pollution*, **159**(2), 474-480.

Beesley, L., Moreno-Jiménez, E., & Gomez-Eyles, J. L. (2010). Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. *Environmental Pollution*, **158**(6), 2282-2287.

Bernai, M. P., Paredes, C., Sanchez-Monedero, M. A., & Cegarra, J. (1998). Maturity and stability parameters of composts prepared with a wide range of organic wastes. *Bioresource Technology*, **63**(1), 91-99.

Bes C, (2008). Phytoremédiation des sols d'un site de traitement du bois contaminés par le cuivre, *Thèse, L'université Bordeaux 1. Nº d'ordre : 3712.*

Bes, C. and Mench, M., (2008). Remediation of copper contaminated topsoils from a wood treatment facility using in situ stabilisation, *Environmental Pollution*, **156**, 1128-1138.

Bes, C., Mench, M., Aulen, M., Gaste, H., & Taberly, J. (2010). Spatial variation of plant communities and shoot Cu concentrations of plant species at a timber treatment site. *Plant Soil*, **330**, 267-280.

Beumer, V., Bardos, P, Menger, P. et al (2014) Decision support system on soft uses. HOMBRE Project Deliverable D5.2. <Online, available at: www.zerobrownfields.eu>.

Biederman, L. A., & Harpole, W. S. (2013). Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. *GCB Bioenergy*, **5**(2), 202-214.

Boisson, J., Ruttens, A., Mench, M., & Vangronsveld, J. (1999). Evaluation of hydroxyapatite as a metal immobilizing soil additive for the remediation of polluted soils. Part 1. Influence of hydroxyapatite on metal exchangeability in soil, plant growth and plant metal accumulation, *Environmental Pollution*, **104**, 225-233.

Bolan, N. S., Kunhikrishnan, A., Choppala, G. K., Thangarajan, R., & Chung, J. W. (2012). Stabilization of carbon in composts and biochars in relation to carbon sequestration and soil fertility. *Science of the Total Environment*, **424**, 264-270.

Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., Kirkham, M. B. & Scheckel, K. (2014). Remediation of heavy metal (loid) s contaminated soils–To mobilize or to immobilize?, *Journal of hazardous materials*, **266**, 141-166.

Borchard, N., Wolf, A., Laabs, V., Aeckersberg, R., Scherer, H. W., Moeller, A., & Amelung, W. (2012). Physical activation of biochar and its meaning for soil fertility and nutrient leaching–a greenhouse experiment. *Soil Use and Management*, **28**(2), 177-184.

Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science*, **277,** 1-18.

Brown, R. A., Kercher, A. K., Nguyen, T. H., Nagle, D. C., & Ball, W. P. (2006). Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. *Organic Geochemistry*, **37**(3), 321-333.

Brown, S., Kurtz, K., Cogger, C., & Bary, A. Land Application-a true path to zero waste. Department of Crop and Soil Sciences, Washington State University Interagency agreement C, 800273. <Online, available at: https://fortress.wa.gov/ecy/publications/publications/0907059.pdf>.

Bruun, E. W., Petersen, C. T., Hansen, E., Holm, J. K., & Hauggaard-Nielsen, H. (2014). Biochar amendment to coarse sandy subsoil improves root growth and increases water retention. *Soil Use and Management*, **30**(1), 109-118.

Burkhead, J. L., Reynolds, K. A. G., Abdel-Ghany, S. E., Cohu, C. M. and Pilon, M., (2009). Copper homeostasis. *New Phytologist*, **182**(4), 799-816.

Busby, R. R., Allen Torbert, H., & Gebhart, D. L. (2007). Carbon and nitrogen mineralization of non-composted and composted municipal solid waste in sandy soils. *Soil Biology and Biochemistry*, **39**(6), 1277-1283.

Buss, W., Kammann, C., & Koyro, H. W. (2012). Biochar Reduces Copper Toxicity in *Chenopodium quinoa* Willd. in a Sandy Soil. *Journal of Environmental Quality*, **41**(4), 1157-1165.

Bustamante, M. A., Said-Pullicino, D., Paredes, C., Cecilia, J. A., & Moral, R. (2010). Influences of winery–distillery waste compost stability and soil type on soil carbon dynamics in amended soils. *Waste Management*, **30**(10), 1966-1975.

Buurman, P., Pape, T., and Muggle, C. C. (1997). Laser grain-size determination in soil genetic studies: Practical problems, *Soil Science*, **162,** 211-218.

Cao, X., Ma, L., Liang, Y., Gao, B., & Harris, W. (2011). Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. *Environmental Science & Technology*, **45**(11), 4884-4889.

Cao, X., & Harris, W. (2010). Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresource Technology*, **101**(14), 5222-5228.

Cao, X., Ma, L., Gao, B., & Harris, W. (2009). Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environmental Science & Technology*, **43**(9), 3285-3291.

Cao, X., Ma, L. Q., & Shiralipour, A. (2003). Effects of compost and phosphate amendments on arsenic mobility in soils and arsenic uptake by the hyperaccumulator *Pteris vittata* L. *Environmental Pollution*, **126**(2), 157-167.

Carter, S., Shackley, S., Sohi, S., Suy, T. B., & Haefele, S. (2013). The impact of biochar application on soil properties and plant growth of pot grown lettuce (Lactuca sativa) and cabbage (Brassica chinensis). *Agronomy*, **3**(2), 404-418.

Chaney, R. L., Angle, J. S., Broadhurst, C. L., Peters, C. A., Tappero, R. V., & Sparks, D. L. (2007). Improved understanding of hyperaccumulation yields commercial phytoextraction and phytomining technologies. *Journal of Environmental Quality*, **36**, 1429-1443.

Charlatchka, R., & Cambier, P. (2000). Influence of reducing conditions on solubility of trace metals in contaminated soils. *Water, Air, and Soil Pollution*, **118**(1-2), 143-168.

Chase, A.R., & Simone, G.W. (1985). Phytotoxicity on foliage ornamentals caused by Batericides and Fungicides. *Plant Pathology Fact Sheet.* Florida, USA: Florida Cooperative Extenstion Service.

Chen, B., Chen, Z., & Lv, S. (2011). A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresource Technology*, **102**(2), 716-723.

Chen, Y., Day, S. D., Wick, A. F., Strahm, B. D., Wiseman, P. E., & Daniels, W. L. (2013). Changes in soil carbon pools and microbial biomass from urban land development and subsequent post-development soil rehabilitation. *Soil Biology and Biochemistry*, **66**, 38-44.

Chen, T., Zhang, Y., Wang, H., Lu, W., Zhou, Z., Zhang, Y., & Ren, L. (2014). Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. *Bioresource technology*, **164**, 47-54.

Chirenje, T., Rivero, C., & Ma, L. Q. (2002). Leachability of Cu and Ni in wood ash-amended soil as impacted by humic and fulvic acid. *Geoderma*, **108**(1), 31-47.

CL:AIRE (2009) Integrated Remediation, Reclamation and Greenspace Creation on Brownfield Land. SUB 11 Su:brim bulletin 11, April 2009. <Online, available at: http://www.forestry.gov.uk/pdf/SUBRIM_bulletin_11.pdf/$FILE/SUBRIM_bulletin_11.pdf>

Clemente, R., & Bernal, M. P. (2006). Fractionation of heavy metals and distribution of organic carbon in two contaminated soils amended with humic acids. *Chemosphere*, **64**(8), 1264-1273.

Cross, A., & Sohi, S. P. (2011). The priming potential of biochar products in relation to labile carbon contents and soil organic matter status. *Soil Biology and Biochemistry*, **43**(10), 2127-2134.

Cui, L., Li, L., Zhang, A., Pan, G., Bao, D., & Chang, A. (2011). Biochar amendment greatly reduces rice Cd uptake in a contaminated paddy soil: A two-year field experiment. *BioResources*, **6**(3), 2605-2618.

Cundy, A. B., Bardos, R. P., Church, A., Puschenreiter, M., Friesl-Hanl, W., Müller, I., Neu, S., Mench, M., Witters, N. & Vangronsveld, J. (2013). Developing principles of sustainability and stakeholder engagement for "gentle" remediation approaches: The European context. Journal of environmental management, 129, 283-291.

Cundy, A.B., Bardos, R.P., Puschenreiter, M. & the GREENLAND project team (2014). The GREENLAND project Decision Support Tool (DST) for Practical Application of Gentle Remediation Options (GRO). <www.greenland-project.eu>.

Cundy, A. B., Hopkinson, L., & Whitby, R. L. (2008). Use of iron-based technologies in contaminated land and groundwater remediation: A review. *Science of the Total Environment*, **400**(1), 42-51.

Debela, F., Thring, R. W., & Arocena, J. M. (2012). Immobilization of heavy metals by co-pyrolysis of contaminated soil with woody biomass. *Water, Air, & Soil Pollution*, **223**(3), 1161-1170.

Department for Communities and Local Government (DCLG). (2008). Woodland Establishment on Landfill Sites: Ten Years of Research. ISBN 9781409801344.

Department for Environment, Food and Rural Affairs (Defra). (2013a). Mechanical Biological Treatment of Municipal Solid Waste. Defra, London, UK. <Online, available at: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/221039/pb13890-treatment-solid-waste.pdf>.

Department for Environment, Food and Rural Affairs (Defra). (2013b). Guidance on complying with the rules for Nitrate Vulnerable Zones in England for 2013 to 2016. PB13935 Defra, UK.

Department for Environment, Food and Rural Affairs (Defra). (2009) Construction Code of Practice for the Sustainable Use of Soils on Construction Sites, PB13298 Defra, UK.

Department for Environment, Food and Rural Affairs (Defra). (2007) Sources and impacts of past, current and future contamination of soil - SP0547. Defra Science Report. Defra, London, UK. <Online, available at: http://randd.defra.gov.uk/Default.aspx?Menu=Menu&Module=More&Location=None&ProjectID=13317&FromSearch=Y&Publisher=1&SearchText=SP0547&SortString=ProjectCode&SortOrder=Asc&Paging=10#Description >

Devi, P., & Saroha, A. K. (2014). Risk analysis of pyrolyzed biochar made from paper mill effluent treatment plant sludge for bioavailability and eco-toxicity of heavy metals. *Bioresource Technology*, **162**, 308-315.

Ding, Y., Liu, Y. X., Wu, W. X., Shi, D. Z., Yang, M., & Zhong, Z. K. (2010). Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. *Water, Air, & Soil Pollution*, **213**(1-4), 47-55.

Dong, X., Ma, L. Q., & Li, Y. (2011). Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. *Journal of Hazardous Materials*, **190**(1), 909-915.

Donovan, S. M., Bateson, T., Gronow, J. R., & Voulvoulis, N. (2010). Characterization of Compost-Like Outputs from Mechanical Biological Treatment of Municipal Solid Waste. *Journal of the Air & Waste Management Association*, **60**(6), 694-701.

Downie, A., Crosky, A. & Munroe. (2009) Physical Properties of Biochar. In: Lehmann, J. & Joseph, S. (Eds.) (2009). *Biochar for Environmental Management: Science and Technology*. London, UK: Earthscan, 13-32.

Du Laing, G. (2010). Analysis and fractionation of trace elements in soils. *Trace Elements in Soils*. Chichester, UK: John Wiley and Sons, 53-70.

Environment Agency. (2011). Sustainable management of biowastes: Compost-Like Output from Mechanical Biological Treatment of mixed source municipal wastes. <Online, available at: http://www.wamitab.org.uk/useruploads/files/waste/waste_resources/ea_documents/sustainable_management_of_biowastes.pdf>.

Environment Agency (2009). A review of human health and environmental risks associated with the land application of mechanical-biological treatment outputs. Science report: SC030144/SR2. Environment Agency, Bristol, UK. <Online, available at: http://publications.environment-agency.gov.uk/pdf/SCHO0609BQER-e-e.pdf >.

Environment Agency (2005). Guidance on sampling and testing of wastes to meet landfill waste acceptance procedures.

Epstein, E., & Bloom, A. J. (2005). *Mineral Nutrition of Plants: Principles and Perspectives*. 2nd ed. Sunderland, MA, USA: Sinauer Associates, Inc.

Eschenbach, A., Mescher, H., Wienberg, R., & Mahro, B. (2001). Humification of PAH and TNT during bioremediation—evaluation of long term risk and sustainability. In: *Treatment of Contaminated Soil*, pp. 271-291. Springer Berlin Heidelberg.

European Commission (EC). (2010). Communication from the Commission to the Council and the European Parliament on Future Steps in Bio-Waste Management in the European Union. <Online, available at: http://ec.europa.eu/environment/waste/compost/pdf/com_biowaste.pdf>.

European Commission (EC). (2003). Applying Compost Benefits and Needs. Seminar Proceedings Brussels, 22 – 23 November 2001. Federal Ministry of Agriculture, Forestry, Environment and Water Management, Austria, and European Communities, 2003. ISBN 3-902 338-26-1. <Online, available at: http://ec.europa.eu/environment/waste/pdf_comments/040119_proceedings.pdf>

European Environment Agency (EEA). (2009). Diverting waste from landfill. Effectiveness of waste-management policies in the European Union. <online, available at: http://www.eea.europa.eu/publications/diverting-waste-from-landfill-effectiveness-of-waste-management-policies-in-the-european-union>.

Evanylo, G., Sherony, C., Spargo, J., Starner, D., Brosius, M., & Haering, K. (2008). Soil and water environmental effects of fertilizer-, manure-, and compost-based fertility practices in an organic vegetable cropping system.*Agriculture, Ecosystems & Environment*, **127**(1), 50-58.

Fabrizio, A., Tambone, F., & Genevini, P. (2009). Effect of compost application rate on carbon degradation and retention in soils. *Waste Management*, **29**(1), 174-179.

Fahd, S., Fiorentino, G., Mellino, S., & Ulgiati, S. (2012). Cropping bioenergy and biomaterials in marginal land: The added value of the biorefinery concept. *Energy*, **37**(1), 79-93.

Farrell, M., & Jones, D.L., (2010). Use of composts in the remediation of heavy metal contaminated soil. *Journal of Hazardous Materials.* **175**, 575-582.

Farrell, M., & Jones, D. L. (2009). Heavy metal contamination of a mixed waste compost: metal speciation and fate. *Bioresource Technology*, **100**(19), 4423-4432.

Farrell, M., Perkins, W. T., Hobbs, P. J., Griffith, G. W., & Jones, D. L. (2010). Migration of heavy metals in soil as influenced by compost amendments. *Environmental Pollution*, **158**(1), 55-64.

Faz, A., Carmona, D. M., Zanuzzi, A., & Mermut, A. R. (2008). Pig manure application for remediation of mine soils in Murcia Province, SE Spain. *The Scientific World Journal*, **8**, 819-827.

Fellet, G., Marchiol, L., Delle Vedove, G., & Peressotti, A. (2011). Application of biochar on mine tailings: effects and perspectives for land reclamation. *Chemosphere*, **83**(9), 1262-1267.

Fenton, G. & Conyers, M. (2002*). Interpreting soil tests for calcium, magnesium and Ca:Mg ratios*. Pamphlet prepared for the New South Wales Acid Soil Action Program. <Online, available at: http://www.dpi.nsw.gov.au/__data/assets/pdf_file/0005/166415/ca-mg-test-ratios.pdf>.

Fernandez, E., Jimenez, R., Lellena, A.M., Aguilar, J. (2004). Evaluation of the BCR sequential extraction procedure applied to two unpolluted Spanish soils. *Environmental Pollution.* **131;** 355-364.

Fischer, D., & Glaser, B. (2012). Synergisms between compost and biochar for sustainable soil amelioration. *Management of Organic Waste*, **10**, 167-198.

Flavel, T. C., & Murphy, D. V. (2006). Carbon and nitrogen mineralization rates after application of organic amendments to soil. *Journal of Environmental Quality*, **35**(1), 183-193.

Fleming, M., Tai, Y., Zhuang, P., & McBride, M. (2013). Extractability of Pb and As in historically contaminated orchard soil: Effects of compost amendments, *Environmental Pollution*, **177,** 90-97.

Fontaine, S., Barot, S., Barré, P., Bdioui, N., Mary, B., & Rumpel, C. (2007). Stability of organic carbon in deep soil layers controlled by fresh carbon supply. *Nature*, **450**(7167), 277-280.

Foot, K. & Sinnett, D. (2006). Imported Soil or Soil-Forming Materials Placement. Best Practice Guidance for Land Regeneration, BPG Note 5. Forest Research, Farnham. <Online, available at: http://www.forestry.gov.uk/pdf/LRU_BPG05.pdf/$FILE/LRU_BPG05.pdf>.

Forest Research (2009). Complete Cultivation, BPG NOTE 13 Best Practice Guidance for Land Regeneration. <Online, available at: http://www.forestry.gov.uk/fr/URGC-7EDCEA>.

Gajić, A., & Koch, H. J. (2012). Sugar beet (*Beta vulgaris* L.) growth reduction caused by hydrochar is related to nitrogen supply. *Journal of Environmental Quality*, **41**(4), 1067-1075.

Gandolfi, I., Sicolo, M., Franzetti, A., Fontanarosa, E., Santagostino, A., & Bestetti, G. (2010). Influence of compost amendment on microbial community and ecotoxicity of hydrocarbon-contaminated soils. *Bioresource Technology*, **101**(2), 568-575.

García-Jaramillo, M., Cox, L., Cornejo, J., & Hermosín, M. C. (2014). Effect of soil organic amendments on the behavior of bentazone and tricyclazole. *Science of the Total Environment*, **466**, 906-913.

Gaskin, J. W., Speir, R. A., Harris, K., Das, K. C., Lee, R. D., Morris, L. A., & Fisher, D. S. (2010). Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. *Agronomy Journal*, **102**(2), 623-633.

Gelfand, I., Sahajpal, R., Zhang, X., Izaurralde, R. C., Gross, K. L., & Robertson, G. P. (2013). Sustainable bioenergy production from marginal lands in the US Midwest. *Nature*, **493**(7433), 514-517.

Gerçel, H. F. (2002). The production and evaluation of bio-oils from the pyrolysis of sunflower-oil cake. *Biomass and Bioenergy*, **23**(4), 307-314.

Giusquiani, P. L., Concezzi, L., Businelli, M., & Macchioni, A. (1998). Fate of pig sludge liquid fraction in calcareous soil: agricultural and environmental implications. *Journal of Environmental quality*, **27**(2), 364-371.

Gomez-Eyles, J. L., Beesley, L., Moreno-Jimenez, E., Ghosh, U. & Sizmur, T. (2013). The Potential of Biochar Amendments to Remediate Contaminated Soils. In: Ladygina, N & Rineau, F. (2013). *Biochar and Soil Biota*, FL, U.S.A: CRC Press.

Grispen, V. M. J., Nelissen, H. J. M., & Verkleij, J. A. C. (2006). Phytoextraction with *Brassica napus* L.: A tool for sustainable management of heavy metal contaminated soils. *Environmental Pollution*, **144**, 77-83.

Gurwick, N. P., Moore, L. A., Kelly, C., & Elias, P. (2013). A systematic review of biochar research, with a focus on its stability in situ and its promise as a climate mitigation strategy. *PloS one*, **8**(9), e75932.

Haefele, S. M., Konboon, Y., Wongboon, W., Amarante, S., Maarifat, A. A., Pfeiffer, E. M., & Knoblauch, C. (2011). Effects and fate of biochar from rice residues in rice-based systems. *Field Crops Research*, **121**(3), 430-440.

Hale, S., Hanley, K., Lehmann, J., Zimmerman, A., & Cornelissen, G. (2011). Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. *Environmental Science & Technology*, **45**(24), 10445-10453.

Hammond, J., Shackley, S., Sohi, S., & Brownsort, P. (2011). Prospective life cycle carbon abatement for pyrolysis biochar systems in the UK. *Energy Policy*, **39**(5), 2646-2655.

Hansmann, R., Mieg, H. A., & Frischknecht, P. (2012). Principal sustainability components: empirical analysis of synergies between the three pillars of sustainability. *International Journal of Sustainable Development & World Ecology*, **19**(5), 451-459.

Harbottle, M. J., Al-Tabbaa, A., & Evans, C. W. (2008). Sustainability of land remediation. Part 2: impact assessment. *Proceedings of the ICE-Geotechnical Engineering*, **161**(3), 117-127.

Harbottle, M. J., Al-Tabbaa, A., & Evans, C. W. (2007). A comparison of the technical sustainability of in situ stabilisation/solidification with disposal to landfill. *Journal of Hazardous Materials*, **141**(2), 430-440.

Hargreaves, J. C., Adl, M. S., & Warman, P. R. (2008). A review of the use of composted municipal solid waste in agriculture. *Agriculture, Ecosystems & Environment*, **123**(1), 1-14.

Harmsen, J. (2007). Measuring bioavailability: from a scientific approach to standard methods. *Journal of Environmental Quality*, **36**(5), 1420-1428.

Hartley, W., Dickinson, N. M., Riby, P., & Lepp, N. W. (2009). Arsenic mobility in brownfield soils amended with green waste compost or biochar and planted with *Miscanthus*. *Environmental Pollution*, **157**(10), 2654-2662.

Hartley, W., Edwards, R., & Lepp, N. W. (2004). Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short-and long-term leaching tests. *Environmental Pollution*, **131**(3), 495-504.

Hasse, J. E., & Lathrop, R. G. (2003). Land resource impact indicators of urban sprawl. *Applied Geography*, **23**(2), 159-175.

Haynes, R. J., & Swift, R. S. (1991). Concentrations of extractable Cu, Zn, Fe and Mn in a group of soils as influenced by air-and oven-drying and rewetting. *Geoderma*, **49**(3), 319-333.

He, Y. D., Zhai, Y. B., Li, C. T., Yang, F., Chen, L., Fan, X. P., Peng, W. F., & Fu, Z. M. (2010). The fate of Cu, Zn, Pb and Cd during the pyrolysis of sewage sludge at different temperatures. *Environmental Technology*, 31(5), 567-574.

Houben, D., Evrard, L., & Sonnet, P. (2013). Beneficial effects of biochar application to contaminated soils on the bioavailability of Cd, Pb and Zn and the biomass production of rapeseed (*Brassica napus* L.). *Biomass and Bioenergy*, **57**, 196-204.

Hsu, J. H., & Lo, S. L. (2000). Characterization and extractability of copper, manganese, and zinc in swine manure composts. *Journal of Environmental Quality*, **29**(2), 447-453.

Husk, B. & Major, J. (2010). Commercial scale agricultural biochar field trial in Québec, Canada, over two years: Effects of biochar on soil fertility, biology, crop productivity and quality. <Online, available at: http://www.blue-leaf.ca/main-en/files/BlueLeaf%20Biochar%20Field%20Trial%2008-09%20Report-1.pdf>

Hwang, T., & Neculita, C. M. (2013). In Situ Immobilization of Heavy Metals in Severely Weathered Tailings Amended with Food Waste-Based Compost and Zeolite. *Water, Air, & Soil Pollution*, **224**(1), 1-9.

Hwang, I. H., Ouchi, Y., & Matsuto, T. (2007). Characteristics of leachate from pyrolysis residue of sewage sludge. *Chemosphere*, **68**(10), 1913-1919.

International Panel on Climate Change (IPCC) (2014). Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Edenhofer, O., Pichs-Madruga, R., Sokona, Y., Farahani, E., Kadner, S., Seyboth, K., Adler, A., Baum, I., Brunner, S., Eickemeier, P., Kriemann, B., Savolainen, J., Schlömer, S. von Stechow, C. Zwickel, T. & Minx, J.C. (eds.) Cambridge, United Kingdom & New York, NY, USA: Cambridge University Press.

Ippolito, J. A., Laird, D. A., & Busscher, W. J. (2011). Environmental benefits of biochar. *Journal of Environmental Quality*, **41**(4), 967-972.

Jia, J., Li, B., Chen, Z., Xie, Z., & Xiong, Z. (2012). Effects of biochar application on vegetable production and emissions of N_2O and CH_4. *Soil Science and Plant Nutrition*, **58**(4), 503-509.

Jin, H., Arazo, R. O., Gao, J., Capareda, S., & Chang, Z. (2014). Leaching of heavy metals from fast pyrolysis residues produced from different particle sizes of sewage sludge. *Journal of Analytical and Applied Pyrolysis*, **109**, 168-175.

Kacprzak, M., Grobelak, A., Grosser, A., & Prasad, M. N. V. (2014). Efficacy of Biosolids in Assisted Phytostabilization of Metalliferous Acidic Sandy Soils with Five Grass Species. *International Journal of Phytoremediation*, **16**(6), 593-608.

Kammann, C. I., Linsel, S., Gößling, J. W., & Koyro, H. W. (2011). Influence of biochar on drought tolerance of Chenopodium quinoa Willd and on soil–plant relations. *Plant and Soil*, **345**(1-2), 195-210.

Karami, N., Clemente, R., Moreno-Jiménez, E., Lepp, N. W., & Beesley, L. (2011). Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. *Journal of Hazardous Materials*, **191**(1), 41-48.

Kashem, M. A., & Singh, B. R. (2001). Metal availability in contaminated soils: I. Effects of floodingand organic matter on changes in Eh, pH and solubility of Cd, Ni and Zn. *Nutrient Cycling in Agroecosystems*, **61**(3), 247-255.

Kauffman, N., Dumortier, J., Hayes, D. J., Brown, R. C., & Laird, D. A. (2014). Producing energy while sequestering carbon? The relationship between biochar and agricultural productivity. *Biomass and Bioenergy*, **63**, 167-176.

Keeney, D. R., & Nelson, D.W. (1982). Inorganic forms of nitrogen. In: A.L. Page (Ed.) *Methods of Soil Analysis: Part 2*. Madison, WI, USA: American Society of Agronomy, pp. 643e698.

Keiluweit, M., Kleber, M., Sparrow, M. A., Simoneit, B. R., & Prahl, F. G. (2012). Solvent-extractable polycyclic aromatic hydrocarbons in biochar: influence of pyrolysis temperature and feedstock. *Environmental Science & Technology*, *46*(17), 9333-9341.

Kiikkilä, O., Pennanen, T., Perkiömäki, J., Derome, J., & Fritze, H. (2002). Organic material as a copper immobilising agent: a microcosm study on remediation. *Basic and Applied Ecology*, **3**(3), 245-253.

Khalil, M. I., Hossain, M. B., & Schmidhalter, U. (2005). Carbon and nitrogen mineralization in different upland soils of the subtropics treated with organic materials. *Soil Biology and Biochemistry*, **37**(8), 1507-1518.

Khan, S., Chao, C., Waqas, M., Arp, H. P. H., & Zhu, Y. G. (2013). Sewage sludge biochar influence upon rice (Oryza sativa L) yield, metal bioaccumulation and greenhouse gas emissions from acidic paddy soil. *Environmental Science & Technology*, **47**(15), 8624-8632.

Kızılkaya, R. (2004). Cu and Zn accumulation in earthworm *Lumbricus terrestris* L. in sewage sludge amended soil and fractions of Cu and Zn in casts and surrounding soil. *Ecological Engineering*, **22**(2), 141-151.

Kleiner, K. (2009). The bright prospect of biochar. *Nature Reports Climate Change*, **3**, 72-74.

Kloss, S., Zehetner, F., Buecker, J., Oburger, E., Wenzel, W. W., Enders, A., Lehmann, J. & Soja, G. (2014). Trace element biogeochemistry in the soil-water-plant system of a temperate agricultural soil amended with different biochars. *Environmental Science and Pollution Research*. DOI 10.1007/s11356-014-3685-y.

Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V., Schwanninger, M., Gerzabek, M. H. & Soja, G. (2012). Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties. *Journal of Environmental Quality*, **41**(4), 990-1000.

Kolbas, A., Marchand, L., Herzig, R., Nehnevajova, E., & Mench, M. (2014). Phenotypic seedling responses of a metal-tolerant mutant line of sunflower growing on a Cu-contaminated soil series: potential uses for biomonitoring of Cu exposure and phytoremediation. *Plant and Soil*, **376**(1-2), 377-397.

Kolbas, A., Marchand., L., Herzig, R., Nehnevajova, & Mench. M. (2013). Phenotypic seedlings responses of a metal-tolerant mutant line of sunflower growing on a Cu-contaminated soil series: potential uses for a biomonitoring of Cu exposure and phytoremediation, *Plant Soil*, **13,** 1974-1978.

Kolbas, A., Mench, M., Herzig, R., Nehnevajova, E., & Bes, C. M. (2011). Copper phytoextraction in tandem with oilseed production using commercial cultivars and mutant lines of sunflower. *International journal of phytoremediation*, **13**(sup1), 55-76.

Kong, L. L., Liu, W. T., & Zhou, Q. X. (2014). Biochar: An Effective Amendment for Remediating Contaminated Soil. In *Reviews of Environmental Contamination and Toxicology*, **228**, 83-99.

Kookana, R. S. (2010). The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review. *Soil Research*, **48**(7), 627-637.

Kumpiene, J., Lagerkvist, A., & Maurice, C. (2008). Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments–a review. *Waste management*, **28**(1), 215-225.

Kumpiene, J., Mench, M., Bes, C. M. and Fitts, J. P. (2011). Assessment of aided phytostabilization of copper-contaminated soil by X-ray absorption spectroscopy and chemical extractions, *Environmental Pollution*, **159,** 1536-1542.

Lagomarsino, A, Mench, M., Marabottini, R., Pignataro, A., Grego, S., Renella, G. and Stazi, S. R. (2011). Copper distribution and hydrolase activities in a contaminated soil amended with dolomitic limestone and compost, *Ecotoxicology and Environmental Safety*, **74**, 2013-2019.

Laird, D. A. (2008). The charcoal vision: a win–win–win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. *Agronomy Journal*, **100**(1), 178-181.

Leggo, P. J. (2013). Enhancing the Growth of Plants on Coal Waste Using a Biological Fertilizer. *International Journal of Environment and Resource*, **2**(3), 59-66.

Lehmann, J. & Joseph, S. (2009). Biochar for Environmental Management: An Introduction. In: Lehmann, J. & Joseph, S. (Eds.) (2009). *Biochar for Environmental Management: Science and Technology*. London, UK: Earthscan, 1-12.

Lehmann, J., Rillig, M. C., Thies, J., Masiello, C. A., Hockaday, W. C., & Crowley, D. (2011). Biochar effects on soil biota–a review. *Soil Biology and Biochemistry*, **9**, 1812-1836.

Lehmann, J., & Rondon, M. (2006). Bio-char soil management on highly weathered soils in the humid tropics. *Biological approaches to sustainable soil systems.* FL, USA: CRC Press, 517-530.

Lehmann, J., da Silva Jr, J. P., Steiner, C., Nehls, T., Zech, W., & Glaser, B. (2003). Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. *Plant and soil*, **249**(2), 343-357.

Leifeld, J., Siebert, S., & Kögel-Knabner, I. (2002). Changes in the chemical composition of soil organic matter after application of compost. *European Journal of Soil Science*, **53**(2), 299-309. In: Ippolito, J. A., Laird, D. A., & Busscher, W. J. (2011). Environmental benefits of biochar. *Journal of Environmental Quality*, **41**(4), 967-972.

Lepp, N. W. (1981). Copper. In: *Effect of heavy metal pollution on plants*. Vol. 1. London, UK: Applied Science Publications, 111-143.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'neill, B., Skjemstad, O., Thies, J., Luizão, F. J., Petersen, J. & Neves, E. G. (2006). Black carbon increases cation exchange capacity in soils. *Soil Science Society of America Journal*, *70*(5), 1719-1730.

Liu, L., Chen, H., Cai, P., Liang, W., & Huang, Q. (2009). Immobilization and phytotoxicity of Cd in contaminated soil amended with chicken manure compost. *Journal of Hazardous Materials*, **163**(2), 563-567.

Lock, K. & Janssen, C. R. (2003). Influence of aging on copper bioavailability in soils. *Environmental Toxicology and Chemistry,* **22**(5), 1162-1166.

Long, Y. Y., Hu, L. F., Fang, C. R., Wu, Y. Y. & Shen, D. S. (2009). An evaluation of the modified BCR sequential extraction procedure to assess the potential mobility of copper and zinc, *Microchemical Journal,* **91,** 1-5.

Lu, A., Shang, S., Qin, X., Wu, Y., Lui, H. (2009). Ageing effect on the mobility and bioavailability of copper in soil, *Journal of Environmental Science,* **21,** 173-178.

Lu, K., Yang, X., Shen, J., Robinson, B., Huang, H., Lui, D., Bolan, N., Pei, J., Wang. (2014). Effects of bamboo and rise straw biochars on the bioavailability of Cd, Cu, Pb and Zn to *Sedum plumbizinicola, Agriculture, Ecosystems and the Environment,* **191,** 124-132.

Lucchini, P., Quilliam, R. S., DeLuca, T. H., Vamerali, T., & Jones, D. L. (2014a). Does biochar application alter heavy metal dynamics in agricultural soil? *Agriculture, Ecosystems & Environment*, **184**, 149-157.

Lucchini, P., Quilliam, R. S., DeLuca, T. H., Vamerali, T., & Jones, D. L. (2014b). Increased bioavailability of metals in two contrasting agricultural soils treated with waste wood-derived biochar and ash. *Environmental Science and Pollution Research*, **21**(5), 3230-3240.

Lui, G., Tao, L., Lui, X., Hou, J., Wang, A., Li, R. (2013). Heavy metal speciation and pollution of agricultural soils along Jishui River in a non-ferrous metal mine area in Jiangxi Province, China, *Journal of Geochemical Exploration*, **132**, 156-163.

Luo, Y., Durenkamp, M., De Nobili, M., Lin, Q., & Brookes, P. C. (2011). Short term soil priming effects and the mineralisation of biochar following its incorporation to soils of different pH. *Soil Biology and Biochemistry*, **43**(11), 2304-2314.

MacNicol, R. D., & Beckett, P. H. T. (1985). Critical tissue concentrations of potentially toxic elements, *Plant and Soil*, **85**, 107-129.

Major, J., Rondon, M., Molina, D., Riha, S. J., & Lehmann, J. (2010). Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. *Plant and Soil*, **333**(1-2), 117-128.

Mallik, A. U., & Karim, M. N. (2008). Roadside revegetation with native plants: Experimental seeding and transplanting of stem cuttings. *Applied Vegetation Science*, **11**(4), 547-554.

Manning, D. A. C., Renforth, P., Lopez-Capel, E., Robertson, S., & Ghazireh, N. (2013). Carbonate precipitation in artificial soils produced from basaltic quarry fines and composts: An opportunity for passive carbon sequestration.*International Journal of Greenhouse Gas Control*, **17**, 309-317.

Mašek, O., Brownsort, P., Cross, A., & Sohi, S. (2013). Influence of production conditions on the yield and environmental stability of biochar. *Fuel*, **103**, 151-155.

Mata-Alvarez, J., Mace, S., & Llabres, P. (2000). Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresource Technology*, **74**(1), 3-16.

McBride, M. B. (1994). *Environmental chemistry of soils.* Oxford, UK: Oxford University Press.

McLaughlin H., Anderson, P. S., Shields, F. E., & Reed, T. B. (2009). All biochars are not created equal and how to tell them apart: Version 2 (October 2009): supersedes the digital reprint issued at the North American Biochar Conference, Boulder, CO – August 2009. <Online, available at: http://www.biochar-international.org/sites/default/files/All-Biochars--Version2--Oct2009.pdf>.

Megharaj, M., Ramakrishnan, B., Venkateswarlu, K., Sethunathan, N., & Naidu, R. (2011). Bioremediation approaches for organic pollutants: A critical perspective. *Environmental International*, **37**, 1362-1375.

Mench, M., & Bes, C. (2009). Assessment of the ecotoxicity of topsoils from a wood treatment site. *Pedosphere*, **19**, 143-155.

Mench, M., Kolbas, A., Marchand, L., Bes, C., Atziria, A., Oustriere, N., Hego, E., Sureau, M., Nibaudeau, M., Rousseau, F., Laffontas, C., Kolbas, N., Herzig, R., Motelica-Heino, M., Hattab, N., Pang, M., Puschenreiter, M. (2013). Solutions de phytoremédiation et pilotes de démonstration sur la plate-forme de phytoremediation BIOGECO (PHYTODEMO) (*Phytoremediation options and trial demonstration on the BIOGECO phytoremediation platform - PHYTODEMO*). Rapport final Convention ADEME 09 72 C0076 / INRA 22000460, Ademe, Département Friches industrielles et sols pollués. 131 p.

Mench, M., Lepp, N., Bert, V., Schwitzguébel, J. P., Gawronski, S. W., Schröder, P., & Vangronsveld, J. (2010). Successes and limitations of phytotechnologies at field scale: outcomes, assessment and outlook from COST Action 859. *Journal of Soils and Sediments*, **10**(6), 1039-1070.

Menger, P., Bardos, P., Ferber, U., Neonato, F., Maring, L. Beumer, V., Track, T., Wendler, K. (2013). Valuation approach for services from regeneration of Brownfields for soft re-use on a permanent or interim basis. HOMBRE Deliverable D5.1. www.zerobrownfields.eu DOI: 10.13140/2.1.3456.4807.

Merckx, R., Brans, K., & Smolders, E. (2001). Decomposition of dissolved organic carbon after soil drying and rewetting as an indicator of metal toxicity in soils. *Soil Biology and Biochemistry*, **33**(2), 235-240.

Mkhabela, M. S., & Warman, P. R. (2005). The influence of municipal solid waste compost on yield, soil phosphorus availability and uptake by two vegetable crops grown in a Pugwash sandy loam soil in Nova Scotia. *Agriculture, Ecosystems & Environment*, **106**(1), 57-67.

Mohan, D., Sarswat, A., Ok, Y. S., & Pittman Jr, C. U. (2014). Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent–a critical review. *Bioresource Technology*, **160**, 191-202.

Montemurro, F., Maiorana, M., Convertini, G., & Ferri, D. (2006). Compost organic amendments in fodder crops: effects on yield, nitrogen utilization and soil characteristics. *Compost Science & Utilization*, **14**(2), 114-123.

Moreno-Jimenez, E., Beesley, L., Lepp, N.W., Dickinson, N.M., Hartley, W., & Clemente, R. (2011). Field sampling of soil pore water to evaluate trace element mobility and associated environmental risk, *Environmental Pollution,* **159,** 3078-3085.

Mulligan, C.N., Yong, R.N., Gibbs, B.F. (2001). Remediation technologies for metal contaminated soils and groundwater: an evaluation. *Engineering Geology*, **60**, 193-207.

Mukherjee, A., & Lal, R. (2014). The biochar dilemma. *Soil Research*, **52**(3), 217-230.

Namgay, T., Singh, B., & Singh, B. P. (2010). Influence of biochar application to soil on the availability of As, Cd, Cu, Pb, and Zn to maize (Zea mays L.). *Soil Research*, **48**(7), 638-647.

Nascimento, C. W. A., Fontes, R. L. F., & Melicio, A. C. F. D. (2001). Availability as related to copper fractions in oxisols under liming, *Scientia Agricola,* **60,** 167-173.

Nason, M., Williamson, J.,Tandy, S., Christou, M., Jones, D. & Healey, J. (2007). Using organic wastes and composts to remediate and restore land: best practice manual. School of the Environment and Natural Resources, Bangor University. ISBN: 978-1-84220-101-5. <Online, available at: http://ies.bangor.ac.uk/TWIRLS/Web%20version%20Manual.pdf>.

Nathanail, C. P. Bardos, R. P., Gillett, A., Mccaffrey, C., Ogden, R., Scott, D., & Nathanail, J. (2013). SP1004 International Processes for Identification and Remediation of

Contaminated Land <Online, available at: http://randd.defra.gov.uk/Default.aspx?Menu=Menu&Module=More&Location=None&Completed=0&ProjectID=16289#Description>

Nathanail, J., Bardos, P, & Nathanail, P. (2007) *Contaminated Land Management Ready Reference*. Update EPP Publications/ Land Quality Press. London, UK: EPP Publications. www.readyreference.co.uk.

Nixon, D. J., Stephens, W., Tyrrel, S. F., & Brierley, E. D. R. (2001). The potential for short rotation energy forestry on restored landfill caps. *Bioresource Technology*, **77**(3), 237-245.

Novak, J. M., Lima, I., Xing, B., Gaskin, J. W., Steiner, C., Das, K. C., Ahmedna, M., Rehrah, D., Watts, D. W., Busscher, W. J., & Schomberg, H. (2009). Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Annals of Environmental Science*, **3**(1), 2.

O'Carroll, D., Sleep, B., Krol, M., Boparai, H., & Kocur, C. (2013). Nanoscale zero valent iron and bimetallic particles for contaminated site remediation, *Advances in Water Resources*, **51**, 104-122.

Ohsowski, B.M., Klironomos, J.N., Dunfield, K.E., Hart, M.M. (2012). Potential of soil amendments for restoring severely disturbed grasslands. *Applied Soil Ecology*. **60**, 77-83.

Olajire, A. A. (2013). A review of mineral carbonation technology in sequestration of CO_2. *Journal of Petroleum Science and Engineering*, **109,** 364-392.

Oleszczuk, P., Jośko, I., & Kuśmierz, M. (2013). Biochar properties regarding to contaminants content and ecotoxicological assessment. *Journal of Hazardous Materials*, **260**, 375-382.

Onwubuya, K., Cundy, A., Puschenreiter, M., Kumpiene, J., Bone, B., Greaves, J., Teasdale, P., Mench, M., Tlustos, P., Mikhalovsky, S. Waite, S., Friesl-Hanl, W., Marschner, B. & Mueller, I. (2009). Developing decision support tools for the selection of "gentle" remediation approaches. *Science of the Total Environment*, **407**(24), 6132-6142.

Oustrière, N., Mench, M., Marchand, L., Bouchardon, J.-L., & Faure, O. (2014). Phytomanagement of a metal-contaminated technosol. Abstract: International Congress of Phytoremediation of Polluted Soils. <Online, available at: http://webs.uvigo.es/phytorem.congress/Abstracts%20book%20-%20PPS%202014.pdf>.

Özçimen, D., & Ersoy-Meriçboyu, A. (2010). Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. *Renewable Energy*, **35**(6), 1319-1324.

Pagliai, M., Vignozzi, N., & Pellegrini, S. (2004). Soil structure and the effect of management practices. *Soil and Tillage Research*, **79**(2), 131-143.

Pardo, T., Clemente, R., Alvarenga, P., & Bernal, M.P. (2014). Efficiency of soil organic and inorganic amendments on the remediation of a contaminated mine soil: II Biological and ecotoxiclogical evaluation, *Chemosphere*, **107,** 101-108.

Park, J. H., Choppala, G. K., Bolan, N. S., Chung, J. W., & Chuasavathi, T. (2011). Biochar reduces the bioavailability and phytotoxicity of heavy metals. *Plant and Soil*, **348**(1-2), 439-451.

Pellera, F. M., Giannis, A., Kalderis, D., Anastasiadou, K., Stegmann, R., Wang, J. Y., & Gidarakos, E. (2012). Adsorption of Cu (II) ions from aqueous solutions on biochars prepared from agricultural by-products. *Journal of Environmental Management*, **96**(1), 35-42.

Petersen, S. O., Henriksen, K., Mortensen, G. K., Krogh, P. H., Brandt, K. K., Sørensen, J., Madsen, T., Petersen, J. & Grøn, C. (2003). Recycling of sewage sludge and household compost to arable land: fate and effects of organic contaminants, and impact on soil fertility. *Soil and Tillage Research*, **72**(2), 139-152.

Powlson, D. S., Whitmore, A. P., & Goulding, K. W. T. (2011). Soil carbon sequestration to mitigate climate change: a critical re-examination to identify the true and the false. *European Journal of Soil Science*, **62**(1), 42-55.

Prendergast-Miller, M. T., Duvall, M., & Sohi, S. P. (2014). Biochar–root interactions are mediated by biochar nutrient content and impacts on soil nutrient availability. *European Journal of Soil Science*, **65**(1), 173-185.

Prognos. (2008)European Atlas of Secondary Raw Material. 2004 status quo and potentials. <Online, available at: http://www.pius-info.de/files/prognos.pdf>.

Puschenreiter, M., and the SUMATECS consortium (2009). Sustainable management of trace element contaminated soils – Development of a decision tool system and its evaluation for practical application, Final report, Project No. SN-01/20, 2009 (SNOWMAN-ERANET). <Online, available at: www.snowman-era.net/downloads/SUMATECS_FINAL_REPORT.pdf>

Qian, K., Kumar, A., Patil, K., Bellmer, D., Wang, D., Yuan, W., & Huhnke, R. L. (2013). Effects of Biomass Feedstocks and Gasification Conditions on the Physiochemical Properties of Char. *Energies*, **6**(8), 3972-3986.

Quilliam, R. S., Marsden, K. A., Gertler, C., Rousk, J., DeLuca, T. H., & Jones, D. L. (2012). Nutrient dynamics, microbial growth and weed emergence in biochar amended soil are influenced by time since application and reapplication rate. *Agriculture, Ecosystems & Environment*, **158**, 192-199.

Redman, A. D., Macalady, D. L., & Ahmann, D. (2002). Natural organic matter affects arsenic speciation and sorption onto hematite. *Environmental Science & Technology*, **36**(13), 2889-2896.

Ro, K. S., Cantrell, K. B., & Hunt, P. G. (2010). High-temperature pyrolysis of blended animal manures for producing renewable energy and value-added biochar. *Industrial & Engineering Chemistry Research*, **49**(20), 10125-10131.

Römkens, P. F. A. M., Bouwman, L. A., & Boon, G. T. (1999). Effect of plant growth on copper solubility and speciation in soil solution samples. *Environmental Pollution*, **106**(3), 315-321.

Ross, S.M. (1996). Retention, transformation and mobility of toxic metals in soils. In Ross, S.M. (1996). *Toxic metals in soil-plant systems*. Chichester, UK: John Wiley and Sons Ltd.

Rowell, D. L. (1994). *Soil Science Methods and Applications.* Harlow: Addison Wesley Longman.

Rulkens, W. H. (2004) Overview of resource recovery technologies for biowastesIn: Lens, P., Hamelers, B, Hoitink, H., & Bidlingmaier, W. (eds.) (2004). *Resource Recovery and Reuse in Organic Solid Waste Management.*r London, UK: IWA Publishing, 225-261.

Ruttens, A., Mench, M., Colpaert, J. V., Boisson, J., Carleer, R., & Vangronsveld, J. (2006). Phytostabilization of a metal contaminated sandy soil. I: Influence of compost and/or inorganic metal immobilizing soil amendments on phytotoxicity and plant availability of metals. *Environmental Pollution*, **144**(2), 524-532.

Samsoe-Petersen, L., Larsen, E.H., Larsen, P.B., Bruun P. (2002). Uptake of trace elements and PAHs by fruit and vegetables from contaminated soils. *Environmental Science and Technology*, **36,** 3057-3063.

Sanderman, J., Baldock, J. A., & Amundson, R. (2008). Dissolved organic carbon chemistry and dynamics in contrasting forest and grassland soils, *Biogeochemistry*, **89,** 181-198.

Savard, J. P. L., Clergeau, P., & Mennechez, G. (2000). Biodiversity concepts and urban ecosystems. *Landscape and urban planning*, **48**(3), 131-142.

Scalenghe, R., & Marsan, F. A. (2009). The anthropogenic sealing of soils in urban areas. *Landscape and Urban Planning*, **90**(1), 1-10.

Schmidt, H.-P., Kammann, C., Niggli, C., Evangelou, M.W.H., Mackie, K.A., Abiven, S. (2014). Biochar and biochar-compost as soil amendments to a vineyard soil: Influences on plant growth, nutrient uptake, plant health and grape quality, *Agriculture, Ecosystems and Environment*, **191**, 117-123.

Scotland and Northern Ireland Forum For Environmental Research (SNIFFER). (2010). Code of Practice for the use of sludge, compost and other organic materials for land reclamation Code ER11, also supporting Technical Document; <Online, available at: www.sniffer.org.uk/files/7413/4183/7993/ER11_Code_of_Practice.pdf>.

Scott, D. I., & Nathanail, C. P. (2004). Application of the operating window concept to remediation-option selection. *Remediation Journal*, **14**(3), 55-64.

Shackley, S., Hammond, J., Gaunt, J., & Ibarrola, R. (2011). The feasibility and costs of biochar deployment in the UK. *Carbon Management*, **2**(3), 335-356.

Shackley, S., Sohi, S., Brownsort, P., Carter, S., Cook, J., Cunningham, C., Gaunt, J., Hammond, J., Ibarrola, R. & Mašek, O. (2010). An assessment of the benefits and issues associated with the application of biochar to soil. *Report for Department for Environment, Food and Rural Affairs*, UK Government, London. <Online, available at: http://www.geos.ed.ac.uk/homes/sshackle/SP0576_final_report.pdf>.

Shackley, S., Sohi, S., Haszeldine, S., Manning, D., & Mašek, O. (2009). Biochar, reducing and removing CO2 while improving soils: A significant and sustainable response to climate change. *UK Biochar Research Centre, School of GeoSciences, University of Edinburgh*. <Online, available at: http://www.geos.ed.ac.uk/homes/sshackle/WP2.pdf>.

Sheldon, A. R. & Menzies, N. W. (2005). The effect of copper toxicity on the growth and root morphology of Rhodes grass (*Chloris gayana* Knuth.) in resin buffered solution culture, *Plant and Soil*, **278,** 341-349.

Shin, J., Lee, S. I., Park, W. K., Choi, Y. S., Hong, S. G., & Park, S. W. (2014). Carbon Sequestration in Soil Cooperated with Organic Composts and Bio-Char during Corn (Zea mays) Cultivation. *Journal of Agricultural Chemistry and Environment*, **3**(04), 151.

Singh, B. P., Hatton, B. J., Singh, B., Cowie, A. L., & Kathuria, A. (2010b). Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *Journal of Environmental Quality*, **39**(4), 1224-1235.

Singh, J., & Kalamdhad, A. S. Bioavailability and Leachability of Heavy Metals during Composting–A Review, *International Research Journal of Environment Sciences*, **2**(4), 59-64.

Singh, B., Singh, B. P., & Cowie, A. L. (2010a). Characterisation and evaluation of biochars for their application as a soil amendment. *Soil Research*, **48**(7), 516-525.

Sissoko, A., & Kpomblekou-A, K. (2010). Carbon decomposition in broiler litter-amended soils. *Soil Biology and Biochemistry*, **42**(4), 543-550.

Sizmur, T., Wingate, J., Hutchings, T., & Hodson, M. E. (2011). *Lumbricus terrestris L.* does not impact on the remediation efficiency of compost and biochar amendments. *Pedobiologia*, **54**, S211-S216.

Smith, S. R. (2009). A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge, *Environment International*, **35**, 142-156

Sneath, H., Wingate, J., Hutchings, T., & De Leij, F. (2009). Remediation of metal, arsenic and phenanthrene contaminated soil using charcoal and iron filings. *Geochimica Et Cosmochimica Acta*, **73**, A1243-A1243.

Sparling, G. P. (1997). Soil microbial biomass, activity and nutrient cycling as indicators of soil health. Pankhurst, C., Doube, B. M., & Gupta, V. V. S. R. (Eds.) *Biological Indicators of Soil Health.* Wallingford, UK: CAB International, 97-119.

Song, Q. J., & Greenway, G. M. (2004). A study of the elemental leachability and retention capability of compost. *Journal of Environmental Monitoring*, **6**(1), 31-37.

Spokas K. A. (2010). Review of the stability of biochar in soils: predictability of O:C molar ratios. *Carbon Management*, **1**(2), 289–303.

Spokas, K. A., Novak, J. M., & Venterea, R. T. (2012). Biochar's role as an alternative N-fertilizer: ammonia capture. *Plant and soil*, **350**(1-2), 35-42.

Stals, M., Thijssen, E., Vangronsveld, J., Carleer, R., Schreurs, S., & Yperman, J. (2010). Flash pyrolysis of heavy metal contaminated biomass from phytoremediation: Influence of temperature, entrained flow and wood/leaves blended pyrolysis on the behaviour of heavy metals. *Journal of Analytical and Applied Pyrolysis*, **87**(1), 1-7.

Stegmann, R., Lotter, S. & Heerenklage, J. (1991). Biological treatment of oil contaminated soils in a bioreactor. In: On-Site Bioreclamation Processes for Xenobiotic and Hydrocarbon Treatment (Hinchee, R.E. and Olfenbuttel, R. Eds), Butterworth-Heinemann, pp. 188-208.

Steiner, C., Teixeira, W. G., Lehmann, J., Nehls, T., de Macêdo, J. L. V., Blum, W. E., & Zech, W. (2007). Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant and Soil*, **291**(1-2), 275-290.

Stevenson, F.J. (1994). *Humus Chemistry – Genesis, Composition, Reactions* (2nd edition). Chichester, UK: John Wiley and Sons.

Streubel, J. D., Collins, H. P., Garcia-Perez, M., Tarara, J., Granatstein, D., & Kruger, C. E. (2011). Influence of contrasting biochar types on five soils at increasing rates of application. *Soil Science Society of America Journal*, **75**(4), 1402-1413.

Stewart, C. E., Paustian, K., Conant, R. T., Plante, A. F., & Six, J. (2008). Soil carbon saturation: Evaluation and corroboration by long-term incubations. *Soil Biology and Biochemistry*, **40**(7), 1741-1750.

SUMATECS Consortium (2008) Sustainable management of trace element contaminated soils – Development of a decision tool system and its evaluation for practical application Project No. SN-01/20. Final Report, version 2.0 Project of the SNOWMAN ERA-Net (Sustainable management of soil and groundwater under the pressure of soil pollution and soil contamination) <Online, available at: http://www.snowmannetwork.com/upload/documents/call1/SUMATECS_project_sheet.pdf>

Taghizadeh-Toosi, A., Clough, T. J., Condron, L. M., Sherlock, R. R., Anderson, C. R., & Craigie, R. A. (2011). Biochar incorporation into pasture soil suppresses in situ nitrous oxide emissions from ruminant urine patches. *Journal of Environmental Quality*, **40**(2), 468-476.

Taghizadeh-Toosi, A., Clough, T. J., Sherlock, R. R., & Condron, L. M. (2012). Biochar adsorbed ammonia is bioavailable. *Plant and Soil*, **350**(1-2), 57-69.

Tang, J., Zhu, W., Kookana, R., & Katayama, A. (2013). Characteristics of biochar and its application in remediation of contaminated soil. *Journal of Bioscience and Bioengineering*, **116**(6), 653-659.

Tang, Y. T., & Nathanail, C. P. (2012). Sticks and stones: the impact of the definitions of brownfield in policies on socio-economic sustainability. *Sustainability*, **4**(5), 840-862.

Tejada, M., Garcia, C., Gonzalez, J. L., & Hernandez, M. T. (2006). Use of organic amendment as a strategy for saline soil remediation: influence on the physical, chemical and biological properties of soil. *Soil Biology and Biochemistry*, **38**(6), 1413-1421.

Thies, J. E. & Rillig, M. C. (2009). Characteristics of Biochar: Biological Properties. In: Lehmann, J. & Joseph, S. (Eds.) (2009). *Biochar for Environmental Management: Science and Technology.* London, UK: Earthscan, 85-106.

Tighe, M., Lockwood, P., & Wilson, S. (2005). Adsorption of antimony (V) by floodplain soils, amorphous iron (III) hydroxide and humic acid. *Journal of Environmental Monitoring*, **7**(12), 1177-1185.

Tong, X. J., Li, J. Y., Yuan, J. H., & Xu, R. K. (2011). Adsorption of Cu (II) by biochars generated from three crop straws. *Chemical Engineering Journal*, **172**(2), 828-834.

Trakal, L., Šigut, R., Šillerová, H., Faturíková, D., & Komárek, M. (2014). Copper removal from aqueous solution using biochar: Effect of chemical activation. *Arabian Journal of Chemistry*, **7**(1), 43-52.

Troeh, F. R. & Thompson, L. M. (2005) *Soils and Soil Fertility*. Iowa, US: Blackwell Publishing. In: Downie, A., Crosky, A., & Munroe, P. (2009). Physical properties of biochar. In: Lehmann, J. & Joseph, S. (Eds.) (2009). *Biochar for Environmental Management: Science and Technology.* London, UK: Earthscan, 13-32.

Uchimiya, M., Bannon, D. I., & Wartelle, L. H. (2012). Retention of heavy metals by carboxyl functional groups of biochars in small arms range soil. *Journal of Agricultural and Food Chemistry*, **60**(7), 1798-1809.

Uchimiya, M., Chang, S., & Klasson, K. T. (2011). Screening biochars for heavy metal retention in soil: role of oxygen functional groups. *Journal of Hazardous Materials*, **190**(1), 432-441.

Uchimiya, M., Lima, I. M., Thomas Klasson, K., Chang, S., Wartelle, L. H., & Rodgers, J. E. (2010). Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil. *Journal of Agricultural and Food Chemistry*, **58**(9), 5538-5544.

U. S. Environmental Protection Agency (US EPA). (2011). Terrestrial Carbon Sequestration, Analysis of Terrestrial Carbon Sequestration at Three Contaminated Sites Remediated and Revitalized with Soil Amendments, EPA-542-R-10-003. <Online, available at: http://www.clu-in.org/download/issues/ecotools/Terrestrial-Carbon-Sequestration-Report.pdf>.

U.S. Environmental Protection Agency (US EPA). (2007). The Use of Soil Amendments for Remediation, Revitalization, and Reuse. EPA 542-R-07-013. <Online, available at: http://www.clu-in.org/download/remed/epa-542-r-07-013.pdf >.

Vangronsveld, J., Herzig, R., Weyens, N., Boulet, J., Adriaensen, K., Ruttens, A., Thewys, T., Vassilev, A., Meers, E., Nehnevajova, E., van der Lelie, D., & Mench, M. (2009). Phytoremediation of contaminated soils and groundwater: lessons from the field. *Environmental Science and Pollution Research*, *16*(7), 765-794.Vangronsveld, J., Herzig, R., Weyens, N. et al. 2009. Phytoremediation of contaminated soils and groundwater: lessons from the field. Env. Sci. Poll. Res, 16, 765-794.

Van Slycken, S., Witters, N., Meiresonne, L., Meers, E., Ruttens, A., Van Peteghem, P., Weyens, N., Tack, F. M. G., & Vangronsveld, J. (2013a). Field evaluation of willow under short rotation coppice for phytomanagement of metal-polluted agricultural soils. International journal of phytoremediation, 15(7), 677-689.

Van Slycken, S., Witters, N., Meers, E., Peene, A., Michels, E., Adriaensen, K., Ruttens, A., Vangronsveld, J., Du Laing, G., Wierinck, I., van Dael, M., van Passel, S. & Tack, F. M. G. (2013). Safe use of metal-contaminated agricultural land by cultivation of energy maize (< i> Zea mays</i>). Environmental Pollution, 178, 375-380.

Verheijen, F., Jeffery, S., Bastos, A. C., Van der Velde, M., & Diafas, I. (2010). Biochar application to soils. A Critical Scientific Review of Effects on Soil Properties, Processes and Function, *JRC Scientific and Technical Reports.* <Online, available at: http://www.biochar.co.nz/pdf/EUR24099.pdf>.

Venegas, A., Rigol, A., & Vidal, M. (2015). Viability of organic wastes and biochars as amendments for the remediation of heavy metal-contaminated soils. *Chemosphere*, **119**, 190-198.

Vegter, J., Lowe, J. & Kasamas, H. (Eds.) (2002). Sustainable Management of Contaminated Land: An Overview. Report Austrian Federal Environment Agency, 2002 on behalf of CLARINET, Spittelauer Lände 5, A-1090 Wien, Austria. <Online, available at: http://www.commonforum.eu/publications_clarinet.asp>.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. G., & Pigna, M. (2010). Mobility and bioavailability of heavy metals and metalloids in soil environments. *Journal of Soil Science and Plant Nutrition*, **10**(3), 268-292.

Vital Earth Ltd. (2009). *Product Information Sheet, 10mm Green Compost.*

Walker, D. J., Clemente, R., & Bernal, M. P. (2004). Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. *Chemosphere*, **57**(3), 215-224.

Wang, Y., Wang, L., Fang, G., Herath, H. M. S. K., Wang, Y., Cang, L., Xie, Z. & Zhou, D. (2013). Enhanced PCBs sorption on biochars as affected by environmental factors: humic acid and metal cations. *Environmental Pollution*, **172**, 86-93.

Warren, G. P., Alloway, B. J., Lepp, N. W., Singh, B., Bochereau, F. J. M., & Penny, C. (2003). Field trials to assess the uptake of arsenic by vegetables from contaminated soils and soil remediation with iron oxides. *Science of the Total Environment*, **311**(1), 19-33.

Waste Resources and Action Programme (WRAP). (2012). Good practice guide for the use of BSI PAS 100 compost in landscape and regeneration. WRAP, Banbury, UK. <Online, available at: http://www.wrap.org.uk/sites/files/wrap/Good%20practice%20guide_Final1.pdf>.

Waste Resources and Action Programme (WRAP). (n.d.) Compost Specifications for the Landscape Industry. <Online, available at: http://www.wrap.org.uk/sites/files/wrap/CompostSpecificationsLandscape1.pdf>.

Weber, J., Karczewska, A., Drozd, J., Licznar, M., Licznar, S., Jamroz, E., & Kocowicz, A. (2007). Agricultural and ecological aspects of a sandy soil as affected by the application of municipal solid waste composts. *Soil Biology and Biochemistry*, **39**(6), 1294-1302.

Weng, L., Temminghoff, E. J., Lofts, S., Tipping, E., & Van Riemsdijk, W. H. (2002). Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil. *Environmental Science & Technology*, **36**(22), 4804-4810.

Wenzel, W. W., & Blum, W. E. H. (1999). Effect of sampling, sample preparation and extraction techniques on mobile metal fractions in soils. In: Adriano, D. C., Chen, Z.-S., Yang, S.-S., Iskandar, I.K. (eds.). *Biogeochemistry of Trace Metals. Advances in Environmental Sciences*, Northwood, UK: Science Reviews, 121-172.

Whalen, J. K., Chang, C., Clayton, G. W., & Carefoot, J. P. (2000). Cattle manure amendments can increase the pH of acid soils. *Soil Science Society of America Journal*, **64**(3), 962-966.

Wild, A., (1993). *Soils and the Environment, an Introduction*. Cambridge, UK: Cambridge University Press.

Witters, N., Mendelsohn, R.O., Van Slycken, S., Weyens, N., Schreurs, E., Meers, E., Tack, F., Carleer, R., & Vangronsveld, J. (2012). Phytoremediation, a sustainable remediation technology? Conclusions from a case study I: Energy production and carbon dioxide. *Biomass Bioenergy*, **39**, 454-469.

Xu, G., Wei, L. L., Sun, J. N., Shao, H. B., & Chang, S. X. (2013). What is more important for enhancing nutrient bioavailability with biochar application into a sandy soil: Direct or indirect mechanism? *Ecological Engineering*, **52**, 119-124.

Yakkala, K., Yu, M. R., Roh, H., Yang, J. K., & Chang, Y. Y. (2013). Buffalo weed (Ambrosia trifida L. var. trifida) biochar for cadmium (II) and lead (II) adsorption in single and mixed system. *Desalination and Water Treatment*, **51**(40-42), 7732-7745.

Yaman, S., Şahan, M., Haykiri-Açma, H., Şeşen, K., & Küçükbayrak, S. (2001). Fuel briquettes from biomass–lignite blends. *Fuel Processing Technology*, **72**(1), 1-8.

Yang, X. E., Peng, H. Y., Jiang, L. Y., & He, Z. L. (2005). Phytoextraction of copper from contaminated soil by Elsholtzia splendens as affected by EDTA, citric acid, and compost. *International Journal of Phytoremediation*, **7**(1), 69-83.

Yang, X. B., Ying, G. G., Peng, P. A., Wang, L., Zhao, J. L., Zhang, L. J., Yuan, P. & He, H. P. (2010). Influence of biochars on plant uptake and dissipation of two pesticides in an agricultural soil. *Journal of Agricultural and Food Chemistry*, **58**(13), 7915-7921.

Yao, Z., Li, J., Xie, H., Yu, C. (2012). Review on remediation technologies of soil contaminated by heavy metals. *Procedia Environmental Sciences,* **16**, 722-729.

Yin Chan, K. & Xu, Z. (2009). Biochar: Nutrient Properties and Their Enhancement. In: Lehmann, J. & Joseph, S. (Eds.) (2009). *Biochar for Environmental Management: Science and Technology.* London, UK: Earthscan, 67-84.

Yruela I (2009). Copper in plants: acquisition, transport and interactions. *Functional Plant Biology*, **36**(5), 409-430.

Yu, X. Y., Ying, G. G., & Kookana, R. S. (2009). Reduced plant uptake of pesticides with biochar additions to soil. *Chemosphere*, **76**(5), 665-671.

Zhang, A., Cui, L., Pan, G., Li, L., Hussain, Q., Zhang, X., Zheng, J. & Crowley, D. (2010). Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice paddy from Tai Lake plain, China. *Agriculture, Ecosystems & Environment*, **139**(4), 469-475.

Zhang, X., Wang, H., He, L., Lu, K., Sarmah, A., Li, J. Bolan, N. S., Pei, J. & Huang, H. (2013). Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. *Environmental Science and Pollution Research*, **20**(12), 8472-8483.

Zhao, X., Monnell, J. D., Niblick, B., Rovensky., C. D., Landis, A. E. (2014). The viability of biofuel production on urban marginal land: An analysis of metal contaminants and energy balance for Pittsburgh's Sunflower Gardens, *Landscape and Urban Planning,* **124,** 22-33.

Zhuang, D., Jiang, D., Liu, L., & Huang, Y. (2011). Assessment of bioenergy potential on marginal land in China. *Renewable and Sustainable Energy Reviews*, **15**(2), 1050-1056.

Ziebell, A. L., Barb, J. G., Sandhu, S., Moyers, B. T., Sykes, R. W., Doeppke, C., Gracom, K. L. Carlile, M., Marek, L. F., Davis, M. F., Knapp, S. J., Burke. Sunflower as a biofuels crop: An analysis of lignocellulosic chemical properties. *Biomass and Bioenergy*. **59;** 208-217.

Zimmerman, A. R., Gao, B., & Ahn, M. Y. (2011). Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biology and Biochemistry*, **43**(6), 1169-1179.

Annex 1 – Contaminants Treated with Biochar as a Single and Combined Amendment

Annex 1 provides an overview of studies trialling biochar as an amendment for the sorption of contaminants. Studies applied biochar to soil unless otherwise highlighted.

Contaminant	Biochar Only	Biochar as a Combined Amendment
Arsenic	• Khan *et al.*, 2013 – sewage sludge biochar • Beesley & Marmiroli, 2011 – hardwood biochar with a pH of 9.9	
Cadmium	• Venegas *et al.*, 2015 – biochar derived from vine shoots and tree bark • Houben *et al.*, 2013 – *Miscanthus* straw biochar • Yakkala *et al.*, 2013 – buffalo weed derived biochar reduced Cd and Pb in wastewater • Beesley & Marmiroli, 2011 • Park *et al.*, 2011 – chicken manure and green waste derived biochars • Debela *et al.*, 2011 – co-pyrolysis of contaminated soil with biomass to create biochar encapsulating contaminant • Fellet *et al.*, 2011 – prune residue derived biochar • Uchimiya *et al.*, 2010 – broiler litter biochar sorption of Cd in soil and water	• Beesley *et al.*, 2010 – hardwood derived biochar as a single amendment and in combination with greenwaste compost reduced water extractable Cd and Zn.
Chromium	• Khan *et al.*, 2013 • Dong *et al.*, 2011 – sugar beet tailing biochar decreased Cr (VI) in water under acidic conditions.	
Cobalt	• Khan *et al.*, 2013	Karami *et al.*, 2011 – reduction in Cu in soil pore water with combined GWC and biochar, although biochar only treatment reduced Cu most significantly.
Copper	• Venegas *et al.*, 2015 • Trakal *et al.*, 2014 – brewers draff biochar, non-activated + activated using KOH reduced Cu	

HOMBRE

Contaminant	Biochar Only	Biochar as a Combined Amendment
	in aqueous solution (synthetic + soil). • Pellera *et al.*, 2012 – Orange peel, rice husk, olive pomace and compost feedstock biochars all adsorbed Cu (II) in water. • Uchimiya *et al*, 2012 • Park *et al.*, 2011 • Sizmur *et al.*, 2011 • Tong *et al.*, 2011 – 3 different crop straw biochars in aqueous solution. • Uchimiya *et al.*, 2011	
Lead	• Venegas *et al.*, 2015 • Houben *et al.*, 2013 • Khan *et al.*, 2013 • Yakkala *et al.*, 2013 (in wastewater) • Park *et al.*, 2011 • Uchimiya *et al.*, 2012 – Oxidised (with concentrated $H_{2S}O_{4)}$ cottonseed hull derived biochar • Cao *et al.*, 2011 – dairy manure biochar • Fellet *et al.*, 2011 • Sizmur *et al.*, 2011 – patented non-activated biochar • Uchimiya *et al.*, 2011 • Uchimiya *et al.*, 2010 (in soil and water) • Cao *et al.*, 2009 – dairy manure derived biochar in aqueous solution	• Karami *et al.*, 2011 – green waste compost and wood-derived biochar reduced Pb concentrations in soil pore water
Nickel	• Venegas *et al.*, 2015 • Khan *et al.*, 2013 • Uchimiya *et al.*, 2010 (in soil and water)	
Zinc	• Venegas *et al.*, 2015 • Houben *et al.*, 2013 • Uchimiya *et al.*, 2012 • Beesley & Marmiroli, 2011 • Debela *et al.*, 2011 • Fellet *et al.*, 2011 • Sizmur *et al.*, 2011	• Beesley *et al.*, 2010
Thallium	• Fellet *et al.*, 2011	
Phosphate	• Chen *et al.*, 2011 – magnetic biochar produced using orange peel as biomass reduced	

Contaminant	**Biochar Only**	**Biochar as a Combined Amendment**
	phosphate in wastewater.	
Atrazine	• Cao *et al.*, 2011 • Cao *et al.*, 2009 (in aqueous solution)	
Naphthalene	• Chen *et al.*, 2011 (in wastewater) • Chen & Chen, 2009 – orange peel biochars produced at a range of temperatures decreased naphthalene and 1-naphthol in water	
PAHs		Beesley *et al.*, 2010 – biochar + compost reduced PAHs, but biochar only treated was significantly more effective.
PCBs	• Wang *et al.*, 2013 – pine needle and wheat straw biochar in soil solution	
p-nitrotoluene	• Chen *et al.*, 2011(in wastewater)	
Pyrene	• Hale *et al.*, 2011 – Corn stover residue biochar	

Annex 2 – Post-Growth Analysis of PAHs and Metals in Soils with Different Amendments.

Annex 2 (below) shows the post growth analysis of PAH and metal content in the P7 soil amended with the treatments specified in 4.5.2.1 (i)

Parameters	Un-amended	BC1 (1%)	BC2 (1%)	BC3 (1%)	BC1 (3%)	BC2 (3%)	BC3 (3%)	C (1%)	C (2%)	BC1 (1%) + C (1%)	BC2 (1%) + C (1%)	BC3 (1%) + C (1%)	BC1 (3%) + C (1%)	BC2 (3%) + C (1%)	BC3 (3%) + C (1%)	BC1 (1%) + C (2%)	BC2 (1%) + C (2%)	BC3 (1%) + C (2%)	BC1 (3%) + C (2%)	BC2 (3%) + C (2%)	BC3 (3%) + C (2%)
TOC (% dry weight)	0.9	1.7	1.0	1.1	1.1	1.1	1.0	1.0	1.1	0.9	0.8	1.1	1.4	1.2	1.1	1.1	1.1	1.1	1.1	1.2	1.1
Metals (mg kg-1 dry weight)																					
As	12.3	16.9	11.5	14.5	10.9	10.7	16.0	11.0	9.4	14.1	10.7	13.8	17.3	9.1	10.4	14.1	18.0	11.7	13.3	11.7	10.5
Ba	31.3	54.8	32.8	60.4	32.7	28.5	45.4	29.5	44.4	47.1	50.8	35.3	65.3	29.8	28.8	40.2	52.4	37.5	58.3	35.8	25.5
Cd	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Cr	21.1	39.7	16.9	25.6	18.2	14.5	24.1	15.7	16.8	23.6	19.5	18.1	27.2	14.0	15.2	20.8	25.6	16.7	23.0	16.7	15.0
Cu	1.1	1.8	306.8	1.3	648.0	309.7	321.1	295.5	259.4	1.0	917.0	627.7	1.2	320.3	1.1	1.1	1.1	298.9	575.7	259.1	309.0
Mo	<1.0	2.1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Ni	9.8	21.3	9.4	13.0	10.2	9.0	12.6	9.1	9.7	11.6	10.4	8.6	12.4	9.3	9.1	11.6	15.4	9.0	12.8	8.5	8.6
Pb	21.4	35.7	21.4	45.8	21.5	28.7	27.5	22.1	18.4	27.0	22.2	20.4	29.6	34.1	20.1	27.9	30.7	19.6	26.4	77.4	20.3
Sb	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.2	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Se	0.4	0.4	0.4	0.7	0.4	0.3	0.5	<0.1	<0.1	1.5	0.6	0.3	0.6	<0.1	<0.1	0.5	0.6	<0.1	0.6	<0.1	<0.1
Zn	44.7	157.3	49.3	33.0	63.7	45.7	46.7	45.7	44.0	41.3	36.7	45.3	50.3	38.0	47.3	49.3	48.3	47.0	47.7	46.0	44.7
Hg	6.2	7.6	6.4	4.6	4.5	5.3	5.6	3.8	4.7	3.5	3.4	7.0	6.5	4.2	4.3	4.5	6.6	5.5	4.1	6.1	5.4
PAHs (mg kg-1 dry weight)																					
Naphthalene	0.7	0.6	0.4	0.6	0.5	0.4	0.5	1.3	0.6	0.3	0.5	0.4	0.5	0.8	0.8	0.6	0.4	0.5	0.3	0.6	0.6
Acenaphthylene	0.7	0.8	0.7	0.5	0.8	0.7	0.8	1.3	0.7	0.7	0.4	0.6	0.4	1.5	1.2	0.7	0.7	0.5	0.4	0.9	0.9
Acenaphthene	0.2	0.2	0.1	0.1	0.3	0.2	0.2	0.2	0.1	0.2	0.1	0.2	0.4	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2
Fluorene	0.6	0.8	0.6	0.4	0.5	0.5	0.8	1.2	0.6	1.0	0.2	0.4	0.3	0.8	0.6	1.0	0.3	0.6	0.2	0.7	0.4
Phenanthrene	3.1	3.7	3.1	2.7	3.8	2.8	4.0	4.6	2.3	4.2	2.0	2.1	1.9	3.8	3.5	3.9	2.4	2.9	1.5	2.6	4.4
Anthracene	7.2	19.0	10.1	5.8	7.6	8.1	10.1	17.0	9.1	12.4	4.1	6.6	4.3	12.7	11.0	10.3	4.8	6.3	3.6	10.0	8.7
Fluoranthene	4.4	6.7	5.8	4.1	7.3	5.5	6.8	7.0	3.6	6.5	2.6	3.3	2.8	8.3	6.7	5.7	5.1	3.6	2.8	4.6	5.7
Pyrene	5.0	7.7	6.6	4.8	8.0	5.9	7.4	7.7	4.2	7.3	3.1	3.5	3.0	9.6	7.8	6.2	5.4	3.7	3.3	5.0	6.4
Benzo[a]anthracene	2.5	3.9	3.6	2.7	4.0	3.8	3.9	4.1	2.2	3.7	1.5	2.0	1.5	5.1	4.0	3.3	2.8	1.9	1.7	2.7	3.2
Chrysene	4.1	6.3	5.2	4.0	6.4	4.6	5.7	6.5	3.6	5.6	2.4	3.3	2.7	8.6	6.5	5.3	4.6	3.0	2.7	4.4	5.1
Benzo[b]fluoranthene	3.9	6.5	6.3	5.0	6.4	6.0	6.6	6.7	3.5	5.7	2.3	3.3	2.5	8.7	6.7	5.1	4.4	2.9	2.7	4.6	4.9

Benzo[k]fluoranthene	1.6	2.6	2.1	1.6	2.6	1.8	2.3	2.7	1.4	2.2	1.0	1.5	1.1	2.9	2.7	2.0	1.9	1.3	1.1	1.9	2.0
Benzo[a]pyrene	1.8	3.0	2.6	2.1	3.1	2.4	2.8	3.2	1.7	2.7	1.1	1.3	1.3	3.4	3.2	2.5	2.2	1.5	1.4	2.2	2.3
Indeno[1.2.3-cd]pyrene	1.6	3.3	3.6	3.0	3.2	3.2	3.3	2.9	1.5	2.5	1.0	1.6	1.2	3.2	3.0	2.4	1.9	1.3	1.3	2.1	2.0
Dibenzo[a.h]anthracene	0.4	0.6	0.6	0.5	0.5	0.6	0.6	0.7	0.4	0.6	0.3	0.4	0.3	0.7	0.6	0.6	0.5	0.4	0.4	0.6	0.5
Benzo[g.h.i]perylene	1.1	1.9	1.7	1.5	1.8	4.2	1.8	2.1	1.1	1.6	0.7	1.0	0.8	2.4	2.2	1.5	1.3	0.9	0.9	1.4	1.4
ΣPAHs	39.0	67.7	53.0	39.3	57.0	48.0	57.7	69.0	36.7	57.3	23.3	31.7	25.0	72.7	60.7	51.3	39.0	31.7	24.3	44.7	48.7