ENVIRONMENTAL ASSESSMENT AND AGRONOMIC PERFORMANCE OF BIOSOLIDS-DERIVED BIOCHAR IN CONTROLLED ENVIRONMENT STUDIES

A Thesis submitted by

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ABSTRACT

Increasing regulatory restrictions on traditional land application of biosolids (treated sewage sludge) in Australia has driven the need to explore alternative treatment technologies that render biosolids (BS) suitable for beneficial use while mitigating environmental risks. Thermal treatment of biosolids is currently being investigated in Australia as an alternative management practice; however, the characteristics of the biochar product is poorly understood. This thesis evaluates the safe land application of biosolids-derived biochar (BDB) produced from the gasification of BS at an Australian wastewater treatment plant using two contrasting Australian soil types (Ferrosol and Chromosol) at three application rates (2.5%, 5% and 10% w/w). Leaching columns were used to assess the environmental risk of heavy metal concentration and mobility in soils treated with BDB compared with BS. The study applied the novel use of p-XRF as a rapid and low-cost technique for investigating leaching behaviour. While BDB-amended soils contained higher total metal concentrations, the leachates showed significantly lower concentrations of soluble copper and chromium compared to those treated with BS. The study underscores a potential mitigation of environmental risks associated when applying BDB as a soil amendment. The combined assessment of agronomic and heavy metal dynamics of BDB was performed using glasshouse studies and compared to BS. BDB significantly increased the dry matter yield of ryegrass, compared to control. At 2.5% w/w application rate BDB increased yield by 180% in Chromosol and 192% in Ferrosol compared to control. Higher application rates of BDB did not affect agronomic efficiency. Importantly, BDB significantly reduced heavy metal uptake (chromium, copper, and zinc) by ryegrass compared to BS. Soil incubation studies supported these findings, showing that 2.5% BDB increased urease activity by 50% in Chromosol and 23% in Ferrosol, relative to control soil, which is beneficial for nitrogen cycling. While BDB at the same rate decreased acid phosphatase activity to 12% in Chromosol and 20% in Ferrosol, which shows a potential impact on phosphorous availability. The study advocates for a 2.5% application rate of BDB to optimize agricultural outputs while safeguarding soil and plant health. The findings also highlight the importance of tailored soil management practices that consider specific soil characteristics, and application rates to optimize benefits and minimize environmental risks. Further research is recommended to explore land application of BDB using field trials to understand long-term impacts and connect the results of the current research observed in controlled environment studies.

CERTIFICATION OF THESIS

I, Payel Sinha declare that the PhD thesis entitled *Environmental assessment and agronomic performance of biosolids-derived biochar in controlled environment studies* is not more than 100,000 words in length including quotes and exclusive of tables, figures, appendices, bibliography, references, and footnotes.

This Thesis is the work of Payel Sinha except where otherwise acknowledged, with the majority of the contribution to the papers presented as a Thesis by Publication undertaken by the student. The work is original and has not previously been submitted for any other award, except where acknowledged.

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STATEMENT OF CONTRIBUTION

Paper 1:

Sinha, Payel, Marchuk, Serhiy, Harris, Peter, Antille, Diogenes L., & McCabe, Bernadette K. (2023). Potential for land application of biosolids-derived biochar in Australia: A review, Sustainability, 15(14), 10909. https://doi.org/10.3390/su151410909.

Payel Sinha contributed 75% to this paper. Collectively, Serhiy Marchuk, Peter Harris, Diogenes L. Antille, Bernadette K. McCabe contributed the remainder.

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TABLE OF CONTENTS

LIST OF FIGURES

ABBREVIATIONS

BDB	Biosolids-derived biochar
BS	Biosolids
$CaCl_2$	Calcium Chloride
Cd	Cadmium
CEC	Cation exchange capacity
Cr	Chromium
Cu	Copper
DMY	Dry matter yield
EBC	European Biochar Certificate
EC	Electrical Conductivity
EPA	Environmental Protection Agency
Hg	Mercury
IBI	International Biochar Initiative
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
NIST	National Institute of Standards & Technology
Ni	Nickel
Pb	Lead
POPs	Persistent organic pollutants
p-XRF	Portable X-Ray Fluorescence
WWTP	Wastewater treatment plant
Zn	Zinc

CHAPTER 1: INTRODUCTION

Biosolids (BS) are the waste organics remaining from the various processes used onsite at wastewater treatment plants (WWTPs). These facilities treat a diverse range of wastewater sources, including both industrial effluents and domestic sewage. These waste biosolids largely consist of waste sludge and organics which are recalcitrant to the anaerobic and/or aerobic wastewater treatment processes employed onsite (Marchuk et al., 2023). While biosolids are rich in organic matter and contain agronomically significant concentrations of plant nutrients, they also contain heavy metals, pathogens, organic contaminants, and other xenobiotics including endocrine disruptors which may pose risks to soil quality and human health when directly applied to land (McLaughlin et al., 2007; Sinha et al., 2023). Due to these risks, biosolids must be stabilised by various combinations of primary, secondary and tertiary treatments with or without composting, alkaline stability or thermal drying prior to land application (Paz-Ferreiro et al., 2018).

Although the application of biosolids (BS) to agricultural land is a common practice, it has potential challenges due to the variability of contaminant levels (Patel et al., 2020). Regulatory frameworks, especially in Australia, impose strict guidelines on BS application to protect public health and the environment (Racek et al., 2020; Sinha et al., 2023). Despite these measures, there are significant knowledge gaps regarding long-term impacts of BS application, including the fate of heavy metals, microplastics, persistent organic pollutants (POPs) and their transport in the environment (Pritchard et al., 2010; Raheem et al., 2018). The development of safer solutions for the disposal and utilisation of BS that better suit the needs of modern agriculture is a key aspect in facilitating a circular economy.

One such innovative avenue gaining attention is the conversion of BS to biochar produced though thermal treatment (i.e., pyrolysis and gasification) (Goldan et al., 2022). Biochar is characterized by its high carbon content, stability in soil and ability to improve soil properties such as water retention and nutrient availability (Lehmann and Joseph, 2015). The highly negative surface charge of biochar enables the retention of cationic nutrients via ion exchange, whereas the relatively extensive surface area, internal porosity, and polarizability facilitate the sorption of anionic nutrients via covalent bonds (Lu et al., 2020). The high cation exchange capacity of biosolids-derived biochar (BDB) has the ability to adsorb heavy metals and organic contaminants such as pesticides and herbicides from the environment. But there is little information on the cycling of heavy metals presented in BDB. Heavy metal contamination of agricultural soils represents a serious environmental issue. Biosolids-derived biochars are characterized by elevated concentrations of total heavy metal and when applied to agricultural land could contaminate soil and groundwater due to potential leaching. Additionally, soil amended with BDB can result in heavy metal accumulation in plant tissues which can enter the food chain. Interactions between biochar, soil, microbes, and plant roots are known to occur within a short period of time after application to the soil (Lehmann and Joseph, 2015). However, the extent, rates, and implications of these interactions are still far from being understood, and this knowledge is needed for an effective evaluation of the use of biochar as a soil amendment (Joseph et al., 2010).

While the use of biochar produced from various green biomass such as rice husk, sugar cane bagasse etc as a soil amendment has been reported in the literature, the application of BDB has not been extensively explored (Lu et al., 2013; Sachdeva et al., 2023). The process of carbonising biosolids to biochar can potentially destroy all pathogens and reduce the mobility and bioavailability of heavy metals and organic pollutants, thus mitigating the environmental risks associated with biosolids land applications (Racek et al., 2020; Sinha et al., 2023). This overview highlights several research gaps:

1. Biosolids-derived biochar-Soil interaction: Studies are required to improve the understanding of how BDB interacts with different soil types. This includes its impact on soil physical properties, fertility, and bioavailability of nutrients and heavy metals to plants. These studies would provide valuable insights into determining the safe application rate of BDB amendments across different soil types, thus promoting sustainable agriculture (Sinha et al., 2023).

2. Environmental risks: Studies are needed to better understand the mobility and leaching risks of heavy metals present in BDB when applied to soil, especially under different environmental conditions such as varying soil types (Marchuk et al., 2021; Patel et al., 2020).

3. Soil health and plant response: The impact of BDB on soil health including changes in soil microbiota and plant heavy metal uptake requires comprehensive longitudinal

studies to assess these impacts over multiple growing seasons (Paz-Ferreiro et al., 2018).

Combined with the current flux of regulatory issues of biosolids in Australia and synthesis of the literature review (presented in Chapter 2), there is a clear knowledge gap in understanding the suitability of land application of BDB in Australia. With current regulatory trends in Australia discontinuing the direct application of BS on land, there is a need to find an alternative technology which further treats BS to render the product suitable for land application both from a nutrient and contamination perspective.

1.1. Research Scope

Thermal treatment of biosolids is currently being investigated in Australia as an alternative management practice; however, the characteristics of the biochar product is poorly understood. To manage biosolids in a more sustainable manner, there is a need for further understanding of interactions between soil, plants and biosolids-derived biochar in different soil types, particularly in the context of their use in agriculture and environmental management. BDB are characterized by elevated level of heavy metal and when applied to agricultural land could contaminate soil and, due to potential leaching, to groundwater (Lehmann and Joseph 2015). However, the extent, rates, and implications of these interactions are still far from being understood, and this knowledge is needed for an effective evaluation of the use of biochar as a soil amendment (Joseph et al, 2010). Consequently, this research evaluates the safe land application of BDB produced from the gasification of BS at an Australian wastewater treatment plant using two contrasting Australian soil types at three application rates (2.5%, 5% and 10% w/w). Two soils from Queensland were used in this laboratory study: Red Ferrosol (Oxisol in the NRCS-USDA Soil Taxonomy) from the Agricultural Field Station Complex at the University of Southern Queensland and a Yellow Chromosol (Alfisol in the NRCS-USDA Soil Taxonomy) from Gatton (Queensland, Australia). Selection of these soils was based on their differences in mineralogy, texture, and soil pH and EC.

The research firstly assessed the impact on heavy metal content, mobility and leaching when BDB is applied to soil. Heavy metals are a group of elements with specific gravities of > 5 g cm^{-3} (Ross, 1994). In excessive concentration those heavy metals regarded as the toxic and environmentally damaging are Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Ni (nickel), Pb (lead) and Zn (zinc) (Ross, 1994) but several of these, especially those that are transition metals, are essential for plant metabolism (e.g., Cu, Ni, Zn). In order to cause a toxic effect, heavy metals must dissolve into soil solution, be taken up by an organism and be transported to cells where a toxic effect can occur. The availability of heavy metals in soils amended with BDB is affected by several factors, including the type of biosolids used for biochar production, pyrolysis temperature and soil characteristics (Figueiredo et al., 2019; Yang et al., 2018). Understanding the dynamics of total heavy metal concentrations in soil treated with amendments is crucial, because regulatory standards focus on this total concentration. Chromium is a heavy metal with known toxic effect on plant growth (Zulfiqar et al., 2023). High level of Cr can lead to chlorosis, necrosis and other growth abnormalities that reduce plant yield and quality (AbdElgawad et al., 2023; Franco et al., 2023). Copper and zinc are essential elements but can be toxic to plants and microorganisms above certain levels (Franco et al., 2023; Meng et al., 2023); therefore, maximum permissible levels in soil must be observed (MAFF, 1998).

The research secondly performed the combined assessment of agronomic performance and heavy metal dynamics of BDB using glasshouse studies and compared to BS to observe the plant yield, agronomic efficiency and heavy metal dynamics in soil amended with BDB. This research will help in developing guidelines for the safe use of BDB in agriculture, contributing to sustainable waste management and agricultural practices.

1.2. Research aims and objectives

The aims of this research are to investigate the concentrations and mobility of heavy metals in two different soil types treated with BDB, and to evaluate the effectiveness of BDB as a soil amendment to increase plant yield and agronomic efficiency, when compared to BS. Part of this research was to assess the suitability of portable X-ray fluorescence (p-XRF) as a rapid, low-cost technique for measuring total heavy metal concentrations in soil and plants treated with such amendments.

The objectives of this research thesis follow:

1. Investigate the effects of BDB on mobility and leaching of heavy metals (Cr, Cu and Zn) in two Australian soils with contrasting physico-chemical properties at varying rates (2.5%, 5%, 10% w/w), and compare these effects with BS application.
2. Evaluate BDB as potential soil amendment with respect to yield, agronomic efficiency and heavy metal uptake in ryegrass (*Lolium perenne* L.) in two Australian

soils with contrasting physico-chemical properties at varying rates (2.5%, 5%, 10% w/w), and compare these effects with BS application.

3. Investigate the effects of BDB on soil enzymatic activity following soil application in two Australian soils with contrasting physico-chemical properties at varying rates (2.5%, 5%, 10% w/w), and compare these effects with BS application.

1.3. Thesis Organization

This thesis is structured as per the guidelines set forth by the University of Southern Queensland with respect to Thesis by Publication. The thesis is organised into six chapters, primarily focused on **Papers 1-3** listed above. Additionally, the thesis includes three appendices that provide supplementary materials relevant to these papers.

Paper 1 is a review of the literature which critically examines the application of biochar derived from biosolids in the context of land application in Australia. **Paper 2** examines the use of portable X- ray fluorescence (p-XRF) to investigate the effects of BS and BDB on heavy metal (Cr, Cu and Zn) mobility and distribution pattern in amended soils (Yellow Chromosol and Red Ferrosol). **Paper 3** investigates the agronomic and environmental impacts of applying BDB at three application rates (2.5%, 5% and 10% w/w) to soils (Yellow Chromosol and Red Ferrosol), focusing on their effects on ryegrass growth, heavy metal uptake and soil enzymatic properties, while comparing it to BS amended soils.

CHAPTER 2: PAPER 1 – LITERATURE REVIEW: POTENTIAL FOR LAND APPLICATION OF BIOSOLIDS-DERIVED BIOCHAR IN AUSTRALIA: A REVIEW

Paper 1 is a published article in *Sustainability* reviewing the utilization of BDB in Australian agriculture, emphasizing the interest in thermal treatment methods such as pyrolysis and gasification with changing legislation and waste reduction objectives. The review highlights the absence of specific legislative standards in Australia for the permissible concentrations of heavy metals in biochar intended for land application. The review notes the existence of voluntary quality standard for biochar internationally, such as the European Biochar Certificate and the International Biochar Initiative., which is focused on ensuring the quality of biochar by regulating organic contaminants and heavy metal concentration.

This review brought together scientific evidence demonstrating that thermal treatment of biosolids can be employed to reduce pathogens, microplastics, and organic pollutants load, while decreasing the bioavailability of heavy metals at environmentally and agronomically safe levels. While the use of biochar produced from various green biomass such as rice husk, sugar cane bagasse as a soil amendment has been reported in the literature, the land application of biochar from biosolids via gasification has not been extensively explored, especially in the Australian context. This highlights several research gaps identified in **Paper 1**.

Potential for land application of biosolids-derived biochar in Australia: A review

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Review

Land Application of Biosolids-Derived Biochar in Australia: A Review

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Abstract: Thermal treatment in Australia is gaining interest due to legislative changes, waste reduction goals, and the need to address contaminants' risks in biosolids used for agriculture. The resulting biochar product has the potential to be beneficially recycled as a soil amendment. On-farm management practices were reviewed to identify barriers that need to be overcome to increase recycling and examine the role of pyrolysis and gasification in effectively improving the quality and safety of biochar intended for land application. Key findings revealed the following: (1) thermal treatment can effectively eliminate persistent organic pollutants, microplastics, and pathogens, and (2) more than 90% of the total heavy metals content in biosolids may become immobilized when these are converted to biochar, thus reducing their bioavailability following land application. While the reported research on the short-term effects of biosolids-derived biochar suggests promising agronomic results, there is a dearth of information on long-term effects. Other knowledge gaps include the optimization of land application rates, understanding of the rate of breakdown, and the fate of contaminants in soil and water, including heavy metal mobility and redistribution in the environment by processes such as erosion and runoff following land application. An improved understanding of nutrients and contaminants dynamics in soils receiving biosolids-derived biochar is a pre-requisite for their safe use in Australian agriculture, and therefore, it is highlighted as a priority area for future research.

Keywords: heavy metals; microplastics; organic pollutants; pyrolysis and gasification; sewage sludge; soil amendment; Australian agriculture

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1. Introduction

Biosolids are the solid end-product of urban wastewater treatment plants, consisting of sewage sludge that is treated to achieve safe environmental and public health standards [1]. While biosolids are rich in organic matter and contain significant concentrations of plant nutrients, they also contain contaminants, including organic compounds, heavy metals, pathogens, and microplastics, which cause concern due to the potential for long-term environmental and public health impacts [2,3]. Biosolids' production increases proportionally to the growth of the population and the adoption of cleaner technology for the treatment of effluents [4]. Annual sewage sludge production has been estimated approximately at 11 million tons of dry solids in Europe, 7 million tons of dry solids in the United States, and China produces 60 million tons of sewage sludge (80% water by weight) with an annual increase rate of 10% [5]. In 2021, Australia generated approximately 380,000 dry tons of biosolids [1], which represented a 24% increase compared with the mean annual production recorded between 2010 and 2019 [6]. Restrictions regarding the use of biosolids in Australia continue to increase with a trend toward diverting their reutilization as a source of carbon and nutrients in agriculture [7]. However, there is renewed interest both nationally and internationally in finding an alternative waste management strategy that applies circular economy principles to recover carbon, nutrients, and energy from biosolids while reducing the need for landfill disposal [8,9].

Thermal treatment including pyrolysis, gasification, and hydrothermal technology can be employed to sustainably process the biosolids intended for land application [8]. The materials that result from these processes offer several advantages compared with biosolids, including the following: (1) reduction in or improved control of odor, pathogens, organic, and inorganic contaminants; (2) mass reduction (range: 30% to 90%), which subsequently reduces handling, transport, and storage costs; and (3) the conversion of biosolids into higher-value products such as bio-oil, syngas, and biochar [10,11]. These advantages should be perceived as opportunities to improve regulatory compliance, reduce existing costs, and generate additional revenue streams.

The work reported in this article was conducted to critically review the potential of biosolids-derived biochar to be used as a soil amendment in Australian agriculture. This assessment was required to identify the knowledge and technology gaps, and inform practice and policy going forward. Current biosolids management practices and regulatory frameworks in Australia were first reviewed to identify the limitations associated with biosolids recycling to land. Subsequently, available thermal treatment methods (pyrolysis and gasification) were studied to determine if they could offer alternative solutions to biosolids' management and reutilization. The physicochemical properties of biosolids-derived biochar and the fate of contaminants were reviewed to assess their potential for land application in comparison with biosolids. The aim of the review was therefore to synthesize the current state of knowledge and to determine if biosolids-derived biochar could be proposed as a promising soil amendment by highlighting the opportunities and challenges for its use in agriculture.

2. Current Biosolids Management Practices and Regulatory Framework in Australia

In 2019, Australia produced approximately 400,000 tons of dry biosolids (DBS) [1,6]. Approximately 70% was applied to agricultural land and around 24% was used for landscaping or land rehabilitation. The remaining 6% was stockpiled, landfilled, or discharged to the ocean [6].

A national regulatory framework strictly controls the land application of biosolids [12], and state guidelines have been developed to ensure a high level of protection for both the environment and public health [13]. However, current guidelines for controlling nutrients, pathogens, and contaminants in land application of biosolids vary between states in Australia, as highlighted by McCabe et al. [14]. As a result, Victoria, Tasmania, and the Northern Territory [1] are faced with the problem of stockpiling biosolids that fail to meet the regulatory criteria [15]. Currently, there are no guidelines in Australia on the issue of microplastics present in biosolids.

3. Limitations with Recycling Biosolids to Land

The concerns around environmental health, food safety, and quality are due to heavy metals and metalloids, persistent organic pollutants (POPs), microplastics, and pathogens [16]. These contaminants can hinder the land application of biosolids.

3.1. Heavy Metals and Metalloids

The risk of metals being released to the environment, transported to ground- or surface waters, being taken up by plants or microorganisms, or transferred to the food chain are key concerns for the land application of biosolids [5,17,18]. Arsenic (As), copper (Cu), lead (Pb), zinc (Zn), and nickel (Ni) present in sewage sludge may be concentrated during treatment [19]. Land application of these elements may result in uptake by plants and subsequently be transferred to the food chain [20,21] or environmental losses by processes such as leaching and runoff [2,22].

The degree of these risks depends on both the concentration of heavy metals and metalloids in the soil amendment, the application rate and method, and timing of application. The elemental concentrations vary depending on the location, wastewater source (commercial, domestic, or industry), and sludge treatment process [15]. However, the most critical factors that affect the mobility and bioavailability of heavy metals in the soil are the mineral components of the soil, such as clay, Fe-Mn-Oxides, and carbonate minerals, along with the soil's redox potential, soil pH, soil permeability, soil organic matter content, and soil microbial activity [23].

3.2. Persistent Organic Pollutants

Persistent organic pollutants (POPs), derived from synthetic organic compounds used in numerous industries, are present in wastewater and accumulate in biosolids [24]. Although primary and secondary treatments in wastewater treatment plants (WWTP) result in the partial removal of organic pollutants (e.g., polyfluorinated alkyl substances (PFAS) [25] and triclosan [26], some may remain in residual concentrations in biosolids and include perfluorinated chemicals (PFOS, PFOA), polychlorinated biphenyls (PCB), polychlorinated alkanes (PCAs), polybrominated diphenyl ethers (PBDE), triclosan, polyaromatic hydrocarbons (PAH), polybrominated diphenyl ethers (PBDEs), dioxins, steroids, and antibiotics [24]. The concentration of total PFOS, PFOA, and total PCB detected in Australian samples of biosolids ranged from 0.021 to 0.386 mg kg^{-1}, 0.003 to 0.05 mg kg^{-1}, 0.27 to 0.77 mg kg^{-1}, and 0.02 to 0.41 mg kg^{-1}, respectively [25]. Consequently, the existence of POPs in land-applied biosolids may result in ecosystem contamination with the potential for bioaccumulation in plants and animals [26] and the risk of human and animal toxicity [27].

To address the risk of environmental persistence, human and animal toxicity, and bioaccumulation of POPs in the food chain, the Australian government introduced strict concentration limits to restrict the land application of biosolids with high concentrations of POPs [28]. In Australia, the allowable limits of POPs in biosolids ranged from: PFOS 0.3–4.2 mg kg^{-1}; PFOA 0.05–33.6 mg kg^{-1}; total DDT 0.5–1 mg kg^{-1}; and total PCBs 0.05–0.5 mg kg^{-1} [12]. Although the disposal of biosolids in Australia complies with these limits, concerns remain regarding their bioavailability and mobility when applied to the soil [27]. More research is required to understand the bioavailability and mobility of heavy metals from biosolids when applied on land in the Australian context.

3.3. Microplastics

Microplastic particles range from 1 mm to 5 mm and can be detected in surface water, soil, sediment, and biota [29]. Microplastics commonly detected in biosolids are generally produced from polyethylene, polypropylene, polystyrene, polyvinylchloride, polyethylene terephthalate, and other polymers [30,31]. These microplastics originate from the synthetic fibers of clothing and plastics used in personal care products which eventually enter WWTPs and can enter the environment via subsequent application of biosolids to land [32,33].

The microplastic contamination of biosolids is widespread in Australia. For example, Okoffo et al. [34] collected biosolids samples from 82 WWTPs across Australia and reported that 99% of samples contained plastics at a concentration between 0.4 and 23.5 mg kg^{-1} DBS. Okoffo et al. [34] further projected that around 4700 Mt of plastics are released into the Australian environment through biosolids end-use each year, of which 3800 Mt is released onto agricultural land.

Microplastics can persist in the environment for decades after their application. Although microplastics are not biodegradable, they are prone to photodegradation and thermo-oxidative degradation [32,34]. The degradation of microplastics to nanoplastics (typically less than 100 nanometers in size, resulting from the degradation and fragmentation of larger plastic) is a concern for plants and animals [35]. At the nanoscale, plastics can pass through cell membranes and enter the food chain [36]. Microplastics and nanoplastics may adversely affect soil physiochemical properties and terrestrial food webs causing growth inhibition in earthworms, lethal toxicity to fungi, mammalian lung inflammation, and broad cytotoxicity [37].

3.4. Pathogens

The transmission of infectious pathogens from biosolids to humans, animals, or plants is a significant public health concern [19]. Biosolids contain pathogenic microorganisms, including viruses, bacteria, protozoa, and helminths [38]. The pathogen load depends on the feedstock, treatment, and stabilization processes used to produce the biosolids [19]. Moderate applications of biosolids can increase the diversity of the soil ecosystem, as the additional organic matter and nutrient inputs support the growth of microbial populations, leading to an increase in diversity [1,39]. However, the impact of biosolids on soil microbial diversity is not always positive. For instance, a study conducted by Mossa et al. [40] found that the increasing application of biosolids resulted in a change in the soil microbial diversity. Soil samples collected from 17 maize fields showed that diversity decreased with increasing zinc concentration in soils with more than 1000 mg kg^{-1} Zn. This indicates that above a certain level of accumulation of biosolids, the positive impact of organic matter on soil microorganisms is offset by the negative effect of high metal contamination [40].

Further inactivation of these pathogens depends on temperature, moisture content, pH, soil type texture, and sunlight [41]. While viral and bacterial pathogens will die in 1–3 months, protozoan oocysts and helminth ova can survive in biosolids for up to a year [42]. Overall, the application of biosolids on soil can have a significant impact on soil microbial diversity and abundance, and its effects depend on the amount of biosolids applied, the level of metal contamination in the sewage sludge, and the soil type [39]. However, the lack of data makes it challenging to review viral and protozoan pathogens in biosolids and is worthy of further research [43].

4. Thermal Treatment of Biosolids

Several factors drive the international uptake of thermal treatment, including current market changes and policy developments, energy generation from waste, waste minimization, and reduced associated disposal costs (Figure 1) [44,45]. Pyrolysis and gasification are the two main thermal processes applied to the management of biosolids and provide two benefits. Firstly, the destruction of POPs [46], microplastics [47], and pathogens [3] and secondly, the technology requires a reduced land footprint relative to other, more hazardous, waste management facilities (i.e., landfill or stockpiles) [8].

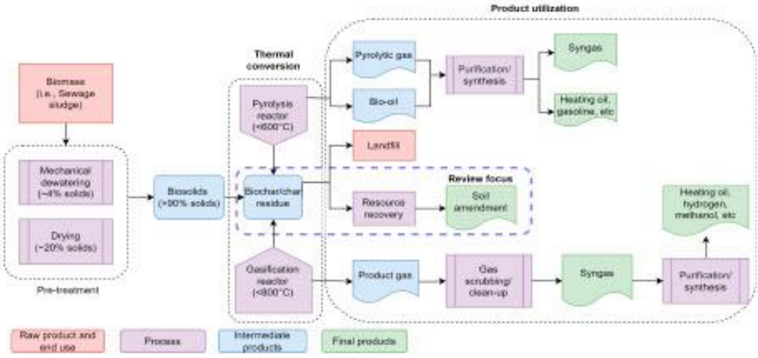

Figure 1. Schematic representation of thermal treatment of biosolids to produce biochar. The blue dotted area illustrates the focus of the literature review.

4.1. Pyrolysis

Pyrolysis involves heating organic materials in the absence of an oxidizing agent in a non-reactive environment (i.e., in the absence of oxygen). Contaminants including POPs, plastics, and pathogens are destroyed during three major stages: (i) dehydration and removal of lightweight volatile compounds at 25–200 °C; (ii) treatment of low and high molecular weight hydrocarbon complexes occurring at 200–600 °C; and (iii) decomposition of inorganics and formation of stable gases at >600 °C [48,49]. Typical processes require a vapor residence time ranging from 3 to 1500 s [10]. The reaction produces the following products: bio-crude oil, solid biochar, and syngas (Figure 1), with the proportion of the products dependent on the pyrolysis method, reaction time, and quality of sewage sludge. Regarding biochar, as the process time and/or temperature increase, the biochar yield decreases [50].

4.2. Gasification

In contrast to pyrolysis, gasification takes place at a much higher temperature ranging from 800 to 1200 °C (Figure 1) and a range of pressures (atmospheric to 35 bar) with controlled introduction of oxygen (~3%) to allow some combustion. Due to the partial combustion of the products of thermal treatment, gasification typically converts organic compounds to 15% biochar and 85% combustible gases which drive the process [51]. Similarly, as with pyrolysis, as process time and/or temperature increase, the biochar yield decreases, and the biochar properties depend on the physicochemical properties of the feedstock biosolids. Currently, biochar generated from biosolids can be used for applications in landfill, agriculture, or in construction [11].

Both pyrolysis and gasification of biosolids reduce volumes and masses, minimize the risk of pathogens, and reduce heavy metals and POPs [52]. However, the implementation of these technologies for large-scale application in WWTPs can be hindered by the high capital and operating costs [53,54].

5. Biosolids-Derived Biochar

5.1. Physicochemical Characteristics of Biosolids-Derived Biochar

The physiochemical characteristics of biosolids-derived biochar are highly variable and depend on the composition of the input feedstock, the thermal treatment process, the temperature, and the residence time [54–57]. Characteristics of particular interest include biochar yield; surface area; porosity; pH; electrical conductivity; concentrations of C, N and H; and N and P content. Table 1 and Figure 2 present data related to the variation in BDB properties as a function of the temperature of pyrolysis/gasification. The data were compiled using UC Davis Biochar [58] and data from published, peer-reviewed articles worldwide [59–66]. The complete data sets used are presented in the Supplementary Materials (Table S1).

5.1.1. Biochar Yield

While significant mass reduction in biosolids is achievable, the amount of biochar produced varies significantly depending on the production procedure and source properties [55,67,68]. During thermal treatment, the high organic content of biosolids is transformed and fixed in the stable carbon phase [69]. The decrease in yield is attributed to the volatilization of hydrocarbons and gasification of the carbonaceous compounds at high temperatures [55,70]. The relative ash content of biochar increases with pyrolysis residence time and temperature, which is expected as ash remains in the solid fraction while organic matter undergoes thermal decomposition [71–73]. Due to the elimination of volatiles, some of the nutrients and metals contained in feedstock biosolids become concentrated in biochar [74].

5.1.2. Surface Area and Porosity

Surface area and porosity play a crucial role in biochar applications, such as wastewater treatment and soil remediation. These properties are decisive to the quantity/quality of the available active sites in biochar and therefore enhance other biochar properties such as cation exchange capacity, water holding capacity, and adsorption capacity [75,76]. The surface area and porosity of BDB are interlinked [77], and generally increase with process temperature due to three factors: (1) an increasing degree of aromatization and rearrangement in the chemical compounds [78]; (2) mass loss during thermal decomposition due to the liberation of water and volatile matter [79]; and (3) the volatilization of moisture content in biosolids could create micropores in the biochar [80]. However, under extreme temperatures, the surface area decreases which is likely due to the destruction of the porous structure and the development of deformation, cracking, or blockage of micropores in BDB [81,82].

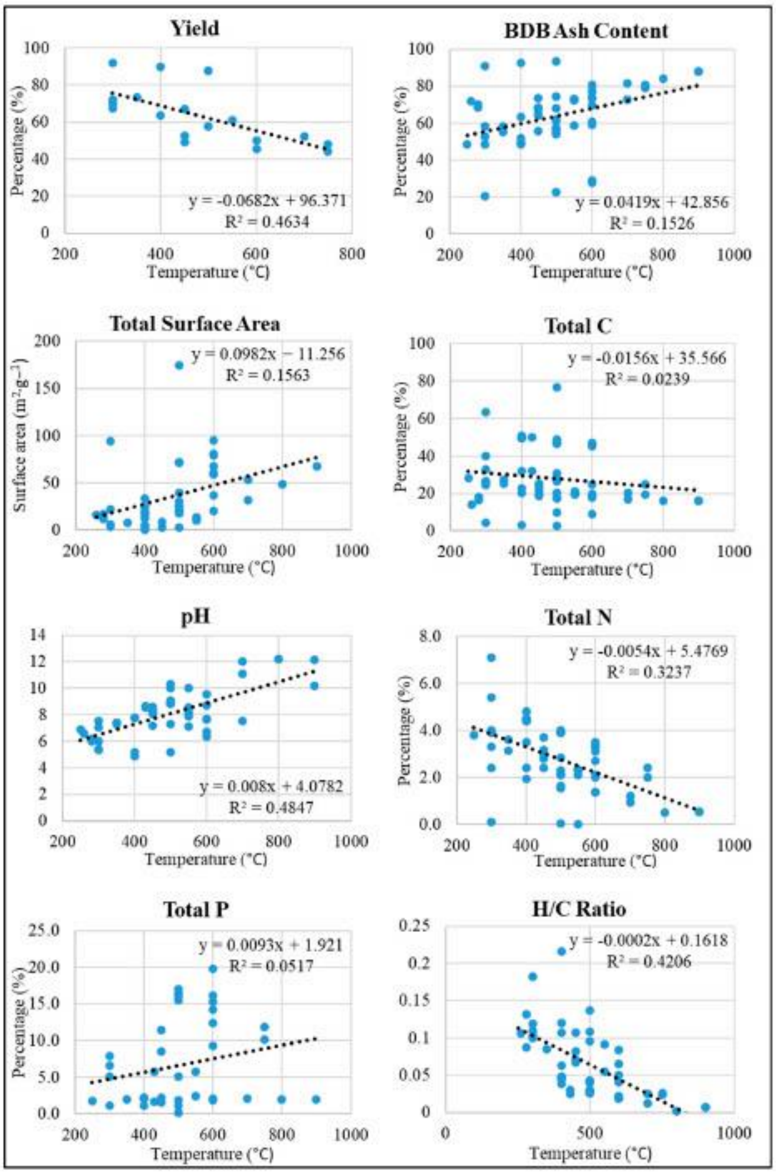

Figure 2. Change in the biosolids-derived biochar (BDB) properties as a function of temperature.

Table 1. Chemical analysis of biochar derived from biosolids at different temperatures. Results reported as average and (standard deviation).

Technology	Sample [a], Temp °C	pH	Elemental Analysis (%)			Nutrient Composition (g kg^{-1})					
			C	H	N	Ca	Fe	K	Mg	P	S
Pyrolysis [1]	BS 25	5.1	25.6	4.1	3.0	26.5 (19.4)	37.0 (22)	4.1 (3.3)	8.1 (9.9)	28.5 (6.8)	23.2 (24.8)
	BDB 300	5.9 (0.6)	23.1 (2.7)	2.7 (0.8)	3.0 (0.6)	31.24 (24)	44.01 (30.4)	4.17 (3.2)	10.18 (12.8)	32.89 (8.2)	23.23 (1.9)
	BDB 400	6 (1.3)	19.9 (0.4)	1	2.2 (0.3)	42.13 (19.7)	48.94 (35.5)	6.52 (3.5)	13.31 (13.4)	32.83 (8.7)	28.46 (26.5)
	BDB 500	7.1 (0.5)	15.3 (5.1)	0.9 (0.8)	1.0 (0.8)	40.41 (32.6)	54.72 (41.6)	5.12 (4.5)	13.19 (17.4)	41.83 (14.9)	24.43 (29.94)
	BDB 550	7	18.6 (12.5)	0.8 (0.2)	2.5 (0.5)	-	-	-	-	-	-
	BDB 600	8.7 (0.7)	-	-	-	24	41.7	13.3	7.86	45.1	-
	BDB 700	9.6 (2.0)	13.9(5.6)	-	1.0 (0.3)	48.96 (21.7)	60.66 (43.3)	12.35 (6.0)	13.99 (12.7)	40.92 (7.8)	35.1 (37.7)
	BDB 900	11	5	-	0	71.82	33.37	9.83	29.06	40.65	9.69
Slow pyrolysis [2]	BS 25	7.1	25.6	4.5	4.5	42.4 (23.6)	30.4 (28.0)	5.1 (2.6)	9.3 (5.9)	38.7 (9.2)	20.9 (10.7)
	BDB 300	7.3 (0.2)	27.5 (4.7)	3.1 (0.3)	4.5. (0.9)	25.76 (28.7)	7.10 (2.9)	3.5 (2.6)	12.40 (7.4)	49.69 (21.6)	7.92 (3.0)
	BDB 400	7.3 (0.2)	22.2 (5.6)	1.9 (0.2)	3.6 (0.8)	7.43 (5)	-	2.17 (0.2)	9.10 (4)	42.03 (15.1)	6.07 (0.6)
	BDB 450	-	22.5 (4.1)	1.7 (0.1)	3.4 (0.5)	-	-	-	-	-	-
	BDB 500	7.4 (0.3)	22.2 (4.0)	1.2 (0.6)	2.8 (1.1)	56.47 (48.5)	63.8 (47.5)	7.59 (5.2)	13.56 (9)	56.73 (19.8)	19.73 (16.9)
	BDB 600	9.6 (1.6)	22.2 (3.9)	0.9 (0.3)	2.6 (0.9)	58.96 (42.5)	48.8 (50.5)	8.32 (4.9)	17.85 (13.5)	68.93 (2.9)	15.6 (13.9)
	BDB 700	12.5 (0.4)	22.5 (3.6)	0.5 (0.1)	2.3 (0.4)	93.05 (24.5)	51.93 (53.4)	11.98 (2.9)	20.42 (9.4)	83.63 (24.7)	24.08 (20)
Fast pyrolysis [3]	BS		43.40	6.99	5.66	27.1	8.5	5.9	6.0	23.9	10.1
	BDB 400	-	29.9	1.1 (0.6)	2.5 (1.4)	-	-	-	-	-	-
	BDB 500	8.8	19.7 (3.14)	1.1 (0.6)	2.5 (1.4)	73.2 (19.8)	28.8 (3.2)	13.2 (6.7)	17.2 (3.6)	46.6 (40.2)	-
	BDB 600	9.5	19.5 (1.6)	0.6 (0.6)	2.3 (1.3)	62.71	33.60	8.40	15.45	18.76	-
	BDB 700	11.1	16.9	0.2	1.0	64.37	35.32	9.30	16.36	20.35	-
	BDB 800	12.2	16.2	0.0	0.5	65.83	35.76	9.20	16.57	19.35	-
	BDB 900	12.2	15.9	0.1	0.5	69.56	37.20	8.60	17.52	20.23	-
Flash Pyrolysis [4]	BDB 350	7.7	20.5	2.4	8.2	17.07	0.4	13.52	9.88	24.12	-
	BDB 400	-	15.4	1.6	6.6	-	-	-	-	-	-
	BDB 450	-	12	1.2	5.9	-	-	-	-	-	-
	BDB 500	-	12.6	1.2	3.9	-	-	-	-	-	-
	BDB 550	-	10.9	0.9	4	-	-	-	-	-	-
	BDB 650	-	10.3	0.7	0.7	-	-	-	-	-	-
	BDB 700	8.7	10	0.5	ND	5.35	ND	23.20	13.6	22.89	-

Table 1. *Cont.*

Technology	Sample [a], Temp °C	pH	Elemental Analysis (%)			Nutrient Composition (g kg^{-1})					
			C	H	N	Ca	Fe	K	Mg	P	S
	BS	-	-	-	-	51	30	5	6	40	8
Two stage gasification	BDB 850	-	5.8	-	0.1	14	7.5	15	17.0	11.2	20
LT-CFB [b] gasification [5]	BDB 750	-	7.2	-	0.6	13	8.1	15	17.0	11	10
	BS	-	-	-	-	49.7	38.7	3	9.6	41.8	9.5
Gasification [6]	BDB 700	12	22.3	0.77	1.9	11	8.8	7.6	24.5	10.2	-
	BDB 900	12	2.9	0.18	0.25	14.5	11.9	10.9	35.1	14.2	-

[a] BS—biosolids; BDB—biosolids-derived biochar; [b] LT-CFB—Low temperature circulating fluidized bed; ND—not detected. [1] [55,83–88]; [2] [89–91]; [3] [92–94]; [4] [95,96]); [5] [97]; [6] [98].

5.1.3. Electrical Conductivity and pH

The electrical conductivity (EC) and pH of biochar influence the mobility of macro- and micro-nutrients and heavy metals [99]. Electrical conductivity indicates the content of soluble salts. Biochar's high-in-ash content typically contains proportionally higher concentrations of salt ions. These salt ions act to reduce the exchangeable hydrogen and aluminum ions in the soil. Consequently, this has the effect of increasing the soil pH [99]. As the treatment temperature increases, the EC of the material reduces dramatically, particularly with temperatures >500 °C [55,71,100]. Biochar EC correlates better with feedstock type than pyrolysis temperature because it is a function of ash content and elemental composition [101,102].

In contrast with EC, resulting biochar pH increases with temperature from around pH 7 at 300 °C to pH 10–12 at 900 °C (Table 1, Figure 1) [55,69,103]. At temperatures higher than 550 °C, cations such as Ca, K, Mg, Na, and Si present in the biosolids will form carbonates and oxides leading to an increase in pH [104]. As pH increases, heavy metals become reduced and are present in residual phases or bound to carbonates, oxides, and organic matter [99].

5.1.4. H:C Molar Ratio

Biosolids-derived biochar is very stable. Estimates of the mean residence time of BDB in soil are in the order of 2000 years [105]. The molar H:C ratio is an indicator of this stability. More specifically, the ratio is an indicator of the degree of carbonization that can be used to characterize the degree of aromaticity of the biochar [77,106]. This is indicated by a reduction in H relative to C, indicating increased aromatization and consequently increased chemical stability [106].

Consequently, biochar stability increases as the degree of aromatic condensation increases [107]. H and C concentration decreases significantly with increases in process temperature (Table 1). This occurs primarily due to the volatilization of elements such as CO, CO_2, H_2O, and hydrocarbons [19]. Additional losses of H occur due to the reduction in hydroxyl (OH-) functional groups, dehydration, and condensation in the thermal treatment processes [108].

5.1.5. Nutrients

Nitrogen, alongside phosphorus, is important for determining the fertilizer value of biosolids-derived biochar but experiences significant losses during thermal treatment (Table 1) [94]. Most nitrogen is lost due to the volatilization of the different nitrogen groups (i.e., NH4-N or NO3-N) at low temperatures [50], and with temperatures above 600 °C, nitrogen is gradually transformed into pyridine-like structures [92,109]. Thomsen et al. [110] operated numerous thermal technologies across a temperature range of 600–850 °C, both with and without oxidation. Without oxidation, nitrogen content decreased from 3.7% in DBS to 2.2% in BDB at 600 °C, 0.6% at 750 °C, and 0.1% at 850 °C. In contrast, the addition of oxidation at 600 °C resulted in a nitrogen content of 0.1% in BDB, which decreased further to 0% at subsequent temperatures. Consequently, a low process temperature without oxidation should be used if biochar with high nitrogen retention is sought [110].

Conversely, while there appears to be a loss of phosphorus during thermal treatment [55], total phosphorus concentration in biochar generally increases with the process temperature (Table 1) [97]. Thomsen et al. [110] measured an increase in total P from 4% in DBS to around 8% in BDB formed at 600 °C and to 11% in BDB formed at 750 °C. This increase could be due to the increased contact of Ca, Mg, and P upon the transformation of organic matter in the biosolids, which would lead to the formation of insoluble Ca-P and Mg-P compounds [71]. However, while total P increases, the available fraction of phosphorus (Colwell P) decreases with an increasing process temperature [55,71]. Unavailable P, however, may become progressively available, albeit slowly [97].

There are several other agronomically essential nutrients contained within BDB. While the total nutrient concentrations of K, Ca, Mg, and Fe typically increase with increasing temperature [55,110], the total H:C ratio and sulfur decreases (Figure 2 and Table S1 in Supplementary Materials) [111].

5.2. Contaminants in Biosolid-Derived Biochar

5.2.1. Fate of Heavy Metals in Biosolids-Derived Biochar

Heavy metals and metalloids contained within biosolids are either volatilized during thermal treatment or become concentrated in the biochar product [112–114]. Mercury, for example, has a low boiling point, and at temperatures above 500 °C, almost all mercury can be volatilized during pyrolysis (Table 1) [88]. Furthermore, Hossain et al. [55] observed the enrichment of Pb, Ni, and Cr in the biochar at temperatures of up to 500 °C, followed by a decrease in concentration at 700 °C, indicating the partial loss of these metals at elevated temperatures. Consequently, the focus has shifted to understanding the conversion of stabilized heavy metals into bioavailable forms and the subsequent mobility of heavy metals in a soil environment [95,105].

High-temperature thermal treatment reduces the ability for heavy metals to leach from biochar into soils, and this phenomenon increases with temperature [78,89,99]. These BDB have high pH and cation exchange capacity (CEC) values (Table 1), along with more chemically stable heavy metal fractions that result in unfavorable conditions for leaching (Table 1) [115]. As a secondary effect of pH increasing with process temperature, heavy metal solubility decreases with increases in pH. Devi and Saroha (2014) [115] demonstrated that pH has a strong effect on water-soluble heavy metals, whereby the extractable rates of Pb, Zn, and Cu decreased from 16%, 82%, and 43% in sewage sludge to 1%, 2%, and 2% in biochar, respectively, as pH increased from 3 to 7.

Consequently, heavy metal bioavailability is reduced by thermal treatment and attributed to reductions in soil pH and the physical changes in both the heavy metals and biochar [116–118]. Yang et al. [88] pyrolyzed eight biosolids from four different wastewater treatment plants in southeast Melbourne, Australia. They produced biochar at two different temperatures (500 and 700 °C) with residence times of 5 h and a heating rate of 5 °C min^{-1}. The concentrations of plant-available Cd, Cu, Pb, and Zn decreased by 93%, 84%, 98%, and 86%, respectively. In this case, treatment at 700 °C was no more beneficial than 500 °C. However, Yang et al. [88] declared that the DTPA method used to estimate plant-available heavy metal content extracts both readily exchangeable and more persistently bound heavy metals. Although the magnitude of reduction in plant-available heavy metals is large, these values may under-represent the benefit of thermal treatment.

Similar to Yang et al. [88]'s work, Hossain et al. [55] thermally treated biosolids from a Sydney (NSW, Australia) WWTP at 300, 400, 500, and 700 °C with an unreported dwell time. Elements including Cu, Cd, and Zn were extracted with DTPA to estimate their plant-available fractions. Copper initially experienced a decrease of at least 99% at a temperature of 300 °C. However, when exposed to 400 and 500 °C, Cu experienced a decrease of only 35% and 24%, respectively, before decreasing back to 99% at 700 °C. Cadmium saw a similar effect at 400 °C, displaying an increase in availability over the feedstock by 33%, while at all other temperatures, Cd was below the limit of detection, with an apparent decrease in the availability of at least 93%. By comparison, Zn followed a temperature-dependent reduction in plant-availability of 52%, 72%, 82%, and 100% at 300, 400, 500, and 700 °C, respectively [55]. Unfortunately, without a dwell time, it is difficult to compare results.

For international comparison, Lu et al. [90] pyrolyzed biosolids from three different wastewater treatment plants in China at 300, 400, and 500 degrees with a dwell time of 2 h and a heating rate of 10 °C min^{-1}. Heavy metal bioavailability was in the range of 0–4%, 0–9%, 0–3%, 0–2%, and 0–4% of total concentrations of Pb, Zn, Cu, Fe, and Mn, respectively (Table 2). DTPA-extractable heavy metals increased at higher treatment temperatures. Across the three WWTPs, a treatment temperature of 300 °C resulted in an average reduction in plant-available extract by 99%, decreasing to 88% at 400 °C, and 89% at 500 °C (Table 2).

The optimum temperature and dwell time appear to be somewhat feedstock specific. For example, both Yang et al. [88] and Lu et al. [90] produced no added benefit from additional treatment temperature (Table 1), while the results from Hossain et al. [55] indicated a higher treatment temperature is more effective at reducing heavy metal bioavailability in the biochar product. Therefore, independent feedstocks should be evaluated for optimum treatment temperature to maximize heavy metal immobilization while ensuring unnecessary energy expense.

Although there are competing results from various investigations, thermal treatment of biosolids can immobilize most of the heavy metals in the resulting biochar, and the expected environmental risk is low (Table 2). However, data explaining the change in heavy metal and metalloid availability that occurs during thermal treatment are scarce [105]. Consequently, the detailed mechanism of how thermal treatment temperature influences the distribution and fraction transformation of heavy metals in sewage sludge still needs further investigation.

Table 2. Heavy metals and organic pollutants in biosolids and biosolids-derived biochar and their allowable range according to guidelines.

Guidelines	Sample	Temp °C	Total Heavy Metals (mg kg^{-1} DBS) [b]								Total PAHs µg kg^{-1} d.b.	Reference
			As	Cd	Cr	Cu	Pb	Hg	Ni	Zn		
AWA-Biosolid	-	-	20–30	1–20	100–600	100–2000	150–420	1–15	60–270	200–2500	-	[12]
IBI-Biochar	Category A	-	13	1.4	93	143	121	1	47	416	6000	[119]
	Category B		100	20	100	6000	300	10	400	7400	300,000	
EBC-Biochar	Premium	-	13	1	80	100	120	1	30	400	4000	[120]
	Basic		13	1.5	90	100	150	1	50	400	12,000	
Technology												
Pyrolysis	BS	N/A	-	2.3–5.3	-	401–611	136–224	-	-	629–1238	-	[19]
	BDB	300	-	3.3–7.5	-	480–043	190–350	-	-	849–1909		
	BDB	400	-	3.8–9.8	-	549–1198	194–438	-	-	912–2104		
	BDB	500	-	4.3–8.9	-	565–1267	212–506	-	-	1014–2305		
Pyrolysis	BS	N/A	-	7.54	-	545	189	-	102	2398	-	[100]
	BDB	400	-	9.67	-	632	239	-	129	2983		
	BDB	600	-	9.76	-	740	253	-	134	3922		
Gasification	BS	N/A	-	1.0–2.5	34–66	-	41	1.5	24	-	-	[97]
	BDB	750	-	1.5–5.5	80–182	-	84–110	0.2	87–158	-		
Gasification	BS	-	-	0.93	80.8	580	78.27			402	-	[121]
	BDB	350		1.5–1.6	218–227	851–900	114–121			597–623		
	BDB	400		1.5–1.7	228–247	886–922	120–125			612–637		
Gasification	BS	-	-	1	36 (7)	529 (8)	45	2	66(2)	423(10)	-	[98]
	BDB	700		ND	98 (1)	1159 (8)	88(1)	ND	122(1)	753 (5)		
	BDB	900		ND	104 (2)	1346 (6)	51(1)	ND	165(4)	757 (4)		
Pyrolysis	BDB	200	7.6–16.7	2–9.1	67.6–281	712–1000	28.4–60		65–635	1964–2940		[122]
Pyrolysis	BDS	25	-	1.0	173	143	51.1		42	698	3339	[123]
	BDB	200		1.1	180	149	54.7		41.1	735	1644	
	BDB	500		1.4	233	193	67.9		55.1	887	70,385	
	BDB	600		1.1	239	198	69.1		56.1	976	1241	
	BDB	700		0.7	247	202	74.2		55.2	986	179	
Pyrolysis	BS	25	-	3.6	-	487	167	-	-	922	-	[90]
	BDB	300		5.5		733	260			1417		
	BDB	500		6.5		841	506			1705		

Table 2. *Cont.*

Guidelines	Sample	Temp °C	Total Heavy Metals (mg kg^{-1} DBS) [b]								Total PAHs µg kg^{-1} d.b.	Reference
			As	Cd	Cr	Cu	Pb	Hg	Ni	Zn		
Pyrolysis	BS BDB	- 550	2.6 12	1.7 2.7	-	160 210	44 82	-	-	1200 2080	3860 900	[124]
Pyrolysis	BS BDB	 550	2.3 11.9	1.5 2.3	-	171 237	53.8 71.9	-	-	1105 1879	5780 1701	[122]
Pyrolysis	BS BDB BDB	Air 400 500	18 9.4 14	ND 3.2 3.2	20 60.7 61	165 357 334	42 83 92.6		23 77.1 68.4	703 1478 1704	-	[72]
Pyrolysis	BDB	550	9.3	3.7	74.1	222	27		34.5	1102	-	[125]
Pyrolysis	BS BDB	- 500	-	-	-	-	-	-	-	-	2950 4350	[126]
Pyrolysis	BS BDB	- 500	-	-	-	-	-	-	-	-	8625–13,333 612–766	[80]
Technology	**Sample [a]**	**Temp °C**	**Available heavy metals (mg kg^{-1} DBS [b])**									**Reference**
			As	**Cd**	**Cr**	**Cu**	**Pb**	**Hg**	**Ni**	**Zn**		
Pyrolysis	BS BDB BDB BDB BDB	25 300 500 600 700	-	7.80 0.45 2.30 5.90 10.5	9 11 9 8.5 8	700 45.5 205 295 365	309 48 27.5 67 115	-	135 20.5 25 37 46.5	3565 280 385 635 970		[123]
Pyrolysis	BS BDB BDB	25 300 500	-	1.8 ND ND	-	139 1.7 0.4	34.9 ND 6.5	-	-	586.6 4.5 50.8		[90]
Pyrolysis	BS BDB	- 550	1.1 0.04	1.1 0.2	-	37 3.4	8.2 2.5	-	-	371 66		[124]
Pyrolysis	BS BDB	- 550	1.07 0.05	1.03 0.17	-	35.3 4.35	9.02 3.41	-	-	387 56.7		[122]
Pyrolysis	SS BDB BDB	Air 400 500	- 0.9 0.6	- ND ND	- 0.2 ND	- 0.3 0.2	- 0.5 0.6	-	- 0.3 ND	- 7.9 1.8		[72]
Pyrolysis	BDB	550	0.04	0.26	1.24	6.5	2.13		2.26	127		[126]

Table 2. *Cont.*

Guidelines	Sample	Temp °C	Total Heavy Metals (mg kg^{-1} DBS) [b]								Total PAHs µg kg^{-1} d.b.	Reference
			As	Cd	Cr	Cu	Pb	Hg	Ni	Zn		
	BS	-		0.62	1.26	22.63	2.74			112		
Gasification	BDB	350	-	0.03–0.12	1–3.91	0.42–1.17	0.58–1.13	-	-	7.67–17.19		[121]
	BDB	400		0.01–0.24	1.2–7.51	0.37–0.97	0.59–1.40			9.05–12.25		
	BS	-			8.89	16.3			3.44			
Gasification	BDB	700	-	-	0.06	0.49	-	-	0.04	-		[98]
	BDB	900			0.04	2.08			<0.01			

[a] BS—biosolids; BDB—biosolids-derived biochar; [b] DBS—dry biosolids; N/A—not applicable; ND—not detected.

5.2.2. Fate of Organic Pollutants and Microplastics in Biosolids-Derived Biochar

Although biosolids are essential vectors for the transfer of POPs and microplastics to the environment, both can be destroyed by thermal treatment. Ross et al. [127] demonstrated that 2.5 min of pyrolysis at 500 °C eliminates some common pollutants, including triclocarban and triclosan from the biochar product. At a temperature of 500 °C, the removal rate of POPs, specifically dioxins (PCDD/PCDF), was 97% in sewage sludge [128]. Conversion of biosolids to biochar reduced PAH content by 95% [91]. Thermal degradation of PAH is further supported in Table 2. Thermal treatment is a promising technology for the decomposition of microplastics at higher temperatures [129]. Ni et al. [47] reported that the microplastic concentration in BDB decreased significantly from 550 to 960 particles per gram to 1.4–2.3 particle per gram with an increase in the pyrolysis temperature up to 500 °C. According to Ni et al. [47], thermal treatment of biosolids at high temperatures (>450 °C) can reduce microplastic concentration by 99%. A recent case study summarized evidence on this topic covering 20 studies and more than 100 different organic pollutants and concluded that pyrolysis reduces the concentration of organic contaminants with an efficacy of >95% to >96% in most cases [130].

While pyrolysis has been demonstrated to be an effective method for removing organic contaminants, it is important to ensure the quality of biochar products meets the established guidelines. This may require an approval process that includes not only chemical analyses, but also bioassays to test the ecotoxicity to soil, water organisms, and plants.

6. Use of Biosolids-Derived Biochar as a Soil Amendment

The current understanding of the agricultural effects of biosolids-derived biochar in Australian agricultural soil is limited and is primarily based on few biomass feedstock materials. Furthermore, commercial biochar in Australia is marketed with only limited (or without) analytical data for the biochar [131]. For the land application of biochar, it is vital to know the composition of the biochar and, consequently, the properties of soils used [132]. Thus, international experiences do not necessarily apply to Australian soils, and research and development must be undertaken to integrate information on Australian soils into management decisions.

There are no legislative standards available in Australia that prescribe limits for the concentrations of heavy metals in biochar intended for soil application. Regulations and standards for composts and biosolids in Australia are based upon an assessment of the total concentration of metals in the material, without any consideration of their mobility in soil and bioavailability. Consequently, inappropriate regulation may limit the use of these nutrient-rich bioresources [105]. Voluntary biochar quality standards exist in Europe, i.e., the European Biochar Certificate [120], and in the USA, i.e., the International Biochar Initiative, and they aim to guarantee the quality of a product. These voluntary schemes define biochar as a material produced by the thermal treatment of biomass under low oxygen conditions, and consequently both these guidelines allow the use of biosolids as feedstocks for biochar production under defined regulation [119]. Importantly, according to these guidelines, organic contaminant and heavy metal concentrations are the major determinants of the end-use of the biochar [119,120].

6.1. *Soil Effects*

Biochar applied to soil can be used for locking carbon in soil, heavy metal immobilization, greenhouse gas reduction, and soil water retention (Figure 3) [131,133,134].

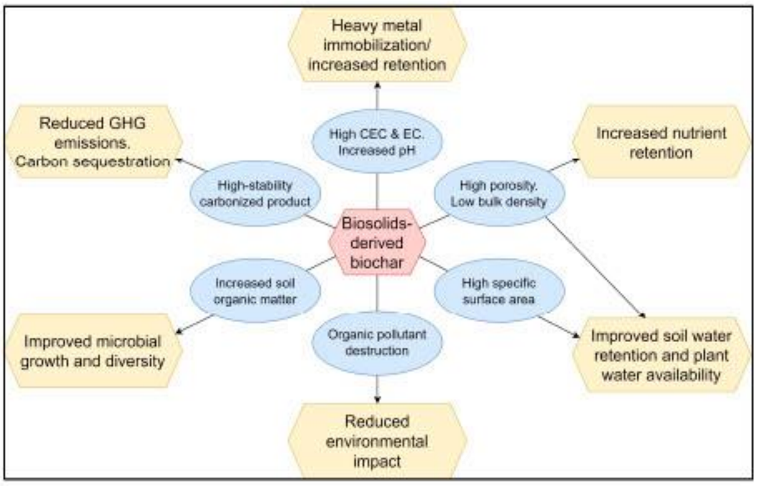

Figure 3. Relevant properties of biosolids-derived biochar that can improve soil properties and reduce environmental risks associated with their use in agriculture.

6.1.1. Soil Acidity and Nutrient Leaching

Naturally, high pH and CEC values for BDB can reduce soil acidity, limit nutrient leaching, and heavy metal release in soil. Hossain et al. [55] demonstrated that by manipulating the temperature of pyrolysis, it is possible to create a range of BDB products with pH values targeted for application in acidic or in alkaline soils. Additionally, the highly negative surface-charge density of biochar enables the retention of cationic nutrients via ion exchange, whereas the relatively extensive surface area, internal porosity, and polarizability facilitate the sorption of anionic nutrients via covalent bonds [135]. Therefore, BDB could adsorb heavy metals and organic contaminants such as pesticides and herbicides from the environment [11].

6.1.2. Soil Hydrology

Biosolids-derived biochar has both a high specific surface area and porosity, which could represent an improvement in soils' nutrient status and physical properties such as water retention and hydraulic conductivity [136]. The bulk density of biochar is lower than that of mineral soils [137], suggesting that the application of biochar can alter soil hydrology and further increase soil porosity, which can result in long-term impacts on soil aggregation [134,138]. Méndez et al. [100] applied the BDB obtained at 600 °C at 8% (*w*/*w*) application rate and observed increases in soil field capacity from 23% to 29%, and available water increased from 10% to 16%.

Typically, high biochar application rates are necessary to improve soil physical and hydraulic properties, such as water-holding capacity or bulk density (e.g., >40 t ha^{-1}, [139]). However, lower biochar application rates (e.g., 10–20 t ha^{-1}) have been also shown to improve physical soil properties [140,141]. There is a lack of research regarding the appropriate level of biochar application for different soil types, particularly in Australia [131,142].

6.1.3. Greenhouse Gas Emissions

Organic materials, such as sewage sludge, added to the soil result in N_2O emissions that are sometimes far greater than equivalent amounts of chemical fertilizer [143,144]. Van Zwieten et al. [144] demonstrated that if biosolids are processed via slow pyrolysis, they do not pose the same greenhouse gas risk as untreated organic material. Biosolids-derived biochar was effective in reducing overall emissions of N_2O compared with the control soil.

The control soil that received an equivalent 165 kg N (in the form of urea) released 15% of this N as N_2O, while amendment of the soil with 5% BDB resulted in only 2% of the N being converted into N_2O (i.e., an 84% decrease). Grutzmacher et al. [145] conducted an incubation experiment in which they applied a range of biochar from different feedstocks to the soil and investigated the potential of biochar to reduce fertilizer induced N_2O emissions. When ammonium nitrate was co-applied with biochar, the smallest emission was observed in soil amended with BDB, which reduced the N_2O emission by 87% [145].

6.1.4. Soil Nutrients, Soil Organic Matter, and Soil Carbon

Pyrolysis makes biosolids very stable against chemical and biological degradation, and biosolids-derived biochar in the soil can store carbon in the form of stable structures for centuries. de Figueiredo et al. [84] evaluated the effects of applying BDB in combination with mineral fertilizer on soil organic carbon fractions (SOC). They demonstrated that the increase in organic C in the soil promoted by biochar varies with the pyrolysis temperature employed [51,146]. The biochar produced under lower pyrolysis temperature (300 °C) affected the more labile fractions of soil organic matter (SOM), whereas the biochar produced under higher pyrolysis temperature (500 °C) influenced the more stable fractions of SOM [84,147]. These differences among biochar greatly influence their mineralization rates, nutrient release, and C accumulation in the soil [148]. Considering the importance of equilibrating the supply of C in both labile and stable forms of SOM, the biochar produced at the 300 °C pyrolysis temperature presents great potential to be used for agro-environmental purposes [84]. Additionally, BDB is beneficial for the soil microbiota. Carbonized organic matter represents energy for microorganisms that inhabit the soil [149], and its application to the soil increases soil microbial activity [150,151]. Furthermore, the high surface area and porosity increase microbial activity by promoting optimal growth conditions [152].

Compared with biochar derived from plant residues, BDB generally contains a higher level of nutrients [153]. Additionally, the high porosity increases the surface area in the structure of the material. It facilitates the adsorption of both hydrophilic and hydrophobic molecules [62], which subsequently improves nutrient retention [72]. In one of the first studies in Australia, Bridle and Pritchard (2004) [154] investigated the effect of BDB on N and P recovery in an incubation experiment over eight weeks. Water-soluble N was retained in the biochar. Biosolids-derived biochar did not initially increase soil mineral N levels, as observed with land application of biosolids, although soil bicarbonate–extractable P levels gradually increased. This study demonstrated that nitrate and ammonium concentrations did not increase in soil within 56 days after application, suggesting that land application can minimize the risk of nitrogen leaching [154].

Biochar also provides a source of P for plant growth and could have applications on soils as a slow-release form of P [154]. Biosolids-derived biochar can be utilized as a reservoir of P for soils, and a certain fraction of this P is in a suitable form available for plant uptake [71,155].

6.2. *Crop Effects*

6.2.1. Crop Yield

All of the above-mentioned soil impacts play an important role in promoting crop yield (Table 3). Sousa and Figueiredo (2016) [156] reported enrichment of nutrients in soil treated with BDB, especially P, available N, and exchangeable cations (Ca and Mg). This enriched soil promoted the development of radish plants with increased plant height, above-ground dry weight, and number of leaves at different rates of BDB application. Furthermore, Hossain et al. [157] studied the use of BDB on the production of cherry tomato and found the addition of biochar (10 $t \cdot ha^{-1}$) increased the average dry weight of shoot production from 62 to 74 $g \cdot plant^{-1}$, and increased yield by 64%.

The interaction between soil and BDB can alter over a long period of time. An extensive search of the literature revealed limited investigations that demonstrated long-term impacts of BDB on soil and crop yield (Table 3). Faria et al. [105] conducted a two-year field experiment which resulted in increased soil fertility, mainly P, Mg, Cu, and Zn, and an increase in CEC, while soil K was not affected. Increased soil fertility resulted in greater crop yield, especially in the second cropping season. Figueiredo et al. [158] investigated the direct (first and second cropping season) and residual (third and fourth cropping season) effects of BDB on soil P fractions, P uptake and corn grain yield. Positive effects of the trial were observed on corn yield and P content in soil. BDB also maintained a high soil P content for two years without re-application, indicating that BDB can behave as a slow-release P-fertilizer [158]. Given that there are limited long-term studies, it is challenging to assess the long-term effect of BDB when applied to land. Despite the increasing research effort in recent years in this area, a sound understanding of the relationship between desired biochar characteristics, production conditions, and feedstock is still lacking. Further work is needed, especially to identify which combination of feedstock and treatment conditions would provide the most appropriate properties for biochar as a soil amendment [77].

Table 3. Effect of biosolids-derived biochar on soil physicochemical characteristics, crop yield and heavy metal bioaccumulation. Thermal treatment process used to biochar from biosolids was pyrolysis.

Temp °C	Plant Species	Soil Fertility	Agronomic Performance		Reference
			Crop Yield	Heavy Metals Bioaccumulation	
300	Radish	Increased soil base saturation, CEC, available P, Ca, and Mg, except K. Soil pH was not affected.	Increased plant height, yields, and above-ground dry weight.	-	[156]
450	Wheat	Increased soil CEC, K, and available P.	Increased plant height, biomass, and grain yield.	-	[46]
500	Rice	Increased pH, EC, total N, C and available P and K. Availability of heavy metals in the soil was reduced.	Increased shoot biomass, grain yields, and above-ground dry weight.	Reduced bioaccumulation of As, Co, Cr, Cu, Ni, and Pb in rice grains, stems, and leaves.	[125]
400–550	Garlic	-	Increased average plant height, plant biomass (stems and leaves) and garlic yield when compared with control.	No heavy metal accumulation was found in stems and leaves. However, higher Zn and Cu content was found in roots and bulbs compared to the control.	[72]
550	Coolatai grass	-	Increased grass yield was observed, specifically when biosolids-derived biochar was combined with chemical fertilizer.	-	[159]
550	Cherry tomatoes	-	Increased plant height and fruit yield.	Heavy metals' concentrations in the fruits were lower in the biochar treatment than the biosolids treatment.	[160]
550	Cucumber	-	Increased plant biomass and fruit yields	Reduced bioaccumulation of As, Cu, Cd, Zn, and Pb in the fruit when compared to the biosolids treatment.	[124]
200–700	Turf grass	Increased soil organic carbon, total N, available P and K, decreased soil pH.	Increased above-ground dry matter and total N, P, and K content.	Reduced bioaccumulation of heavy metals was observed in above-ground biomass	[161]

6.2.2. Bioavailability and Bioaccumulation of Pollutants

The main limitation in using biosolids and BDB as a soil amendment is the presence of heavy metals and PAH (Table 2). To cause a toxic effect, heavy metals must dissolve in soil solution, be taken up by organisms, and transported to cells where a toxic effect can occur [162]. Through conversion of biosolids to biochar, it is possible to decrease PAH concentrations (Table 2) and the bioavailability of heavy metals (Table 4). Waqas et al. [124] conducted research on contaminated soil from farmland near an iron refinery plant in Fujian Province, China, in which the researchers applied both biosolids and BDB. The conversion of biosolids to biochar significantly decreased the concentration of PAH and available heavy metal concentration (Table 2). Additionally, the application of BDB to soil was much more effective in reducing the availability of PAHs and heavy metals than biosolids, and therefore reducing pollutant transfer from soil to water and subsequently to plants. Consistent with these observations, plants with biochar application were less prone to PAH accumulation. Studies that involved growing lettuce [126], tomatoes [122], and cucumber [124] with biosolids and BDB, revealed that the PAH concentration in plant biomass was lower in the biochar trials (Table 3).

In a Mediterranean context, Mendez et al. [162] evaluated the effects of biochar from pyrolyzed sewage sludge applied on agricultural soil. The evaluated properties included heavy metal solubility and bioavailability in BDB-treated soils compared to those treated with raw sewage sludge. The risk of leaching of Cu, Ni, and Zn were lower in the soil treated with BDB than in the sewage sludge treatment [162]. Biochar-amended samples also reduced the availability of Ni, Zn, Cd, and Pb in plants compared to amended samples of sewage sludge (Tables 3 and 4).

While the bioaccumulation of heavy metals in plants grown in BDB is a potentially concerning pathway for them to enter the food chain, the bioavailability of heavy metals represents a low risk. Jin et al. [107] and Lu et al. [163] reported that although carbonization leads to the enrichment of heavy metals in the matrix of BDB, they exist mostly in oxidizable and residual forms. This results in a significantly reduced bioavailability of these pollutants and presents a very low ecological risk [107]. Hossain et al. [157] investigated the effect of BDB on cherry tomatoes and concluded that, while heavy metals were taken up by the plant, there was no significant bioaccumulation in the fruit (Table 4). In contrast, an experiment conducted by Song et al. [72] reported the accumulation of heavy metals, mostly Ni, in garlic tissues in soil amended with BDB. It should be noted that this study used high application rates of BDB (50%), which are unrealistic from an agronomic point of view. However, this does indicate that plants undertake preferential storage of heavy metals in different tissues. More research is required to understand the specifics of preferential heavy metal storage in edible crops. Furthermore, interactions between biochar, soil, microbes, and plant roots are known to occur within a short period of time after application to the soil [134]. However, the extent, rates, and implications of these interactions are still far from understood, and this knowledge is needed for an effective evaluation of the use of biochar as a soil amendment [44,101].

Despite increasing the concentration of total heavy metals in relation to the raw material, pyrolysis reduces the bioavailability of metals [3,84]. Due to the reduced metal leaching resulting from immobilization during thermal treatment, BDB is generally understood to be safe, and hence, several researchers recommend establishing limit values in Australian regulations on the leachability of metals instead of total metal concentrations [88,89]. For example, in an Australian study by Hossain et al. [157], 10 t ha^{-1} of BDB was used, which were over the maximum concentrations allowed by the Australian food standards. Although total metal concentrations in the soil exceeded the guidelines, tomatoes grown in this environment did not result in the accumulation of potentially toxic concentrations of heavy metals (Tables 3 and 4).

Table 4. Heavy metal accumulation in plants. All treatments were applied as % *w/w* basis and are represented as mg kg^{-1}.

Plants	Treatments	As	Cd	Cr	Cu	Ni	Pb	Zn	References
Rice grain	Control	0.45	0.4	ND	20	ND	0.95	54	[164]
	5% BDB	0.19	0.32	ND	17	ND	0.6	44	
	10% BDB	0.17	0.28	ND	16	ND	0.5	41	
Tomato	Control	0.35	0.26	ND	2.8	ND	0.5	85	[157]
	2% BDB	0.17	2.6	ND	4	ND	0.25	20	
	5% BDB	0.16	2.5	ND	2	ND	0.2	12	
	10% BDB	0.12	2	ND	1.2	ND	0.17	8	
Rice grain	Control	0.14	0.02	0.3	4.8	0.68	0.35	8	[125]
	5% BDB	0.05	0.12	0.21	4.7	0.55	0.1	26	
	10% BDB	0.04	0.13	0.17	4.6	0.49	0.05	28	
Turnip	2% BDB	0.12	0.11	ND	3.2	ND	0.22	48	[165]
	5% BDB	0.11	0.1	ND	1.9	ND	0.19	36	
Turf grass	Control	0.14	0	0.19	0.25	ND	0.18	0.59	[161]
	1% BDB	0.08	0.02	0.08	0.12	ND	0.2	0.23	
	5% BDB	0.03	0	0.04	0.1	ND	0.05	0.11	
	10% BDB	0.07	0	0.06	0.14	ND	0.14	0.18	
	20% BDB	0.06	0	0.05	0.1	ND	0.08	0.11	
	50% BDB	0.05	0	0.04	0.1	ND	0.05	0.05	

BDB—Biosolids-derived biochar; ND—not detected.

7. Conclusions and Future Research Needs

Options for beneficially using biosolids in Australia are centered on application to arable land. The presence of contaminants such as heavy metals, persistent organic pollutants, microplastics, and pathogens are of concern, and represent a risk to the environment, human, and animal health. It is anticipated that measures implemented towards achieving a low- or neutral-carbon economy, assisted by technological advances for the treatment of sewage sludge (e.g., improved removal of contaminants and energy recovery from treatment processes), coupled with the volatility of fertilizer and energy markets, will stimulate increased uptake of biosolids in Australian agriculture. Increased recycling of biosolids and biosolids-derived products to land may go some way to reduce the reliance on synthetic and mineral fertilizers and help improve the carbon balance of arable land. The use of biosolids is leaning towards nutrient recovery and power generation, as witnessed, for example, in some European Union countries and the United States.

This review brought together scientific evidence showing that thermal treatment (e.g., pyrolysis and gasification) of biosolids can be employed to reduce pathogens, microplastics, and organic pollutants' load, and decrease the bioavailability of heavy metals maintaining them within environmentally and agronomically safe levels. Where biosolids or biochar are used, on-farm implementation of the best (or recommended) management practices for crops, soil, and applied nutrients must always be exercised to mitigate risks. While research into the short-term effects (e.g., <10 years) of biosolids-derived biochar on crop, soil, and environment appears to support their use in agriculture, the longer-term effects are less known, and therefore longer-term studies will be beneficial. Nutrient and contaminant dynamics in soils receiving biosolids-derived biochar, and the inherent risk of transferring these contaminants to the food chain need to be determined together with measures to mitigate such risks. Key research gaps identified by this review are summarized below:

1. Exploration of the potential for cost-effective thermal technology to treat biosolids, including alternatives for recovering energy for electricity generation and conversion of biosolids to biochar;
2. Thermal treatment appears to be effective at eliminating persistent organic pollutants, microplastics, and pathogenic contaminants from biosolids. However, the efficacy of

thermal treatment in reducing (or avoiding) soil contamination from these sources is not well documented. This information is critical for supporting the safe use of biosolids-derived biochar as a soil amendment and for removing concerns associated with recycling;

3. There is potential to customize biochar products to suit specific users' needs (e.g., soil and crop type, farm application method), which will require understanding of the relationship between the desired biochar characteristics and the production conditions and feedstock. The optimal combination of feedstock and treatment conditions to match specific crop and soil requirements needs to be determined. Optimization of the physical and mechanical properties of biosolids-derived biochar will enable field application with standard fertilizer applicators, improving field delivery efficiency and logistics, and their acceptability by farmers.

A comprehensive analysis of the strengths, weakness, opportunities, and threats associated with the conversion of biosolids to biochar in the Australian market is presented in Figure 4. The circular economy approach and closing the waste-loop gap are identified as opportunities. However, challenges such as the lack of long-term studies, understanding nutrient and contaminant dynamics, and the cost of equipment for the thermal treatment are recognized as weaknesses.

Strengths	**Weakness**
• Reduction in waste volume, which can decrease disposal costs and alleviate pressures on landfills. • Thermal treatment of biosolids can produce energy, which can be used to power the treatment process. • Biosolids-derived biochar has the potential to improve soil health and fertility, leading to increased crop yields and reduced need for synthetic fertilisers. • The production of biochar from biosolids can contribute to the greenhouse gas emissions by sequestering carbon in the soil.	• Concerns about potential contaminates in biosolids may limit public acceptance of the use of biochar in agriculture. • Thermal treatment facilities may require significant capital requirement. • The lack of long-term studies on the effects of biosolids-derived biochar on soil health and contaminant transfer may limit the adoption of the technology.
Opportunities	**Threats**
• The global shift towards a low-carbon economy and increasing demand for sustainable products may create new markets for biosolids-derived biochar. • The ability of biochar to sequester carbon can be used to generate carbon credits, providing additional revenue streams. • The development of custom biochar products tailored to specific crops and soil types may create niche markets and increase demand. • Research into the long-term effects of biosolids-derived biochar on soil health and contaminant transfer can help to address concerns and increase acceptance.	• Fluctuations in the prices of fossil fuels may affect the competitiveness of biochar as the energy source. • Regulatory barriers or lack of clear guidelines for the safe use of biosolids-derived biochar may hinder market growth. • Competition from other waste-to-energy technlogies and alternative fertilisers may limit the market for biosolids-derived biochar • Lack of awareness or education about the benefit of biosolids-derived biochar may limit market uptake.

Figure 4. SWOT analysis of conversion of biosolids–biochar in the Australian market.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su151410909/s1, Table S1: Variation in BDB properties as a function in pyrolysis/gasification temperature. The data were compiled using the UC Davis Biochar Database and data from published peer-reviewed articles from around the world.

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Abbreviations

BDB: Biosolids-derived biochar; CEC: Cation exchange capacity; DBS: Dry biosolids; WWTP: Wastewater treatment plant; POPs: Persistent organic pollutants; PFOS, PFOA: Perfluorinated group of chemicals; PCBs: Polychlorinated biphenyls; PCAs: Polychlorinated alkanes; PBDEs: Polybrominated diphenyl ethers; PAHs: Polyaromatic hydrocarbons; PBDEs: Polybrominated diphenyl ethers.

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Supporting information

Land application of biosolids-derived biochar in Australia: A review

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Table S1

References

Table S1: Variation in BDB properties as a function in pyrolysis/gasification temperature. The data were compiled using UC Davis Biochar Database (http://biochar.ucdavis.edu/) and data from published peer-reviewed articles from around the world.

Reference	T°C	Yield, %	Total Surface Area m^2/g	Total Ash Content %	Total C %	Total H %	Total N %	Total P %	pH	EC dS/m	CEC cmolc/kg	K g/kg	Na g/kg	Ca mg/kg	Mg mg/kg	Al mg/kg	Fe mg/kg
Méndez et al. (2013) [1]	400		33.4						7.8	3.04	29.9						
Méndez et al. (2013) [1]	600		37.2						8.7	1.46	11.7						
Zhao, L et al. (2013) [2]	500		71.6	61.9	26.6			0.2	8.8		168.0	0.5		6.6	0.6	1.9	2.2
Agrafioti et al. (2013) [3]	300		4.0		39.7	4.1	7.1		6.0								
Agrafioti et al. (2013) [3]	500		18.0		9.8	0.4	2.1										
Liu et al. (2014) [4]	450				21.3		3.2	1.5	8.6			13.8					
Chen et al. (2014) [5]	500		25.4	74.2	17.5	0.7	1.5	1.8	8.8		76.8	8.5	1.2	59.3	14.7	28.4	31.1
Chen et al. (2014) [5]	600		20.3	77.9	18.4	0.3	1.4	1.9	9.5		30.8	8.5	1.7	62.7	15.5	28.3	33.6
Chen et al. (2014) [5]	700		32.2	81.5	16.9	0.2	1.0	2.0	11.1		50.3	9.9	1.4	64.4	16.4	32.8	35.3
Chen et al. (2014) [5]	800		48.5	83.9	16.2	0.0	0.5	1.9	12.2		126.6	9.3	1.9	65.8	16.6	34.5	35.8
Chen et al. (2014) [5]	900		67.6	88.1	15.9	0.1	0.5	2.0	12.2		247.5	8.7	3.4	69.6	17.5	35.5	37.2
Cely et al. (2014) [6]	600		59.2	73.6					7.7	3.70	24.2						
Zhao et al. (2014) [7]	500		71.6		30.6	3.3	2.9										
Xu et al. (2014) [8]	500		71.6	61.4	27.7				8.9			5.2		65.7	6.5	19.3	22.1
Oh et al. (2015) [9]	400		19.5		31.8	3.4	4.4										
Song et al. (2014) [9]	400		0.1	52.0	22.6	2.7	3.5		7.8								
Song et al. (2014) [9]	450		2.9	55.6	18.6	2.0	2.4		8.3								
Song et al. (2014) [9]	500		3.2	57.6	17.7	1.7	2.3		9.1								
Song et al. (2014) [9]	550		13.3	58.5	19.6	1.8	2.1		10.0								
de la Rosa et al. (2014) [10]	600		67.3	69.5	17.9	1.5	2.0		6.7								
Pituello et al. (2015) [11]	250			48.6	28.3		3.8	1.7	6.9	0.69		4.2					
Pituello et al. (2015) [11]	350			58.1	27.5		3.6	2.0	7.3	0.09		4.4					
Pituello et al. (2015) [11]	450			67.0	22.5		2.8	2.2	7.2	0.13		4.9					
Pituello et al. (2015) [11]	550			73.2	20.1		2.3	2.4	7.1	0.21		4.2					
Chen et al. (2015) [12]	900			88.1	15.9	0.1	0.5		10.2		247.5			69.6	17.5		
Ojeda et al. (2015) [13]	500							5.1	10.0			9.1	3.8	89.1			42.7

Leng et al. (2015) [14]	280		12.0	68.6	18.0	1.6			6.2								
Leng et al. (2015) [14]	280		17.0	70.2	16.5	2.2			6.0								
Leng et al. (2015) [14]	260		16.0	71.9	14.1	1.5			6.6								
Liang et al. (2016) [15]	300		6.4	20.6	63.4		0.1		7.5	0.31	26.0						
Liang et al. (2016) [15]	500		174.6	22.5	76.7		0.0		10.3	0.95	15.2	1.9					
van Zveiten et al. (2010) [16]	550				21.0		0.0	5.7	7.9							11.0	
Rahman et al. (2021) [17]	600				9.1		1.4	2.1	6.4	2.18		5.6	1.0	12.4	5.6	50.2	25.8
Netherway et al. (2019) [18]	300	91.9	21.6	91.1	4.4	0.8	2.4	1.1	5.4		34.5	1.3	1.9	4.5	2.9		43.0
Netherway et al. (2019) [18]	400	89.8	24.6	92.7	3.1	0.7	2.0	1.1	5.2		38.3	1.3	2.0	5.1	3.0		43.4
Netherway et al. (2019) [18]	500	87.7	25.3	93.4	2.7	0.4	1.7	1.1	5.2		36.6	1.7	2.2	5.6	3.1		46.7
Hossain et al. (2021) [19]	300	64.7	93.9		26.7		3.9	5.1	7.1	0.46		2.2		20.4	7.2		
Hossain et al. (2010) [20]	550						2.3		8.2	1.90	35.0						
Roberts et al. (2017) [21]	300	67.5		58.4	24.5	2.9	4.0	6.6									
Roberts et al. (2017) [21]	450	52.5		73.5	19.6	1.6	3.0	8.5									
Roberts et al. (2017) [21]	600	50.2		80.8	19.8	1.0	2.7	9.3									
Roberts et al. (2017) [21]	750	48.1		79.0	19.4	0.5	2.0	10.1									
Roberts et al. (2017) [21]	300	70.1		48.6	32.8	3.6	5.4	7.9									
Roberts et al. (2017) [21]	450	49.1		68.4	25.4	1.7	3.7	11.4									
Roberts et al. (2017) [21]	600	45.5		76.6	24.7	1.0	3.1	12.4									
Roberts et al. (2017) [21]	750	44.4		80.6	24.9	0.6	2.4	11.9									
Hossain et al. (2011) [22]	300	72.3		52.8	25.6	2.6	3.3		5.3	4.12							
Hossain et al. (2011) [22]	400	63.7		63.3	20.2	1.3	2.4		4.9	4.15							
Hossain et al. (2011) [22]	500	57.9		68.2	20.3	0.9	2.1		7.3	4.70							
Hossain et al. (2011) [22]	700	52.4		72.5	20.4	0.5	1.2		12.0	2.50							
Wang et al. (2021) [23]	350	73.3	8.0	55.1	25.3	2.2	3.2		7.4								
Wang et al. (2021) [23]	450	67.1	8.8	64.4	24.3	1.7	3.0		8.1								
Wang et al. (2021) [23]	550	61.3	10.2	72.4	19.9	1.1	2.4		8.5								
Frišták et al. (2018) [24]	430				31.9	0.8		5.7	8.6	0.35							
Frišták et al. (2018) [24]	430				49.9	1.5		1.7	8.7	0.32							
Adhikari et al. (2019) [25]	400		4.0	48.6	50.1	2.4	4.5	2.0									
Adhikari et al. (2019) [25]	400		5.0	49.5	50.6	2.4	4.4	2.2									
Adhikari et al. (2019) [25]	400		13.0	49.9	49.5	2.2	4.8	2.2									
Adhikari et al. (2019) [25]	400		17.0	49.4	49.5	1.9	4.5	2.1									

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Adhikari et al. (2019) [25]	500		21.0	54.7	46.7	1.4	3.9	17.0									
Adhikari et al. (2019) [25]	500		19.0	54.2	48.5	1.4	4.0	15.5									
Adhikari et al. (2019) [25]	500		39.0	56.3	47.0	1.2	3.9	16.5									
Adhikari et al. (2019) [25]	500		30.0	56.5	47.1	1.2	3.9	16.1									
Adhikari et al. (2019) [25]	600		79.5	59.1	45.5	0.9	3.4	16.1									
Adhikari et al. (2019) [25]	600		80.5	27.7	47.1	1.0	3.5	14.2									
Adhikari et al. (2019) [25]	600		95.0	29.1	46.3	0.9	3.3	19.8									
Adhikari et al. (2019) [25]	600		60.5	60.8	45.4	0.9	3.3	15.3									

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CHAPTER 3: GENERAL METHODS

To address the objectives, the experimental design comprised of three sets of interconnected experiments, which were conducted under controlled conditions of temperature and soil moisture both in the laboratory and glasshouse. This methodology section details: (1) soil, biosolids and biosolids-derived biochar characterisation, (2) soil leaching experiment, (3) glasshouse experiment, and (4) incubation experiment which are described in detail in **Paper 2** and **Paper 3**.

3.1. Soil, biosolids and biosolids-derived biochar characterisation

A general characterisation of soil, BS and BDB were conducted by the analytical tests described in **Paper 2** and **Paper 3**. Presence of heavy metals (Cr, Cu, and Zn) were characterised by analysing the samples by inductively coupled plasma mass spectrometry (ICP-MS) (Figure 1) and p-XRF (

Figure *2*).

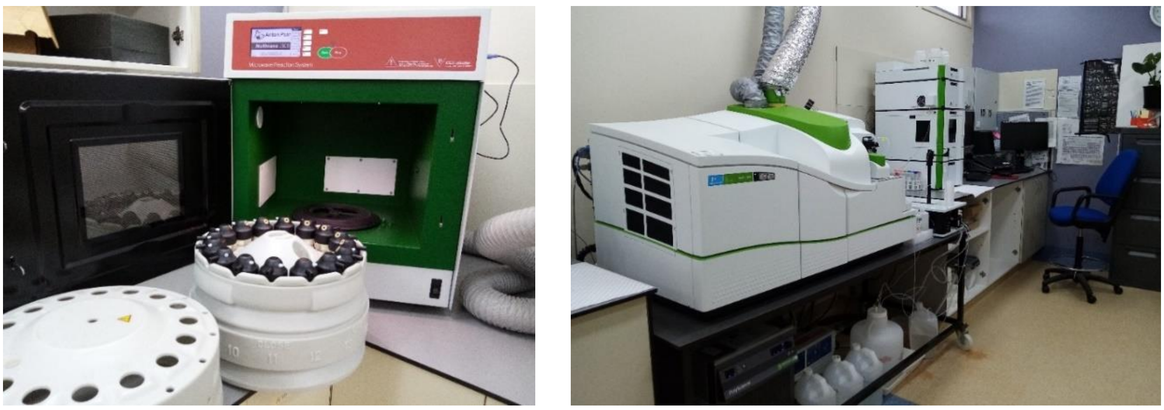


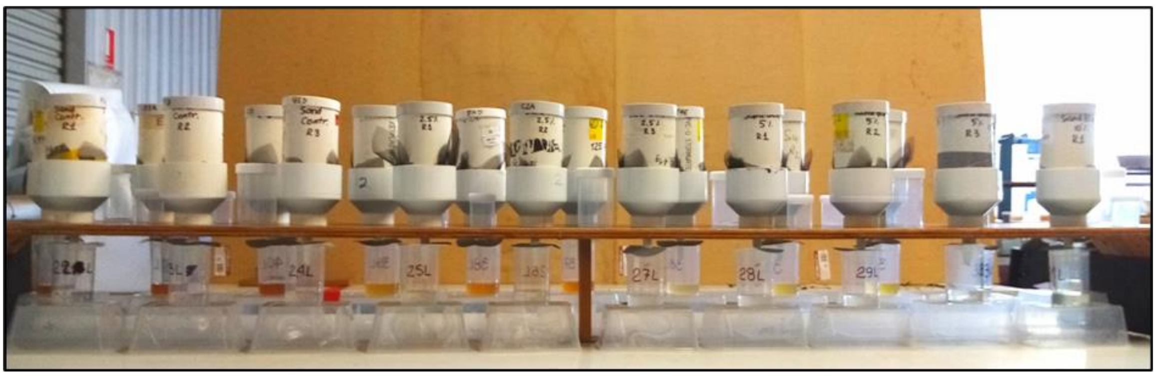
Figure 1. Microwave Digestion system and ICP-MS

Figure 2. Portable X-ray fluorescence spectroscopy

3.2. Leaching column experiment

The effect of biosolids and biochar on heavy metal leaching was assessed by monitoring calcium chloride-extractable metal concentrations released by soil, soil-biosolids, and soil-biochar mixtures during the leaching experiment described in detail in **Paper 2**. The 0.01 M calcium chloride extraction provides information about the soil solution and exchangeable metal pools and can be regarded as an indicator of metal solubility, bioavailability and mobility in soils (Houba et al., 2000; Pueyo et al., 2004; Kalis et al., 2007).

Prior to their use in the experiment, both soils were sieved (2mm aperture) and thoroughly mixed with either biosolids-derived biochar or biosolids in appropriate proportions (according to the application rates). The treated and original soil samples (500 g each) were evenly packed into Plexiglas columns (8.7 cm inner diameter and 300 cm long) at a bulk density of 1.33 Mg m-3 (in triplicates). Columns fitted with Whatman grade 4 filter paper supported by wire mesh caps fixed to the base of each column. Three columns per treatment (untreated control, medium rates and high rates), two soils and two amendments (BDB and BS), placed on a stand above leaching funnels (Figure 3). Initially the columns



were wetted with the deionized water to saturation for 48 hours from the base by slow capillary rise. Moisture contents during experiment maintained around 80% of measured field capacity via application of deionized water. At each leaching event, 250 mL of deionized water applied and leachate collected in plastic containers and analysed for the concentration of Cr, Zn and Cu on ICP-MS. Leaching was repeated at days 0, 7, 15, 30 and 60 of the experiment.

Figure 3. Leaching experiment in controlled laboratory condition.

3.3. Glasshouse experiment

Ryegrass (*Lolium perenne* L.) was used in a pot study conducted in a glasshouse facility at the Centre for Agricultural Engineering at the University of Southern Queensland (Toowoomba, Australia) using the Yellow Chromosol and Red Ferrosol described earlier (Figure 4). Plastic pots, 10 cm in height, 10 cm in diameter at the bottom and 10 cm in diameter at the top were used for the pot trial. The experimental design was a factorial randomised block design with 3 treatments: i) control soil (CS), ii) soil with BDB, and iii) soil with BS. Soils were amended with BS and BDB at three different rates in mass: 2.5% (10 t/ha), 5% (20 t/ha) and 10%(40 t/ha) w/w referred to here as BS 2.5%, BS 5%, BS 10%, BDB 2.5 %, BDB 5%, and BDB 10%, respectively. Each treatment was carried out in triplicates. In each pot, 400g of air-dried soil was mixed uniformly with the respective rates of the treatments. Ryegrass seeds (20 g) were spread uniformly on the soil surface. The experiment commenced on March 20, 2022, and was conducted over a period of twelve months. Water (pH = 7.01) was supplied to maintain the soil between field capacity and approximately 70% of field capacity throughout the experiment (Yellow Chromosol – 15% w/w & Red Ferrosol – 21% w/w). Leaching was always avoided. The ambient temperature and relative humidity in the glasshouse were maintained at 25 ± 3°C and 55-65%, throughout

the experiment. A total of twelve cuts were performed at regular time intervals of 30 days over a period of one year. The grass was cut at 20-mm above the soil surface (Cordovil et al., 2007) and the harvested plant material was oven-dried at 60°C for 48 hours (MAFF (1998), Method No.: 1) for determination of dry matter yield (DMY) and heavy metal uptake.

Figure 4. Overview of the pots experiment in the glasshouse (Agricultural Sciences and Engineering Precinct, University of Southern Queensland, Toowoomba, Australia)

3.4. Soil incubation experiment

This study investigated the enzymatic activity after 60 days at constant temperature and moisture conditions in soil following the application of BS and BDB. This method is described in **Paper 3**. From this laboratory study, likely patterns of enzymatic activity in field conditions can be inferred.

Soil incubation was conducted to determine the effect of biochar on the enzymatic activity in soil. Soils were amended with BS and BDB at three different rates: 2.5%, 5% and 10% w/w referred to here as BS 2.5%, BS 5%, BS 10%, BDB 2.5 %, BDB 5%, and BDB 10%, respectively. A zero-amendment control was also used for each soil type. The experiment followed a fully randomized design with three replications (*n* = 3) for each treatment. Treated and control soil samples (200 g each) were evenly packed into plastic pots (6.5 cm inner diameter and 10 cm in height). The soils were maintained at a soil water content equivalent to 70% of field capacity and incubated at a constant temperature of 25 ± 2°C for 60 days. Sampling was conducted at 0, 10, 20, 40 and 60 days from the start of the experiment by collecting subsoil samples weighing 20 g. Soil samples collected on day 60 were used for laboratory analysis of enzymatic activity.


Figure 5. Incubation experiment (left) and environmental chamber (right)

3.5. Plant and soil measurements and analyses

Standard methods were used for the determination of pH, electrical conductivity (1:5 soil:water) and particle size distribution (Gee and Bauder, 1986). Total carbon and nitrogen concentration were measured by ignition with a Leco elemental analyser (Leco Corporation, St. Joseph, MI, USA). The chemical composition of soil, BDB and BS, and heavy metal content were analysed by ICP-MS (ELAN 6000, Perkin Elmer, Switzerland) after acidic digestion ("Aqua regia" HNO_3:HCl, 3:1) in a microwave oven (Multiwave, 3000 Anton Paar, USA). For X-ray diffraction (XRD) analysis the clay fractions (< 2 µm) were separated from the bulk soils through sedimentation according to Stokes' law (Jackson, 2005). The XRD patterns for randomly oriented air-dried samples were recorded with a PANalytical X'Pert Pro Multi-purpose diffractometer. XRD data were collected and displayed using CSIRO software XPLOT for Windows (Raven, 1990).

Portable X-ray Fluorescence: Portable X-ray fluorescence is a non-destructive analytical technique widely used for its in-situ soil and plant analysis, due to its rapid and cost-effective nature. However, the application of p-XRF in detecting heavy metals in soils is subject to certain limitations that stem from the inherent properties of the technique, the complex nature of soil matrices, and the presence of soil amendments. p-XRF has specific detection limits for various elements, which may not be sensitive enough to detect low concentrations of heavy metals, especially in complex matrixes. Additionally, soil amendments can alter the soil matrix, potentially affecting the p-XRF readings due to changes in soil's physical and chemical properties. The presence of organic matter, moisture, or other elements, particularly those with higher concentrations, can interfere with detection of target heavy metals (Alqattan et al., 2023; Hu et al., 2017). High iron (Fe) content, for example, can affect the p-XRF's efficiency in reporting the actual amount of Cr due to lower absorption edge in energy than the fluorescent peak of Fe (Alqattan et al., 2023). Furthermore, alterations in the form or binding of heavy metals within the soil matrix, along with chemical transformations, such as oxidation-reduction reactions, complexation and precipitation, can change the speciation of heavy metals, affecting their detectability by p-XRF, even though they remain present in the soil. (Li et al., 2022). Understanding these limitations is crucial for interpreting p-XRF data accurately in environmental and agricultural research.

Soil and plant samples: Plant samples: Oven dried soil and plant samples were packed into XRF sample cups and scanned with the OLYMPUS Vanta M Series portable X-ray fluorescence spectrometer (VMR-CXC-G2-A) for the total elemental concentration in the SOILEXTRA and GEOCHEM modes. The Olympus Vanta p-XRF features a (Rhodium/Tungsten (Rh/W)) anode X-ray tube of 10 to 50 kVp at 10-200 µA. This analyser uses a factory-installed calibration procedure with Compton Normalisation to estimate soil elemental concentrations in % or mg kg^{-1}. The SOIL mode is equipped with a three-beam configuration at 50 kV, 40 kV and 15 kV whereas the GEOCHEM mode has a two-beam configuration at 50 kV and 10 kV. To enable lower atomic number elements to be measured, such as magnesium, silicon, aluminium, and iron (Limit of detection of 1%), GEOCHEM mode uses longer count rates. The National Institute of Standards & Technology (NIST) certified standard, NIST 2711a (moderately elevated trace elements) soil standard was used to verify the performance of the instrument.

p-XRF was calibrated against calcium (Ca), titanium (Ti), rubidium (Rb), potassium (K), iron (Fe) and strontium (Sr). The recovery of elements via the p-XRF was high when comparing instrument measured values to the NIST standard (over 98% for all reference elements). In GEOCHEM Mode, Ca recovery was 105% (NIST certified material, Ca 2.42%), Ti recovery was 103% (NIST certified material, Ti 0.317%) and Rb recovery was 98% (NIST certified material, Rb 120 ppm) for the reference soil. In the SOIL EXTRA Mode, K recovery was 104% (NIST certified material, K 2.53%), Fe recovery was 100% (NIST certified material, Fe 2.82%) and Sr recovery was 97% (NIST certified material, Sr 242 ppm) for the reference soil.

Enzymatic analysis: Soil urease activity (BC0120 Soil Urease (UE) Activity Assay Kit), and acid phosphatase activity (BC0140 Soil Acid Phosphatase (S-ACP) Activity Assay Kit) were all determined by using the corresponding kit produced by Solarbio (http://www.solarbio.net/). The stopping procedure was operated according to the product manual provided by Solarbio using a spectrophotometer.

3.6. Statistical analyses

The statistical package GenStat Release® 19th Edition (VSN International Ltd., 2020) was used to analyze data for heavy metal concentrations in soil and plant dry matter. Analyses involved ANOVA and repeated measurement of ANOVA. The least significant differences were used to compare means with a probability level of 5%. Figures were created using Graphpad Prism 9.1.2 (https://www.graphpad.com/updates/prism-912-release-notes). Statistical analyses were graphically assessed by means of residual plots. Log, natural log, or square root transformations of the data were applied to meet assumptions of normality or homoscedasticity for ANOVA analyses.

CHAPTER 4: PAPER 2 –HEAVY METAL DYNAMICS IN SOILS AMENDED WITH BIOSOLIDS AND BIOSOLIDS DERIVED BIOCHAR USING PORTABLE X-RAY FLUORESCENCE SPECTROSCOPY

4.1. Introduction

Paper 1 indicated that during the thermal conversion of biosolids to biochar, while pathogens, microplastics and organic pollutants are eliminated or greatly reduced in concentration, the process concentrates heavy metals. Due to the loss of water and organics, heavy metal concentration can increase by 2.5-3.5 fold (Jin et al., 2016). Heavy metal contamination of agricultural soils represents a serious environmental issue. BDB are characterized by elevated level of heavy metal and when applied to agricultural land could contaminate soil and groundwater via leaching events (Lehmann and Joseph 2015). However, the extent, rates, and implications of these interactions are still far from being understood, and this knowledge is needed for an effective evaluation of the use of biochar as a soil amendment (Joseph et al, 2010).

Paper 1 identified that the mobility of heavy metals is of critical importance as this dictates the potential risk to soil, surface water and groundwater contamination. Addressing this research gap, the first objective of this study is to "Investigate the effects of BDB on mobility and leaching of heavy metals (Cr, Cu and Zn) in two Australian soils with contrasting physico-chemical properties at varying rates (2.5%, 5%, 10% w/w), and compare these effects with BS application".

The novelty of **Paper 2** lies in its comprehensive approach to understanding the environmental impact of a commercially produced BDB when applied to soils, and the effect on heavy metal mobility and leaching. The work aimed to investigate heavy metal concentrations and mobility in soil treated with BDB using leaching columns and compared to BS amended soil. Specifically, the objectives of this work were twofold. First, to evaluate p-XRF as a cost-effective tool for measuring heavy metal mobility as compared to conventional ICP-MS analysis. Second, to investigate the effect of BDB on heavy metal mobility in two Australian soils and compare the results to BS amended soils. Successful application of p-XRF to the study of heavy metal mobility in soil could significantly reduce the cost of laboratory analyses potentially allowing for in-situ characterization of soil and soil amendments. The dual focus helps in advancing the understanding of BDB environmental impacts on heavy metal leaching when applied to soils but also contributes to methodological advancements in soil analysis.

4.2. Manuscript submitted to *Pedosphere*.

Heavy metal dynamics in soils amended with biosolids and biosolids derived biochar using portable X-ray fluorescence spectroscopy

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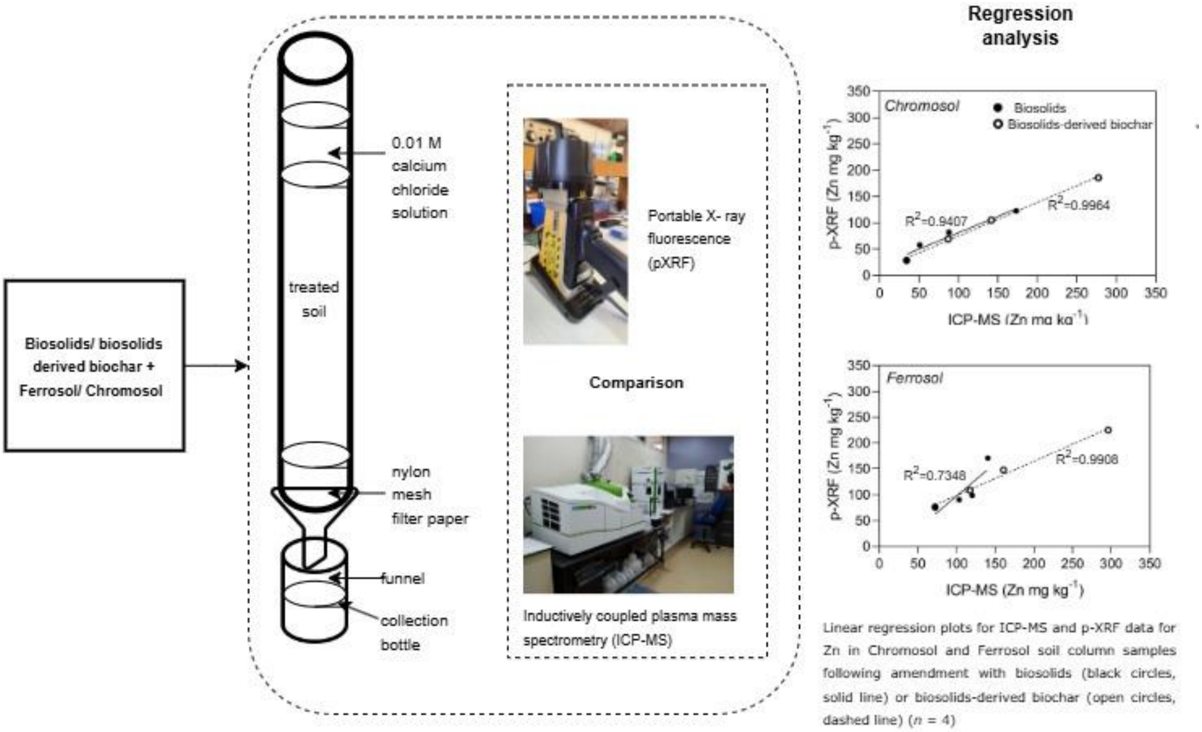
Abstract

This study reports on the novel use of portable X- ray fluorescence (p-XRF) as a rapid and low-cost technique for investigating leaching behaviours of heavy metals in soils amended with biosolids (treated sewage sludge) and biosolids-derived biochar at three application rates (2.5%, 5% and 10% w/w). The measurement of zinc, copper, and chromium in two soils of contrasting mineralogy and physico-chemical properties (Yellow Chromosol and Red Ferrosol) was quantified in a laboratory setup using leaching columns. Analysis of total heavy metal movement in soil columns after six leaching events revealed decreased copper and chromium mobility in both soils, while zinc mobility decreased in Chromosol but increased in Ferrosol for biosolids treatment. These findings stress the complex dynamics of heavy metal mobility and emphasize the importance of understanding specific patterns in different soil types. Regression analyses between p-XRF and ICP-MS (Inductively coupled plasma mass spectrometry) results affirmed the reliability of p-XRF, particularly for determining total zinc and copper concentrations, although discrepancies were noted for chromium in Chromosol due to low elemental concentrations. The study underscores the nuances related to environmental risk assessment, emphasizing the need for comprehensive evaluations beyond total heavy metal concentrations to inform sustainable soil management practices.

Graphical abstract



Keywords

Sewage sludge; ICP-MS; zinc; copper; chromium

Abbreviations

BS, Biosolids; BDB, Biosolids-Derived Biochar; p-XRF, Portable X-Ray Fluorescence; ICP-MS, Inductively Coupled Plasma Mass Spectrometry; ICP-OES, Inductively Coupled Plasma Optical Emission Spectroscopy; EPA, Environmental Protection Agency, PFAS, Per- and Polyfluoroalkyl Substances; Zn, Zinc; Cu, Copper; Cr, Chromium; $CaCl_2$, Calcium Chloride; EC, Electrical Conductivity; CO, Carbon Monoxide; CO_2, Carbon Dioxide; NH_4-N, Ammonium; NO_3-N, Nitrate Nitrogen; Pb, Lead; Cd, Cadmium.

1. Introduction

Biosolids (BS) are commonly used in agriculture as soil amendments due to their high nitrogen and phosphorus concentrations. However, land applications are regulated to manage the associated risks with a range of contaminants, including heavy metals and emerging contaminants such as microplastics and per- and polyfluoroalkyl substances (PFAS). While biosolids provide numerous beneficial effects on soil biophysical and chemical properties (Jones and Healey, 2010), the concentration of potentially harmful heavy metals has resulted in heavy environmental restrictions. Due to Environmental Protection Agency (EPA) regulations, beneficial use of biosolids in Australia has declined from 94% in 2017 to 91% in 2019, and 83% in 2021 (Dean et al., 2020). Consequently, the stockpiling and landfilling of biosolids is increasing while industry searches for an alternative management solution.

One potential solution for managing biosolids is thermal conversion. Principally, these technologies include pyrolysis and gasification, whereby the main difference lies in the presence of oxygen during the processes. Gasification is achieved in an environment containing sub-stoichiometric oxygen, where organic matter is converted into carbon char and syngas. Conversely, pyrolysis is the process of sublimating organic matter in the absence of oxygen, leading to the production of char, tar, and gas (Rada, 2017). The primary benefits of these technologies include: (i) mass and volume reduction of biosolids thereby lowering associated transport cost, (ii) production of liquid and gaseous energy carriers, and (iii) generation of 'biochar', a solid product rich in stable carbon and plant nutrients (Joseph et al., 2021; Mierzwa-Hersztek et al., 2018; Sinha et al., 2023). While the primary pathway for disposal of biochar derived from biosolids (BDB) is landfill, the high nutrient content his piqued interest in application as a soil additive.

Although biochars are commonly reported to be beneficial for soils, concerns remain regarding the safe application of BDB to agricultural land. While thermal conversion of BS to BDB eliminates or greatly reduces pathogens, microplastics and organic pollutants (i.e., PFAS), heavy metals become concentrated (Raheem et al., 2018; Sinha et al., 2023). Due to the loss of water and organics, heavy metal concentration can increase by 2.5-3.5-fold (Jin et al., 2016). However, the mobility of heavy metals is of critical importance as this dictates the potential risk to soil, surface water and groundwater contamination. Although heavy metal concentrations in the BDB are increased compared to the BS feedstock, heavy metal mobility in BDB is significantly lower than BS when applied to the environment (Jin et al., 2016). Specifically, biochar has a relatively high cation exchange capacity which allows for adsorption of heavy metals and organic contaminants (Hill, 2005). There are few works which explore the interactions between BDB in Australian soils. Consequently, as there is substantial variation in both soil and biochar characteristics, there is need to explore the interactions between BDB and heavy metals in various Australian soil applications.

Regulation of BS and BDB is emerging in Australia. Sinha et al. (2023) provided a critical review of the use of biosolids-derived biochar in Australian agriculture, highlighting the increased interest in thermal treatments as a management method due to legislative changes and waste reduction goals. The review highlighted the absence of specific legislative standards in Australia for the permissible concentrations of heavy metals in biochar intended for land application. The review noted the existence of voluntary quality standards for biochar internationally, such as the European Biochar Certificate and the International Biochar Initiative, which focus on ensuring the quality of biochar by regulating organic contaminants and heavy metal concentration. Consequently, there is need to understand how these materials interact with Australian soils to better inform policy and regulation.

To better inform regulation policy in a timely manner, there is need for cheaper, more rapid analysis of heavy metal mobility in soil. While inductively coupled plasma mass spectrometry (ICP-MS) is currently the gold standard for this application (Schneider et al. 2016; Messager et al. 2021), portable X-ray fluorescence spectrometry (p-XRF) is emerging as a viable alternative (Al Maliki et al., 2017; Madden et al., 2022). X-ray fluorescence spectrometry has several advantages when compared to other multi-element techniques such as ICP-MS (McComb et al., 2014). Although ICP-MS is an EPA approved method for determining trace metals in soil and water due to its reliability and sensitivity, it is expensive and time consuming to prepare and analyse samples. In comparison, p-XRF is a comparably rapid, cheap and non-destructive technique to measure heavy metal concentrations in environmental samples (Ravansari et al., 2020). Additionally, p-XRF analysis requires limited preparation for solid samples, does not produce hazardous waste, and is portable (McLaren et al., 2012). Due to these advantages, p-XRF is commonly viewed as field equipment, and has been widely used for environmental assessment of soils and plants (Antonangelo and Zhang, 2021). While p-XRF results are often validated with wet chemistry techniques, McLaren et al. (2012) and Borges et al. (2020) demonstrated good correlation between wet chemistry and p-XRF performance for total element concentration in plant and soil matrices. Similarly, McComb et al. (2014) used both X-ray fluorescence and inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine phosphorus concentration in raw materials and ceramics and results were comparable between the two analytical methods. The same study showed that detection limits values obtained with p-XRF were higher than those obtained with ICP-OES/MS. Consequently, the application of p-XRF to lab-based research has potential to equip researchers with the capability to rapidly screen for heavy metal mobility in various Australian soil types.

The work aimed to investigate heavy metal concentrations and mobility in soil treated with BS and BDB using leaching columns. Specifically, the objectives of this work were twofold. First, to compare p-XRF against ICP-MS as tools for measuring heavy metal mobility in two Australian soils. Second, to investigate the effect of biosolids and biosolids-derived biochar on heavy metal mobility in two Australian soils. Successful application of p-XRF to the study of heavy metal mobility in soil could significantly reduce the cost of laboratory analyses potentially allowing for in-situ characterization of soil and soil amendments.

2. Materials and methods

2.1. Description of soils and soil amendments

Both BS and BDB were produced from the same BS sourced from Pyrocal Pty Ltd. (Toowoomba, Queensland, https://www.pyrocal.com.au/). The BDB was industrially produced in a Pyrocal continuous carbonisation technology gasifier. Dried Biosolids were gasified at a temperature of 400°C increasing to 700°C over a residence time of 100 seconds. Biochar was quenched with water upon exiting the gasifier. Both the dry BS and BDB materials were crushed, dried at 40°C and sieved to pass 2 mm.

Two soils from Queensland were used in this laboratory study (Table 1): clayey Ferrosol (Rhodoxeralf in the US Soil Taxonomy description) from the Agricultural Field Station Complex at the University of Southern Queensland and acidic sandy Yellow Chromosol (Alfisol in the US Soil Taxonomy description) from the Gatton area (Queensland, Australia). Selection of these soils was based on their differences in mineralogy, texture, and pH. Soil samples were collected from the 0.0–0.20 m depth by a hand auger, air-dried, and sieved to 2 mm. All measurements reported as w/w and mg kg^{-1} are on a dry matter basis.

Table 1. Physicochemical characterization of the soils used in the leaching study.

Description	Analytical method	Red Ferrosol	Yellow Chromosol
GPS Location		27°36'32.27" S, 151°55'52.96" E	27°35'44.9" S, 152°18'20.1" E
pH (1:5 soil:water), %	4A1[1]	6.0	5.5
EC (1:5 soil:water), dS m^{-1}	3A1[1]	0.03	0.01
Total C, % (w/w)	6B2[1]	3.51	1.69
Total N, % (w/w)	7A5[1]	0.27	0.16
Clay (<0.002 mm), % (w/w)	Gee and Bauder, 1986	57	14
Silt (0.002–0.02 mm), % (w/w)	Gee and Bauder, 1986	11	11
Sand (0.02–2 mm), % (w/w)	Gee and Bauder, 1986	32	75
Total Zn, mg kg^{-1}	17A2[1]	89.80	42.70
Soluble Zn, mg kg^{-1}	1:5 soil:water suspension, then ICP-MS	0.19	0.23
Total Cu, mg kg^{-1}	17A2[1]	46.20	8.50
Soluble Cu, mg kg^{-1}	1:5 soil:water suspension, then ICP-MS	BDL[2]	BDL[2]
Total Cr, mg kg^{-1}	17A2[1]	331.0	13.5
Soluble Cr, mg kg^{-1}	1:5 soil:water suspension, then ICP-MS	0.12	0.01
Dominant clay mineral	X-ray Diffraction	Kaolinite	Kaolinite, Montmorillonite

[1]Rayment and Lyons, 2011

[2]BDL-Below detection limit

2.2. Soil columns and leaching study

Soils were amended with BS and BDB at three different rates: 2.5%, 5% and 10% w/w referred to here as BS 2.5%, BS 5%, BS 10%, BDB 2.5%, BDB 5%, and BDB 10%, respectively. A control (zero-amendment) for each soil type was also used. The experiment was carried out under laboratory conditions, in a fully randomized design with triplicate replications for each treatment tested. The treated and original soil samples (500 g each) were evenly packed into columns to achieve uniform density within the PVC tubes (87 mm inner diameter by 200 mm long). The bottom of the soil columns was fitted with a nylon mesh screen and filter paper to prevent soil loss. Another filter paper was placed on the top of the soil to reduce surface disturbance while pouring the leaching solution to the soil. The columns were first wetted with a 0.01 M calcium chloride ($CaCl_2$) solution from the base of the column to reach saturation by capillary rise, which was achieved after about 48 hours and then leached with 0.01 M $CaCl_2$ solution. The leaching of zinc (Zn), copper (Cu) and chromium (Cr) through the soil was evaluated under saturated/near-saturated soil conditions using vertically oriented plexiglass columns placed in funnels with draining tubes. Soil water content in the soil columns were maintained between saturation and field capacity (corresponding to suctions between 0 and -100 cm) over the entire experiment to minimize the risk of by-pass flow between the soil matrix and the inner wall of the PVC tube due to swelling, and to allow for gravitational drainage (Ngo-Cong et al., 2021). The soil columns were allowed to drain freely during the leaching events and water was not observed to pool on the soil surface for extended periods. A total of six leaching events were conducted at 1, 3, 7, 14, 30 and 60 days respectively after the experiment was established.

2.2.1. Leaching with Calcium chloride solution

The effect of BS and BDB on heavy metal leaching was assessed by monitoring $CaCl_2$-extractable metal concentrations released from soil (control without amendment), soil-BS and soil-BDB mixtures during the experiment. The 0.01 M $CaCl_2$ extraction provided information about the soil solution and exchangeable metal pools, and it can be regarded as an indicator of metal solubility, mobility, and bioavailability in soils (Houba et al., 2000; Pueyo et al., 2004; Kalis et al., 2007). At days 1, 3, 7, 14, 30 and 60 from the start of the experiment, columns were leached with approximately 150 mL of 0.01 M $CaCl_2$ solution. Leaching was performed by slowly pouring the solution into the columns above the soil covered with filter paper. Columns were covered with plastic cups to minimize evaporation during the leaching events, and they were allowed drain into plastic containers placed beneath each column. The receiving containers had a cap with a small hole drilled through it that allowed the funnel’s drain tube to be inserted into the container to minimize evaporative losses. The amount of leachate collected at each leaching event was determined volumetrically. Leachate samples were filtered and analysed for pH, electrical conductivity (EC), Zn, Cu and Cr concentrations.

2.3. Analytical methods

Standard methods were used for the determination of pH, EC (1:5 soil:water) (Rayment and Lyons, 2011) and particle size distribution (Gee and Bauder, 1986) (Table 1). Total carbon and nitrogen concentrations were measured by ignition with a Leco elemental analyser (Leco Corporation, St. Joseph, MI, USA).

2.3.1. Inductively coupled plasma mass spectrometry

The chemical composition of the soils, BS and BDB, including heavy metal concentrations, were analysed by ICP-MS (ELAN 6000, Perkin Elmer, Switzerland) following microwave-assisted acid digestion (aqua regia, 3:1 HNO_3:HCl) (Multiwave, 3000 Anton Paar, USA).

2.3.2. *Portable X-ray Fluorescence*

Air-dried soil samples were packed into XRF sample cups and scanned with the OLYMPUS Vanta M Series p-XRF Spectrometer (VMR-CXC-G2-A) for the total elemental concentration in the SOILEXTRA and GEOCHEM modes. The Olympus Vanta p-XRF features a (Rhodium/Tungsten (Rh/W)) anode X-ray tube of 10 to 50 kVp at 10-200 µA. This analyser uses a factory-installed calibration procedure with Compton Normalisation to estimate soil elemental concentrations in % or mg kg^{-1}. The SOIL mode is equipped with a three-beam configuration at 50 kV, 40 kV and 15 kV whereas the GEOCHEM mode has a two-beam configuration at 50 kV and 10 kV. To enable lower atomic number elements to be measured, such as magnesium, silicon, aluminium and iron (Limit of detection of 1%), GEOCHEM mode uses longer count rates. The National Institute of Standards & Technology (NIST) certified standard, NIST 2711a (moderately elevated trace elements) soil standard was used to verify the performance of the instrument.

p-XRF was calibrated against calcium (Ca), titanium (Ti), rubidium (Rb), potassium (K), iron (Fe) and strontium (Sr). The recovery of elements via p-XRF was high when comparing instrument measured values to the NIST standard (over 98% for all reference elements). In GEOCHEM Mode, Ca recovery was 105% (NIST certified material, Ca 2.42%), Ti recovery was 103% (NIST certified material, Ti 0.317%) and Rb recovery was 98% (NIST certified material, Rb 120 ppm) for the reference soil. In the SOIL EXTRA Mode, K recovery was 104% (NIST certified material, K 2.53%), Fe recovery was 100% (NIST certified material, Fe 2.82%) and Sr recovery was 97% (NIST certified material, Sr 242 ppm) for the reference soil.

2.4. *Statistical analyses*

The statistical package GenStat Release® 19th Edition (VSN International Ltd., 2020) was used to analyse data of heavy metal concentrations in soil and leachate, and pH. Analyses involved ANOVA and repeated measurement of ANOVA. Two Way ANOVAs were done in GraphPad Prism 9.1.2. Log, natural log or square root transformations were applied to ensure data met assumptions of normality and homoscedasticity. A Tukey's or Sidak's post hoc test was applied to assess multiple comparisons where ANOVA results were significant. The least significant differences (LSD) were used to compare means with a probability level of 5%. Figures were created using GraphPad Prism 9.1.2 (https://www.graphpad.com/updates/prism-912-release-notes). Statistical analyses were graphically assessed by means of residual plots.

3. Results and Discussion

3.1. Characterization of the element concentrations in biosolids and biosolids-derived biochar

The elemental compositions of biochars are related to the thermal treatment temperature, retention time, water content, and biomass constituents of feedstock (Srinivasan et al., 2015). Biosolids-derived biochar contained higher concentrations of total Zn, Cu and Cr compared to BS, however, the soluble fractions of Zn, Cu and Cr are significantly decreased in BDB as these metals precipitate under alkaline conditions (Table 2). Agrafioti et al. (2013) and Hossain et al. (2011) observed similar trends on the effect of higher temperature on pH and available/extractable heavy metals. Total carbon and nitrogen concentrations decreased in BDB when compared to BS, although the total phosphorus concentration increased. This was due to the volatilization of different carbon and nitrogen groups (i.e., carbon monoxide, carbon dioxide, water, hydrocarbon, ammonium-nitogen, or nitrate-nitrogen) at higher temperatures during thermal treatment (Yang et al., 2018). This increase in total phosphorus in BDB is due to the loss of water and organic material from biosolids during the thermal treatment (Adhikari et al., 2019).

Table 2. Physicochemical characterization of biosolids and biochar used in the leaching experiment.

Description	Analytical method	Biosolids	Biosolids-derived biochar
pH (1:5 soil:water)	4A1[1]	5.6	9.5
EC (1:5 soil:water), dS m^{-1}	3A1[1]	5.38	0.51
Total C, % (w/w)	6B2[1]	40.59	34.55
Total N, % (w/w)	7A5[1]	7.07	4.65
Total P, g kg^{-1}	17A2[1]	49.90	78.90
Soluble P, g kg^{-1}	1:5 soil:water suspension, then ICP-MS	7.13	0.13
Total Zn, mg kg^{-1}	17A2[1]	957.0	1,517.4
Soluble Zn, mg kg^{-1}	1:5 soil:water suspension, then ICP-MS	1.43	0.20
Total Cu, mg kg^{-1}	17A2[1]	580.1	692.3
Soluble Cu, mg kg^{-1}	1:5 soil:water suspension, then ICP-MS	0.05	0.02
Total Cr, mg kg^{-1}	17A2[1]	53.0	98.7
Soluble Cr, mg kg^{-1}	1:5 soil:water suspension, then ICP-MS	0.31	0.01

[1]Rayment and Lyons, 2011

3.2. Evaluation of p-XRF as a suitable tool for rapidly measuring heavy metal concentration in soil

To assess the suitability of p-XRF as a suitable analytical tool, the relationship between ICP-MS analyses and p-XRF laboratory readings for total concentrations of Zn, Cu and Cr in soil after six leaching events were analysed (Fig. 1). There were strong correlations (R^2) between ICP-MS and p-XRF results for Zn and Cu in both soil types as well as for both BS and BDB treatments (Table 3). However, there were poor correlations for Cr in the Chromosol for both BS and BDB treatments. In the Ferrosol, there was a strong correlation for Cr in BDB treatments, but only moderately strong correlation for Cr from BS. These results align with previous investigations which indicated that p-XRF is effective in accurately detecting Cu and Zn as compared to Cr. For example, Adler et al. (2020) focused on predicting soil concentrations of Cu, Zn, and cadmium (Cd) through p-XRF measurements and reported high suitability for Zn concentrations. Similarly, Borges et al. (2020) compared p-XRF measurements with laboratory-based methods and suggested that p-XRF measurements were accurate for the measurement of Cu, lead (Pb) and Zn concentrations, while Cd and Cr may be more effectively screened using alternative laboratory methods.

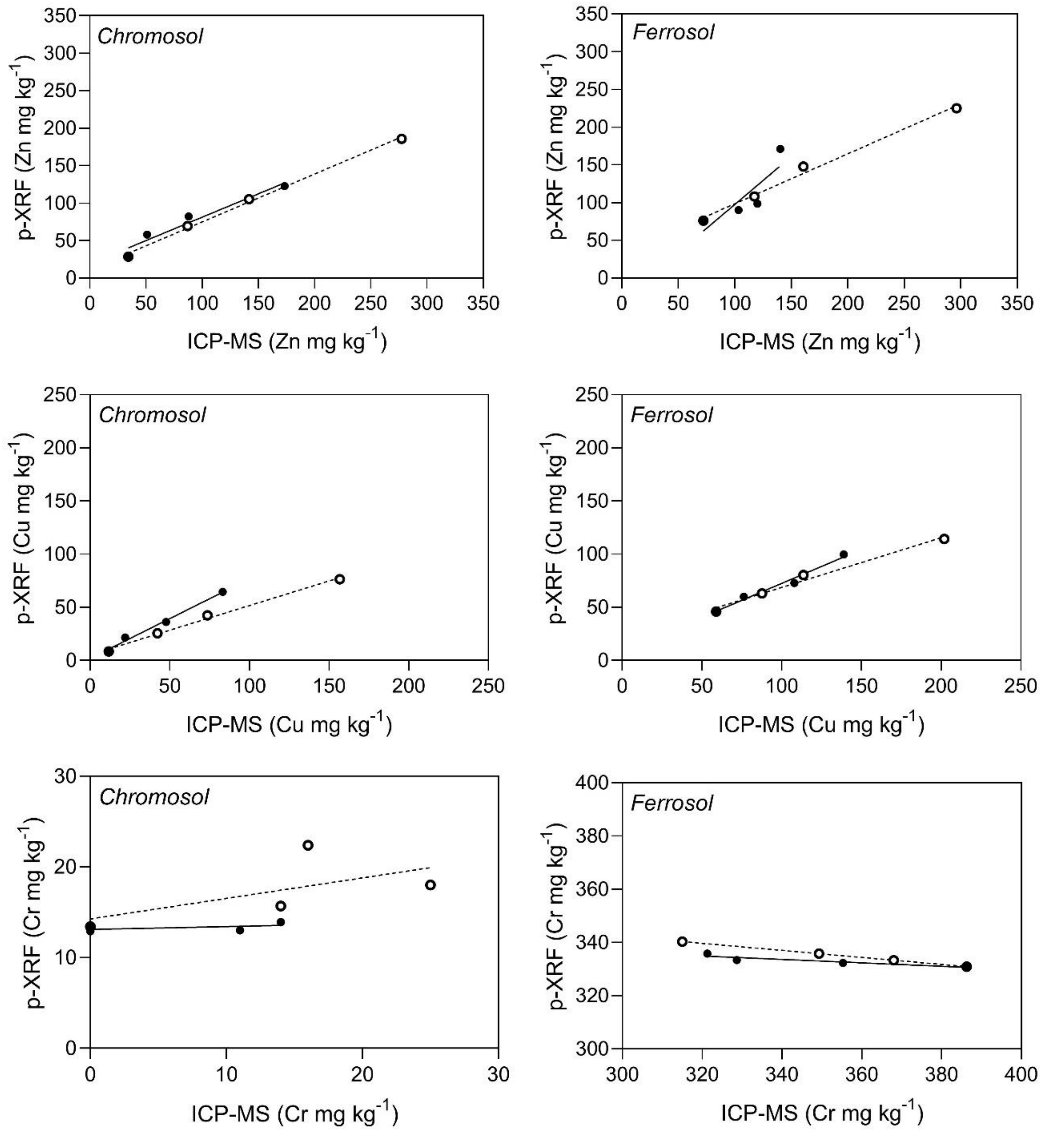


Fig. 1. Linear regression plots for ICP-MS and p-XRF data for Zn, Cu and Cr in Chromosol and Ferrosol soil column samples following amendment with biosolids (black circles, solid line) or biosolids-derived biochar (open circles, dashed line) (n = 4).

Table 3. Linear regression results for ICP-MS and p-XRF data for Zn, Cu and Cr in Chromosol and Ferrosol soil columns following biosolids (BS) or biosolids-derived biochar (BC) amendments.

Element	Parameter	*Chromosol*		*Ferrosol*	
		BS	***BDB***	***BS***	***BDB***
Zn	Equation	y = 0.6238x + 18.72	y = 0.6389x + 10.89	y = 1.269x - 29.53	y = 0.6621x + 32.17
	R^2	0.9407	0.9964	0.7348	0.9908
	p	* (0.0301)	* (0.0018)	ns (0.1428)	* (0.0046)
	SE	0.11	0.03	0.54	0.05
Cu	Equation	y = 0.7491x + 1.808	y = 0.4633x + 5.235	y = 0.6381x + 8.584	y = 0.4672x + 21.91
	R^2	0.9899	0.9934	0.9779	0.9822
	p	* 0.0051	* 0.0033	* 0.0111	* 0.0089
	SE	0.05	0.03	0.07	0.04
Cr	Equation	y = 0.03173x + 13.10	y = 0.2263x + 14.26	y = -0.06447x + 355.5	y = -0.1319x + 381.9
	R^2	0.2610	0.3711	0.8421	1.000
	p	ns 0.4891	ns 0.3908	ns 0.0823	*** <0.0001
	SE	0.04	0.21	0.02	3.2×10^{-4}

Asterisks indicate significance levels ($p<0.05$ = *, $p<0.001$ = **, $p<0.0001$ = ***); ns indicates not significant; SE indicates standard error.

3.3. Distribution of heavy metal in soil columns as determined by p-XRF

In order to understand the environmental and agricultural impact of BDB addition, it is important to understand the distribution of heavy metals in the soil matrix and the movement of heavy metals at different soil depths. This is important for informing practices and policies due to the potential for bioaccumulation through plant uptake and/or leaching of heavy metals into the water table. The movement of Cu, Cr and Zn was distinctly different between the Chromosol and Ferrosol when treated with BS and BDB (Fig. 2). Under the BDB treatment, the total concentration of Cu, Cr and Zn movement increased in Ferrosol but decreased in Chromosol. Similarly, with biosolids treatment, the total concentration of Cu and Cr increased in Ferrosol but decreased in Chromosol, whereas Zn concentrations decreased in Ferrosol and increased in Chromosol. These results demonstrate the importance in understanding the contribution of soil characteristics toward heavy metal mobility in different soil types and at different soil depths, and this is currently a key knowledge gap which warrants further investigation.

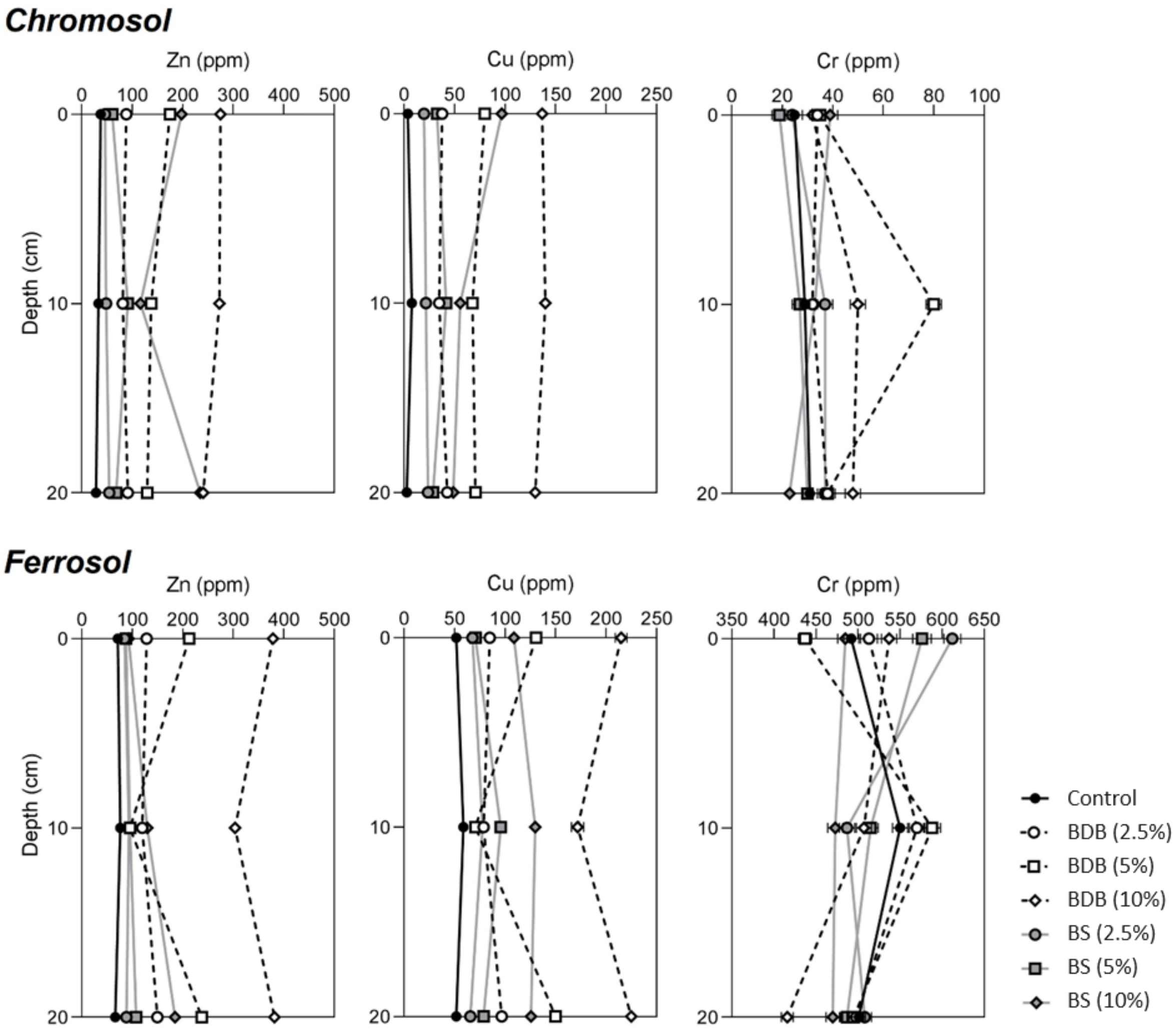


Fig. 2. Mobility of heavy metals through soil columns after 6 leaching events for Chromosol and Ferrosol amended with biosolids and biosolids-derived biochar. Error bars show standard deviation (n = 3).

3.4. Effects of biosolids and biosolids-derived biochar on heavy metals mobility in amended soils

Throughout the leaching experiment, changes in the pH of the soil leachates were observed following the application of BS and BDB to the soils (Fig. 3). These changes were dependent on time and soil type, but application rate produced no significant impact. The increase in leachate pH in the Chromosol was more pronounced due to lower buffering capacity of sandy Chromosol compared with clayey Red Ferrosol. Biosolids-derived biochar may increase soil pH due to its inherent alkalinity, making it a promising amendment for acidic soils. The ability of BDB to increase soil pH can also reduce the leaching of heavy metals and other contaminants into groundwater.

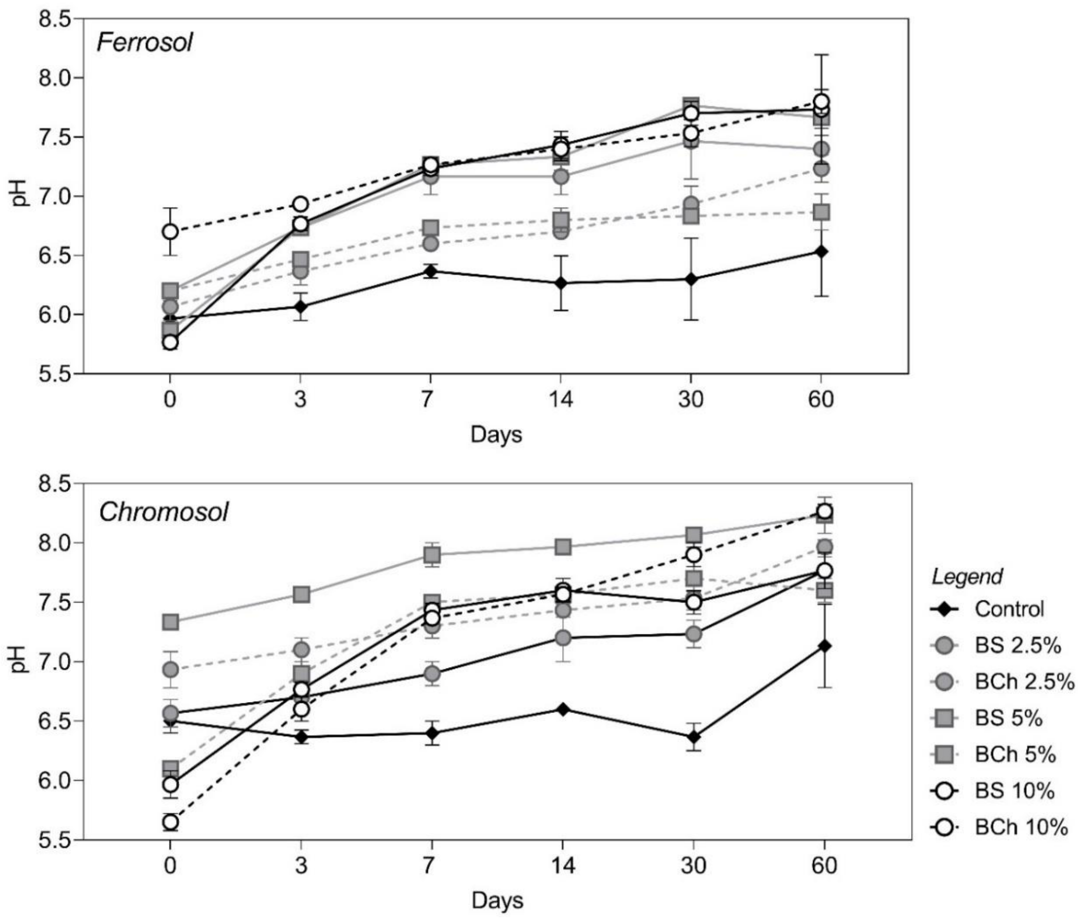


Fig. 3 pH of leachate following sequential leaching events over time (60 days). Error bars show standard deviation (n = 3).

The accumulated mass of each metal in the leachate varied depending on the soil and the treatment applied (Fig. 4, Table 4). Minimal metal leaching occurred from control Ferrosol and Chromosol, particularly for Cu and Cr. The addition of biochar to the soils reduced the metal concentration in the leachate, especially for Zn in Chromosol. Zn concentration in the leachate reduced from 14.3 mg kg^{-1} to 8.69 mg kg^{-1} upon a 10% w/w biochar application rate (Table 4). However, when biosolids and biochar were independently applied to both soils, there was an increased release of Cu and Cr into the leachate. This increase was most significant when biosolids was applied at different rates to both the soil types. In this study, Cr was the most mobilized metal when biosolids is applied at the highest rate of 10% w/w in both soil types. Specifically, in comparison to the control soil, the concertation of Cr released in the leachate increased from 0.07 to 4.95 mg kg^{-1} for Chromosol and from 0.09 to 5.88 mg kg^{-1} for Chromosol and Ferrosol (Fig. 3, Table 4).

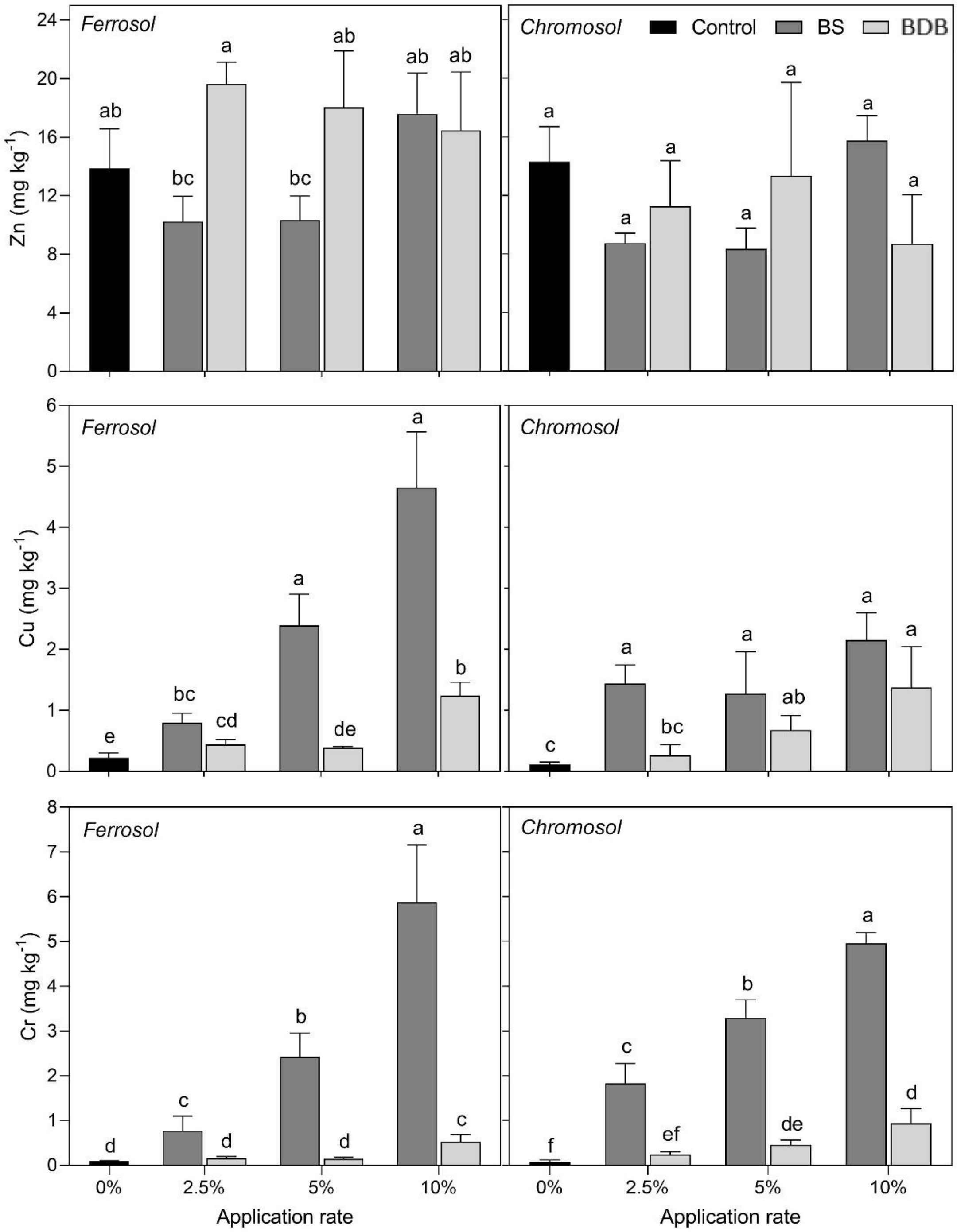


Fig. 4. Total mass of Zn, Cu and Cr leached from the columns after 6 leaching events for Red Ferrosol and Yellow Chromosol treated with different application rate of biosolids and biosolids-derived biochar. Error bars show SD (n = 3). Letters denote statistically significant differences between means.

Table 4. Leaching behaviour of heavy metals in soil amendments: added amounts, leachate concentrations and leached ratios.

	Ferrosol			Chromosol		
Treatment	**Total Zn mg kg^{-1}**	**Zn Leached mg kg^{-1}**	**%**	**Total Zn mg kg^{-1}**	**Zn Leached mg kg^{-1}**	**%**
Soil 0%	410.00	13.88	3.39	42.70	14.31	33.51
BC 2.5%	447.94	19.63	4.38	80.60	11.24	13.95
BC 5%	485.87	18.02	3.71	118.60	13.33	11.24
BC 10%	561.74	16.45	2.93	194.40	8.69	4.47
Soil 0%	410.00	13.88	3.39	42.70	14.30	33.49
BS 2.5%	433.93	10.32	2.38	66.60	8.74	13.12
BS 5%	457.85	17.58	3.84	90.60	8.36	9.23
BS 10%	505.70	14.31	2.83	138.40	15.77	11.39
Treatment	Total Cu **mg kg^{-1}**	**Cu Leached mg kg^{-1}**	**%**	**Total Cu mg kg^{-1}**	**Cu Leached mg kg^{-1}**	**%**
Soil 0%	46.20	0.22	0.48	8.50	0.11	1.29
BC 2.5%	63.50	0.44	0.69	25.80	0.26	1.01
BC 5.0%	80.80	0.39	0.48	43.10	0.68	1.58
BC 10%	115.40	1.24	1.07	77.70	1.37	1.76
Soil 0%	46.20	0.22	0.48	8.50	0.10	1.18
BS 2.5%	60.70	0.80	1.32	23.00	1.44	6.26
BS 5.0%	75.20	2.39	3.18	37.50	1.27	3.39
BS 10%	104.20	4.65	4.46	66.50	2.15	3.23
Treatment	**Total Cr mg kg^{-1}**	**Cr Leached mg kg^{-1}**	**%**	**Total Cr mg kg^{-1}**	**Cr Leached mg kg^{-1}**	**%**
Soil 0%	331.00	0.09	0.03	13.50	0.07	0.52
BC 2.5%	333.50	0.16	0.05	16.00	0.24	1.50
BC 5.0%	335.90	0.15	0.04	18.40	0.46	2.50
BC 10%	340.90	0.53	0.16	23.40	0.94	4.02
Soil 0%	331.00	0.09	0.03	13.50	0.07	0.52
BS 2.5%	332.30	0.07	0.02	14.80	1.83	12.36
BS 5.0%	333.70	0.24	0.07	16.20	3.29	20.31
BS 10%	336.30	0.46	0.14	18.80	4.95	26.33

The main risk associated with applying biochar derived from biosolids is the potential leaching of heavy metals from the biochar into the soil and, subsequently, the environment. This study demonstrated that the utilization of biochar as compared to direct biosolids application results in lower Cu and Cr leaching. When biochar is added to control soils, there is consistently lower Cu and Cr leaching in comparison to using biosolids at the same application rates. For instance, when biosolids and biochar were applied to Ferrosol at a rate of 10% w/w, the accumulated Cu in the leachate was 4.65 mg kg^{-1} and 1.24 mg kg^{-1}

respectively. A similar trend was also observed in Chromosol. This aligns with other research which stated that thermal treatment of biosolids can immobilize most of the heavy metals in the resulting biochar via multiple mechanisms such as high pH, high surface area and stable carbonized matrix (Hernandez et al., 2011; Li et al., 2012).

3.4.1. Zinc

Zinc concentrations in leachate varied significantly depending on the treatments (i.e., biosolids and biochar) and the two soil types ($p<0.01$) (Fig. 5). During the initial sampling events, especially in soils treated with different rates of biochar, Zn concentrations were highest in comparison to Cu and Cr. Subsequently, this concentration gradually decreased from the second to the fourth sampling event. By the fifth and sixth sampling events, Zn leachate concentrations ranged between 0 – 1 mg kg^{-1} in both the soil types. It is also important to highlight that during the leaching events, the pH in the leachate samples from both soil types increased gradually, especially in the fifth and sixth sampling events (pH from ~7 to 8.5) (Fig. 4). Importantly, Zn is particularly sensitive to changes in pH compared to other metals like Pb and Cd (Antonangelo et al., 2023). The observed pH elevation, especially during the fifth and sixth leaching events, might have limited the movement of Zn from the biochar matrix (Fig. 3). Furthermore, it is also worth noting that biochars produced at high temperatures tend to contain increased amount of ash, which could play an important role in immobilizing Zn and reducing its mobility from the biochar matrix (Qian et al., 2016).

Contrastingly, throughout the leaching events the concentration of Zn in the leachates from both soil types increased in soils amended with 10% biosolids (Fig. 3). This increase, especially noticeable from the fourth sampling event, suggesting that biosolids, containing high organic matter have higher degradability compared to biochar (Adhikari et al., 2019). As biosolids degrade more rapidly in soil over time, they release more unavailable forms of heavy metals, which subsequently become bioavailable in the soil for plant uptake and leaching into groundwater.

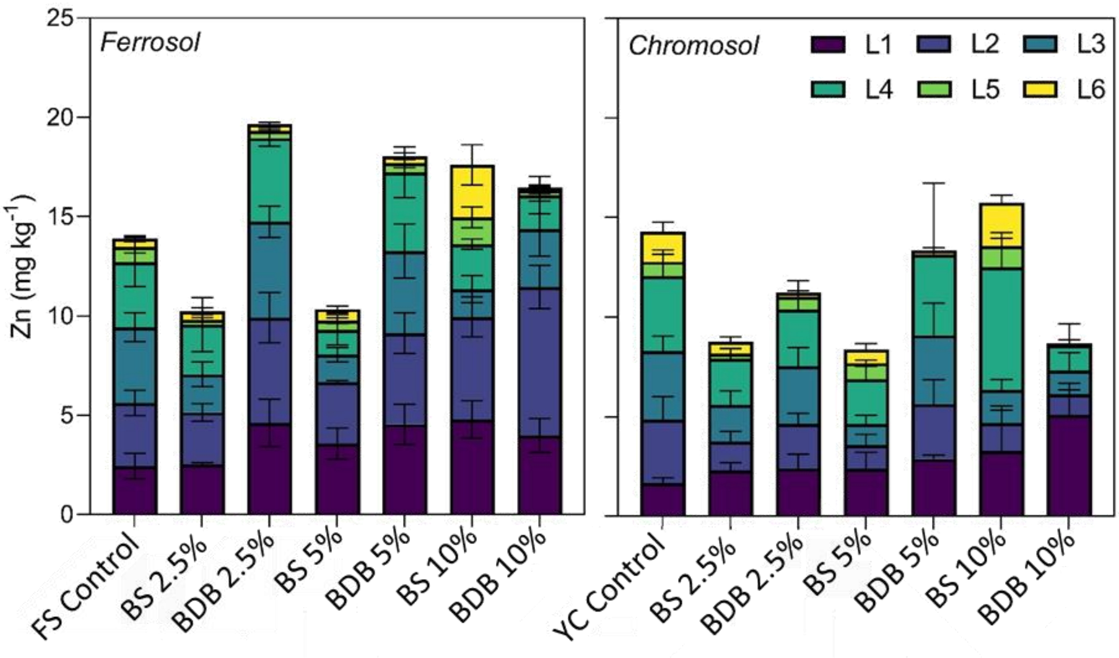


Fig. 5. Zinc (Zn) recovered in leachate (as total Zn, mg kg^{-1}) over six leaching events. Notation: FS, Red Ferrosol; YC, Yellow Chromosol; BDB, Biosolids-Derived Biochar; BS, Biosolids; the number that follows BDB and BS denotes the application rate of the amendment expressed in % (by weight). Error bars on mean values ($n = 3$) denote the standard deviation, $p<0.001$, LSD: 0.317 (Soil type), $p>0.05$, LSD: 0.453 (Control *vs*. Treatment), $p<0.011$, LSD: 0.484 (Amendment type), $p>0.05$, LSD: 0.513 (Amendment rate), $p<0.001$, LSD: 0.388 (Leaching events). LSD values were estimated using a 5% probability level.

3.4.2. Copper

In the initial sampling, the concentrations of Cu in leachates were notably higher across all leaching events in both soil types and across different rates of both biosolids and biochar applications. Following the six leaching events, the concentration of Cu in leachates increased in the following treatment order: control soil<biochar-amended soils<biosolids-amended soils (Fig. 6). Biosolids applications increased Cu concentrations in leachates more than biochar applications at all application rates (Fig. 6). There were significant differences between control and treated samples ($p<0.0001$), as well as significant differences between amendment types and amendment rates ($p<0.001$). During leaching events 1 to 4, Cu concentrations in leachates for both soils increased with increasing application rates, as expected. However, Cu leaching was not observed in leaching events 5 and 6. The amount of Cu recovered in leachate from biochar-treated soil was about one-third the amount recovered from biosolids-treated soil. Biochar showed reduced concentrations of Cu recovered in leachate, but to greater extent in clay Red Ferrosol than in Sandy Chromosol. Application of biochar significantly reduced the leachability of heavy metals at all application rates likely due to higher pH (Fig. 3) and surface area (Hossain et al., 2011). The above results are consistent with leachate studies which have reported that extractable concentrations of all the elements including Cu in the biosolid derived-biochar were lower than those in the original raw wastewater sludge samples (Hossain et al., 2011).

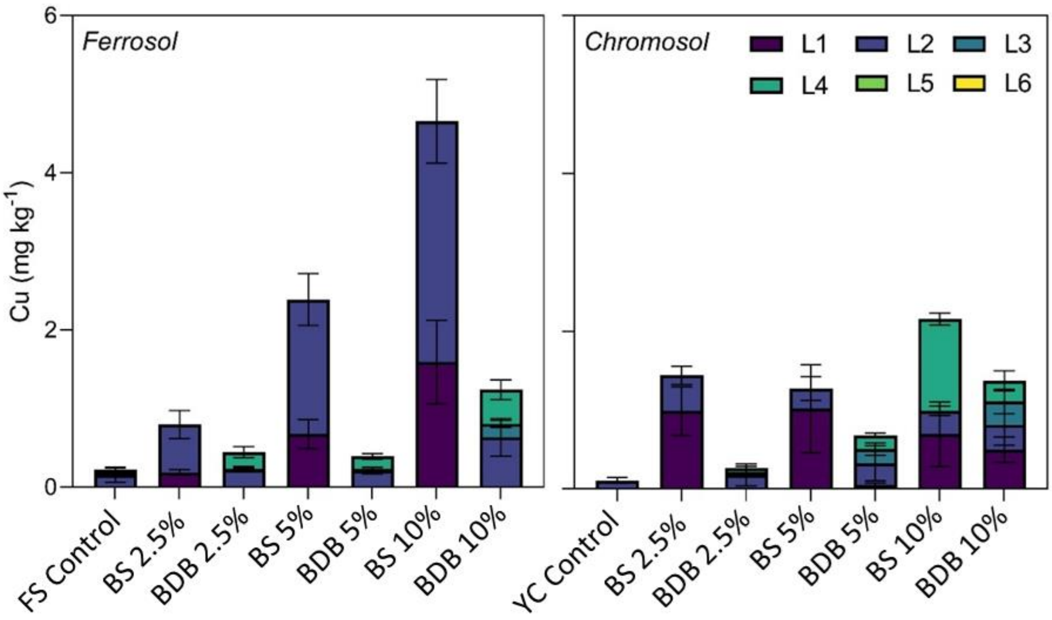


Fig. 6. Copper (Cu) recovered in leachate (as total Cu, mg kg-1). Note that after the fourth leaching event, the amount of Cu recovered in leachate was below detection limits. Notation: FS, Red Ferrosol; YC, Yellow Chromosol; BDB, Biosolids-Derived Biochar; BS, Biosolids; the number that follows BDB and BS denotes the application rate of the amendment expressed in % (by weight). Error bars on mean values (n = 3) denote the standard deviation, p<0.05 LSD: 0.044 (Soil type), p<0.001, LSD: 0.0636 (Control vs. Treatment), p<0.001, LSD: 0.068 (Amendment type), p<0.001, LSD: 0.072 (Amendment rate), p<0.001, LSD: 0.067 (Leaching events). LSD values were estimated using a 5% probability level.

3.4.3. Chromium

Cr recovered in leachate was similar in both soils and between-leaching events (Fig. 7). Most of the mobile fraction of Cr was extracted during leaching events 1-4 of the experiment. In both soils, Cr recovered in leachate increased with the application rate. Total Cr recovered in leachate from biochar-treated soil was about eight times lower than from biosolids-treated soil. There were no differences between soil types, but there were significant differences between control and all biosolid and biochar treatments (p<0.001) as well as significant differences between amendment types and amendment rates (p<0.001). There were lower concentrations of Cr in the leachate from soils amended with biochar compared to biosolids amended for all rates applied. For both soils treated with 10% biochar, Cr concentrations were lower than soils amended with 2.5% of biosolids. Lower Cr concentrations in these leachates indicated lower Cr mobility in biochar amended soils, confirming the efficiency of biochar in reducing environmental risk. It is important to note that despite the higher total Cr levels in biochar compared to biosolids (98.7 mg kg^{-1} vs 53 mg kg^{-1}, Table 2), the mobility, leaching risk, and bioavailability of Cr would be greatly reduced in biochar amended soils compared to biosolids.

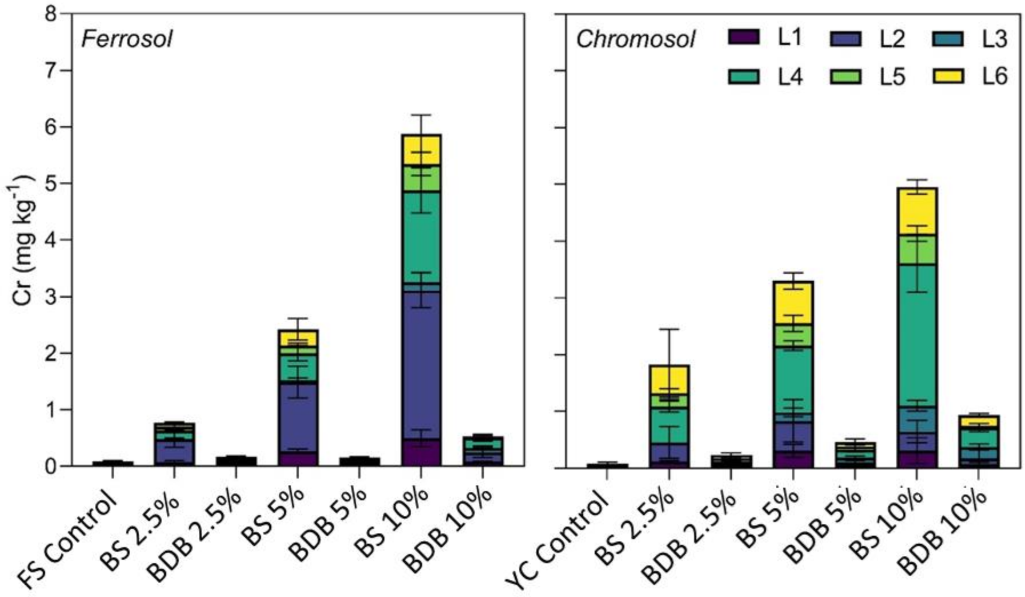


Fig. 7. Chromium (Cr) recovered in leachate (as total Cr, mg kg^{-1}). Notation: FS, Red Ferrosol; YC, Yellow Chromosol; BDB, Biosolids-Derived Biochar; BS, Biosolids; the number that follows BDB and BS denotes the application rate of the amendment expressed in % (by weight). Error bars on mean values ($n = 3$) denote the standard deviation, $p>0.065$, LSD: 0.045 (Soil type), $p<0.001$, LSD: 0.064 (Control vs. Treatment), $p<0.001$, LSD: 0.069 (Amendment type), $p<0.001$, LSD: 0.073 (Amendment rate), $p<0.001$, LSD: 0.066 (Leaching event). LSD values were estimated using a 5% probability level.

4. Conclusions

This study investigated the impact of biosolids and biosolids-derived biochar on the mobility of heavy metals in soils. While higher total metal concentrations were observed in biochar-amended soils, the leachates showed significantly lower concentrations of soluble copper and chromium compared to those treated with biosolids. This underscores a potential mitigation of environmental risks associated when applying biosolids-derived biochar as a soil amendment. However, the varying zinc concentration leaching patterns at different application rates of biosolids-derived biochar versus biosolids, highlights the need for further research to understand the complex relationship between application rates and leaching behaviours. In order to understand the distribution of these heavy metals within the two soil matrices at different depths the movement of total heavy metal concentrations was observed after 6 leaching events in constructed soil columns. Movement of heavy metals, specifically copper and chromium, decreased in both Ferrosol and Chromosol and zinc decreased in Chromosol for biosolids-derived biochar treatment but increased in Ferrosols for biosolids treatment. More research needs to be done in this area to understand the pattern of zinc leaching and movement in different soil types.

Additionally, this study evaluated the efficacy of portable X-ray fluorescence as a rapid and cost-effective measurement tool for heavy metal concentrations, comparing it with measurements obtained via ICP-MS. This study established a relationship between two analytical techniques, ICP-MS and pXRF for soil elemental analysis, with a focus on three heavy metal concentrations. Regression analyses conducted between these methods reaffirmed the reliability of p-XRF, particularly for determining total Zn, Cu, and Cr concentrations in soil, although with variations depending on soil type. Discrepancies observed between p-XRF and ICP-MS results for Cr in the Chromosol were attributed to low elemental concentrations approaching the limit of detection for p-XRF.

In a broader context, this study highlights the importance of recognising that total metal concentrations alone do not provide a complete understanding of environmental risk. The observed reduction in the solubility of Cu and Cr in biochar treatments, despite higher total concentrations, suggests a potential mitigation of environmental risks associated with leaching. This nuanced understanding is essential for informed decision-making in agricultural practices and environmental management, striking a balance between the benefits of soil amendments and potential environmental impacts. Ultimately, the study highlighted the importance of conducting comprehensive assessments that extend beyond total metal concentrations to evaluate the environmental sustainability of soil amendments.

Credit authorship contribution statement

Payel Sinha; Conceptualization, Methodology, Visualisation, Data curation, Investigation, Writing – Original Draft, Presentation, Formal analysis, Writing – Review & Editing. Maja Arsic; Presentation, Formal analysis, Writing – Review & Editing. Serhiy Marchuk; Conceptualization, Methodology, Writing – Review & Editing, Supervision. Diogenes L. Antille; Conceptualization, Methodology, Writing – Review & Editing, Resources, Supervision. Peter Harris; Conceptualization, Methodology, Writing – Review & Editing, Supervision. Seija Tuomi; Methodology, Technical assistance, Analysis; Bernadette McCabe; Conceptualization, Methodology, Writing – Review & Editing, Resources, Funding acquisition, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Heavy metal dynamics in soils amended with biosolids and biosolids derived biochar using portable X-ray fluorescence spectroscopy

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Supplementary Material

Table A1. Change in leachate pH during experiment.

Treatment	pH					
	Day 0	Day 3	Day 7	Day 14	Day 30	Day 60
Ferrosol Control Soil	6.0	6.1	6.4	6.3	6.3	6.5
Ferrosol+BDB 2.5%	6.1	6.4	6.6	6.7	6.9	7.2
Ferrosol+BDB 5%	6.2	6.5	6.7	6.8	6.8	6.9
Ferrosol+BDB 10%	6.7	6.9	7.3	7.4	7.5	7.8
Ferrosol+BS 2.5%	6.2	6.7	7.2	7.2	7.5	7.4
Ferrosol+BS 5%	5.9	6.7	7.3	7.3	7.8	7.7
Ferrosol+BS 10%	5.8	6.8	7.2	7.4	7.7	7.7
Chromosol Control Soil	6.5	6.4	6.4	6.6	6.4	7.1
Chromosol+BDB 2.5	6.6	6.7	6.9	7.2	7.2	7.8
Chromosol+BDB 5	6.9	7.1	7.3	7.4	7.5	8
Chromosol+BDB 10	7.3	7.6	7.9	8.0	8.1	8.2
Chromosol+BS 2.5	6.1	6.9	7.5	7.6	7.7	7.6
Chromosol+BS 5	6.0	6.8	7.4	7.6	7.5	7.8
Chromosol+BS 10	5.7	6.6	7.4	7.6	7.9	8.3

Table A2: Leaching of Zn (mg kg^{-1} of soil)

Treatment	Leaching Events (mg kg^{-1})						Total Zn (mg kg^{-1})
	1	2	3	4	5	6	
Ferrosol Control Soil	2.44	3.17	3.82	3.29	0.75	0.41	13.88
Ferrosol+BDB 2.5%	4.61	5.30	4.82	4.22	0.37	0.31	19.64
Ferrosol+BDB 5%	4.53	4.59	4.14	3.97	0.45	0.34	18.03
Ferrosol+BDB 10%	3.98	7.47	2.92	1.70	0.24	0.14	16.47
Ferrosol+BS 2.5%	2.52	2.62	1.92	2.50	0.23	0.44	10.23
Ferrosol+BS 5%	3.56	3.10	1.37	1.25	0.47	0.57	10.33
Ferrosol+BS 10%	4.79	5.15	1.40	2.27	1.34	2.63	17.60
Chromosol Control Soil	1.66	3.21	3.43	3.76	0.72	1.53	14.30
Chromosol+BDB 2.5	2.41	2.25	2.89	2.83	0.64	0.22	11.25
Chromosol+BDB 5	2.88	2.75	3.45	4.05	0.00	0.20	13.33
Chromosol+BDB 10	5.10	1.05	1.16	1.28	0.00	0.10	8.69
Chromosol+BS 2.5	2.31	1.45	1.84	2.30	0.26	0.58	8.75
Chromosol+BS 5	2.38	1.19	1.06	2.25	0.81	0.67	8.36
Chromosol+BS 10	3.28	1.40	1.68	6.15	1.08	2.18	15.76

Table A3: Leaching of Cu (mg kg^{-1} of soil)

Treatment	Leaching Events (mg kg^{-1}) 1	2	3	4	5	6	Total Cu (mg kg^{-1})
Ferrosol Control Soil	0.00	0.16	0.03	0.04	0.00	0.00	0.22
Ferrosol+BDB 2.5%	0.00	0.23	0.01	0.21	0.00	0.00	0.44
Ferrosol+BDB 5%	0.00	0.21	0.02	0.16	0.00	0.00	0.39
Ferrosol+BDB 10%	0.00	0.64	0.17	0.44	0.00	0.00	1.24
Ferrosol+BS 2.5%	0.19	0.61	0.00	0.00	0.00	0.00	0.80
Ferrosol+BS 5%	0.68	1.71	0.00	0.00	0.00	0.00	2.39
Ferrosol+BS 10%	1.59	3.06	0.00	0.00	0.00	0.00	4.65
Chromosol Control Soil	0.00	0.11	0.00	0.00	0.00	0.00	0.11
Chromosol+BDB 2.5	0.00	0.18	0.04	0.05	0.00	0.00	0.26
Chromosol+BDB 5	0.05	0.28	0.18	0.17	0.00	0.00	0.68
Chromosol+BDB 10	0.50	0.32	0.29	0.26	0.00	0.00	1.37
Chromosol+BS 2.5	0.99	0.45	0.00	0.00	0.00	0.00	1.44
Chromosol+BS 5	1.02	0.26	0.00	0.00	0.00	0.00	1.27
Chromosol+BS 10	0.69	0.30	0.00	1.16	0.00	0.00	2.15

Table A4: Leaching of Cr (mg kg^{-1} of soil)

Treatment	Leaching Events (mg kg^{-1}) 1	2	3	4	5	6	Total Cr (mg kg^{-1})
Ferrosol Control Soil	0.05	0.01	0.00	0.02	0.00	0.01	0.09
Ferrosol+BDB 2.5%	0.06	0.03	0.01	0.04	0.01	0.01	0.16
Ferrosol+BDB 5%	0.05	0.03	0.01	0.05	0.01	0.00	0.15
Ferrosol+BDB 10%	0.08	0.16	0.08	0.18	0.01	0.02	0.53
Ferrosol+BS 2.5%	0.08	0.40	0.01	0.14	0.07	0.07	0.77
Ferrosol+BS 5%	0.27	1.21	0.03	0.49	0.13	0.28	2.42
Ferrosol+BS 10%	0.49	2.61	0.15	1.62	0.47	0.53	5.88
Chromosol Control Soil	0.02	0.02	0.00	0.02	0.00	0.02	0.07
Chromosol+BDB 2.5	0.04	0.03	0.04	0.07	0.00	0.05	0.24
Chromosol+BDB 5	0.05	0.05	0.09	0.14	0.06	0.08	0.46
Chromosol+BDB 10	0.07	0.10	0.20	0.34	0.04	0.19	0.94
Chromosol+BS 2.5	0.12	0.34	0.00	0.63	0.24	0.50	1.83
Chromosol+BS 5	0.31	0.52	0.15	1.18	0.39	0.75	3.29
Chromosol+BS 10	0.31	0.34	0.46	2.51	0.52	0.83	4.95

Table A5: Two Way ANOVA results for total metal concentrations in ferrosol and chromosols amended with different application rates of biosolids or biosolids-derived biochars.

Element	Source of variation	Ferrosol	Chromosol
		P value	P value
Zn	Treatment	** 0.0081	ns
	Application rate (%)	ns	ns
	Interaction	** 0.0027	* 00244
Cu	Treatment	*** <0.0001	** 0.0014
	Application rate (%)	*** <0.0001	*** <0.0001
	Interaction	*** <0.0001	* 0.0213
Cr	Treatment	*** <0.0001	*** <0.0001
	Application rate (%)	*** <0.0001	*** <0.0001
	Interaction	*** <0.0001	*** <0.0001

4.3. Links and implications

Paper 1 indicated that biochar can immobilize heavy metals and reduce their solubility in soils. Future investigations should focus on understanding how specific soil characteristics and application rate affect the mobility and distribution of heavy metals in soil environments.

Paper 2 aimed to fill the above research gap using a controlled experimental setup with leaching columns and two contrasting soil types to provide a greater understanding of these interactions. Additionally, the study seeks to validate the use of p-XRF as a rapid and cost-effective method for measuring heavy metal concentrations in soils treated with different soil amendments, comparing its effectiveness with the more established ICP-MS.

Links:

1. Heavy metal immobilization by biochar: The study reinforces previous findings that BDB immobilizes heavy metals, reducing their solubility and potential for leaching when applied to soils. This is particularly relevant in the context of the real time use of commercially produced biochar as a soil amendment on agricultural soils, especially considering the evolving regulations that may ban the use of biosolids on Australian agricultural land.

2. Soil type and application rate impact: The study highlights that soil type and application rates affect the mobility and distribution of heavy metals. This link is crucial for tailoring BDB application to different soil types to minimize heavy metal leaching risks in the environment. The findings in **Paper 2** suggest that specific soil characteristics and application rates must be considered to optimize the benefits of BDB while mitigating potential environmental risks.

3. Comparison of measurement techniques: By validating the use of p-XRF against the established ICP-MS, **Paper 2** demonstrated a link between rapid, cost-effective measurement techniques and more traditional, costly laboratory methods. The validation supports the use of p-XRF as a reliable tool for real-time soil analysis, facilitating more extensive and frequent monitoring soil health and contamination.

Implications:

1. Environmental risk mitigation: **Paper 2** suggests that using BDB as a soil amendment can potentially mitigate environmental risks associated with heavy metal contamination and leaching. This is due to observed reduction in the solubility and mobility of copper and chromium in BDB-amended soils, despite higher total concentration present in BDB.
2. Tailored soil amendment strategies: The varying results of zinc leaching depended on soil type and application rate, indicated the need for customized soil amendment strategies. Understanding these dynamics can help in developing specific guidelines for applying commercial scale production of BDB to different soil types, ensuring optimal outcomes. The tailored approach can enhance the effectiveness of BDB in reducing heavy metal mobility and improving soil health.
3. Cost effective environmental analysis: The successful application of p-XRF for measuring heavy metal concentrations provides a more cost-effective method for soil analysis. This could facilitate more widespread monitoring of soil contamination risks.
4. Long-term soil health and food safety: Highlighting the need for further research on the long-term field studies to understand heavy metal dynamics of BDB-amended soil, the study underscores the importance of ongoing monitoring to ensure soil ecosystem and food safety. This is crucial for maintaining sustainable agricultural practices over time and ensuring that the benefits of using BDB do not come at the cost of long-term environmental health.
5. Policy and regulatory frameworks: The results observed in **Paper 2** can inform policy makers and regulatory bodies about the benefits and potential risks of using BDB in sustainable agriculture. This could lead to the development of regulations that promote the safe and effective use of BDB balancing the benefits of waste recycling as soil amendments with potential environmental impacts. Such informed policies can help in the widespread adoption of BDB while ensuring environmental protection.

CHAPTER 5: PAPER 3 – AGRONOMIC PERFORMANCE OF RYEGRASS AND HEAVY METAL DYNAMICS IN SOIL AMENDED WITH BIOSOLIDS-DERIVED BIOCHAR

5.1. Introduction

Studies, reviews, and meta-analysis have generally found that biochar tends to be more effective in promoting plant growth and mitigative heavy metal bioavailability in acidic soils rather than alkaline soils. Despite these advancements, a critical research gap identified in **Paper 1** persists regarding the direct comparison of agronomic efficiency and soil health outcomes of utilizing biosolids-derived biochar versus biosolids application in contrasting soil types at different rates. This comparison allows for the evaluation of two soil amendments with distinct properties, nutrient release properties and environmental impacts, providing a comprehensive understanding of their role in sustainable agriculture. This direct comparison is crucial for determining the most effective and environmentally responsible practices for enhancing agronomic performance, thereby guiding agricultural stakeholders and policy makers in making informed decisions for long-term sustainability.

Understanding the dynamics of total heavy metal concentrations in soil treated with amendments is crucial, because regulatory standards focus on this total concentration as stated in **Paper 2**. As positive effect has been observed in **Paper 2** in terms of BDB amended soils exhibited lower concentrations of soluble copper and chromium in leachates compared to soil treated with biosolids, further research is required in understand around heavy metal uptake in plant.

This paper focuses on two objectives: Firstly, “Evaluate BDB as potential soil amendment with respect to yield, agronomic efficiency and heavy metal uptake in ryegrass (*Lolium perenne* L.) in two Australian soils with contrasting physico-chemical properties at varying rates (2.5%, 5%, 10% w/w), and compare these effects with BS application”. Secondly, “Investigate soil enzymatic activity following soil application of BDB in two Australian soils with contrasting physio-chemical properties at varying rates (2.5%, 5%, 10% w/w), and compare these effects with BS application”.

5.2. Manuscript submitted to *Archives of Agronomy and Soil Science*

Agronomic performance of ryegrass and heavy metal dynamics in soil amended with biosolids-derived biochar

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Abstract

This paper investigates, for this first-time, to our knowledge, the combined assessment of agronomic and environmental impacts of applying biosolids-derived biochar (BDB) in two soil types (Chromosol and Ferrosol) when compared to biosolids. Glasshouse experiments revealed that biosolids-derived biochar significantly increased the dry matter yield of ryegrass, although biosolids performed better overall. At 2.5% w/w application rate of BDB increased yield by 180% in Chromosol and 192% in Ferrosol compared to control, while biosolids increased yield by 562% in Chromosol and 179% in Ferrosol. Higher application rates of BDB did not affect agronomic efficiency. Importantly, BDB significantly reduced heavy metal uptake (chromium, copper, and zinc) by ryegrass compared to biosolids. Soil incubation supported these findings, showing that 2.5% BDB increased urease activity by 50% in Chromosol and 23% in Ferrosol, relative to control soil, which could be beneficial for nitrogen cycling. While at the same rate BDB decreased acid phosphatase activity 12% in Chromosol and 20% in Ferrosol, potentially affecting phosphorous availability. The study advocates for a 2.5% application rate of biosolids-derived biochar to optimize agricultural outputs while safeguarding soil and plant health. Further research is recommended to explore land application of BDB using field trials to understand long-term impacts and connect the results of the current research observed in controlled environment studies.

Keywords

Sewage sludge; p-XRF (Portable X-Ray Fluorescence); dry matter yield; urease; acid phosphatase

Abbreviations

BS, Biosolids; BDB, Biosolids-Derived Biochar; p-XRF, Portable X-Ray Fluorescence; Zn, Zinc; Cu, Copper; Cr, Chromium; Fe, Iron

1. Introduction

Maintenance of soil carbon (C) and soil fertility are vital components of sustainable agriculture system, which address global challenges in terms of food security and environmental resilience (Shang et al., 2014). Soil fertility directly affects crop yield, making it a focus area for land use management to achieve long-term agricultural sustainability (Tuğrul, 2019). A range of soil and crop management strategies are available to improve agricultural sustainability (Shah and Wu, 2019). Among such strategies is the combination and use of organic and inorganic fertilizers which can improve crop productivity and soil fertility (Shah and Wu, 2019).

Biosolids (BS), the organic materials derived from the treatment of wastewater sludge, have long been used as soil amendments in agricultural practices. Use of biosolids in agriculture is beneficial due to the high nutrient content of biosolids, and the cost effectiveness and efficiency for managing this waste (Marchuk et al., 2023). However, the safe use of biosolids is becoming a global concern due to potential environmental implications, especially regarding persistent organic pollutants, microplastic and heavy metal accumulation (Sinha et al., 2023). To address these challenges, the conversion of biosolids to biochar (i.e., a carbon rich product obtained through the thermal treatment of organic materials under limited oxygen conditions) presents a promising option for effectively managing the risks associated with biosolids (Patel et al., 2020; Raheem et al., 2018).

Biochar is generally more effective in acidic soils than alkaline soils at promoting plant growth and mitigating heavy metal bioavailability (Hossain et al., 2021; Méndez et al., 2013; Faria et al., 2018; Jeffery et al.,2011). Also, they found that manure- and grass-based biochar are more effective than those made from wood (Jeffery et al.,2011; Macdonald et al.,2014). Despite these advancements, a critical research gap persists regarding the direct comparison of soil fertility and crop production outcomes of utilizing biosolids-derived biochar (BDB) versus biosolids application in contrasting soil types at different rates (Sinha et al., 2023). This comparison allows for the evaluation of two soil amendments with distinct properties, nutrient release properties and environmental impacts, providing a comprehensive understanding of their role in sustainable agriculture. This direct comparison is crucial for determining the most effective and environmentally responsible practices for enhancing soil fertility and crop productivity, thereby guiding agricultural stakeholders in making informed decisions for long-term sustainability.

Understanding the dynamics of total heavy metal concentrations in soil treated with amendments is crucial, because regulatory standards focus on this total concentration. Chromium (Cr) is a heavy metal with known toxic effect on plant growth (Zulfiqar et al., 2023). High level of Cr can lead to chlorosis, necrosis and other growth abnormalities that reduce plant yield and quality (AbdElgawad et al., 2023; Franco et al., 2023). Copper (Cu) and zinc (Zn) are essential elements but can be toxic to plants and microorganisms above certain levels (Franco et al., 2023; Meng et al., 2023); therefore, maximum permissible levels in soil must be observed (MAFF, 1998). This research study also highlights research gap in comprehending the behaviour of total heavy metal concentration in soil and plants treated with biochar and biosolids using portable X-ray fluorescence (p-XRF) spectrometry, one of the essential components for compliance and informing regulation.

The study explores the effects of biosolids-derived biochar on ryegrass growth and soil health, compared to BS. The research was conducted at three different application rates (2.5%, 5%, and 10% w/w) to determine the optimal use of BDB for enhanced crop productivity while minimizing environmental risks. The primary objectives were to evaluate the response of ryegrass to BDB in terms of dry matter yield (DMY) and agronomic efficiency, and to assess the uptake of heavy metals (Cr, Cu, and Zn) by the plants in glasshouse experiment. Additionally, the study aimed to investigate the impact of BDB on soil enzymatic properties (urease and acid phosphatase) in a controlled soil incubation experiment. It is envisaged that the results derived from this work will inform the design of future field-scale experimentation aimed at improving on-farm use of BDB in the development of practical management recommendations.

2. Material and methods

2.1. Description of soils and soil amendments

Both BS and BDB were produced from the same BS material sourced from Pyrocal Pty Ltd. (Toowoomba, Queensland, https://www.pyrocal.com.au/). The biochar was produced on site at a wastewater treatment plant using Pyrocal's Continuous Carbonisation Technology (CCT) gasifier. Dried Biosolids were gasified at a temperature of 400°C increasing to 700°C over a residence time of 100 seconds. BDB was quenched with water upon exiting the gasifier. Both the dry biosolids and derived biochar materials were crushed, dried at 40°C and sieved to pass 2mm. Physicochemical properties are presented in Table S1. Heavy metal analyses were performed on BS and BDB samples and the resulting values were compared with guidelines relevant to BS and BDB in land applications (Table 1).

Table 1: Heavy metals in biosolids and biosolids-derived biochar used in the experiment and their allowable range according to guidelines.

	Grade/Quality	Total heavy metals ($mg\ kg^{-1}$)			Analytical method/ Reference
		Cr	**Cu**	**Zn**	
Amendments					
Biosolids-derived biochar		98.7	692.3	1,517.4	172A2[1]
Biosolids		53.0	580.1	957.0	172A2[1]
Guidelines					
AWA-Biosolid	Category A	100	150	300	Natural Resource Management Ministerial Council (2004)
	Category B	250	375	700	
	Category C	500	2,000	2,500	
IBI -Biochar	Category A	93	143	416	International biochar initiative (2015)
	Category B	100	6,000	7,400	
EBC-Biochar	Premium	80	100	400	Schmidt et al. (2013)
	Basic	90	100	400	

[1]Rayment and Lyons, 2011

Two soils from Queensland were used in this laboratory study: Red Ferrosol (Oxisol in the NRCS-USDA Soil Taxonomy) from the Agricultural Field Station Complex at the University of Southern Queensland and a Yellow Chromosol (Alfisol in the NRCS-USDA Soil Taxonomy) from Gatton (Queensland, Australia). Selection of these soils was based on their differences in mineralogy, texture, pH and total carbon content. Soil samples were collected from 0.0–0.20 m depths, air-dried, and sieved to pass 2 mm sieves. Physicochemical properties, clay mineralogy by X-ray diffraction and locations of the soils are presented in Table S2.

2.2. Glasshouse experiment

Ryegrass (*Lolium perenne* L.) was used in a pot study conducted in a glasshouse facility at the Centre for Agricultural Engineering at the University of Southern Queensland (Toowoomba, Australia) using the Yellow Chromosol and Red Ferrosol described earlier. Plastic pots, 10 cm in height, 10 cm in diameter at the bottom and 10 cm in diameter at the top were used for the pot trial. The experimental design was a factorial randomised block design with 3 treatments: i) control soil (CS), ii) soil with BDB, and iii) soil with BS. Soils were amended with BS and BDB at three different rates in mass: 2.5%, 5% and 10% w/w referred to here as BS 2.5%, BS 5%, BS 10%, BDB 2.5 %, BDB 5%, and BDB 10%, respectively. Each treatment was carried out in triplicates. In each pot, 400g of air-dried soil was mixed uniformly with the respective rates of the treatments. Ryegrass seeds (20 g) were spread uniformly on the soil surface. The experiment commenced on March 20, 2022, and was conducted over a period of twelve months. Water (pH = 7.01) was supplied to maintain the soil between field capacity and approximately 70% of field capacity throughout the experiment (Yellow Chromosol – 15% w/w & Red Ferrosol – 21% w/w). Leaching was always avoided. The ambient temperature and relative humidity in the glasshouse were maintained at 25 ± 3°C and 55-65%, throughout the experiment. A total of twelve cuts were performed at regular time intervals of 30 days over a period of one year. The grass was cut at 20-mm above the soil surface (Cordovil et al., 2007) and the harvested plant material was oven-dried at 60°C for 48 hours (MAFF (1998), Method No.: 1) for determination of DMY and heavy metal uptake.

2.3. Soil incubation experiment

Soil incubation was conducted to determine the effect of biochar on the enzymatic activity in soil. Soils were amended with BS and BDB at three different rates: 2.5%, 5% and 10% w/w referred to here as BS 2.5%, BS 5%, BS 10%, BDB 2.5 %, BDB 5%, and BDB 10%, respectively. A zero-amendment control was also used for each soil type. The experiment followed a fully randomized design with three replications (n = 3) for each treatment. Treated and control soil samples (200 g each) were evenly packed into plastic pots (6.5 cm inner diameter and 10 cm in height). The soils were maintained at a soil water content equivalent to 70% of field capacity and incubated at a constant temperature of 25 ± 2°C for 60 days. Sampling was conducted at 0, 10, 20, 40 and 60 days from the start of the experiment by collecting subsoil samples weighing 20 g. Soil samples collected on day 60 were used for laboratory analysis of enzymatic activity.

2.4. Plant and soil measurements and analyses

Standard methods were used for the determination of pH, electrical conductivity (1:5 soil:water) and particle size distribution (Gee and Bauder, 1986). Total carbon and nitrogen concentration were measured by ignition with a Leco elemental analyser (Leco Corporation, St. Joseph, MI, USA). The chemical composition of soil, BDB and BS, and heavy metal content were analysed by inductively coupled plasma mass spectrometry (ICP-MS) (ELAN 6000, Perkin Elmer, Switzerland) after acidic digestion ("Aqua regia" HNO_3:HCl, 3:1) in a microwave oven (Multiwave, 3000 Anton Paar, USA). For X-ray diffraction (XRD) analysis the clay fractions (< 2 µm) were separated from the bulk soils through sedimentation according to Stokes' law (Jackson, 2005). The XRD patterns for randomly oriented air-dried samples were recorded with a PANalytical X'Pert Pro Multi-purpose diffractometer. XRD data were collected and displayed using CSIRO software XPLOT for Windows (Raven, 1990).

2.4.1. Portable X-ray fluorescence Spectrometry

Plant samples: Oven dried plant samples were packed into XRF sample cups and scanned with the OLYMPUS Vanta M Series portable X-ray fluorescence spectrometer (VMR-CXC-G2-A) for the total elemental concentration in the SOILEXTRA and GEOCHEM modes. The Olympus Vanta p-XRF features a (Rhodium/Tungsten (Rh/W)) anode X-ray tube of 10 to 50 kVp at 10-200 µA. This analyser uses a factory-installed calibration procedure with Compton Normalisation to estimate soil elemental concentrations in % or mg kg^{-1}. The SOIL mode is equipped with a three-beam configuration at 50 kV, 40 kV and 15 kV whereas the GEOCHEM mode has a two-beam configuration at 50 kV and 10 kV. To enable lower atomic number elements to be measured, such as magnesium, silicon, aluminium, and iron (Limit of detection of 1%), GEOCHEM mode uses longer count rates. The National Institute of Standards & Technology (NIST) certified standard, NIST 2711a (moderately elevated trace elements) soil standard was used to verify the performance of the instrument.

p-XRF was calibrated against calcium (Ca), titanium (Ti), rubidium (Rb), potassium (K), iron (Fe) and strontium (Sr). The recovery of elements via the p-XRF was high when comparing instrument measured values to the NIST standard (over 98% for all reference elements). In GEOCHEM Mode, Ca recovery was 105% (NIST certified material, Ca 2.42%), Ti recovery was 103% (NIST certified material, Ti 0.317%) and Rb recovery was 98% (NIST certified material, Rb 120 ppm) for the reference soil. In the SOIL EXTRA Mode, K recovery was 104% (NIST certified material, K 2.53%), Fe recovery was 100% (NIST certified material, Fe 2.82%) and Sr recovery was 97% (NIST certified material, Sr 242 ppm) for the reference soil.

2.4.2. *Enzymatic analysis*

Soil urease activity (BC0120 Soil Urease (UE) Activity Assay Kit), and acid phosphatase activity (BC0140 Soil Acid Phosphatase (S-ACP) Activity Assay Kit) were all determined by using the corresponding kit produced by Solarbio (http://www.solarbio.net/). The stopping procedure was operated according to the product manual (Catalog Number: BC0120 and Catalog Number: BC0140 attached in the supplementary document) provided by Solarbio using a spectrophotometer.

2.4.3. *Agronomic efficiency and heavy metal uptake*

A total of twelve cuts were performed at regular time intervals of 30 days. Grass was cut at 20 mm above the soil surface and the harvested plant material oven-dried at 60°C for 48 hours for determination of DMY. Cumulative DMY over twelve cuts was subsequently used to derive the agronomic efficiency of the amendments applied to soil as per Equation (1) after Antille and Moody (2021)

Equation 1: Determination of agronomic efficiency

$$AE = \frac{DMY(Treatment) - DMY(Control)}{Amendment\ application\ rate} \ldots\ldots (1)$$

where: AE is the agronomic efficiency of the amendment applied to soil and DMY is dry matter yield, all expressed in kg kg^{-1}.

2.4.4. *Statistical analyses*

The statistical package GenStat Release® 19th Edition (VSN International Ltd., 2020) was used to analyse data for heavy metal concentrations in soil and plant dry matter. Analyses involved ANOVA and repeated measurement of ANOVA. The least significant differences were used to compare means with a probability level of 5%. Figures were created using Graphpad Prism 9.1.2 (https://www.graphpad.com/updates/prism-912-release-notes). Statistical analyses were graphically assessed by means of residual plots. Log, natural log, or square root transformations of the data were applied to meet assumptions of normality or homoscedasticity for ANOVA analyses.

3. Results and discussion

3.1. Glasshouse experiment

3.1.1. Effect of treatments on dry matter yield and agronomic efficiency

The impact of biochar application on plant yield varies significantly across different studies, with some showing positive effects (Junior and Guo, 2023; Song et al., 2014) while others showing no improvement or even negative effect at higher application rates (Regmi et al., 2022; Suppadit et al., 2012; You et al., 2019). The variability in response to biochar application highlights the importance of considering specific soil type, crop type, and biochar characteristics when determining the optimal application rate.

Soil amended with BDB enhanced ryegrass growth and subsequent DMY compared to control in both soil types (Figure 1). Mean cumulative DMY was significantly higher in BS and BDB than in control soil ($p<0.001$) in both soil types. Higher application rates of BDB generally did not increase DMY yielding in both soil types. Differences between control and amendments at each cut were significant, and there were also significant differences in amendment type on DMY ($p<0.001$). Biosolids-derived biochar is known to improve soil structure, increase water retention and enhance nutrient availability, which can lead to increased plant growth and yield (Agegnehu et al., 2015; Lehmann and Joseph, 2015).

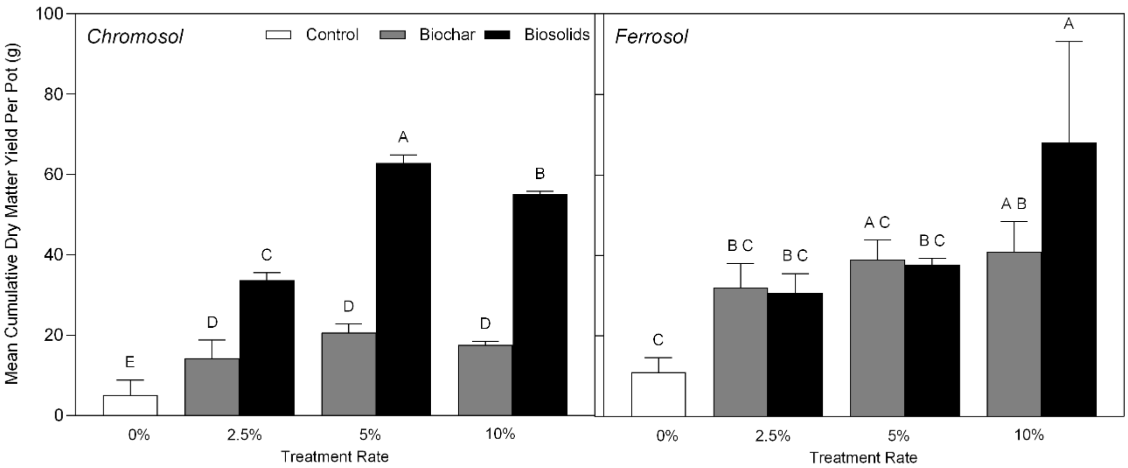

Figure 1: The effect of biosolids and biosolids-derived biochar on dry matter yield of ryegrass grown in pots over twelve cuts. Different letters indicate significant differences between treatments.

In Chromosol, BS was more effective than BDB at enhancing DMY across all tested application rates (p<0.001). At lower application rate of 2.5%, BS significantly increased DMY by 562%, while at the same rate for BDB resulted in a 180% increase. These findings contrast with Hossain et al. (2015), who reported no significant difference in the growth and production of cherry tomatoes when comparing wastewater sludge and sludge biochar application in Chromosol. The discrepancy may be attributed to the variations in biochar characteristics influenced by temperature and the initial feedstock characteristics. Notably, while BS showed the highest yield increase at 5% application rate, there was a decrease observed at 10% application rate. Gutiérrez-Ginés et al. (2023) reported similar findings, where higher application rates of BS (12.8% w/w) decreased growth in *Leptospermum scoparium* plants. Conversely, increasing the application rate of BDB did not significantly affect the DMY aligning with studies reported in literature (Junior and Guo, 2023; You et al., 2019).

In Ferrosol addition of BDB and BS were equally beneficial in enhancing DMY across all application rates. At lower application rates of 2.5% and 5%, BDB demonstrated slightly higher, although not significant, DMY compared to BS. Specifically, addition of 2.5% and 5% BDB resulted in a DMY increase of 192% and 256%, respectively, while BS resulted in DMY yield increase by 179% and 244% respectively. Although not specific to Ferrosol, broader research has reported that biochar application generally increases crop yields (Carter et al., 2013; Junior and Guo, 2023; Song et al., 2014). Given Ferrosol's high fertility and robust physical properties, it is likely to respond positively to BDB application, similar to other fertile soils at lower application rates. At lower application rates of BS (2.5% and 5%), there was no significant difference in yield, although at 10% application rate, BS exhibited the most substantial increase in DMY by 521%. These results align with the findings by Shan et al. (2021) reported similar findings, who observed grain yield of rice increased to 811.7% with sewage sludge application at the rate of 7.4% w/w. The higher rates of nitrogen, phosphorous and potassium in biosolids along with high organic matter may be the reason for higher yields (Agegnehu et al., 2015). Similar to the trend in Chromosol, the application rate of BDB in Ferrosol had no significant effect on DMY, corroborating with studies reported in literature (Junior and Guo, 2023; You et al., 2019).

Biochar decreases soil bulk density and may have acted as a soil conditioner that retained more available water and nutrients, and improved root growth which subsequently enhanced crop yield (Obia et al., 2016; You et al., 2019). The different responses of BDB application in Chromosol and Ferrosol can be attributed to difference in soil physicochemical properties (such as pH, total carbon content and clay content) which lead to Chromosol's lower fertility and nutrient status comparing to Ferrosol (Table S2). Although some studies have shown a clear effect of BDB on crop yield in sandy soil with low fertility (Agegnehu et al., 2015), this experiment evidenced that the increase in application rate in BDB, had no significant effect on DMY yield in either Chromosol or Ferrosol. Consequently, the optimum rate observed in this study was 2.5% w/w for both soil types. The significant differences in yield observed in this study can be attributed to several factors and conditions that may not be commonly reported in the broader literature. While both soil types benefit from BDB at lower application rate of 2.5%, the degree and efficiency of response can vary, suggesting the need for tailored soil management practices that consider the specific soil characteristics, amendment type and application rates.

Comparison of agronomic efficiency between BS and BDB revealed that BS generally offered higher efficiency across the tested application rates, with highest rate at 2.5% in Chromosol (Figure 2). The higher efficiency of BS can be attributed to its faster mineralization rate, which likely releases nutrients more rapidly to support plant growth (Liao et al., 2020). Whereas in Ferrosol, although not significant BDB offered slightly higher efficiency at 2.5% application rate (Figure 2). This subtle difference might be due to the varying mineralization dynamics in different soil types, with Ferrosol potentially providing conditions that enhance BDB's nutrient release (Alkharabsheh et al., 2021). Biosolids-derived biochar, while beneficial at lower application rates, shows no significant effect on efficiency as the rate increased, suggesting its benefits in Chromosol are maximised at lower application rates. This trend aligns with BDB's more stable and slower mineralization process, which limits its short-term nutrient contribution even at higher application rates (Alkharabsheh et al., 2021). Similarly, in Ferrosol BDB showed a moderate level of efficiency that decreased (non-significant) with higher application rate (Figure 2). This pattern further supports the hypothesis of BDB's slower mineralization rate, as increasing its application rate does not proportionally increase nutrient availability in the short term. The observed trends for both the amendments are consistent with findings from other studies. Biochar can reduce soil nitrogen losses, which could explain the initial increase in agronomic efficiency at lower application rate (Jeffery et al., 2015; Wei et al., 2020). Integration of biochar into poor soil enhances soil fertility, crop development, and productivity (Zeeshan et al., 2020). On the other hand, the high agronomic efficiency observed with biosolids can be attributed to their rich nutrient content, particularly nitrogen, phosphorus and potassium which are essential for plant growth (Hossain et al., 2010; Méndez et al., 2012).

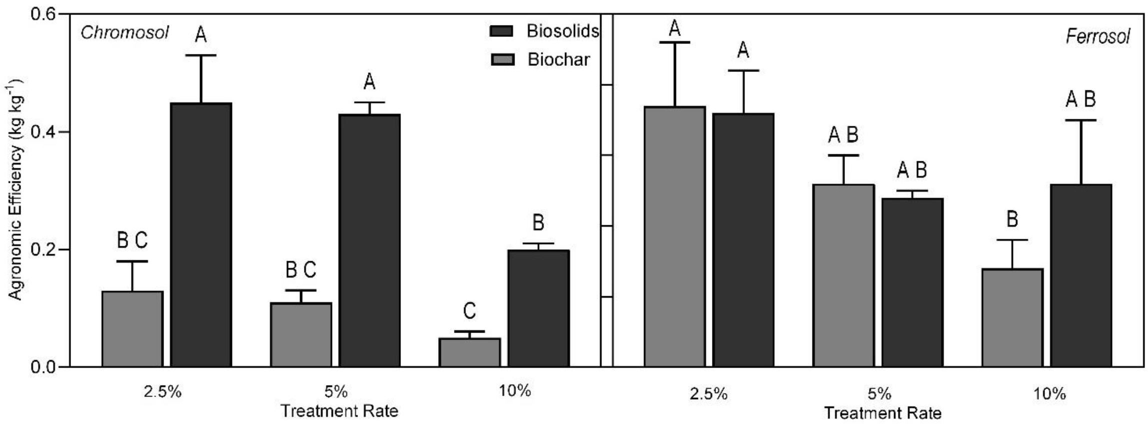

Figure 2: Agronomic efficiency for biosolids and biosolids derived biochar as derived from cumulative dry matter yield. Different letters indicate significant differences between treatments.

3.1.2. Effect of treatments on plant uptake of heavy metals

Heavy metal uptake in plants refers to the absorption and accumulation of metal contaminants from the soil into the plant tissues (Arif et al., 2016). This process is influenced by the bioavailability of the metals in the soil, which can be altered by addition of soil amendments such as biosolids and biosolids-derived biochar (Yan et al., 2020). Cumulative mean of total heavy metal uptake concentrations of Cr, Cu and Zn in the above ground part of ryegrass after 12 cuts were analysed over a period of 1 year (Figure 3).

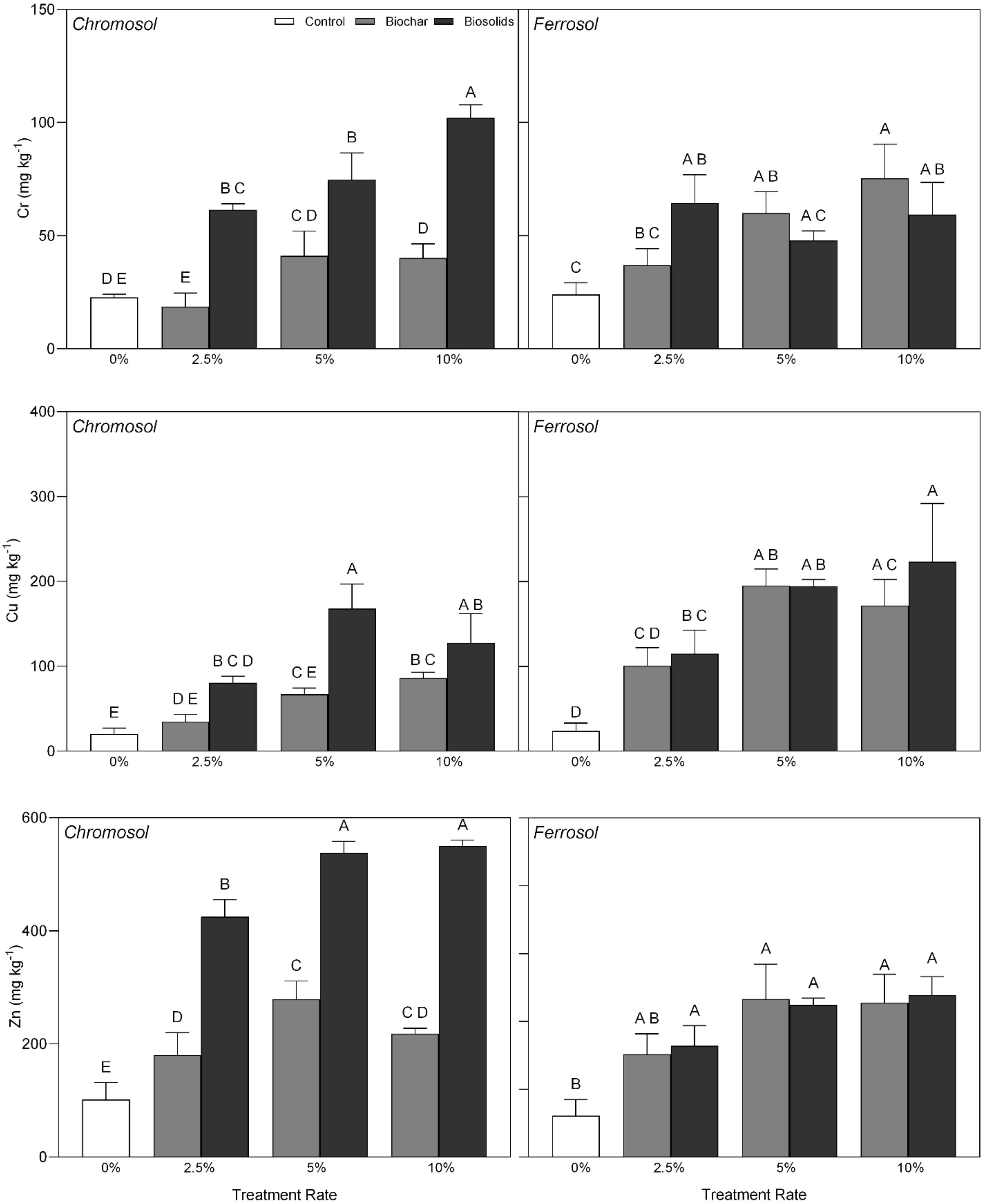

Figure 3: Effect of biosolids and biosolids-derived biochar rate on total heavy metals uptake by aboveground part of ryegrass after 12 cuts. Error bars on mean values (n = 3) denote the standard deviation.

Chromium Uptake Dynamics: While soil type alone did not significantly affect Cr uptake, the addition of BS or BDB amendments and their application rates significantly influenced the Cr uptake in the plant dry biomass (p<0.001). In Chromosol, the application rate of BS generally led to higher Cr uptake, with values approximately increasing from 70 mg kg^{-1} at 2.5% to over 100 mg kg^{-1} at 10%. BDB showed a less consistent increase with application rate, with the highest uptake around 40 mg kg^{-1} at 5% and slightly lower at 10%. In Ferrosol, the application rate of BS and Cr uptake is not directly proportional, with some decrease in rate observed at 5% when compared to 2.5%. Biosolids-derived biochar showed a similar trend as BS with highest uptake at 10% application rate. Overall, BS tend to result in higher Cr uptake compared to BDB at higher application rates. This could be due to different nutrient compositions and properties of the amendments affecting Cr availability and uptake mechanisms (Gutiérrez-Ginés et al., 2023). Biosolids-derived biochar has high surface area and porosity, which can adsorb Cr ions, reducing their availability in soil solution and thus their uptake by plants (Bashir et al., 2021; Namdari et al., 2024).

Copper Uptake Dynamics: Soil type significantly influences Cu uptake, as does the combination of BS and BDB amendments and their application rate (p<0.001). In Chromosol, the application rate of BS generally led to higher Cu uptake, while BDB shows less consistent increases in Cu uptake with application rate. In Ferrosol, the increasing application rate of BS correlates with higher Cu uptake, the highest uptake observed at 10%. BDB shows less consistent increases with application rate in Ferrosol. Notably, in both soil types, Cu uptake was lower in BDB when compared to BS at equivalent application rates. Consistent with the findings, BDB typically reduces Cu bioavailability through adsorption and immobilization mechanisms (Liu et al., 2023; Liu et al., 2024; Majaule et al., 2020).

Zinc Uptake Dynamics: Similar to Cr, the effect of soil type on Zn uptake is not statistically significant, although the combination of BS and BDB amendments and their application rate significantly influences the Zn uptake (p<0.001). In Chromosol, BS show a more consistent increase of Zn uptake with increasing application rate with the highest value observed at 10% application rate, while BDB showed less consistent increase in Zn uptake with application rate. In Ferrosol, the increasing application rate of BS and BDB leads to higher Zn uptake. Similar to Cr and Cu uptake, Zn uptake was lower in BDB when compared to BS at equivalent application rates in both soil type. BS increases Zn availability and uptake possibility due to their nutrient rich composition and influence on soil chemistry, as stated in Gutiérrez-Ginés et al. (2023), where the application of BS in soil, increased exchange Zn. Similar observation was also supported by from Gartler et al. (2013), where biosolids mixed with biochar significantly increased Zn uptake by some crop species. Biosolids-derived biochar typically reduces Zn bioavailability through adsorption and immobilization mechanisms (Namdari et al., 2024; Qian et al., 2016).

The findings from this study are consistent with other research which indicates that BDB exerts a more pronounced effect on immobilizing heavy metals and reducing their bioavailability when compared to BS especially in Chromosol (de Figueiredo et al., 2019; Hossain et al., 2010; Namdari et al., 2024), this can be attributed to the physiochemical properties of BDB, such as high surface area, porosity and pH modifying ability (Liu et al., 2023; Majaule et al., 2020). These findings underscore the importance of considering both amendment types and specific amendment rates when managing certain heavy metal uptake in agricultural systems.

The effectiveness of BDB in altering the heavy metal bioavailability can be influenced by soil properties such as pH and clay content (Table S1). Although soil was not a significant factor in influencing Cr and Zn uptake, for Cu the soil type was significant. While biosolids and biosolids-derived biochar can be beneficial for plant growth, their use in different soil types should be carefully managed to avoid excessive heavy metal uptake. Long-term research is imperative for comprehensively understanding the continued impacts of the amendments in different soil types.

3.2. Incubation experiment

3.2.1. Effect of treatments on soil enzyme activity

Enzyme activity serves as a crucial indicator for monitoring the impact of soil management, agricultural practices, and contamination on soil health (Adetunji et al., 2017). After the incubation with biosolids and biosolids-derived biochar, ureases and acid phosphatase activity was measured (Figure 4). Urease and acid phosphatase are closely linked through their roles in nutrient cycling and soil health.

Urease plays an important role in the transformation of soil nitrogen, with its activity being influenced by factors such as soil pH and texture. Ureases activity was significantly increased following incubation with BDB and BS in both Chromosol and Ferrosol soil compared to control soil. The application of BDB at a 2.5% w/w rate increased ureases activity by 50% in Chromosol and 23% in Ferrosol, relative to control soil. Similarly, the addition of biosolids at the same rate led to an increase in the rate of urease activity by 100% in Chromosol and 37% in Ferrosol relative to control soil. The greater increase in urease activity observed with BS compared to BDB can be attributed to higher nutrient content, particularly total nitrogen (Table S1) and the enhanced microbial activity promoted by the organic matter present in biosolids (Medina-Herrera et al., 2020). This observation underscores the significance of soil amendments in modulating enzyme activities, particularly in the context of nitrogen cycling.

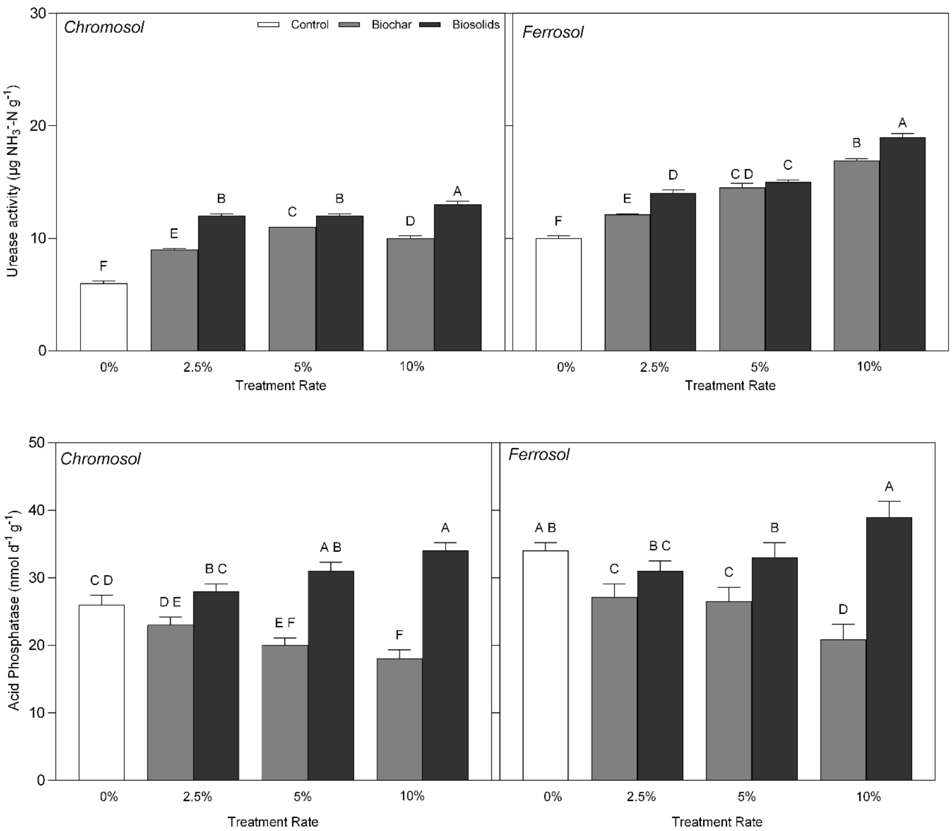

Figure 4. Effect of biosolids and biochar addition on the urease, and acid phosphatase in soil. Error bars on mean values (n = 3) denote the standard deviation. Different letters indicate significant differences between treatments at p<0.001 level.

Phosphatase enzymes are involved in the mineralization of organic P in soil, facilitating the conversion of complex organic P compounds to inorganic forms that are readily available for plant uptake. A significant decrease (p<0.001) in acid phosphatase activity in both Chromosol and Ferrosol was observed following the addition of BDB compared to control. Conversely, biosolids addition to Chromosol increased the enzyme activity, but decreased in Ferrosol at lower application rates. The application of BDB at a 2.5% w/w rate decreased acid phosphatase activity by 12% in Chromosol and 20% in Ferrosol, relative to control soil.

While addition of BS at 2.5% increased acid phosphatase activity by 8% in Chromosol, but decreased by 9% in Ferrosol, relative to control soil. The rise in pH resulting from addition of BDB may contribute to the observed decrease in the acid phosphatase activity as observed by Chen et al. (2013). Based on the urease activity in this incubation study, the application of BDB and BS improved the soil microbial activity and soil quality.

The combined effect of increased acid phosphatase and urease activities with biosolids application enhances the overall nutrient availability in soil, particularly nitrogen and phosphorous, which are critical for plant growth and development (Adetunji et al., 2017). This improved nutrient availability is a key factor that can contribute to the higher yields observed in soils treated with BS and BDB, across both Chromosol and Ferrosol soils (Figures 1 & 2). Incorporating BS also can increase microbial activity, likely due to biosolids-borne microbes (Medina-Herrera et al., 2020). These findings align with previous research that demonstrated the beneficial effects of biochar and biosolids on soil nutrient dynamics and plant growth outcomes (You et al., 2019; Medina-Herrera et al., 2020; Silva-Leal et al., 2021). The synergistic effect of increased microbial activities facilitates the breakdown and mineralization of organic compounds, thereby making essential nutrients more accessible to plants.

The higher enzymatic activities observed in BS is more likely attributed to the presence of particulate organic matter (POM) (Wang et al., 2020; Chen et al., 2018). POM is the liable fraction of soil organic matter that significantly influences soil enzymatic activities and is strongly correlated with urease and proteases (Wang et al., 2020). This increase in liable organic matter fraction may stimulate microbial growth and enzyme synthesis, leading to overall enzymatic activities in BS compared to BDB. Given these observations further research is required to understand the relative contributions of POM and mineral associated organic matter to enzyme activities in biochar amended soils. This approach would provide a more comprehensive understanding of the mechanisms in driving increases enzymatic activities in BS and help develop strategies to enhance soil fertility and ecosystem functions through organic matter management.

4. Conclusion

This study demonstrated several agronomically important concepts for the safe re-use of biosolids-derived biochar as a fertiliser. Specifically, this study explored aspects of dry matter yield, agronomic efficiency, heavy metal uptake, and enzyme activity. Regarding yield and agronomic efficiency, BDB significantly enhanced dry matter yield of ryegrass at lower application rates of 2.5%. With respect to heavy metal bioavailability, application of BDB to pot trials significantly decreased heavy metal uptake in above-ground biomass compared with BS. The incubation study regarding enzyme activity, both BDB significantly increased urease activity, important for nitrogen cycling in soil. By comparison to control, BDB application decreased acid phosphatase activity, which could have implications for phosphorous-limited applications. These enzymatic responses are important indicators of soil health and nutrient availability, which directly affect plant growth and productivity.

The study also identified research gaps needing further exploration, including the long-term effects of biosolids-derived biochar on soil and plant systems, the underlying mechanism of overall observed changes and broader environmental impacts. The importance of these interconnected results lies in their implications for sustainable agriculture. By demonstrating that biosolids-derived biochar can enhance plant growth while also mitigating heavy metal uptake and influencing soil enzyme activity, the study provides a scientific basis for the development of soil amendment strategies that promote plant productivity and environmental health.

5. Credit authorship contribution statement

Payel Sinha; Conceptualization, Methodology, Visualisation, Data curation, Investigation, Writing – Original Draft, Presentation, Formal analysis, Writing – Review & Editing. Diogenes L. Antille; Conceptualization, Methodology, Writing – Review & Editing, Resources, Supervision. Peter Harris; Conceptualization, Methodology, Writing – Review & Editing, Supervision. Serhiy Marchuk; Conceptualization, Methodology, Writing – Review & Editing, Supervision. Seija Tuomi; Methodology, Technical assistance; Bernadette McCabe; Conceptualization, Methodology, Writing – Review & Editing, Resources, Funding acquisition, Supervision.

6. Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Agronomic performance of ryegrass and heavy metal dynamics in soil amended with biosolids-derived biochar

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Table S1: Physicochemical characterization of biosolids and biochar

.

Description	Analytical method	Biosolids	Biochar
pH (1:5 soil:water)	4A1[1]	5.6	9.5
EC (1:5 soil:water), dS m^{-1}	3A1[1]	5.38	0.51
Total C, % (w/w)	6B2[1]	40.59	34.55
Total N, % (w/w)	7A5[1]	7.07	4.65
Total P, g kg^{-1}	17A2[1]	49.90	78.90
Soluble P, g kg^{-1}	1:5 soil:water suspension, then ICP-MS	7.13	0.13
Total Zn, mg kg^{-1}	17A2[1]	957.0	1517.4
Soluble Zn, mg kg^{-1}	1:5 soil:water suspension, then ICP-MS	1.43	0.20
Total Cu, mg kg^{-1}	17A2[1]	580.1	692.3
Soluble Cu, mg kg^{-1}	1:5 soil:water suspension, then ICP-MS	0.05	0.02
Total Cr, mg kg^{-1}	17A2[1]	53.0	98.7
Soluble Cr, mg kg^{-1}	1:5 soil:water suspension, then ICP-MS	0.31	0.01

[1]Rayment and Lyons, 2011

Table S2. Physicochemical characterization of the soils

Description	Analytical method	Red Ferrosol	Yellow Chromosol
GPS Location		27°36'32.27" S, 151°55'52.96" E	27°35'44.9" S, 152°18'20.1" E
pH (1:5 soil:water), %	4A1[1]	6.6	5.5
EC (1:5 soil:water), dS m^{-1}	3A1[1]	0.03	0.01
Total C, % (w/w)	6B2[1]	3.51	1.69
Total N, % (w/w)	7A5[1]	0.27	0.16
Clay (<0.002 mm), % (w/w)	Gee and Bauder, 1986	57	14
Silt (0.002–0.02 mm), % (w/w)	Gee and Bauder, 1986	11	11
Sand (0.02–2 mm), % (w/w)	Gee and Bauder, 1986	32	75
Total Cr, mg kg^{-1}	Digestion, ICP-MS, 17A2[1]	331	14
Total Cu, mg kg^{-1}	Digestion, ICP-MS, 17A2[1]	46	9
Total Zn, mg kg^{-1}	Digestion, ICP-MS, 17A2[1]	90	43
Dominant clay mineral	X-ray Diffraction	Kaolinite	Kaolinite, Montmorillonite

[1]Rayment and Lyons, 2011

Soil Urease(UE) Activity Assay Kit

Note: It is necessary to predict 2-3 large difference samples before the formal determination.

Operation Equipment: Spectrophotometer

Catalog Number: BC0120

Size: 50T/24S

Components:

Reagent I: Liquid 10 mL×1. Methylbenzene. Storage at 4°C. Required but not provided.

Reagent II: Powder ×1. Dissolved with 20 mL of distilled water before use. Storage at 4°C.

Reagent III: Liquid 65 mL×1. Storage at 4°C.

Reagent IV Solution A: Liquid 2 mL×1. Storage at 4°C.

Reagent IV Solution B: Liquid 8 mL×1. Storage at 4°C. Before using, mix Solution A and Solution B according to the volume ratio of 1:4 for use; mix the amount with how much.

Reagent V: Liquid 0.5 mL×1. Storage at 4°C. The liquid is placed in the EP tube in the reagent bottle. Before use, add 9.5 mL of distilled water, mix well and wait for use; store the reagent that cannot be used up at 4°C;

Standard: Liquid 1 mL×1, 1 mg/mL standard solution.

Product Description

Urease is an enzyme that catalyzes the hydrolysis of urea into carbon dioxide and ammonia. The microbial quantity of soil, organic matter content, total nitrogen and available nitrogen content have positive correlation with soil urease activity. Soil nitrogen status is determined by soil urease activity.

The ammonia is determined by the indophenol blue method, resulting in blue indophenol produced is proportional to the concentration of ammonia.

Reagents and Equipment Required but Not Provided.

Spectrophotometer, thermostat water bath, transferpettor, 1 mL glass cuvette, ice, 30-50 mesh sieve (or smaller), distilled water, Methylbenzene (Express delivery not allowed), distilled water.

Procedure

I. Sample processing:

The fresh soil sample shall be dried by naturally or in an oven at 37°C, and shall be screened through 30-50 mesh.

II. Determination procedure:

1. Preheat the spectrophotometer for more than 30 minutes, adjust the wavelength to 630 nm, set zero with distilled water.
2. Sample Preparation

Reagent	Test tube	Contract tube

Air drying soil sample (g)	0.25	0.25
Reagent I (μL)	125	125
Mix thoroughly, wetting all the soil, place at room temperature for 15 minutes.		
Reagent II (μL)	625	-
Distilled water (μL)	-	625
Reagent III (μL)	1250	1250
Mix thoroughly, culture for 24 hours in 37℃ water-bath. Centrifuge at 10000 ×g for 10 minutes at room temperature. Take the supernatant for test.		

3. Dilute the supernatant 10 times. (Add 0.9 mL of distilled water to 0.1 mL of the supernatant). Dilute until the absorbance less than 1.5.
4. Prepare standard solution: Diluted the standard to 8, 6, 4, 2, 1, 0.5, 0.25, 0 μg/mL.
5. Ammonia concentration test

Reagent	Test tube(T)	Contract tube(C)	Standard tube
Diluted supernatant solution/ Standard solution	360	360	360
Reagent IV (μL)	120	120	120
Reagent V (μL)	120	120	120
Mix thoroughly, incubate at room temperature for 20 minutes.			
Distilled water (μL)	400	400	400

Mix thoroughly, set the counter to zero with distilled water at 630 nm and measure the absorbance which noted as A, ΔA=A(T)-A(C). Set a contract cube for each test tube.

Make standard curve: Get the standard curve according to standard concentration (y) and absorbance (x, subtract the blank).

Calculation

According to the standard curve, take ΔA(x) into the formula to get the concentration (μg/mL) of sample(y).

Unit definition: One unit of enzyme activity is defined as the amount of enzyme catalyzes the production of 1 μg of NH_3-N in the reaction system per day every gram of dry soil sample.

Urease activity (U/g soil sample) = y×10×Vrv÷W÷T=80×y

10: Dilution factor;

T: Reaction time, 1 day;

Vrv: Total reaction volume, 2 mL;

W: Sample weight ,0.25 g.

Recent Product Citations:

[1] Hou Q, Wang W, Yang Y, et al. Rhizosphere microbial diversity and community dynamics during potato cultivation[J]. European Journal of Soil Biology, 2020, 98: 103176.

References:

[1] Kandeler E, Gerber H. Short-term assay of soil urease activity using colorimetric determination of ammonium[J]. Biology and fertility of Soils, 1988, 6(1): 68-72.

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Related Products:

BC0110/BC0115 Soil Polyphenoloxidase (S-PPO) Activity Assay Kit

BC0280/BC0285 Soil Alkaline Phosphatase(S-AKP/ALP) Activity Assay Kit

BC4040/BC4045 Soil Neutral Invertase(S-NI) Activity Assay Kit

Soil Acid Phosphatase (S-ACP) Activity Assay Kit

Note: Take two or three different samples for prediction before test.

Operation Equipment: Spectrophotometer

Catalog Number: BC0140

Size: 50T/48S

Components:

Reagent I: Liquid 21 mL×1 , storage at 4℃. Protect from light.

Reagent II: powder×1 bottle, storage at 4℃. Dissolve with 50 mL of distilled water before use.

Reagent III: Liquid 11 mL×1, storage at 4℃.

Reagent IV: Powder×1, storage at 4℃. Dissolve with 1152 μL of absolute ethyl alcohol (required but not provided) and 48 μL of distilled water before use. Do not use any more if it turns brown.

Standard: Liquid 1 mL×1 bottle, storage at 4℃, 0.5 μmol/mL phenol standard solution, storage at 4℃.

Product Description:

Soil phosphatase is an enzyme which catalyze soil organic phosphate mineralization, the activity influence directly the decomposition and transformation of organic phosphate and its bio-availability. The activity is the indicator of evaluating the direction and intensity of soil phosphorus bio-transformation. Soil phosphatase is influenced by the content of carbon, nitrogen, available phosphorus in the soil and pH. Soil phosphatase is divideded into three types: acidic, neutral and alkaline phosphatase according to the optimum pH.

In acidic condition, soil acid phosphatase (S-ACP) can hydrolyze disodium phenyl phosphate to phenol and disodium hydrogen phosphate. The activity of S-ACP can be calculated by measuring the amount of phenol produced.

Reagents and Equipments Required but Not Provided:

Spectrophotometer, 37℃ incubator, centrifuge, transferpettor, table centrifuge, 1 mL glass cuvette, analytical balance, toluene, alcohol, ice and distilled water.

Procedure:

I. Crude enzyme preparation:

Add 0.05 mL of methylbenzene to 0.1 g of dry soil sample, shake slightly for 15 minutes. Add 0.4 mL of Reagent I, mix thoroughly and keep in 37℃ incubator for 24 hours. Then add 1 mL of Reagent II immediately and mix thoroughly to stop the catalysis. Centrifuge at 8000 rpm for 10 minutes at room temperature, take the supernatant on ice for testing.

II. Determination procedure:

1. Preheat Spectrophotometer for 30 minutes, adjust the wavelength to 660 nm, set zero with distilled water.

2. Blank tube: Take a 1 mL glass cuvette, add 50 μL of Reagent I, 200 μL of Reagent III, 20 μL of Reagent IV, mix thoroughly. Then add 730 μL of distilled water after color development. Mix thoroughly and place for 30 minutes at room temperature. Determine the absorbance at 660 nm and record as A_B.

3. Standard tube: Take a 1 mL glass cuvette, add 50 μL of standard solution, 200 μL of Reagent III, 20 μL of Reagent IV, mix thoroughly. Then add 730 μL of distilled water after color development. Mix thoroughly and place for 30 minutes at room temperature. Determine the absorbance at 660 nm and record as A_S.

4. Test tube: Take a 1 mL glass cuvette, add 50 μL of supernatant, 200 μL of Reagent III, 20 μL of Reagent IV, mix thoroughly. Then add 730 μL of distilled water after color development. Mix thoroughly and place for 30 minutes at room temperature. Determine the absorbance at 660 nm and record as A_T.

Note: Blank tubes only need to be tested 1-2 times.

III. S-ACP activity calculation:

Unit definition: One unit of enzyme activity is defined as the amount of enzyme catalyzes the production of 1 nmol of phenol in the reaction system per day every gram soil sample.

$$S\text{-}ACP(nmol/d/g)=[C\times(A_T-A_B)\div(A_S-A_B)]\times Vrv\times 1000\div W\div T$$
$$=725\times(A_T-A_B)\div(A_S-A_B)\div W$$

C: Standard concentration, 0.5 μmol/mL;
Vrv: Total volume in catalyze system, 1.45 mL;
W: Soil sample weight, g;
T: Reaction time, 24 hours=1 day;
1000: 1 μmol=1000 nmol.

Recent Protect Citations:

[1] Liu B, Wang S, Wang J, et al. The great potential for phytoremediation of abandoned tailings pond using ectomycorrhizal Pinus sylvestris[J]. Science of The Total Environment, 2020, 719: 137475.

[2] Hou Q, Wang W, Yang Y, et al. Rhizosphere microbial diversity and community dynamics during potato cultivation[J]. European Journal of Soil Biology, 2020, 98: 103176.

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[1] 关松荫.土壤酶及其研究法[M].北京：科学出版社，1982.

Related Products:

5.3. Links and implications

Promising evidence provided in **Paper 2** supported the potential of BDB to mitigate environmental risks associated with heavy metal leaching in a controlled environment setting. **Paper 3** expanded on these findings by comparing yield, agronomic efficiency, and heavy metal uptake in ryegrass (*Lolium perenne* L.) usind soil amended with BDB and compared to BS. The novelty of **Paper 3** lies in its dual focus on agronomic performance of ryegrass and enzymatic activity in BDB-amended in two physiologically contrasting Australian soils. This capstone paper combines the knowledge gaps identified in **Paper 1** and key findings in **Paper 2** and attempts to integrate findings related to soil-BDB-plant interaction.

Links:

1. Dry matter yield and agronomic efficiency: BDB significantly enhances the dry matter yield of ryegrass, particularly at lower application rates of 2.5%. This suggests that BDB can effectively promote plant growth and increase agronomic efficiency, potentially leading to higher crop yields and improved agricultural productivity.
2. Heavy metal uptake: Application of BDB can lead to significant decrease in heavy metal uptake in above ground biomass compared with BS. These findings highlight the potential of BDB to mitigate the risks associated with heavy metal contamination in agricultural soils, thereby informing the concerns around food safety.
3. Enzyme activity: BDB application results in increased urease activity, crucial for nitrogen cycling in soil. However, it also decreases acid phosphatase activity, which may have implications for phosphorus limited applications This enzymatic activity indicates alterations in soil microbe and nutrition availability, directly impacting soil health, plant growth and productivity.
4. Research gaps: The study identifies several research gaps that require further exploration, including the long-term effect of BDB on soil and plant systems, the underlying mechanisms driving observed changes, and broader environmental impacts. Addressing these gaps is crucial for a comprehensive understanding of the implications of using BDB as a soil amendment and ensuring its sustainable application in agriculture.

Implications:

1. Promotion of sustainable agriculture: The interconnected results of the study emphasize the potential of BDB to promote sustainable agriculture. By enhancing plant growth, reducing heavy metal uptake, and influencing soil enzyme activity, BDB offers promising avenue for developing soil amendment strategies that simultaneously boost plant productivity and addresses food safety concerns.
2. Policy and regulatory frameworks: The results demonstrated in **Paper 3** supported heavy metal dynamics revealed in **Paper 2,** which can inform policy makers and regulatory bodies in Australia about the potential risks of using commercially produced BDB in sustainable agriculture. This could lead to the development of regulations that promote the safe and effective use of BDB balancing the advantages of waste recycling as soil amendments with potential environmental impacts. Such informed policies can help in the widespread adoption of BDB while ensuring environmental protection.
3. Need for continued research: The identification of research gaps emphasizes the need for continued investigation into the long-term effects and broader implications of BDB produced at commercial scale at wastewater treatment plants and recycled back on agricultural land. Addressing these gaps will assist in facilitating the development of informed soil management practices and ensure the integration of BDB into sustainable agriculture.

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CHAPTER 6: DISCUSSION AND CONCLUSIONS

This chapter reports the overall result and discussion of this research thesis. They are described sequentially, synthesising insights from the literature review and addressing the research objectives identified in the introduction. The conclusion of this research is then presented, along with recommendations for future work.

6.1. Land application of biosolids-derived biochar in Australia: A review

Paper 1 provided a critical review of the use of biosolids-derived biochar in Australian agriculture, highlighting the increased interest in thermal treatments as a management method due to legislative changes and waste reduction goals. Currently, there are no legislative standards available in Australia that prescribe limits for the concentrations of heavy metals in biochar intended for land application. Regulations and standards for composts and biosolids in Australia are based upon an assessment of the total concentration of metals in the material, without any consideration of their mobility in soil and bioavailability. Voluntary biochar quality standards exist in Europe (i.e., the European Biochar Certificate) (Schmidt et al., 2013) and in the USA (i.e., the International Biochar Initiative) (International biochar initiative, 2015) and they aim to guarantee the quality of the biochar product. Importantly, according to these guidelines, organic contaminants and heavy metal concentrations are the major determinants of the end-use of the biochar.

This review brought together scientific evidence showing that thermal treatment (such as pyrolysis and gasification) of biosolids can be employed to reduce pathogens, microplastics, and organic pollutants load, and decrease the bioavailability of heavy metals maintaining them within environmentally and agronomically safe levels. Where biosolids or biochar are used, on-farm implementation of best (or recommended) management practices for crops, soil and applied nutrients must always be exercised to control such risks. While research into the short-term effects (e.g., <10 years) of BDB on crop, soil and environment appears to support its use in agriculture, the longer-term effects are less known. Therefore, longer-term studies are required for better understanding the viability of using BDB as a safe soil amendment. The nutrient and contaminant dynamics in soils receiving BDB, and the inherent risk of transferring these contaminants to the food chain need to be determined together with measures to mitigate such risks. Key research gaps identified by this review are summarized below:

1. Exploration of potential for cost-effective thermal technology to treat biosolids, including alternatives for recovering energy for electricity generation and conversion of biosolids to biochar.
2. Thermal treatment appears to be effective at eliminating persistent organic pollutants, microplastics, and pathogenic contaminants from biosolids. However, the efficacy of thermal treatment in reducing (or avoiding) soil contamination from these sources is not well documented. This information is critical for supporting the safe use of BDB as a soil amendment and for removing concerns associated with recycling.
3. There is potential to customize biochar products to suit specific users' needs (e.g., soil and crop type, farm application method), which will require understanding of the relationship between the desired biochar characteristics and the production conditions and feedstock. The optimal combination of feedstock and treatment conditions to match specific crop and soil requirements needs to be determined. Optimization of the physical and mechanical properties of BDB will facilitate field application with standard fertilizer applicators, improving field delivery efficiency and logistics, and their acceptability by farmers.

A comprehensive analysis of the strengths, weakness, opportunities, and threats associated with the conversion of biosolids to biochar in the Australian market is discussed in Sinha et al., 2023.

Strengths	Weakness
• Reduction in waste volume, which can decrease disposal costs and alleviate pressures on landfills. • Thermal treatment of biosolids can produce energy, which can be used to power the treatment process. • Biosolids-derived biochar has the potential to improve soil health and fertility, leading to increased crop yields and reduced need for synthetic fertilisers. • The production of biochar from biosolids can contribute to the greenhouse gas emissions by sequestering carbon in the soil.	• Concerns about potential contaminates in biosolids may limit public acceptance of the use of biochar in agriculture. • Thermal treatment facilities may require significant capital requirement. • The lack of long-term studies on the effects of biosolids-derived biochar on soil health and contaminant transfer may limit the adoption of the technology.

Opportunities	Threats
• The global shift towards a low-carbon economy and increasing demand for sustainable products may create new markets for biosolids-derived biochar. • The ability of biochar to sequester carbon can be used to generate carbon credits, providing additional revenue streams. • The development of custom biochar products tailored to specific crops and soil types may create niche markets and increase demand. • Research into the long-term effects of biosolids-derived biochar on soil health and contaminant transfer can help to address concerns and increase acceptance.	• Fluctuations in the prices of fossil fuels may affect the competitiveness of biochar as the energy source. • Regulatory barriers or lack of clear guidelines for the safe use of biosolids-derived biochar may hinder market growth. • Competition from other waste-to-energy technlogies and alternative fertilisers may limit the market for biosolids-derived biochar • Lack of awareness or education about the benefit of biosolids-derived biochar may limit market uptake.

Figure 6. SWOT analysis of biosolids-biochar conversation on the Australian market.

These insights from **Paper 1** informed the aims and objectives of this thesis, focusing on exploring the direct comparison of mobility and leaching of heavy metals, crop production, agronomic efficiency, heavy metal uptake by plants and soil enzymatic activity outcomes of utilizing BDB versus BS amendments in two contrasting soil types at three different rates. **Paper 2** and **Paper 3** addressed these objectives through experimental studies. **Paper 2** focused on the mobility and leaching of heavy metals in soils amended with this novel BDB at different rates and comparing it with BS. Promising evidence supporting the potential of BDB to mitigate environmental risks associated with heavy metal leaching in agricultural settings supporting the studies in **Paper 1**. **Paper 3** expanded on these findings by comparing yield, agronomic efficiency, and heavy metal uptake in ryegrass (*Lolium perenne* L.) of BDB at three different rates in contrasting soil and comparing it with BS. The results showed that BDB significantly increased the dry matter yield of ryegrass, although BS performed better overall. Higher application rates of BDB did not affect agronomic efficiency. Importantly, BDB significantly reduced heavy metal uptake (chromium, copper, and zinc) by ryegrass compared to biosolids. Highlighting and correlating with the findings in **Paper 2** demonstrating the role of BDB in immobilizing and reducing the bioavailability of heavy metals to plants, thereby enhancing food safety and environmental protection. Significant difference was observed in **Paper 2** and **Paper 3** regarding mobility and leaching of heavy metals, yield, agronomic efficiency, and heavy metal uptake responses between the two soil types, when amendments were applied, which can be attributed to inherent soil properties. This suggests the need for tailored soil management practices that consider the specific soil characteristics, amendment type and application rates.

6.2. Heavy metal dynamics in biosolids and biosolids-derived biochar amended soils following sequential leaching events.

Paper 1 indicated that during the thermal conversion of biosolids to biochar, while pathogens, microplastics and organic pollutants are eliminated or greatly reduced in concentration, the process concentrates heavy metals. Due to the loss of water and organics, heavy metal concentration can increase by 2.5-3.5-fold (Jin et al., 2016). The highly negative surface charge of biochar enables the retention of cationic nutrients via ion exchange, whereas the relatively extensive surface area, internal porosity, and polarizability facilitate the sorption of anionic nutrients via covalent bonds (Lu et al., 2020). Heavy metal contamination of agricultural soils represents a serious environmental issue. BDB are characterized by elevated level of heavy metal and when applied to agricultural land could contaminate soil and, due to potential leaching, to groundwater (Lehmann and Joseph 2015). However, the extent, rates, and implications of these interactions are still far from being understood, and this knowledge is needed for an effective evaluation of the use of biochar as a soil amendment (Joseph et al, 2010). **Paper 1** identified that the mobility of heavy metals is of critical importance as this dictates the potential risk to soil, surface water and groundwater contamination.

It was hypothesized that BDB application would lead to a reduction in the mobility and leaching of heavy metals compared to BS application in diverse soil types at varying rates leading to the investigation outlined in **Paper 2**.

6.2.1. Effects of biosolids and biosolids-derived biochar on heavy metals mobility and leaching in amended soils

The research findings in **Paper 2** were encouraging. The key finding being BDB-amended soils exhibited lower concentrations of soluble copper and chromium in leachates compared to soil treated with biosolids. Hence supporting the alternative hypothesis that BDB application would lead to a reduction in the mobility and leaching of heavy metals compared to biosolids application in diverse soil types at varying rates.

pH changes and heavy metal mobility: Application of BDB and BS to soils led to changes in the pH of soil leachates. These changes varied depending on the soil type, but not with application rate. The increase in pH was more pronounced in Chromosol due to the lower buffering capacity compared to Ferrosol. The pH elevation is particularly notable with BDB application, which is attributed to the inherent alkalinity of biochar, which can mitigate heavy metal leaching by reducing their solubility (Hernandez et al., 2011; Li et al., 2012). The effect is especially beneficial for acidic soils, where the risk of heavy metal mobility into the ground water is a concern.

Zinc mobility: Zinc concentrations in leachates varied significantly with the type of soil amendments and soil type. Initially Zn concentrations were highest in soil treated with BDB, gradually decreasing over subsequent leaching events. The reduction in Zn mobility is attributed to the elevated pH levels in leachates particularly in the later stage of the leaching events, which likely limited Zn movements from BDB matrix. Conversely, soils amended with BS exhibited increased Zn mobility, particularly at higher application rates, suggesting that the degradability of BS contributes to the release of bioavailable heavy metals over time.

Copper mobility: Copper mobility was significantly influenced by the type of soil amendment. Biosolids-amended soils showed higher Cu concentration in leachates compared to BDB-amended soils. The reduced copper mobility in BDB-amended soil can be attributed to the biochar's higher pH and surface area, which likely immobilized Cu, reducing its leachability.

Chromium Mobility: Chromium mobility was also affected by the soil amendments, with BDB-amended soil exhibiting significantly lower chromium concentrations in leachates compared to BS-amended soils. Despite the high chromium levels in biosolids-derived biochar, the mobility of chromium was greatly reduced in BDB-amended soils. This reduction in Cr mobility highlighted the effectiveness of BDB in immobilizing heavy metals, presenting a lower environmental risk compared to BS application.

While biochar-amended soils contained higher total metal concentrations, the leachates showed significantly lower concentrations of soluble Cu and Cr compared to those treated with BS. This highlights a potential mitigation of environmental risks associated when applying BDB as a soil amendment. However, the varying Zn concentration leaching patterns at different application rates of BDB versus BS, highlights the need for further research to understand the complex relationship between application rates and leaching behaviours. These findings emphasize the importance of considering BDB as a viable soil amendment for sustainable agricultural practices. Further research is warranted to explore the long-term effects of these amendments on heavy metal dynamics in soils and determine their implications for food safety and ecosystem health.

6.3. Effect of biosolids and biosolids-derived biochar on plant and soil established with ryegrass

Studies, reviews, and meta-analysis have generally found that biochar tends to be more effective in promoting plant growth and mitigative heavy metal bioavailability in acidic soils rather than alkaline soils. Despite these advancements, a critical research gap identified in **Paper 1** persists regarding the direct comparison of crop yield and agronomic efficiency outcomes of utilizing BDB. This comparison allows for the evaluation of two soil amendments with distinct properties, nutrient release properties and environmental impacts, providing a comprehensive understanding of their role in sustainable agriculture. This direct comparison is crucial for determining the most effective and environmentally responsible practices for enhancing agronomic performance and soil health, thereby guiding agricultural stakeholders in making informed decisions for long-term sustainability.

Paper 2 contributes to this discourse by focusing on the dynamics of total heavy metal concentrations in soil treated with amendments, a critical factor given that regulatory standards often prioritize these contractions. It was observed that soils amended with BDB exhibited lower concentrations of certain heavy metals (copper and chromium) in leachates compared to those treated with BS. This finding highlights the need for further investigation into the mechanism of heavy metal uptake in plants following soil amended with BDB and BS at varying rates.

Understanding the dynamics of total heavy metal concentrations in soil treated with amendments is crucial, because regulatory standards focus on this total concentration as stated in **Paper 2**. As positive effect has been observed in **Paper 2** in terms of BDB amended soils exhibited lower concentrations of soluble Cu and Cr in leachates compared to soil treated with BS, further research is required in understand around heavy metal uptake in plant. Hence **Paper 3** investigated the agronomic performance and heavy metal uptake by ryegrass after applying BDB to soil, focusing on their effects on ryegrass growth, heavy metal uptake by plants and soil enzymatic properties, while comparing to BS application.

Building on the research gaps identifies in **Paper 1** and the key findings of **Paper 2**, **Paper 3** was designed to investigate the agronomic and environmental impacts of applying BDB to soil, with a particular focus on their effects on ryegrass growth, heavy metal uptake and soil enzymatic properties. It was hypothesized that BDB application would (i) increase in yield and agronomic efficiency compared to control soil; (ii) reduction in the uptake of heavy metals by plants compared to BS application; and (iii) increase in soil enzymatic activity in diverse soil types at varying rates.

6.3.1. Dry matter yield and agronomic efficiency

The impact of biochar application on plant yield varies significantly across different studies. Junior and Guo (2023) and Song et al. (2014) showing positive effects while Regmi et al. (2022), Suppadit et al. (2012) and You et al. (2019) show no improvement or even negative effect at higher application rates. The variability in response to biochar application highlights the importance of considering specific soil type, crop type, and biochar characteristics when determining the optimal application rate.

The research findings in **Paper 3** were encouraging. The key finding indicated that BDB significantly increased dry matter yield and agronomic efficiency, although their effectiveness varies with the type of soils and rate of amendments applied. Hence supporting the alternative hypothesis that BDB application increased plant yield and agronomic efficiency compared to control soil.

In Chromosol, at application rate of 2.5%, BDB significantly increased DMY by 180% increase when compared to control. Increasing the application rate of BDB did not significantly affect the DMY aligning with studies reported in literature (Junior and Guo, 2023; You et al., 2019). BDB was less effective at enhancing DMY across all tested application rates when compared to BS (p<0.001). These findings contrast with Hossain et al. (2015), who reported no significant difference in the growth and production of cherry tomatoes when comparing wastewater sludge and sludge biochar application in Chromosol. The discrepancy may be attributed to the variations in biochar characteristics influenced by temperature and the initial feedstock characteristics.

In Ferrosol the addition of BDB enhanced the DMY significantly at 10% application rate. Although an increase was observed at 2.5% and 5% application rate, it was not significant when compared to control. Notably, at lower application rates of 2.5% and 5%, BDB demonstrated slightly higher, although not significant, DMY compared to BS. Specifically, addition of 2.5% and 5% BDB resulted in a DMY increase of 192% and 256%, respectively, while BS resulted in DMY yield increase by 179% and 244% respectively. Broader research has reported that biochar application generally increases crop yields, particularly in fertile soils like Ferrosol, which are likely to respond positively to BDB application (Carter et al., 2013; Junior and Guo, 2023; Song et al., 2014). Similar to the trend in Chromosol, the application rate of BDB in Ferrosol had no significant effect on DMY, corroborating with studies reported in literature (Junior and Guo, 2023; You et al., 2019).

Biosolids-derived biochar showed higher agronomic efficiency at 2.5% w/w. BDB, showed no significant effect on efficiency as the rate increased, suggesting its benefits are maximised at lower application rates. While there appears to be a trend toward lower agronomic efficiency at higher loading rates, insufficient data was available to support such a trend. Comparison of agronomic efficiency between BS and BDB revealed that BS generally offered higher efficiency across the tested application rates, with highest rate at 2.5% in both soils.

The study demonstrated that BDB application resulted in higher DMY and agronomic efficiency at an application rate of 2.5% w/w when compared to control. Integration of biochar into poor soil enhances soil fertility, crop development, and productivity (Zeeshan et al., 2020). While both soil types benefit from BDB, the degree and efficiency of response can vary, suggesting the need for tailored soil management practices that consider the specific soil characteristics, amendment type and application rates.

6.3.2. Plant uptake of heavy metals

The research findings in **Paper 3** were encouraging. The key finding indicated that application of BDB to pot trials significantly decreased heavy metal uptake in above-ground biomass compared with BS, although their effectiveness varies with the type of soils and rate of amendments applied. Hence supporting part of the alternative hypothesis that BDB application leads to a reduction in the uptake of heavy metals by plants compared to BS application.

The effectiveness of BDB in altering the heavy metal bioavailability can be influenced by soil properties such as pH and clay content (Bashir et al., 2021; Namdari et al., 2024). Soil type significantly influenced Cu uptake, although the uptake of Cr and Zn was not influenced by the soil type. This understanding of heavy metal uptake highlights the importance of considering soil characteristics when applying soil amendments to reduce heavy metal bioavailability.

Consistent with **Paper 2**, the research in **Paper 3** highlights that BDB has more pronounced effect on immobilizing heavy metals, thereby reducing their solubility and bioavailability in comparison to BS. This can be attributed to the physiochemical properties of BDB, such as high surface area, porosity and pH modifying ability. These characteristics of BDB contribute to its effectiveness in binding heavy metals, making them less available for plant uptake and thus reducing their potential for heavy metal accumulation in plants as discussed in **Paper 1**.

6.3.3. Soil enzyme activity

The primary finding revealed that the application of BDB significantly increased urease activity but decreased acid phosphatase activity in the soil incubation study compared to control soil. Additionally, when compared to BS application, the enzymatic activity in the soil decreased. Consequently, these results do not support the hypothesis that the application of BDB leads to an increase in enzymatic activity.

Urease plays an important role in the transformation of soil nitrogen, with its activity being influenced by factors such as soil pH and texture. Ureases activity was significantly increased following incubation with BDB and BS in both Chromosol and Ferrosol soil compared to control soil. The application of BDB at a 2.5% w/w rate increased ureases activity by 50% in Chromosol and 23% in Ferrosol, relative to control soil. Similarly, the addition of BS at the same rate led to an increase in the rate of urease activity by 100% in Chromosol and 37% in Ferrosol relative to control soil. The greater increase in urease activity observed with BS compared to BDB can be attributed to higher nutrient content, particularly total nitrogen (**Paper 1**) and the enhanced microbial activity promoted by the organic matter present in BS (Medina-Herrera et al., 2020). This observation supports evidence that soil amendments modulate enzyme activities, particularly in the context of nitrogen cycling.

Phosphatase enzymes are involved in the mineralization of organic P in soil, facilitating the conversion of complex organic P compounds to inorganic forms that are readily available for plant uptake. A significant decrease ($p<0.001$) in acid phosphatase activity in both Chromosol and Ferrosol was observed following the addition of BDB compared to control. Conversely, BS addition to Chromosol increased the enzyme activity, but decreased in Ferrosol at lower application rates. The application of BDB at a 2.5% w/w rate decreased acid phosphatase activity by 12% in Chromosol and 20% in Ferrosol, relative to control soil. While addition of BS at 2.5% increased acid phosphatase activity by 8% in Chromosol, but decreased by 9% in Ferrosol, relative to control soil. The rise in pH resulting from addition of BDB may contribute to the observed decrease in the acid phosphatase activity as observed by Chen et al. (2013). Based on the urease activity in this incubation study, the application of BDB and BS improved the soil microbial activity and soil quality.

The combined effect of increased acid phosphatase and urease activities with BS application enhances the overall nutrient availability in soil, particularly nitrogen and phosphorous, which are critical for plant growth and development (Adetunji et al., 2017). This improved nutrient availability is a key factor that can contribute to the higher yields observed in soils treated with BDB, across both Chromosol and Ferrosol soils. Incorporating soil amendments also can increase microbial activity, likely due to biosolids-borne microbes (Medina-Herrera et al., 2020). These findings align with previous research that demonstrated the beneficial effects of biochar on soil nutrient dynamics and plant growth outcomes (**Paper 1**). The synergistic effect of increased microbial activities facilitates the breakdown and mineralization of organic compounds, thereby making essential nutrients more accessible to plants.

The addition of BDB increased the total heavy metal concentration in the soil, which is another critical factor which may influence the enzyme activity (Wang et al., 2007). The presence of heavy metals in soil can inhibit enzymatic activity. This inhibition may be due to direct interaction of heavy metals with enzyme active sites, thereby inhibiting the enzyme function (Giller et al., 2009). Additionally, heavy metals may exhibit microbial toxicity leading to lower microbial population and consequently lower enzyme activity (Giller et al., 2009). Given these observations further research is required to understand how heavy metal concentration in different soil types affect the activity of enzymes which can help in developing strategies to mitigate the negative impacts of heavy metal concentration on soil ecosystems.

6.4. Limitations and future research recommendations

The comprehensive study present in the thesis papers have several limitations that need to be assessed in future research:

1. Unknown long-term effects: One significant limitation noted across the studies on the effects of BS and BDB on soil and plant systems. While short-term effects are documented, the long-term impacts on soil health, crop productivity and environment safety remain less understood. This gap in knowledge could affect the sustainability and advisability of using these amendments extensively in agriculture.

2. Complexity in heavy metal leaching patterns: The research has identified complex and varying patterns in the leaching of heavy metals, specifically zinc, when using BDB compared to BS in **Paper 2**. This variability suggests that the relationship between amendment application rates and heavy metal leaching behaviours are not completely understood, which complicates the management and mitigation of potential environmental risks.

3. pH buffering capacity: The pH role on BS and BDB dynamics in the two soil types was not explored deep enough in the study in **Paper 2** and **Paper 3**

4. Variability in soil responses: **Paper 2** and **Paper 3** highlight that the effectiveness of BDB varies significantly depending on soil type. This variability indicates that a one-size fit all approach may not be effective, and tailored soil management practices are necessary to optimize the befits of these amendments when minimizing risks.

5. Measurement discrepancies: The use of p-XRF for measuring heavy metal concentration showed some discrepancies when compared to ICP-MS, particularly for Cr in Chromosol in **Paper 2**. These discrepancies suggest limitation in detection capabilities of p-XRF at lower concentrations, which would impact the accuracy of assessments regarding heavy metal mobility and environmental risks.

6. Impact on soil enzyme activity: **Paper 3** indicate that while BDB can enhance certain soil enzymes activities, such as urease, they may also decrease others, like

acid phosphatase. This differential impact on soil enzymatic activities could have implications for nutrient cycling and soil health, particularly in phosphorous-limited systems.

7. Narrow scope of heavy metal analysis: Only three heavy metals (Cr, Cu and Zn) were investigated in this study. As noted in **Paper 2** and **Paper 3**, each heavy metal exhibits its own interaction style within the soil environment. Therefore, further research is necessary in this area to comprehensively understand the behaviours and mobility and potential impacts of broader range of heavy metals.
8. Scalability: The findings from controlled experimental setting such as leaching columns (**Paper 2**), glasshouse trials and incubation study (**Paper 3**) do not fully translate to field conditions. The scalability of these findings to different agricultural settings and larger geographic area could limit the practical application of these findings.

While application of BDB and BS offer significant opportunities for improving soil health and agricultural productivity, the identified limitations and knowledge gaps highlight the need for a cautious and well-informed approach. Addressing these gaps through further research will enhance the scientific basis for the sustainable use of BDB in agriculture and environmental management.

6.5. Conclusion

This investigation demonstrated that BDB produced at an Australian wastewater treatment plant utilizing gasifier system, has the potential to be used as a viable soil amendment for sustainable agricultural practices. The key findings highlight the potential of BDB to mitigate environmental risks associated with heavy metal leaching. Biosolids-derived biochar-amended soils exhibited lower concentrations of soluble Cu and Cr in leachate compared to BS-amended soil. The application of BDB led to an increase in pH, particularly in Chromosol soil, which helped reduce the solubility and mobility of these heavy metals. This effect is beneficial for acidic soils where heavy metal leaching into ground water is a concern. In terms of plant yields and agronomic efficiency revealed that BDB significantly increased the DMY of ryegrass. At 2.5% w/w application rate BDB increased yield by 180% in Chromosol and 192% in Ferrosol compared to control. Unlike previous work, higher application rates of BDB did not affect yield or agronomic efficiency. Importantly, BDB significantly reduced heavy metal uptake (chromium, copper, and zinc) by ryegrass compared to BS. Soil incubation supported these findings, showing that 2.5% BDB increased urease activity by 50% in Chromosol and 23% in Ferrosol, relative to control soil, beneficial for nitrogen cycling. While at the same rate BDB decreased acid phosphatase activity 12% in Chromosol and 20% in Ferrosol, potentially affecting phosphorous availability. Consequently, the study advocates for a 2.5% application rate of BDB to optimize agricultural outputs while safeguarding soil and plant health. The findings also highlight the importance of tailored soil management practices that consider specific soil characteristics, amendment types and application rates to optimize benefits and minimize environmental risks.

The study also acknowledges several limitations, including the need for long-term impact assessment, understanding complex heavy metal leaching patterns, variability in soil types, differential impacts on soil enzymatic activity and scalability of findings to field conditions. Addressing these gaps through further research will enhance the scientific basis for sustainable use of industrially produced BDB in agriculture and environmental managements.

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APPENDIX A: BIOSOLIDS-DERIVED FERTILISERS: A REVIEW OF CHALLENGES AND OPPORTUNITIES

Contribution was made to the following paper, “Biosolids-derived fertilisers: A review of challenges and opportunities,” providing contribution in formal analysis and writing.

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Review

Biosolids-derived fertilisers: A review of challenges and opportunities

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HIGHLIGHTS

- Land application of biosolids is a cost effective way to reuse nutrient in soils.
- Ever changing nature of biosolids contaminants dictates regulatory guidelines.
- Nutrient content in biosolids provides an understanding of baseline agronomic value.
- Extractive technologies can recover and purify valuable constituents from biosolids.
- Prospects for novel granulated fertilisers derived from biosolids are significant.

GRAPHICAL ABSTRACT

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ABSTRACT

Soil application of biosolids as an organic fertiliser continues to be a cost-effective way to beneficially utilise its carbon and nutrient contents to maintain soil fertility. However, ongoing concerns over microplastics and persistent organic contaminants means that land-application of biosolids has come under increased scrutiny. To identify a way forward for the ongoing future use of biosolids-derived fertilisers in agriculture, the current work presents a critical review of: (1) contaminants of concern in biosolids and how regulatory approaches can address these to enable on-going beneficial reuse, (2) nutrient contents and bioavailability in biosolids to understand agronomic potential, (3) developments in extractive technologies to preserve and recover nutrients from biosolids before destructive dissipation when the biosolids are thermally processed to deal with persistent contaminants of concern (e.g. microplastics), and (4) use of the recovered nutrients, and the biochar produced by thermal processing, in novel organomineral fertilisers that match specific equipment, crop and soil requirements of broad-acre cropping. Several challenges were identified and recommendations for prioritisation of future research and development are provided to enable safe beneficial reuse of biosolids-derived fertilisers. Opportunities include more efficient technologies to preserve, extract and reuse nutrients from sewage sludge and biosolids, and the production of organomineral fertiliser products with characteristics that enable reliable widespread use across broad-acre agriculture.

Abbreviations: ACT, Australian Capital Territory; ANZBP, Australian and New Zealand Biosolids Partnership; AWA, Australian Water Association; COD, chemical oxygen demand; CSIRO, Commonwealth Scientific and Industrial Research Organisation; EBPR, enhanced biological phosphorus removal; EoWC, End of Waste Code; EPA, Environmental Protection Authorities; EU, European Union; FRV, fertiliser replacement value; NBRP, National Biosolids Research Program; NLBAR, nitrogen limiting application rate; NSW, New South Wales; NT, Northern Territory; OMF, organomineral fertiliser; PFAS, perfluoroalkyl and polyfluoralkyl substances; PFOA, perfluorooctanoic acid; PFOS, perflurorooctane Sulfonate; PRR, partition-release-recover; QLD, Queensland; SA, South Australia; TAS, Tasmania; VIC, Victoria; WA, Western Australia; WWTP, Waste Water Treatment Plants.

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Contents

1. Introduction

Biosolids are the main solid end-product of urban wastewater treatment, comprised of sewage sludge treated to achieve a certain quality that reduces or eliminates health and environmental risks and improves beneficial use characteristics. Biosolids production is unavoidable, roughly proportional to population size, and therefore will continue to increase with an increasing global population. In Australia, around 350,000 dry megagrams (Mg) of biosolids were generated in 2021 (Vero, 2022). Biosolids continue to be widely applied as an organic fertiliser and soil conditioner, as this is still the most economical way to beneficially reuse its nutrient and carbon content in soils (Okoffo et al., 2020; Kanteraki et al., 2022). For example, the proportion of biosolids applied to land in the European Union (EU) is about 35 % (Hušek et al., 2022), application of biosolids to arable land is common in the United States (55 %), Canada and New Zealand, (Lu et al., 2012; Raheem et al., 2018), and in Australia, its use in agriculture has increased from 55 % in 2010 to 73 % in 2021, but varies by State and Territory (Vero, 2022).

Biosolids applied to agricultural land can increase crop yield through improvements in soil physico-chemical properties, and agronomic responses are reported to be greater in weathered soils, which are common across Australia (Reid, 2002; Torri and Cabrera, 2017). Beneficial reuse of nutrients from biosolids is important to offset the demand for chemical fertilisers as this can provide a dual benefit, namely: reducing fertiliser price pressures on agriculture, and decreasing greenhouse gas emissions associated with chemical fertiliser production. Since the beginning of 2020, nitrogen (N) fertiliser prices have increased fourfold, while phosphate and potash prices have increased over threefold, and these prices will likely continue to rise (www.cnbc.com, 2022). Between January–December 2021, urea prices increased from AUD256 Mg^{-1} to AUD1026 Mg^{-1}; mono-ammonium phosphate increased from AUD420 Mg^{-1} to 952AUD Mg^{-1} and potassium chloride increased from AUD357 Mg^{-1} to AUD822 Mg^{-1} (Austrade, 2022). Prices have continued to rise in January and February 2022 (Austrade, 2022). Additionally, global demand for fertilisers will continue to increase concurrently with increased demand for food, fibre, and biofuels (FAO, 2019). Studies on the emissions avoided by use of nutrients in biosolids have shown that for every Mg of dry biosolids used, around 6 Mg of CO_2 can be avoided (Darvodelsky, 2012). This includes the avoidance of imbedded emissions associated with N fertiliser production via the energy-intensive Haber-Bosch process. There is also global concern over the long-term availability of non-renewable mineral nutrient resources, especially phosphorus (P) (Cordell et al., 2013; Battisti et al., 2022) and potassium (K) (Dawson, 2011; Mehta et al., 2016). It is critical to efficiently recover and safely recycle these nutrients wherever possible to reduce dependency on non-renewable sources, and thereby create sustainable agriculture that also protects the environment (Johnston et al., 2014; Weikard and Seyhan, 2009). This is especially important given that about 80 % of the total phosphate extracted worldwide is used for mineral fertilisers and animal feed additives (Dawson and Hilton, 2011) and >90 % of P ingested by people is excreted and therefore may be recoverable from wastewaters and biosolids into biosolids (Cordell et al., 2009;). Moreover, Australia is a net exporter of food, but is heavily reliant on imported nutrients (Mehta et al., 2016). However, whilst the total nutrient value in biosolids has been widely recognised, limited emphasis has been placed to date on the release and bioavailability of those nutrients, which considerably and directly impacts on the fertiliser replacement value (FRV) of nutrients in biosolids. These aspects are critically evaluated in the current work, to quantify and demonstrate the true agronomic value of biosolids.

The Australian and New Zealand Biosolids Partnership (ANZBP) was established by the Australian Water Association (AWA) to track, promote and support the sustainable management of biosolids in Australia and New Zealand. The ANZBP surveyed community attitudes to the use and management of biosolids in 2010 and 2020 (Jones et al., 2020) with biosolids defined similarly as the treated by-product of wastewater treatment that can be applied to land or used as fuel for power generation. The ANZBP survey results (Jones et al., 2020) showed that the awareness of the term biosolids had increased over time from 33 % in 2010 to 45 % in 2020, and that a large majority of respondents (73 %) were positively disposed toward the use of biosolids for the purposes above. Additionally, over 50 % of community members said that they would be very likely to use biosolids products in their own garden (Jones et al., 2020). The community respondents generally felt comfortable in the knowledge that biosolids use is controlled and regulated (Jones et al., 2020).

In the USA, Canada, and the EU, application of biosolids to land continues to be a dominant practice (Lu et al., 2012), but current legislation imposes varying degrees of restriction to their use in agriculture. In all those countries the most common contaminants emphasized in regulations are heavy metal concentrations in biosolids and soil, and organic contaminants and pathogens in biosolids (Christodoulou and Stamatelatou, 2016). Many differences exist in specific requirements, and, in general, current legislation in the USA focuses on reduction of both pathogens and of pollutants, whereas the EU legislation is directed more toward the regulation of pollutants (Iranpour et al., 2003). The processes involved in the development of the regulatory framework in Australia were based on, or modified from European and North American guidelines (Hill, 2005). However, the soils, climatic conditions, and agricultural practices in Australia are sufficiently different to those in other parts of the world to justify use of locally developed guidelines in Australia to protect the environment and the human food chain (Whatmuff and Osborne, 1992; McLaughlin et al., 2000; Hill, 2005). There are several features of soils in Australia that distinguish them from soils commonly found in Europe and North America: specifically, many of the soils of Australia are pedologically very old and highly weathered, have a very low level of soil fertility and consist of variable charge minerals. The above differences are important when considering the reactions of metals in soil (McLaughlin et al., 2000). Heavy metals are one key contaminant class addressed by regulatory frameworks, which is important for agricultural use of biosolids. However, the impact of regulations on source control and heavy metals in Australian biosolids has not been previously investigated, and this is illustrated in the current work by tracking heavy metals in biosolids by consolidating and presenting literature data published over several years. In addition, the review considers the concept of bioavailability of heavy metals and the impact that this may have on the risks associated with the agricultural use of biosolids-derived fertilisers.

Typically, biosolids have been applied to land in their original form. Sustainable farming practice aims to balance nutrient inputs with outputs. An 'ideal' fertiliser supplies nutrients only on the basis of plant demand, in relation to its phenological stage (Trinchera et al., 2011), and to prevent environmental impacts associated with over-application or poorly timed application (Sakrabani, 2020). There are significant differences in nutrient availability between biosolids and mineral fertilisers. Nutrients in mineral fertilisers are generally in a soluble form, and when applied are immediately plant-available. In contrast, a large proportion of nutrients in biosolids are in organic forms which must first to be mineralised to be plant-available. This presents both a challenge and an opportunity by blending or reacting mineral fertilisers with organic fertilisers to produce so-called organo-mineral fertilisers (OMF). Such fertiliser mixes or products could balance the rapid release properties of nutrients from mineral fertilisers with sustained slow mineralisation and release of nutrients from an organic component (e.g. composted manure, Abbott et al., 2018), and, additionally, could improve soil structure, drainage, water availability, and increase soil carbon to promote crop growth (Sakrabani, 2020; Antille et al., 2013b). The use of such products represents a technological advancement but requires consideration of several important product and application-related factors to enable successful use in broad-acre agriculture. To date, there has not been a review and evaluation of these important considerations, and this is addressed in the current paper.

Despite the benefits to date of regulations to ensure that stability classes are met, vector attraction potential is minimised, and contaminants are restricted to below levels where significant environmental impacts would be expected, challenging contaminants in biosolids continue to emerge and these are threatening the long-term viability of the direct agricultural use of biosolids. Regulatory approaches have attempted to engage with such emerging contaminants, but microplastics and nano-plastics have become a significant concern for environmental and human health due to their ubiquitousness and because of new research suggesting links to significant adverse impacts (Section 3). Consequently, there have been indications that thermal processing of biosolids (e.g. gasification, pyrolysis or incineration) may be a convenient way forward to destroy persistent contaminants of concern (Hušek et al., 2022). For this reason, there has been increased research interest in technologies to extract valuables (N, P, K, and others) from biosolids or its precursor sewage sludge (Gianico et al., 2021) before the biosolids or sludge is sent to thermal process. To date, there has not been a targeted review on such extraction technologies specifically in support of recovery and preserving of nutrients before thermal processing of biosolids to use in balanced organic fertiliser formulations; as such, these aspects are addressed in the current work.

The current review was conducted to promote the safe beneficial reuse of organic fertilisers derived from biosolids in agriculture. This is done by providing, for the first time, a critical evaluation of the above-named important aspects of agronomic value and bioavailability of nutrients in biosolids, regulatory influences and opportunities for benefits in contaminant levels due to tighter catchment control, targeted extractive technologies to recover and preserve nutrients before thermal processing of biosolids, and using these nutrients together with biochar from thermal processing to formulate balanced OMF suitable for broad-acre agriculture.

2. Agronomic value of biosolids constituents

Application of biosolids for agriculture has significant potential because of the volumes produced that could be used for its nutrients and carbon content (fertilizing and- soil conditioning), at comparatively lower costs. A substantial body of past research in Australia has focussed on biosolids effects on soils and plants (Table 1), including important work dating as far back as the 1980–1990s (De Vries, 1983; Jakobsen and Willett, 1986; Dann et al., 1989; Barry et al., 1998). Included in this has been the Australian National Biosolids Research Program (NBRP) established in 2002 by the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO). The NBRP conducted national trials of biosolids under a wide range of conditions, including various soil types, climates, and cropping systems, to evaluate the true agronomic benefits of biosolids in agriculture, and to understand how well overseas research findings might translate into the Australian context. For this, a total of 17 field sites were established in five Australian States and examined both potential beneficial and

Table 1
Physico-chemical and biological responses of soil amended with biosolids. Outcomes of Australia based published scientific experiments.

Soil property	Effect	References
Aggregate stability	No effect	Ives, 2012
Bulk density	No effect	Ives, 2012
CEC	Increased	Munn et al., 2001; Sarooshi et al., 2002;
EC	Increased	Sarooshi et al., 2002; Rajendram et al., 2011; Ives, 2012; Antille et al., 2020
Heavy metals	Increased, but below regulatory threshold levels	Joshua et al., 1998; Dumbrell, 2005; Munn et al., 2001; Whatmuff, 2002; Cooper, 2005b; Bell et al., 2006; Pritchard and Collins, 2006; Warne et al., 2008; Eldridge et al., 2009; Nash et al., 2011; Rajendram et al., 2011; Qi et al., 2011;
Infiltration/Surface runoff	Decreased	Joshua et al., 1998
Macronutrients: N, P, K, S	Increased	Munn et al., 2001; Pu et al., 2004; Stokes et al., 2004; Cooper, 2005a; Pritchard and Collins, 2006; Pu et al., 2008; Beshah, 2010; Nash et al., 2011; Rajendram et al., 2011; Ives, 2012; Pu et al., 2012; Albuquerque, 2018; Antille et al., 2020; Rahman et al., 2021
Microbial biomass	Increased	Madejón et al., 2010; Ives, 2012; Thangarajan et al., 2015; Chowdhury et al., 2016; Wijesekara et al., 2017.
pH	Decreased	Rajendram et al., 2011; Nash et al., 2011
	Increased	Munn et al., 2001; Sarooshi et al., 2002; Cooper, 2005a; Murtaza et al., 2011; Rahman et al., 2021
Total or organic C	No effect	Pu et al., 2004; Ives, 2012
	Increased	Munn et al., 2001; Sarooshi et al., 2002; Pritchard and Collins, 2006; Nash et al., 2011; Bolan et al., 2013; Wijesekara et al., 2017; Albuquerque, 2018
Water holding capacity	Increased	Belyaeva et al., 2012
Yields	Increased	Pu et al., 2004; Stokes et al., 2004; Cooper, 2005a; Corrêa et al., 2005; Pritchard, 2005; Warne et al., 2008; Beshah, 2010; Madejón et al., 2010; Lamb et al., 2012; Murtaza et al., 2012; Bolan et al., 2013; Antille et al., 2020

deleterious effects. Across all NBRP sites, biosolids were applied to supply nutrients at similar levels to historic fertiliser use. In general, biosolids were applied according to States and Territories guidelines that specify the N-limiting biosolids application rate (NLBAR) and was found to deliver sufficient nutrients for at least 1–2 annual cropping cycles (averaged across all sites in the NBRP) without needing mineral fertiliser (McLaughlin et al., 2008). Moreover, the application of biosolids was observed to have a positive effect on crop yields and plant nutrient contents with the main benefits probably being due to N and P addition with biosolids (Stokes and Surapaneni, 2004; McLaughlin et al., 2008). The NBRP continues to be the most comprehensive and significant program of research to date concerning biosolids use in Australian agriculture.

Typically, biosolids contain high concentrations of N, P, K, and sulphur (S), and several micronutrients, including copper (Cu), zinc (Zn), calcium (Ca), magnesium, boron (Bo), molybdenum (Mo), and manganese (Mn). The application rate of biosolids in Australia is determined by total N and NLBAR. However, one concern with NLBAR is typical low N:P ratios in biosolids in terms of crop fertiliser requirements, so that biosolids application based on N could result in excess P. When biosolids are routinely applied, this can result in progressive build-up in soil P levels, increasing the risk of P transport to water courses by erosion and runoff (Warne et al., 2008; Pritchard et al., 2010). To demonstrate variability of nutrients content in biosolids across Australia, data from over 70 relevant peer-reviewed articles, technical reports and PhD studies were compiled for the present review (Supplementary Materials, Tables S1, S4, and S5). Biosolids properties and composition was observed to vary between analysis batches and between wastewater treatment plants (WWTPs). This was plausibly due to differences in the specific treatment processes in place and wastewater conditions changing with time or being different across locations (McLaughlin et al., 2000; Ukwatta and Mohajerani, 2015).

The agronomic value of biosolids can be estimated based on total nutrient content and per unit nutrient price. For the current work and using the average quantities of biosolids applied to agriculture in Australia over 2010–2021 and N, P and K contents in Australian biosolids (Table S1), the total maximum nutrient value was estimated could be up to 33 million AUD per year for nominal prices of AUD2.23 kg^{-1} N; AUD3.63 kg^{-1} P, and AUD1.37 kg^{-1} K (Supplementary Material, Table S2).

To determine true FRV, it is important to consider nutrient plant-availability (Warne et al., 2008), which for biosolids can vary considerably (Table 2). Nutrients in biosolids are typically slow-release, for example, with 15–50 % of the N and P becoming available within the first year and an additional proportion in subsequent years (McLaughlin et al., 2008; Pritchard et al., 2010). The slow mineralisation of biosolids can help maintain plant-available N during periods of rainfall when conventional fertiliser is at significant risk of leaching from the crop root zone (Pampana et al., 2021). The efficiency of N input from industrial fertiliser to agriculture is also generally poor, with an estimated 40–70 % N typically dissipated into the environment (Chojnacka et al., 2022). Guidelines in Australia define N mineralisation rates for biosolids applied to land over one year of application at 15 % for anaerobically digested biosolids and 25 % for aerobically digested biosolids. However, a study conducted by Eldridge et al. (2008) in NSW found that up to 50 % of total N in land applied biosolids could mineralise in the first 2 months after application. In TAS, Ives et al., 2010 observed that 35 % of total N in anaerobically digested biosolids being land applied could mineralise in 59 days. In warm, subtropical QLD, mineralisation rates also averaged 55–60 % of the applied organic N in the first 6–9 months following biosolids application, with at least 30 % (and in some cases 60 %) of the applied organic N being mineralised within the first 6–8 weeks after incorporation (McLaughlin et al., 2007). These results indicate a need to understand nutrient release characteristics to better understand the true FRV of biosolids, including globally.

Table 2
Availability[a] of N and P in biosolids applied to land across Australia. Data from multiple sources with references given in the Supplementary Material, Table S4.

Nutrient	Availability (% of total nutrient concentration)					Number of data points
	Min	Max	Mean	Std. Dev.	Median	
N	0.01 %	38.7 %	11.2 %	9.3 %	9.4 %	52
P	0.37 %	35.0 %	13.5 %	11.4 %	10.8 %	10

[a] Calcium chloride extractable.

Other macro and micro nutrients in biosolids (e.g., S, Ca, magnesium, Fe, Mn, Cu, Zn, B, Cl and Mo) may also become increasingly valued into the future, together with the potential soil amelioration effects of biosolids applied to degraded soils (e.g. lacking soil carbon, or with poor moisture holding capacity) and/or nutrient-depleted soils. These benefits are not currently well quantified and requires further research investigation, including under relevant field conditions, and climate context. In general, it is expected that multiple benefits of biosolids will gain in importance over time, as will the perceived value of biosolids as organic fertiliser, especially as these factors become better understood.

3. Environmental and health concerns with biosolids use in agriculture, current regulatory controls

Production and application of biosolids in Australia is regulated by State-based Environmental Protection Authorities (EPA) or equivalent bodies, according to guidelines specific to each State or Territory (Supplementary Material, Table S3). These guidelines set out quality assurance requirements and best management practices for reuse, and gain legal standing where they may be called up in relevant legislation or referred to in an environmental license of a facility. New South Wales was the first state in Australia to develop guidelines for the beneficial reuse of biosolids (New South Wales Environmental Protection Authority, 1997), and the subsequent development of guidelines in other states and the national biosolids guidelines that followed, largely mirrored the NSW guidelines (McLaughlin et al., 2007). The basic structure of all the guidelines is similar, comprising contaminant grading; stabilization grading (i.e., pathogen and vector attraction, odour potential); and management controls, including sampling and monitoring. An overall combined quality grade (stability and contaminant) determines permissible uses for the classified biosolids. The Australian approach to managing contaminants in biosolids has been relatively similar to that used in the USA, except for the actual limits imposed. Australian guidelines have been suggested to include significantly stricter requirements than that required in the USA (Reid, 2002). Also, to ensure that excessive levels of contaminants are not added to otherwise clean soils, guidelines specify that both biosolids and the soils to which they are to be applied are to be monitored for the levels of relevant contaminants. The guidelines also include several further controls relating to soil pH, soil slope, soil water regime, and proximity to watercourses, roads, property boundaries, and sensitive receptors (e.g. residences), as these influence the risk of adverse environmental and amenity impacts. To demonstrate the level of biosolids-specific guidance provided, the example in the Australian State of Queensland (2020) is where an End of Waste Code (EoWC) for Biosolids deals with various controls and factors and in fact includes trigger values in soils for perfluoroalkyl and polyfluoroalkyl substances (PFAS) (Hall et al., 2021) (see further below).

Unfortunately, organic contaminants are common in industrial, medical, and household products and applications and therefore usually end up in human-derived wastewater (Kinney et al., 2006), many of which are persistent and potentially bioaccumulative. Organic contaminants can include pharmaceuticals, hormones, detergent metabolites, fragrances, plasticizers, and pesticides. Organic pollutants of primary interest include organochlorine pesticides, polychlorinated byphenyls and polychlorinated dioxins/furans. Importantly, most organic chemicals are present in biosolids in Australia at low concentrations (Smith, 2009) (often below detection limit) and have therefore been suggested as unlikely to pose an issue for land application of biosolids to soils (Clarke et al., 2008; Clarke et al., 2010). However, the nature and types of pollutants found in biosolids are constantly evolving with improvements in measurement and identification capabilities, and this is an on-going global challenge for policy to manage 'unknown' or 'emerging' contaminants. Three options to do this have been previously suggested (Clarke, 2014): (1) regular national biosolids surveys for emerging pollutants; (2) development of an Unregulated Contaminant Monitoring Regulation program; and (3) development and application of biological-based assays for generalised toxicity that can be related to relevant human/ecological receptors.

One emerging area of research interest is the link between effects of land-applied materials such as biosolids, on soil microbial health. Moderate applications of biosolids have been suggested could increase the diversity of the soil ecosystem, as the additional organic matter and nutrient inputs support the growth of microbial populations, leading to an increase in diversity (Goyal et al., 2008). However, the observed impact of biosolids on soil microbial diversity may not always been positive (Markowicz et al., 2021; Goyal et al., 2008). For example, the field application study of Mossa et al. (2017) using biosolids indicated that for soil samples collected from 17 maize fields, soil microbial diversity decreased with increasing zinc (Zn) concentrations in soils. This suggests that above a certain level, heavy metals accumulation of biosolids might offset the positive impact of organic matter on soil microorganisms. Currently, regulatory approaches do not address soil microbial ecotoxicity effects, whereas into the future the further development and use of ecotoxicity tests may become more prominent in combination with traditional chemical analyses. In the future this may enable the evaluation of the potential effect of toxic substances (including those in amendments such as biosolids) on soil microorganisms (Giannakis et al., 2021). However, soil microbial ecotoxicological data for the effect of pollutants from biosolids on Australian soils and organisms still are sparce (Broos et al., 2007).

One group of emerging contaminants which has received increasing attention is PFAS and Perfluorooctane Sulfonate (PFOS). PFAS substances are used in a wide variety of applications in industry and household products. The ANZBP conducted a national survey on the presence of PFAS in biosolids in which major utilities voluntarily shared data for over 100 samples from 13 different sewage treatment plants around Australia (Hopewell and Darvodelsky, 2017). This data found that PFAS concentrations were well below proposed biosolids limits, and therefore may be posing a low level of risk when land applied. Similarly, the average level of PFOS measured in biosolids was around 0.5 % of the suggested safe level for agricultural use, and the maximum level of PFOS measured at all sites was also lower than the suggested safe level by a factor of about 11, including for two sites with a known history of elevated PFOS (Darvodelsky and Hopewell, 2018). The ANZBP investigation hence concluded that: a) PFOS and PFAS were present in biosolids at detectable levels; b) average values of PFOS measured in Australian biosolids were around 7 % of the calculated Health Investigation Level; and c) levels of Perfluorooctanoic acid (PFOA) detected were significantly lower than Health Investigation Levels suggested by the Australian Government (Hopewell and Darvodelsky, 2017). Accordingly, it was recommended that limits in biosolids be adopted and be routinely reviewed as further data became available (Hopewell and Darvodelsky, 2017).

Heavy metals in soil and their transfer to the food chain has long been a key consideration for land application of biosolids and biosolids-derived fertiliser products (Hušek et al., 2022). For this reason, a significant amount of data was found in the literature for the heavy metal content of biosolids across Australia (Supplementary materials, Table S6). These data were collated and assessed for the current work to determine whether progress in regulatory controls of heavy metals, such as via pressure on industrial catchments to reduce heavy metals discharged to sewer, could have led to changes in heavy metals in biosolids over time. Encouragingly, total heavy metal content in biosolids were observed to reduce over time (Fig. 1). This could have been caused by improved technologies/products/practices, and due to more stringent source control for domestic WWTP catchment (e.g., industrial flows), and shows a potential for developments to positively influence biosolids quality over time.

Most biosolids regulations around the world have thresholds for total heavy metal concentrations in biosolids (being the readily measurable quantity) and some in Australia (e.g. EoWC in Queensland) also include adjustments for background soil heavy metal levels. During the NBRP research study, critical soil concentrations of Cu and Zn were assessed in terms of adverse effects on microbial processes and plant productivity, and found to be affected by soil pH, clay content, organic carbon content and cation exchange capacity (Warne et al., 2008). This led to a set of soil-specific threshold limits being proposed for Cu and Zn. The properties of biosolids also play a crucial role in determining the mobility of heavy metals in soil (Merrington et al., 2003; Haynes et al., 2009) and heavy metal mobility can be highly variable. This was demonstrated by data from our own work and that of Oliver et al., 2005, (Table 3) and indicated that heavy metal mobility is ideally assessed on a case-by-case basis to determine the potential for detrimental environmental impacts and benefits (Oliver et al., 2005). Although it is understood that the available concentration controls the contaminant toxicity, this issue remains a key knowledge gap, and accordingly biosolids guidelines may be imposing excessively conservative threshold levels if based on total heavy metals.

Microplastics and nano-plastics are an emerging contaminant in biosolids of major concern to the safe direct beneficial reuse of biosolids in agriculture. Both microplastics and nanoplastics are small plastic particles, with respective diameters of 1–5000 μm and 1–1000 nm, and are now ubiquitous in the environment (Leusch and Ziajahromi, 2021). Plastics in domestic wastewater, which end up in biosolids, originate from plastic-containing household products via normal household cleaning and washing (e.g. synthetic fibers from clothes washing), plastics from cosmetics and personal care products, and abrasive plastics in cleaning agents (Okoffo et al., 2020). An investigation of microplastics in Australian biosolids sampled 82 WWTPs across Australia and detected plastics concentrations ranging from 0.1 to 9.6 mg. g^{-1} dry weight, with polyethylene being the predominant plastic detected (Okoffo et al., 2020). When biosolids are land applied in agriculture, microplastics become part of the soil and can influence its properties, and can be bioavailable to animals and plants, or can migrate into aquatic ecosystems (Hušek et al., 2022). Microplastics can be hazardous and elicit chemical, physical, and biochemical toxicity (Bläsing and Amelung, 2018; Okoffo et al., 2020). Currently, there is unfortunately a lack of standardized and applicable methods to identify and quantify microplastics in complex samples such as wastewater and biosolids, and this has increased uncertainty in microplastics assessments (Ziajahromi et al., 2017). However, despite this, it will be challenging to completely eliminate microplastics from domestic wastewater and biosolids, and accordingly, some have suggested the direct application to agriculture may not be a viable future option (Hušek et al., 2022). Instead, thermal processing of biosolids (e.g. pyrolysis, gasification) has been proposed for the full destruction of plastics and other persistent contaminants (Hušek et al., 2022).

4. Extractive technologies for preparation of biosolids-derived fertilisers

Unfortunately, thermal processes are destructive to soil-active carbon compounds (e.g. humic substances) and N (see Section 4.1) and can be detrimental to the bioavailability and purity of P (see Section 4.2). Accordingly, there has been increasing interest in technologies for upstream extraction of nutrients and carbon compounds before the biosolids are sent to thermal processing. These can then be safely beneficially reused (Gianico et al., 2021). These technologies are reviewed in this section.

4.1. Nitrogen recovery

Into the future, when WWTPs are converted into resource recovery facilities, the destructive dissipation of carbon and N via the activated sludge process will likely be replaced with energy-efficient extractive technologies to recover N and carbon in useful forms. In this regard, a useful partition–release–recover (PRR) framework has been previously described for the efficient selection and integration of such technologies (Batstone et al., 2015), whereby; (1) N is partitioned from the main water line of the WWTP to the sludge line via bioassimilation; (2) N in the sludge is then released via a digestion (ideally anaerobic with simultaneous energy recovery) and; (3) is finally N is recovered in forms suitable for the intended

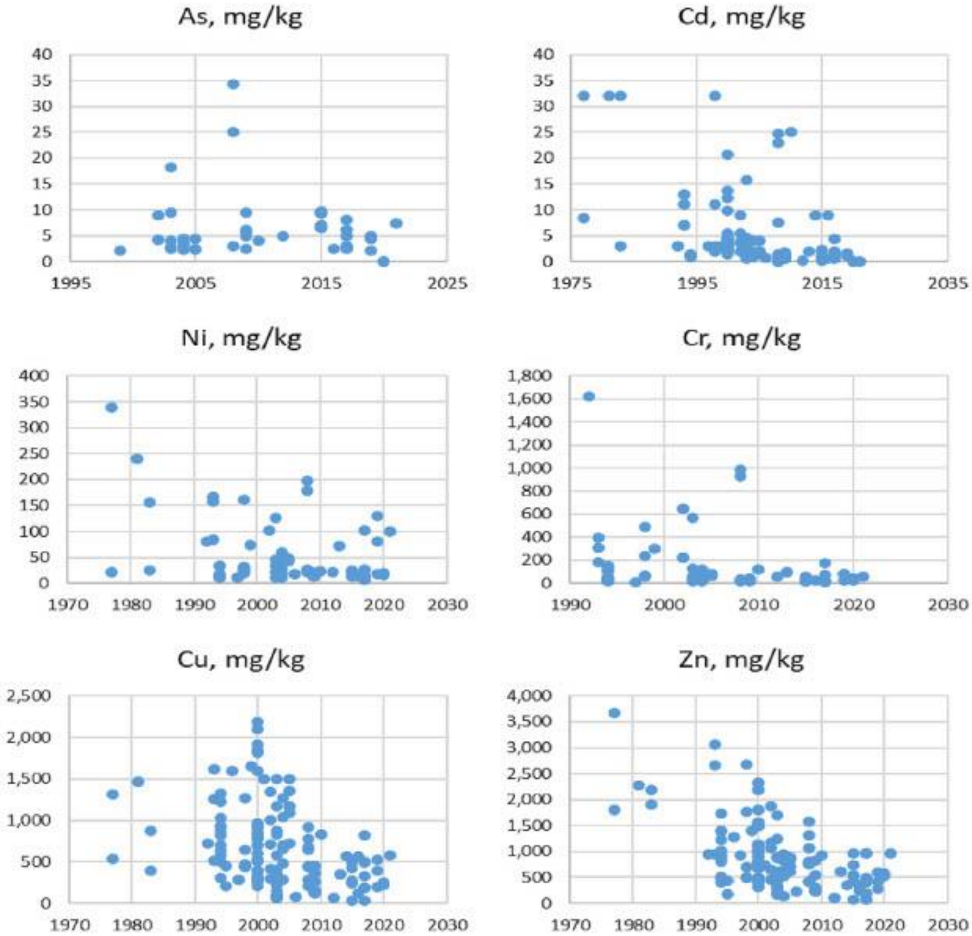

Fig. 1. Total heavy metal content in Australian biosolids over the period 1970–2022, mg/kg dry solids. Data were collated from a large range of literature sources as cited in the Supplementary Material, Table S5.

end-use (e.g., fertiliser). For the partition step (step 1), anaerobic photoheterotrophic mediators have been of particular interest, efficiently using light energy to assimilate carbon and nutrients from wastewater into a protein-rich microbial biomass (Capson-Tojo et al., 2020). Limited investigations using pot trials have already shown that such microbial biomass almost performed as well as chemical fertilisers as a nutrient source for pasture grass (Zarezadeh et al., 2019). For the release step (step 2 above), soluble products from a first-stage fermentation at lower pH and short hydraulic retention time may be useful as the biodegradable carbon for bio-assimilation in the partition step (Batstone et al., 2015). A recent novel process also explored the direct enhanced recovery of up to 50 % ammonia from sludge fermentation under vacuum (Okoye et al., 2022). Such developments will be important to reduce the energy consumption for N recovery so that it at least becomes comparable with that used for N

Table 3
Percentage of bioavailable[a] to total concentration of selected heavy metals in Australian biosolids.

Biosolids location	Cd	Pb	Cr	Ni	Cu	Zn	References
Site A	0.84	0.00	0.06	6.58	0.53	0.66	Unpublished data, Waste to Profit project, Ramirez et al., 2021
Site B	1.33	0.00	0.12	2.52	0.87	0.07	Unpublished data, Waste to Profit project, Ramirez et al., 2021
Werribee	6.90	n.a.[b]	n.a.[b]	8.70	0.50	8.30	Oliver et al., 2005
Chelsea	0.20	n.a.[b]	n.a.[b]	3.40	0.60	0.70	Oliver et al., 2005
Bolivar	1.60	n.a.[b]	n.a.[b]	5.90	4.70	0.40	Oliver et al., 2005

[a] Calcium chloride extractable.
[b] Not reported.

manufacturing as chemical fertiliser (Batstone et al., 2015). This remains an important aspect for future research and development.

4.2. Phosphorus recovery

Globally, it has been estimated that 20 % of mineral P consumed is excreted by humans and thus potentially recoverable (Cordell et al., 2009; Batstone et al., 2015), whilst about 80 % of the total non-renewable rock phosphate extracted worldwide is used for mineral fertilisers and animal feed additives (Dawson and Hilton, 2011). With a likely increase in thermal processing of biosolids into the future, the impact of such processing on plant availability of P would be important. For example, the study of Mackay et al. (2017) showed that extractable P in by-products of biosolids converted via four thermal conversion processes (pyrolysis, incineration, and two forms of gasification) was lower than in unprocessed biosolids. Moreover, it has been suggested (Mehta et al., 2015) there could be a competition with incineration between operating at low temperatures (<700 °C) to ensure a high fertiliser efficiency of P (Thygesen et al., 2011) vs. operating at higher temperatures >900 °C to minimise nitrous oxide emissions (Gutierrez et al., 2005). For these reasons, it is important to target the upstream recovery of P via wastewater treatment or from sewage sludge before biosolids is sent to thermal processing. Phosphorus can be recovered from the sludge line of a WWTP via minerals precipitation, albeit at high and somewhat limiting operational cost (Raheem et al., 2018). However, the recovery of P can be facilitated by accumulation of P into biomass via enhanced biological P removal (EBPR), and with a subsequent release step (e.g. thermochemical or biochemical), this P can be solubilised to be more efficiently recovered at higher concentration via mineral precipitation (e.g. struvite) (Yuan et al., 2012). Struvite technology is already commercially available, producing struvite fertiliser with favourable characteristics and generally low levels of contamination (Muys et al., 2021).

4.3. Humic substances

There has been significant interest in extraction/recovery of molecules from sewage sludge with an organic soil amendment benefit (Núñez et al., 2022). Humic substances is one such class of molecules found in sludge, said to make up an estimated 10–15 % of the total sludge dissolved organic matter (Li et al., 2013; Xiao et al., 2020), and comprised of humic acids and fulvic acids (Xiao et al., 2020). The benefits of humic substances as biostimulants of plant growth have been well-documented (Jindo et al., 2020). Humic substances are inherent components in sludge produced via biological release during anaerobic digestion and are also produced and/or chemically altered via thermal or chemical pre-treatment of sludge (Xiao et al., 2020). Humic acid is said to be recoverable from sludge in an up-concentrated liquid form via membrane filtration (Núñez et al., 2022).

4.4. Section summary

Overall, to recover nutrients and organic amendment compounds from wastewater and sludge before biosolids is thermally processed, various upstream recovery technologies would need to be integrated into or replace conventional WWTP processes that currently destructively dissipate carbon and N (Fig. 2). Several PRR technologies are commercially available and have been reasonably widely applied as individual technologies. However, their successful integration into a whole of plant context at full-scale remains a development gap (Batstone et al., 2015). Following the description of technologies above, there is an opportunity to extract/recover P and N into chemical fertiliser forms which are readily bioavailable, and these

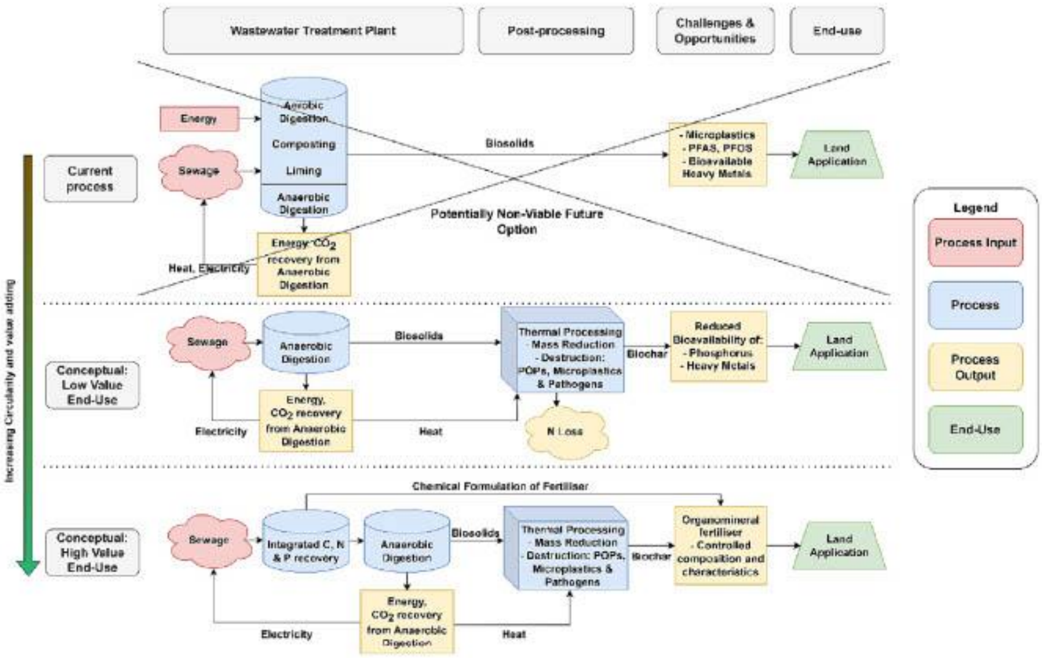

Fig. 2. Schematic overview of an alternative future scenario where conventional WWTPs are converted into closed-loop resource recovery centres, in this case to produce balanced biofertilisers for broad-acre cropping applications.

can then be used in novel OMF formulations with properties that target broad-acre cropping applications.

5. Biosolids-derived fertiliser products tailored for broad-acre farming

Key drivers for organic-based fertilisers in agriculture are (1) technological developments that are enabling the production of high-quality products, (2) improvements in application techniques for field spreading, cost advantages compared with mineral or synthetic fertilisers, and (3) the need to maintain soil carbon and fertility levels thus allowing for increased circularity of carbon and nutrients (Chambers et al., 2003; McCabe et al., 2020; Burggraaf et al., 2020). The following section reviews key considerations associated with biosolids-derived fertilisers in agriculture, to facilitate their widespread adoption and use for broad-acre crop production (Antille et al., 2013b; Antille et al., 2017).

5.1. Physical and mechanical properties

For solid fertiliser products, the physical (e.g., density properties, particle size and size distribution) and mechanical (e.g., static particle strength) properties are very important to enable successful handling, transport, storage and mechanized application. For example, materials that exhibit a moderately high crushing strength are also able to resist forces imposed by handling, storage, and spreading without significant shattering, dust formation, or caking. A breaking force of 15 Newton has been suggested as a lower limit to avoid particle fracture during handling and field spreading (Hignett, 1985). Unlike fertiliser spreading equipment, machinery used for application of solid organic materials (and likely biosolids-derived organic fertilisers) does not necessarily allow for high degree of control over the placement and uniformity of the material being applied. Consequently, the distribution of the material on the ground can be less uniform than conventional (granular or liquids) fertilisers, both along the direction of travel and across the working width of the machine. The application rates are controlled by the forward speed and the calibration of the metering system, and the physical properties of the material being applied are important for a single application (e.g., changes in moisture content, density, particle size). Dimensional analyses (e.g., Gregory and Fedler, 1987) have shown that granular materials flow, such as during discharge from a fertiliser spreader or during loading/unloading operations, depends on density properties. Density properties are also related to the volume needed for storage and transport, and together with particle size and size distribution are important for field-spreading equipment (Antille et al., 2015). For example, the uniformity of distribution of fertiliser materials during field spreading is influenced by particle size and size distribution and particle density, because these properties influence particle segregation and aerodynamics (Hofstee and Huisman, 1990; Bradley and Farnish, 2005). This is important because uneven spreading increases the risk of nutrient losses to the environment and can influence nutrient use efficiency (Jensen and Pesek, 1962). For this, a coefficient of variation of about 10–12 % in particle size has been suggested to be a threshold above which a loss in yield and potentially reduced quality in grain in terms of protein content could impose financial penalties (Miller et al., 2009). Studies by Antille et al. (2013a, 2015) showed that the optimum particle size range of granular biosolids and biosolids-derived fertilisers were between 1.10 and 5.50 mm in diameter for conventional twin-disc spreaders.

5.2. Chemical composition

Biosolids generally have low N:P ratios (Section 2). Moreover, biosolids are generally well-supplied with P (range: 5–12 % total P as P_2O_5) but have less K (typically, <2 % total K as K_2O) (Krogmann and Chiang, 2002). This is important because land application based on crop N or K requirements then risks the progressive build-up of soil P levels. While high soil P levels do not necessarily result in plant toxicity, elevated P increases environmental risk associated with potential soil P transport to surface water and groundwater. Blending with mineral or synthetic fertilisers can be used to correct for imbalance and/or inconsistent chemical composition (nutrients and C:N ratio) between different batches (Sommers, 1977) to achieve a desirable N:P:K ratio. This may be required to suit specific soil and crop requirements. By optimizing the nutrient composition and adjusting the nutrient application rate, the nutrient recovery in the crop and therefore use-efficiency can be improved (Antille et al., 2013c; Antille et al., 2017). Potential build-up of heavy metals in soil and uptake by crops grown on the soil can lead to their subsequent transfer to the food chain (Jones and Johnston, 1989; Jones, 1991). The associated risks should be appropriately managed, also by considering background soil heavy metal levels and heavy metal mobility (see Section 3).

5.3. Agronomic efficacy

Information available in the scientific literature suggests that FRV of organic materials, including biosolids and biosolids-derived fertilisers, can often be <40–60 % of that using urea or ammonium nitrate (e.g., Lalor et al., 2011; Petersen, 2003; Ashekuzzaman et al., 2021). However, some nutrients present in organic materials are in organic forms and therefore could undergo delayed or slow mineralisation to become plant-available. Research to date has been particularly interested in understanding the mineralisation-release characteristics, and how the application of straight fertilisers and organic sources (e.g. composted manures) in splits could be used to increase the overall nutrient recovery in crops and mitigate potential yield penalties by inadequate nutrient supply with organic materials alone. The correct synchronization of nutrient supply (from the soil/organic material) with demand (from the plant) is a key factor influencing nutrient use efficiency. Knowledge of the soil/crop/environment specific factors governing nutrient transformations in soil and the ability to predict such processes is a key requirement for improved nutrient use efficiency of organic materials, and for timely field application.

Agronomic performance may also be improved by blending with mineral fertilisers until the desired nutrient ratio and appropriate mineralisation-nutrient release characteristics can be obtained. This has included the reactive conversion of the blend to a compound referred to as an OMF. The product specifications for OMF by coating biosolids granules with mineral sources of N (as urea) and K (as potash) was reported in a series of studies by Antille et al. (2013b, 2015), as shown in Fig. 3), with N:P:K ratios of approximately 10:5:5 and 15:5:5. The main advantage of OMF vs. conventional blending is that the physical and mechanical properties of OMF particles can be made more consistent, which can provide greater certainty with handling and field application. For blended materials, if the physical and mechanical properties of the constituents in the blend are significantly different, segregation can occur (Bridle et al., 2004), which could affect aerodynamic behaviour and uniformity of distribution during field spreading (Grift et al., 1997). Moreover, for OMF, the mineral fraction represents a source of nutrients that are rapidly released and are readily available for crop uptake, whilst the organic fraction undergoes slower mineralisation to provide more sustained nutrient supply following soil application (Smith et al., 2020). Unfortunately, the rate of nutrient release from the organic fraction of OMF can be difficult to predict and this will be important into the future to manage benefits and impacts from agronomic and environmental perspectives (Antille et al., 2014a, 2014b). The conversion of biosolids into OMF products tailored to meet specific soil and crop needs represents a technological advancement compared with ways that biosolids have been traditionally used in agriculture.

5.4. Biochar as a co-component of OMF

Incineration of sewage sludge is still a common practise across Europe since restrictions to landfilling of sewage sludge were introduced with the EU Landfill Directive (99/31/EC) (CEC (Council of the European Commission), 1999). However, due to a high cost and poor public perception of sludge incineration (Raheem et al., 2018) pyrolysis and gasification have attracted increasing interest as well-known thermal processing alternatives. Pyrolysis and gasification produce biochar as a co-product (Raheem et al.,

Fig. 3. OMF granules and biosolids, after Antille et al., 2013b, with permission.

2018). The use of biochar in soils and agriculture has attracted considerable research interest in recent years (Abbott et al., 2018), because due to its unique physicochemical features, biochar from sewage sludge or biosolids has the potential to be utilised as a soil amendment fertiliser (Lehmann and Joseph, 2015). For example, depending on its characteristics, biochar could increase soil structure, water retention capacity and nutrient retention as a soil conditioner, and as a fertiliser it could deliver nutrients to plants, increase microbial activity and reduce nutrient losses due to leaching and volatilisation (Cayuela et al., 2013; Kloss et al., 2012). Biochar can also have sorption properties that mitigate N leaching, and influence relevant soil microbial processes to reduce N losses in some soils (Shanmugam et al., 2021). Lastly, biochar has also previously been suggested as a means to sequester carbon in soils (Marris, 2006).

Thermal processing results in mass destruction/volume reduction/up-concentration of contaminants in ash or biochar. Some studies have been concerned that use of biochar from biosolids may increase the heavy metal accumulation in the soil-plant system, posing a potential threat to agricultural soil (Song et al., 2014; Yue et al., 2017). However, several studies have demonstrated that heavy metals can be immobilised in biochar derived from biosolids, reducing their bioavailability and reducing the risk of soil-plant contamination (Hossain et al., 2010; Faria et al., 2017; Sousa and Figueiredo, 2015); albeit that it is important to note that heavy metals may be immobilised to varied extents depending on the pyrolysis conditions, the resulting biochar characteristics, and soil and crop effects (Jin et al., 2016; Patel et al., 2020). Considering that biochar would likely be available as a by-product from end-of-pipe thermal processing of biosolids, the interest in inclusion of biochar in soil amendments or as fertiliser co-component will likely increase over time. There has already been a move to include biochar as a co-ingredient in amendments, including with conventional fertilisers (Abbott et al., 2018).

Other than understanding the agronomic benefits of using biochar, future research will need to identify preferred pyrolysis conditions that produce biochars with the desired physical structure and composition for soil amendments (Abbott et al., 2018). This can then develop targeted and sustainable fertiliser formulations to support soil health and provide plant benefits (e.g., Yeboah et al., 2017).

6. Opportunities, and recommendations for further work

There has been global concern over the long-term availability of non-renewable mineral fertiliser resources, and over the substantial energy consumption and greenhouse gas emissions from conventional N fertiliser production. Biosolids produced from treatment of domestic sewage has long been applied to agriculture as a source of nutrients to displace mineral fertilisers. For example, biosolids use in Australian agriculture has seen a 73 % increase in total production from 2010 to 2021. Significant Australian studies, such as the National Biosolids Research Program (2002–2008), have highlighted the potential FRV, crop returns and overall benefits and risks of biosolids use in agriculture. However, although the direct agricultural recycling of biosolids is still the most practicable option for beneficial reuse, it poses several notable logistical, practical, environmental and performance difficulties. These include (1) an imbalance of fertiliser nutrients in biosolids, and properties of biosolids that do not enable well-controlled field-application, with risk of over-supply or under-supply of nutrients and associated financial and environmental risks; and (2) emerging contaminants such as micro-plastics and nano-plastics which are ubiquitous in biosolids and could pose a significant future threat to the direct agricultural use of biosolids. Instead, thermal processing (e.g. incineration, pyrolysis or gasification) of biosolids has been explored to destroy such organic contaminants. Policy guidance regarding the safe use of biosolids in Australian agriculture has been well established and has been successful for >20 years to reduce potential adverse human health and environmental impacts associated with its beneficial use. For example, via a collation of data from several Australian literature studies, the current work demonstrates that heavy metal concentrations in biosolids have progressively declined over time, likely at least partly influenced by tighter control over industrial catchments. Due to recent scientific advancements on the role of soil microbiota on soil health, regulations for biosolids application to land could into the future consider the impact of contaminants (i.e., heavy metals, organic pollutants and microplastic) on the soil microbiota by the implementation of ecotoxicological analysis on soils.

As an alternative to destructive dissipation of potentially valuable carbon and nutrients by thermal processing, the current paper highlighted commercially-available extraction technologies as an alternative to instead recover such constituents from sewage sludge or biosolids upstream in the wastewater treatment plant, to make these available for agronomic use. However, although commercially available and applied in isolation, extractive technologies need to be researched and developed in an integrated whole-of-plant context and at a relevant scale, including to address key challenges such as a current high energy demand of N recovery, and a generally high comparative cost of extractive recovery.

Nutrients and carbon made available by extraction, put together with by-products from thermal processing (e.g. biochar), represent potential ingredients for the future production of balanced organic fertilisers, whether these be blends of mineral fertilisers and organic fertilisers, or whether instead reactive mixtures of these as formed, referred to as OMF. The understanding and further development of such products will be important to address current limitations, including variable nutrient mineralisation, release and supply, but also to provide fertiliser products suitable for broad-acre cropping applications. For example, conventional spreading equipment used for mineral fertilisers with appropriate particle size and strength. Moreover, there are particular opportunities to balance the rapid plant-available nutrient supply of mineral fertilisers with slow-release organic fertiliser forms to provide sustained nutrient supply for enhanced crop growth.

This represents a research opportunity and need to develop tailored fertiliser products with the desired product and nutrient supply characteristics. Research and investigations should particularly seek to resolve important links between processes that produce and extract nutrient and carbon constituents, and the agronomic benefits and risks posed when these constituents are formulated into targeted fertilisers and, importantly, applied to land at reasonable/viable application rates. This development could ensure the safe and beneficial use of nutrient and carbon resources in sewage sludge and biosolids across broad-acre agriculture into the future.

CRediT authorship contribution statement

Conceptualization B.K.M, S.M. S.T. and D.L.A.; methodology, S.M., S.T., and B.K.M.; formal analysis, S.M., S.T, P.S., and P.H.; investigation S.M and S.T.; data curation, S.M.; writing—original draft preparation, S.M.; writing—review and editing, S.M., S.T., P.S., P.H., D.L.A., and B.K.M.; visualization, S.M., S.T., D.L.A and B.K.M. supervision, B.K.M., project administration, B.K.M; funding acquisition, B.K.M. All authors have read and agreed to the published version of the manuscript.

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Data availability

No data was used for the research described in the article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.162555.

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APPENDIX B: AN INVESTIGATION INTO THE MOBILITY OF HEAVY METALS IN SOILS AMENDED WITH BIOSOLIDS-DERIVED BIOCHAR

Contribution was made to the following conference paper, “An investigation into the mobility of heavy metals in soils amended with biosolids-derived biochar,” providing contribution in experimentation and formal analysis.

Marchuk, Serhiy., Antille, Diogenes L., Sinha, Payel., Tuomi, Seija., Harris, Peter.W., McCabe, Bernadette K., 2021.An investigation into the mobility of heavy metals in soils amended with biosolids-derived biochar. In: 2021 ASABE Annual International Meeting; ASABE Paper No.: 2100103; American Society of Agricultural and Biological Engineers. St. Joseph, MI, USA. https://doi.org/10.13031/aim.202100103

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An investigation into the mobility of heavy metals in soils amended with biosolids-derived biochar

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ABSTRACT. *A laboratory experiment that was conducted to gain an understanding of heavy metals dynamics in soils amended with biosolids (treated sewage sludge) and biochar produced from biosolids. The findings of this study, albeit limited in scope, go some way to inform the development of a scientific-based framework that supports practical and cost-effective management of biochar intended for land application. The risk of heavy metals (Zn, Cu, Cr) leaching in two soils of contrasting mineralogy and physico-chemical properties (Yellow Chromosol and Red Ferrosol) was quantified in a laboratory setup using leaching columns. Application of biosolids and biochar to soil increased pH of the leachate solution, and it increased with the rate of biosolids or biochar applied to soil. Differences in pH of leachate between biosolids and biochar-treated soil were not significant. Zinc (Zn) recovered in leachate was higher in the Red Ferrosol than the Yellow Chromosol, but total Zn recovered after six leaching events was less than 20 mg kg^{-1}, and there was no clear effect of rate. There was a little more Zn recovered in leachate from biochar- compared with biosolids-treated soil. Copper (Cu) recovered in leachate was higher in the Red Ferrosol than the Yellow Chromosol, but no Cu was recovered after the fourth leaching event, and in both soils Cu in leachate increased with the application rate. The amount of Cu recovered in leachate from biochar-treated soil was about one-third the amount recovered from biosolids-treated soil. Chromium (Cr) recovered in leachate was similar in both soils and recoveries were fairly consistent between-leaching events. In both soils, Cr recovered in leachate increased with the application rate. Total Cr recovered in leachate from biochar-treated soil was about eight times lower than from biosolids-treated soil. There is a need to extend the work reported here and to consider other soil types (e.g., Vertisols) that may respond differently from the physico-chemical and hydrological perspectives, and to capture the dynamics of other heavy metals as well as phosphorus, which were not part of this study. Based on the results of this work, there appears to be potential for future use of biochar in these two Queensland soils.*

Keywords. *Copper, Chromium, Land application of biosolids, Leaching, Potentially toxic elements, Sewage Sludge, Zinc.*

Introduction

Biochar is a carbon-rich solid material produced by heating biomass in an oxygen-limited environment and can be applied to soil as a means to sequester carbon, improve soil condition and function (Joseph et al., 2010). The negative high surface charge density of biochar enables the retention of cationic nutrients via ion exchange, whereas the relatively extensive surface area, internal porosity, and polarizability facilitate anionic nutrient sorption via covalent bonds (Lu et al., 2020). The relatively high cation exchange capacity of some char materials, such as biosolids-derived biochar, have the ability to adsorb heavy metals and organic contaminants that may be present in the soil environment (Hill, 2005). There is limited information on the cycling and mobility through the soil of heavy metals present in biochar derived from sewage sludge. The risk of heavy metal contamination following application of waste to agricultural soils is a serious environmental concern (Jones and Johnston, 1989; Yeboah et al., 2017). Biochar derived from biosolids may carry an elevated level of heavy metals, and therefore, land application of such material may result in soil contamination and subsequent transfer of heavy metals to surface and underground waters through leaching and runoff (Clarke et al., 2016; Antille et al., 2017). There is also a risk of plant uptake in soil enriched with heavy metals, which may be then transferred to the food chain (Singh et al., 1984; Dudka and Miller, 1999). This risk can be higher in soils with acidic reaction (Kookana et al., 2011; Torri and Corrêa, 2012). The interaction between biochar, soil, microbes and plant roots are known to occur within a short period of time after application (Lehmann and Joseph, 2009) and are highly influenced by soil pH (Gorovtsov et al., 2020). Understanding the extent and implications of these interactions is necessary for effective assessment of risks associated with biochar use in agriculture and for improved use efficiency of such materials (Joseph et al., 2010; Agegnehu et al., 2015).

In Australia, commercially available biochar materials are marketed with limited or no analytical data disclosing their chemical composition (Singh et al., 2014). Such information is critical when these materials are used for land application together with the physico-chemical properties of the soil being treated with biochar; including, but not limited to: mineralogy, soil pH, and background level of heavy metals in soil (Verheijen et al., 2010; Oni et al., 2019).

Heavy metals

Heavy metals are a group of elements with specific gravities of higher than 5 g cm^{-3} (Ross, 1994). At high concentration, some heavy metals; namely: cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn), are regarded as toxic and environmentally damaging (Johnston, 2008; Johnston and Jones, 1995), but Cu, Ni and Zn (transition metals) are also essential for plant metabolism (Antille et al., 2013; Yue et al., 2017). The availability of heavy metals in soils amended with biochar derived from biosolids is affected by the type and composition of biosolids used in their production, the pyrolysis temperature and soil properties, particularly soil pH (Yang et al., 2018; Figueiredo et al., 2019). The process of pyrolysis increases the concentration of heavy metals in biochar relative to that of the raw material (Phoungthong et al., 2018), but also reduces their bioavailability (Paz-Ferreiro et al., 2018; Figueiredo et al., 2020).

The risk of heavy metal leaching in soil amended with biochar is also reduced during the pyrolysis for which biosolids-derived biochar may be regarded as safe (Mendez et al., 2012). Hence, proposals have been put forward to consider limit values in the Australian regulations based on leachability of heavy metals instead of their concentration in biochar (e.g., Roberts et al., 2017; Yang et al., 2018). Such proposals also imply soil type and soil pH are considered when determining the risk of leaching. For example, a study by Hossain et al. (2011) in Australia applied 10 Mg ha^{-1} of biosolids-derived biochar, but recovery of heavy metals in tomatoes did not exceed the maximum allowable concentrations stated in the Food Standards Australia and New Zealand (https://www.foodstandards.gov.au/Pages/default.aspx), despite the fact that heavy metal concentrations (as total elements) in soil exceeded current guidelines (Edgerton and Buss, 2019).

Objectives

The work reported in this paper was conducted to quantify the risk of heavy metals (Zn, Cu, Cr) leaching in soils amended with biosolids-derived biochar. The study was conducted under controlled laboratory conditions using two different soil types from Queensland (Australia), which are commonly used for arable cropping. This preliminary study aims to inform the development of a scientific-based framework that supports practical and cost-effective management of biochar intended for land application.

Materials and Methods

Soils

Two soils from southern Queensland (Australia) were used in this laboratory study, namely: Red Ferrosol (Oxisol in the NRCS-USDA Soil Taxonomy) from Toowoomba and Yellow Chromosol (Alfisol in the NRCS-USDA Soil Taxonomy) from Gatton, respectively. The selection of these soils was mainly based on their contrasting mineralogy, texture, pH and carbon contents (Table 1). Soil samples were collected from the 0-200 mm depth interval, air-dried at 40°C and sieved to pass 2-mm.

Table 1. Physicochemical characterization of the soils used in the leaching experiment. 'BDL': below detection limit.

Description	Red Ferrosol	Yellow Chromosol
GPS Location	27°36'32.27" S, 151°55'52.96" E	27°35'44.9" S, 152°18'20.1" E
pH (1:5 soil/water), %	6.0	5.5
EC (1:5 soil/water), dS/m	0.03	0.01
Total C, % (w/w)	3.51	1.69
Total N, % (w/w)	0.27	0.16
Clay (<0.002 mm), % (w/w)	57	14
Silt (0.002–0.02 mm), % (w/w)	11	11
Sand (0.02–2 mm), % (w/w)	32	75
Total Zn, mg/kg	89.80	42.70
Soluble Zn, mg/kg	0.19	0.23
Total Cu, mg/kg	46.20	8.50
Soluble Cu, mg/kg	BDL	BDL
Total Cr, mg/kg	331.0	13.5
Soluble Cr, mg/kg	0.12	0.01
Dominant clay mineral	Kaolinite	Kaolinite, Montmorillonite

Biosolids and biochar

Both biosolids and biochar produced from the same biosolids material (henceforth referred to as biochar) were sourced from Pyrocal Pty Ltd. (Toowoomba, Queensland, https://www.pyrocal.com.au/). The biochar was industrially produced in a commercial thermal gasification system. Both materials were air-dried at 40°C and sieved to pass 2-mm. The physico-chemical properties of biochar and biosolids are presented in Table 2.

Table 2. Physicochemical characterization of biosolids and biochar used in the leaching experiment.

Description	Biosolids	Biochar
pH (1:5 soil/water)	5.6	9.5
EC (1:5 soil/water), dS/m	5.38	0.51
Total C, % (w/w)	40.59	34.55
Total N, % (w/w)	7.07	4.65
Total P, % (w/w)	4.99	7.89
Soluble P, g/kg	7.13	0.13
Total Zn, mg/kg	957.0	1517.4
Soluble Zn, mg/kg	1.43	0.20
Total Cu, mg/kg	580.1	692.3
Soluble Cu, mg/kg	0.05	0.02
Total Cr, mg/kg	53.0	98.7
Soluble Cr, mg/kg	0.31	0.01

Analytical methods

Standard analytical methods were used for determination of pH and EC (1:5 soil/water ratio) (Rayment and Lyons, 2011), and particle size distribution (Gee and Bauder, 1986). Total carbon (C) and total nitrogen (N) were measured by ignition with a LECO Elemental Analyser (LECO Australia, https://leco.com.au/). The chemical composition of soil, biochar and biosolids, and heavy metal content were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (ELAN 6000, Perkin Elmer, Switzerland) after digestion in *Aqua regia* (HNO_3:HCl, 3:1 ratio) in a microwave oven (Multiwave, 3000 Anton Paar, USA). X-ray diffraction (XRD) was used for clay (<2 μm) fraction analysis; this fraction was separated from the bulk soil through sedimentation (Jackson, 2005). The XRD patterns for randomly oriented air-dried samples were recorded with a PANalytical X'Pert Pro Multi-purpose diffractometer. XRD data were collected and displayed using the CSIRO software XPLOT for Windows (Raven, 1990).

Soil columns and leaching experiment

Soils were mixed with biosolids (BS) and biochar (BCh) at three different rates, expressed as % (by weight) as follows: 2.5, 5 and 10 referred to here as BS2.5, BS5, BS10, BCh2.5, BCh5 and BCh10, respectively. A control (zero-amendment) for each soil type was also used. All treatments were replicated three times ($n = 3$). The transport of Zn, Cu and Cr through the soil was evaluated under saturated/near-saturated soil conditions using vertically oriented Plexiglas columns (87 mm inner diameter by 200 mm long). Soil in columns was maintained between saturation and 90% saturation (corresponding to suctions between 0 and -50 cm; Ngo-Cong et al., 2021) over the entire experiment; this minimized the risk of by-pass flow between the soil matrix and the inner wall of the PVC tube. The soil columns were allowed to drain freely during the leaching events and there was never water ponding on the soil surface. Over time, the soils in the columns consolidated due to the effect of gravity and successive leaching events. A total of six leaching events were conducted at days 1, 3, 7, 14, 30 and 60, respectively after the experiment was established. Soil in columns (500 g each) was carefully packed to achieve uniform density within the PVC tube and in triplicates; this process was repeated with both soil types and for all treatments, including controls (Figure 1). The bottom of the soil columns was fitted with a nylon mesh screen and filter paper, and another filter paper placed on the top of the soil to reduce surface disturbance while pouring the leaching solution to the soil. To achieve uniform packing, the air-dried soil sample was carefully placed into the columns using a spatula and then gently vibrated. The columns were first wetted-up with a 0.01M $CaCl_2$ solution from the base of the column to reach saturation by capillary rise, which was achieved after about 48 hours.

Leaching with $CaCl_2$ solution

The effect of biosolids and biochar on heavy metal leaching was assessed by monitoring $CaCl_2$-extractable metal concentrations released from soil (control without amendment), soil-biosolids and soil-biochar mixtures during the experiment. The 0.01 M $CaCl_2$ extraction provides information about the soil solution and exchangeable metal pools, and it can be regarded as an indicator of metal solubility, bioavailability and mobility in soils (Houba et al., 2000; Pueyo et al., 2004; Kalis et al., 2007). At days 1, 3, 7, 14, 30 and 60 from the start of the experiment, columns were leached with approximately 150 mL of 0.01M $CaCl_2$ solution. Leaching was performed by slowly pouring the solution into the columns above the soil covered with filter paper. Columns were covered with plastic cups to minimize evaporation during the leaching events, and they were allowed drain into plastic containers at the bottom of stands. The receiving containers had a cap with a small hole drilled through it that allowed the drain tube to be inserted into the container to minimize evaporative losses. The amount of leachate collected at each leaching event was determined volumetrically. Leachate samples were filtered and analyzed for pH and EC, Zn, Cu and Cr concentration as indicated earlier.

Figure 1. Overview of the leaching experiment conducted under controlled laboratory conditions.

Statistical analyses

The statistical package GenStat Release® 19th Edition (VSN International Ltd., 2020) was used to analyze heavy metal concentration and leachate pH data and involved repeated measurement of ANOVA. The least significant differences (LSD) were used to compare means with a probability level of 5%. Statistical analyses were graphically assessed by means of residual plots and normalization of data was not required.

Results and Discussion

pH of leachate

The addition of soil amendments tended to increase the pH in the leachate recovered; the maximum pH in leachate samples was recorded after the last leaching event (Table 3). The increase in leachate pH in the Yellow Chromosol was more significant than the Red Ferrosol, which was attributed to lower soil buffering capacity.

Table 3. Changes in pH of leachate observed during the experiment. Biochar (BCh) and biosolids (BS) applied to soil columns at rates of 2.5%, 5%, and 10% (w/w). Values shown are means (n =3) for each leaching event, P<0.001, LSD: 0.054 (Soil type), P<0.001, LSD: 0.077 (Control *vs*. Treatment), P>0.987, LSD: 0.082 (Amendment type), P<0.001, LSD: 0.087 (Amendment rate), P<0.001, LSD: 0.055 (Leaching events). LSD values were estimated using a 5% probability level.

Soil type	Red Ferrosol						Yellow Chromosol					
Treatment, leaching event	**1**	**2**	**3**	**4**	**5**	**6**	**1**	**2**	**3**	**4**	**5**	**6**
Control	6.0	6.1	6.4	6.3	6.3	6.5	6.5	6.4	6.4	6.6	6.4	7.1
BCh2.5	6.1	6.4	6.6	6.7	6.9	7.2	6.6	6.7	6.9	7.2	7.2	7.8
BCh5	6.2	6.5	6.7	6.8	6.8	6.9	6.9	7.1	7.3	7.4	7.5	8.0
BCh10	6.7	6.9	7.3	7.4	7.5	7.8	7.3	7.6	7.9	8.0	8.1	8.2
BS2.5	6.2	6.7	7.2	7.2	7.5	7.4	6.1	6.9	7.5	7.6	7.7	7.6
BS5	5.9	6.7	7.3	7.3	7.8	7.7	6.0	6.8	7.4	7.6	7.5	7.8
BS10	5.8	6.8	7.2	7.4	7.7	7.7	5.7	6.6	7.4	7.6	7.9	8.3

Zinc

The concentrations of Zn recovered in leachate are shown in Figure 2. Overall, there were no differences in Zn concentration in leachate between control and treatments, which was observed in both soil types (P >0.05). There were significant differences between amendment types (P <0.01), but there was no amendment rate effect on Zn recovered in leachate (P >0.05). Total recovery of Zn across all leaching events was fairly low, ranging from 10.2 to 19.6 mg kg^{-1} in the Red Ferrosol and from 8.4 to 14.8 mg kg^{-1} in the Yellow Chromosol. These differences between soil types were significant (P <0.001). Differences between amendment types were mainly due to the effect of biochar applied to the Red Ferrosol, which yielded consistently higher recoveries than the same soil amended with biosolids. For the Yellow Chromosol, Zn recoveries in leachate were similar with both amendments. Approximately, 96% (biochar-treated soil) and 85% (biosolids-treated soil) of the Zn recovered in leachate were measured in the first four leaching events.

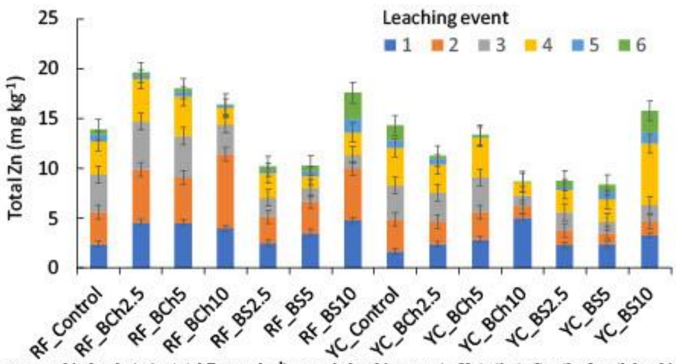

Figure 2. Zinc (Zn) recovered in leachate (as total Zn, mg kg^{-1}) over six leaching events. Note that after the fourth leaching event, the amount of Cu recovered in leachate was below detection limits. Notation: RF, Red Ferrosol; YC, Yellow Chromosol; BCh, Biochar; BS, Biosolids; the number that follows BCh and BS denotes the application rate of the amendment expressed in % (by weight). Error bars on mean values (n = 3) denote the standard deviation, P<0.001, LSD: 0.317 (Soil type), P>0.05, LSD: 0.453 (Control *vs*. Treatment), P<0.011, LSD: 0.484 (Amendment type), P>0.05, LSD: 0.513 (Amendment rate), P<0.001, LSD: 0.388 (Leaching events). LSD values were estimated using a 5% probability level.

Copper

The concentrations of Cu recovered in leachate are shown in Figure 3. After six leaching events, the concentration of Cu in leachate increased in the following order: control soil < biochar amended soil < < biosolids amended soil. Overall, there were significant differences between control and treatments (P <0.001), amendment types and rates (P-values <0.001). Differences in Cu recovered between-leaching events were significant (P <0.001). Total recovery of Cu across all leaching events was also fairly low, ranging from 0.4 to 4.7 mg kg^{-1} in the Red Ferrosol and from 0.3 to 2.2 mg kg^{-1} in the Yellow Chromosol. Differences between soil types were significant (P = 0.004).

The amount of Cu recovered in leachate tended to increase between the first and the fourth leaching events, which was observed in both soils, and recoveries were proportional to the application rate. There was no Cu recovered in leaching events 5 and 6 (below detection limits). Overall, application of biochar reduced the amount of Cu recovered in leachate, particularly in the Red Ferrosol.

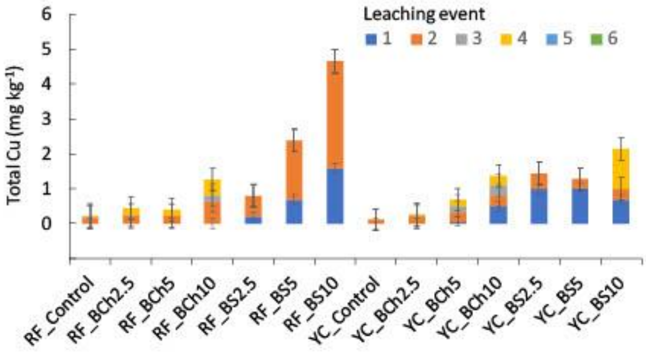

Figure 3. **Copper (Cu) recovered in leachate (as total Cu, mg kg^{-1}). Note that after the fourth leaching event, the amount of Cu recovered in leachate was below detection limits. Notation: RF, Red Ferrosol; YC, Yellow Chromosol; BCh, Biochar; BS, Biosolids; the number that follows BCh and BS denotes the application rate of the amendment expressed in % (by weight). Error bars on mean values (n = 3) denote the standard deviation, P=0.004, LSD: 0.044 (Soil type), P>0.001, LSD: 0.0636 (Control *vs*. Treatment), P<0.001, LSD: 0.068 (Amendment type), P>0.001, LSD: 0.072 (Amendment rate), P<0.001, LSD: 0.067 (Leaching events). LSD values were estimated using a 5% probability level.**

Chromium

The concentrations of Cr recovered in leachate are shown in Figure 4. Overall, there were significant differences between control and treatments, amendment types and rates (P-values <0.001). Differences in Cr recovered between-leaching events were significant (P <0.001). Total recovery of Cr across all leaching events ranged from 0.3 to 3.0 mg kg^{-1} in the Red Ferrosol and from 0.5 to 3.4 mg kg^{-1} in the Yellow Chromosol, but differences between soil types were not significant (P>0.05). In biochar-treated soil, between 74% (Yellow Chromosol) and 91% (Red Ferrosol) of the Cr was recovered in the first four leaching events. In biosolids-treated soil, between 66% (Yellow Chromosol) and 82% (Red Ferrosol) of the Cr was recovered in the first four leaching events. As observed for Zn and Cu, Cr recoveries were proportional to the application rate.

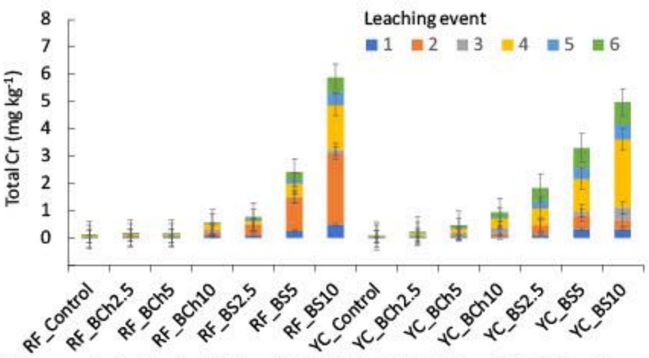

Figure 4. **Chromium (Cr) recovered in leachate (as total Cr, mg kg^{-1}). Notation: RF, Red Ferrosol; YC, Yellow Chromosol; BCh, Biochar; BS, Biosolids; the number that follows BCh and BS denotes the application rate of the amendment expressed in % (by weight). Error bars on mean values (n = 3) denote the standard deviation, P>0.065, LSD: 0.045 (Soil type), P<0.001, LSD: 0.064 (Control *vs*. Treatment), P<0.001, LSD: 0.069 (Amendment type), P<0.001, LSD: 0.073 (Amendment rate), P<0.001, LSD: 0.066 (Leaching event). LSD values were estimated using a 5% probability level.**

Summary

This paper presented preliminary results of a laboratory experiment that was conducted to gain an understanding of heavy metals dynamics in soils amended with biosolids (treated sewage sludge) and biochar produced from biosolids. The findings of this study, albeit limited in scope, will go some way to inform the development of a scientific-based framework that supports practical and cost-effective management of biochar intended for land application. The risk of heavy metals (Zn, Cu, Cr) leaching in soils of contrasting mineralogy and physico-chemical properties was quantified in a laboratory setup using leaching columns. The main results from this work are summarized here below:

- Application of biosolids and biochar to soil increased the pH of the leachate solution, and it increased with the rate of biosolids or biochar applied to soil. The pH of the leachate solution was consistently higher in the Yellow Chromosol compared with the Red Ferrosol (by about 0.5 pH units on average across treatments). Differences in pH of leachate between biosolids and biochar-treated soil were not significant.
- The amount of zinc (Zn) recovered in leachate was higher in the Red Ferrosol than the Yellow Chromosol (by about 30%), but total Zn recovered after six leaching events was less than 20 mg kg^{-1}, and there was no clear effect of rate. Overall, there was a little more Zn recovered in leachate from biochar- compared with biosolids-treated soil.
- The amount of copper (Cu) recovered in leachate was higher in the Red Ferrosol than the Yellow Chromosol (by about 30%), but no Cu was recovered after the fourth leaching, and in both soils Cu in leachate increased with the application rate. On average, the amount of Cu recovered in leachate from biochar-treated soil was about one-third the amount of Cu recovered from biosolids-treated soil.
- The amount of chromium (Cr) recovered in leachate was similar in both soils and recoveries were fairly consistent between-leaching events. In both soils Cr recovered in leachate increased with the application rate. Overall, total Cr recovered in leachate from biochar-treated soil was about eight times lower than from biosolids-treated soil.

There is a need to expand the work reported here to other soil types used for cropping in Queensland (e.g., Vertisols), which will likely respond differently from the physico-chemical and hydrological perspectives, and to capture the dynamics of other heavy metals as well as phosphorus, which were not considered as part of this study. Based on the results of this work, there appears to be potential for future use of biochar in these two Queensland soils.

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