Using Biochar to Manage and Remediate an Urban Soil Contaminated by Lead

A thesis submitted in fulfilment of the requirements for the degree of Master of Engineering

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Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed. I acknowledge the support I have received for my research through the provision of an Australian Government Research Training Program Scholarship.

Pacian Netherway

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I would like to dedicate this thesis to my late dad, who inspired my interest in science and motivated me to undertake research.

This work would not have been possible without my supervisor, Dr Jorge Paz-Ferreiro, whose guidance and support was unwavering throughout the duration of my studies .I would like to thank my associate supervisor, Dr Suzie Reichman for her valuable guidance and for welcoming me in to her laboratory group.

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Abstract

The contamination of soils by lead (Pb) is a widespread issue which poses a risk to urban communities globally. Recently, the remediation of this contaminant in-situ using chemical immobilisation has emerged as a promising option. This approach to remediation works by adding an amendment, usually phosphorus-based, in aim of inducing a shift in Pb speciation to a form which poses a lower risk to human health. A wide range of conventional phosphorus-based amendments, mostly mined or manufactured phosphates have been assessed for this purpose in the past. This approach is not without critique, with an increasing number of studies bringing in to question the sustainability of using these types of amendments. Specifically, there is concern that excess phosphorus could enter the environment and result in poor environmental outcomes.

Biochar has garnered attention as a means to sequester carbon, manage waste and remediate contamination. Biogenic waste products are often rich in phosphorus and the conversion of these wastes streams to biochar has emerged as a method to capture phosphorus so that it can be applied to the land and recycled back in to the soil system for one or more of the aforementioned benefits.

This study is motivated by recent efforts to immobilise Pb contaminated soils in-situ by adding phosphorus based amendments. Phosphorus plays an important role in the immobilisation of this element and there is a growing need to appraise alternative P sources for this use. Specifically, this study aims at assessing biochars produced from poultry litter and biosolids as sources of P to reduce the risk which Pb in soil poses to human health by comparing their efficacy in reducing *in vitro* bioaccessible Pb against conventional treatments. In order to understand any improved environmental outcomes by using these biochars for this purpose, impacts on soil quality were assessed, together with the potential for the release of excess P in to the environment.

Overall, this research has identified two problematic waste streams (poultry litter and biosolids) that could be valorised towards the remediation of Pb contaminated soils and signals acidic biochars, a product which to date has found less applications than their alkaline counterparts, as more suitable for Pb remediation.

The results of this research indicate that the application of biochars produced at 500°C increased the activity of soil enzymes, signaling an increase in soil quality. Consistent with previous authors, the results indicate that phosphorus-rich biochars act as a slow release source of P, whereby the availability of P in the receiving soil was not affected following treatment with biochar, indicating poor environmental outcomes such as the release of excess P in to the environment could be avoided using biochars for this purpose.

The application of an amendment for the purposes of immobilizing heavy metals in soil should consider wider environmental outcomes to ensure that a net environmental benefit is achieved. Under a holistic approach to assessing remediation options, these wider environmental outcomes will help to equip researchers and industry alike in their endeavour to reduce the burden posed by contaminated soils in to the future.

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1.0 Preface

This thesis has been prepared for submission as a thesis with publications to fulfil the requirements for a Masters by Research in Environmental Engineering.

1.1 Publications and Recognition

1.1.1 Journal Publications

At the time of submission of this thesis, the author has an article accepted for publication at the Journal of Environmental Quality:

Pacian Netherway; Suzie Reichman; Kirk Scheckel; Nick Pingitore; Gabriel Gasco; Ana Mendez, Aravind Surapaneni; Jorge Paz-Ferreiro. *Phosphorus rich riochars can transform lead in an urban contaminated soil,* Accepted for publication May 2019, Journal of Environmental Quality.

Chapter 2 Section 6 of this thesis was included in a review article which was published in the journal *Applied Geochemistry*:

Mark Laidlaw; Gabriel Filippelli; Sally Brown; Jorge Paz-ferreiro; Suzie Reichman; **Pacian Netherway**; Adam Truskewycz; Andrew Ball; Howard Mielke. Case studies and evidence-based approaches to addressing urban soil lead contamination, Applied Geochemistry, January 2017 http://dx.doi.org/10.1016/j.apgeochem.2017.02.015

1.1.2 Conference presentations and other

CleanUp Conference, Melbourne 2017, Using Biochar to Remediate Lead Contaminated Soil. **Pacian Netherway**, Suzie Reichman and Jorge Paz-Ferreiro

EcoForum, Perth 2016: Using Biochar to Manage and Remediate Lead Contaminated Soil. **Pacian Netherway,** Suzie Reichman and Jorge Paz-Ferreiro. **Awarded Best Poster**.

Chronicle Magazine Issue No. 49, Australian Land and Groundwater Association, February 2017 Using Biochar to Manage and Remediate Lead Contaminated Soil. **Pacian Netherway,** Suzie Reichman and Jorge Paz-Ferreiro.

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2.0 Introduction

2.1 Lead

Lead (Pb) is one of the first known metals (Morrison and Murphy, 2005); it is very resistant to corrosion so does not biodegrade, instead it can bioaccumulate in the human body where it serves no known biological benefit (Morrison and Murphy, 2005). A significant amount of Pb ha been released in to the environment, for example in 1998, it was suggested to have been released more than any other heavy metal (Nriagu, 1998). In the environment Pb generally exists in a +2 oxidation state in the form of galena (PbS), anglesite ($PbSO_4$) and cerussite ($PbCO_3$).

Pb is relatively insoluble at common environmental pH and readily adsorbs to the surface of particulate matter (Morrison and Murphy, 2005). Consequently soils and sediments commonly act as a sink of Pb in the environment (Calow, 1998).

2.2 Sources of lead in urban soil

Globally, soils in urban environments are a significant sink for environmental Pb resulting from both point and diffuse anthropogenic sources. The historical use of leaded fuel and leaded paints has left an ubiquitous mark on urban soils, whilst the industrial activities of mining and smelting leave behind a legacy of Pb (Filippelli et al., 2015). With respect to the deposition of lead in soil from its use as an additive in fuel, In Melbourne, Australia, De Silva et al. (2016) reported lead concentrations up to 144 mg kg^{-1} in an urban roadside soil, whilst in another urban part of Melbourne, Laidlaw et al. (2018) found lead at concentrations up to 710 mg kg^{-1}. This is consistent with other studies around the world, for example Mielke (1994) found that in New Orleans, USA, inner city soils contained Pb ranging from 600 – 1200 mg kg^{-1}. With respect to industrial sources including mining and smelting, as an example, Broken Hill, is a town in Australia which was established around one of the largest lead mines in the world. Here the mean concentration of Pb in urban topsoil is around 700 mg kg^{-1} with a maximum concentration of over 6,000 mg kg^{-1} (Yang and Cattle, 2015). Whilst in Shenyang city, China, near a former Pb smelter, Pb concentrations in soil range from 26 – 2,911 mg kg^{-1} (Wang et al., 2006).

Despite the considerable effort taken to eliminate paint-related sources and leaded petrol over the last 60 years (Filippelli et al., 2015) and the drive to reduce exposure in communities living nearby to point sources of Pb (Lyle et al., 2006), environmental Pb poisoning persists as a principal environmental threat to human health (Mushak, 2011) and the need to mitigate this threat remains.

2.3 Risk Based remediation

Land contamination is an issue facing communities all over the world. For example, the United Nations Assembly for the environment estimates that there are over 340,000 contaminated sites which require remediation (United Nations Environment Program, 2017). The remediation of contaminated soils does not have a one-size-fits-all solution; instead it is scenario-based, depending upon the characteristics of the contaminant, the fate and transport of the contaminant in the environment and the human or ecological receptor at potential risk of harm. This concept is referred to as the source-pathway-receptor model and underpins the risk-based management and remediation of contaminated sites in several countries, for example in Australia and the United States (ASC NEPM, 2013; USEPA, 1989).

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With respect to the management and/or remediation of soil contamination, approaches generally aim at breaking a linkage to reduce the risk at the receptor. For example, a straight forward approach involves source removal, however this is often cost prohibitive, generates significant volumes of waste and is likely to face community backlash (Hettiarachchi and Pierzynski, 2004). With respect to the pathway contamination takes to a receptor, this can be managed using physical barriers or by using chemical amendments to immobilize or sequester the contaminant in-situ. In recent times, a risk-based approach to soil remediation by has been preferred as a sustainable yet pragmatic way to managing the risk posed to the receptor (Henry et al., 2015).

In Australia the management of land contamination is underpinned by the National Environmental Protection Measure (NEPM) (ASC NEPM, 2013). Schedule B7 of the NEPM sets out soil investigation levels to enable contamination to be assessed in terms of potential risks to human health and ecosystems. With respect to assessing potential human health risks posed by Pb in soil, the screening criteria vary according to the current or proposed use of the land. For Pb, the most conservative criteria, health investigation level (HIL) A is 300 mg kg^{-1} which has been derived using the Integrated Exposure Uptake Biokinetic Model (IEUBKM) as described in (NEPC, 2014). Bioaccessibility (discussed in Sections 2.5 and 2.6) is the key parameter in this model; commonly a default value of 50% bioaccessibility is adopted. Importantly, in NEPC (2014) it is stated that the "risk management of elevated Pb levels at contaminated sites will become increasingly the focus of site investigation and remediation where Pb levels are above HILs.

2.4 Human Pb exposure pathways and risks

In 2015 the National Health and Medical Research Council released a statement titled Evidence on the Effects of Lead on Human Health (NHMRC, 2015). This statement was based on findings from comprehensive independent evaluation of evidence and advises that blood Pb level greater than 5 micrograms per decilitre is above background levels in Australia. The review found that blood Pb levels less than 10 µg dL^{-1} are associated with several health effects. In the United States, the Centres for Disease Control recently reduced the definition of elevated blood Pb from 10 to 5 µg dL^{-1}, with some researchers suggesting that this could lead to a lowering of the current screening level of Pb in soil (Henry et al., 2015, Obrycki et al., 2016). The lowering of regulatory levels could trigger the clean-up of sites, including vast tracts of urban soils (Laidlaw et al., 2017), which was not required previously.

The primary route which humans are exposed to Pb is via ingestion of Pb contaminated soils (Calabrese et al., 1997, Hooker and Nathanail, 2006), although recent works have suggested that the inhalation of Pb containing dusts represents a significant exposure pathway (Kastury et al., 2017, Kastury et al., 2018, Laidlaw et al., 2017). Children are at particular risk of being exposed to Pb as they are known to ingest considerable amounts of soil via hand-to-mouth activity (Calabrese et al., 1997) whilst playing in soil.

In Tong et al. (2000), exposure to environmental Pb was presented as "…a major public health hazard of global dimensions". Exposure to Pb can result a wide range of adverse health outcomes for example, motor neuron disease (Laidlaw et al., 2015) and preeclampsia (Kennedy et al., 2012).

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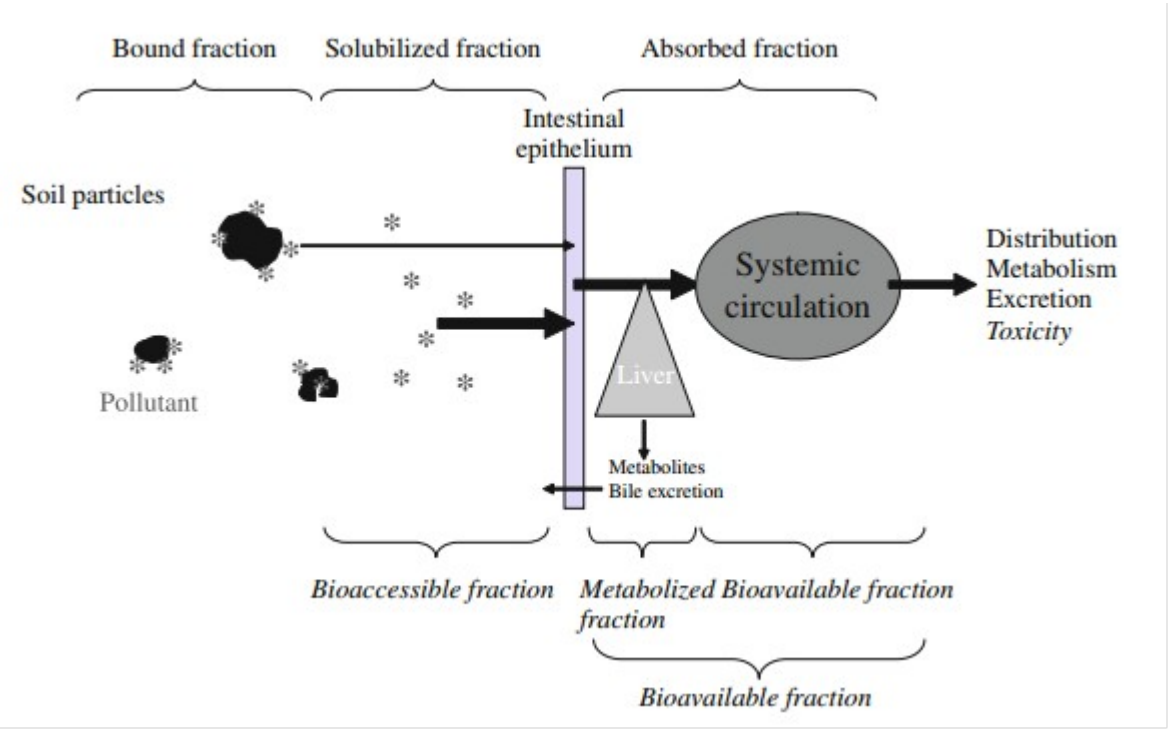
2.5 Human bioavailability of lead in soil

Oral bioavailability is defined by mammalian toxicologists as “the fraction of the administered dose that reaches the blood compartment from the gastrointestinal tract” (Ruby et al., 1999) In terms of contamination, Cave et al. (2011) defined oral bioavailability as “the fraction of an ingested contaminant that is absorbed and reaches the systemic circulation where it may then cause adverse effects on human health”.

Bioaccessibility refers to fraction of ingested contaminant that is soluble in the gastrointestinal environment and therefore available for absorption (Cave et al., 2011). In the case of Pb, this bioaccessible fraction is predominantly produced in the stomach, where low pH conditions can act to dissolve Pb. Once in solution, this contaminant can travel down in to the intestines, where it can transit through the intestinal epithelium and be absorbed in to the blood stream (Cave et al., 2011). This route is summarised in Figure 1.

Figure 1 Oral bioavailability (Cave et al., 2011)



2.6 *In vitro* bioaccessibility

There are the considerable monetary and ethical constraints associated with *in vivo* experimentation involving contaminant bioaccessibility, and, consequently, a significant body of research exists in the development of *in vitro* bioacessibility (IVBA) tests as a proxy for in *vivo tests*. The methodologies broadly stem from the physiologically based extraction test (PBET) developed by Ruby et al. (1996). Broadly these aim at mimicking the conditions of the human gastrointestinal tract to gain an understanding of how the contaminant will behave if ingested. Generally, available IVBA tests can be grouped as either single phase (i.e mimic the stomach only) or multiple phase (i.e. mimic the stomach, intestines and other parts of the gastrointestinal tract). An overview of parameters of established IVBA methods is discussed in the following sections, with a particular focus on these

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accepted by regulatory bodies in human health risk assessment which have been correlated with *in vivo* studies.

2.6.1 The role of pH

The pH of the stomach is dependent on the ingestion of food. For example, when food enters a previously empty stomach the pH rises from 2.0 to 4.0 units (Ruby et al., 1996). The solubility of Pb is dependent upon acidity, for example, in Ruby et al. (1996), IVBA soluble Pb decreased by 65% when pH was increased from 1.3 – 2. As such the pH adopted during the IVBA test bioaccessibility is a key parameter. Generally, a stomach pH between 1.5 and 2.5 has been employed in previous studies (Ryan et al., 2004, Brown et al., 2003, Scheckel and Ryan, 2004).

There are many different procedures which have been proposed to measure *in vitro* bioaccessibility of Pb, some of which are summarised in table 1. The single phase (stomach) method proposed by Drexler and Brattin (2007) was standardized as an *in vitro* bioaccessibility assay for Pb in soil (USEPA, 2013). Briefly, in this method 0.4 mol L^{-1} glycine ($C_2H_5NO_2$) solution is adjusted to pH 1.5 by hydrochloric acid (HCl). 37°C Deionised water is adjusted to pH 2.5 using trace metal grade HCl. The extraction involves mixing 1 g of the 250 µm fraction of soil with 200 mL of solution in a 125 mL wide mouth HDPE bottle. The bottles are sealed and placed on a rotating shaker in an incubation chamber at 37°C. The rotations are at 30 ±2 rpm. The pH is adjusted to 2.5 at 5 min and 30 min. After 60 min of rotating the samples are removed and 10 mL is extracted, filtered and analysed by a relevant analytical method.

With respect to intestinal pH, generally the pH used in IVBA Pb tests adopts a near neutral pH. The intestinal phase extraction is conducted following the stomach phase, so the pH of the system shifts from highly acidic to near neutral. This could potentially induce the precipitation of Pb which was previously solubilised in the stomach phase. As such the single stomach phase extraction is regarded as being more conservative than a multiple phase extraction (Juhasz, 2016).

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Table 1 Overview of *in vitro* bioaccessibility methods

Abbreviation	Name	Metal(oids) tested	1,2 or 3 phase extraction	Extractant solution composition	Validated with *in vitro* results (Y or N)	pH	S:S	Temperature (°C)	Mixing	Reference
PBET	Physiologically based extraction test	Pb, As	Two phase	*Stomach:* Pepsin, citrate, malate, lactic acid, acetic acid *Intestinal:* Bile and pancreatin	Y	*Stomach:* 1.3 – 4.0 *Intestinal:* 7.0	1:100	37	Argon at 1.0 L/min	(Ruby et al., 1996)
UBM	Unified barge method	As, Cd, Pb	Three phase	Saliva: α-amylase,uric acid,mucin Stomach: BSA, pepsin, mucin *Intestinal:* BSA, pancreatin, lipase, bile	Y	*Saliva:* 6.5 *Stomach:* 1.07 *Intestinal:* 6.3	1:100	37	End-over-end (55rpm)	(Oomen et al., 2003)
RBALP	Relative bioaccessibility leaching procedure	Pb	Single phase	Glycine	Y	1.5	1:100	37	End-over-end (30rpm)	(Drexler and Brattin, 2007)
Table notes S:S = soil to extractant ratio										

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2.6.2 Pb species and particle size

The factors affecting bioavailability are shown in Figure 2 and described as follows.

Pb species

There are a wide range of Pb minerals found in the environment. Pyromorphite is a highly insoluble form of Pb across a wide pH range. Solubility constants (K_{sp}) of some common Pb minerals found in the environment are presented in Table 2 below. As such the IVBA of Pb depends upon its mineral form which is generally governed by its source. For example cerussite type minerals are commonly encountered in shooting range soils due to the chemical weathering of Pb shot (Sanderson et al., 2016).

Table 2 Solubility product of various Pb minerals

Pb species	Chemical Formula	Log K_{sp}
Pb sulphate	$PbSO_4$	-7.67
Cerussite	$PbCO_3$	-13.13
Galena	PbS	-26.77
Hydroxypyromorphite	$Pb_{10}(PO_4)_6(OH)_2$	-76.78
Chloropyromorphite	$Pb_{10}(PO_4)_6(Cl)_2$	-84.43

Particle size

Particle size plays an important role in IVBA Pb. The smaller the particle size, the more surface area available for reaction with the extractant. Commonly 250 μm is adopted as the particle size most likely to stick to the hands children and be incidentally ingested via hand-to-mouth activity (Oomen et al., 2003, Drexler and Brattin, 2007, Ruby et al., 1996)

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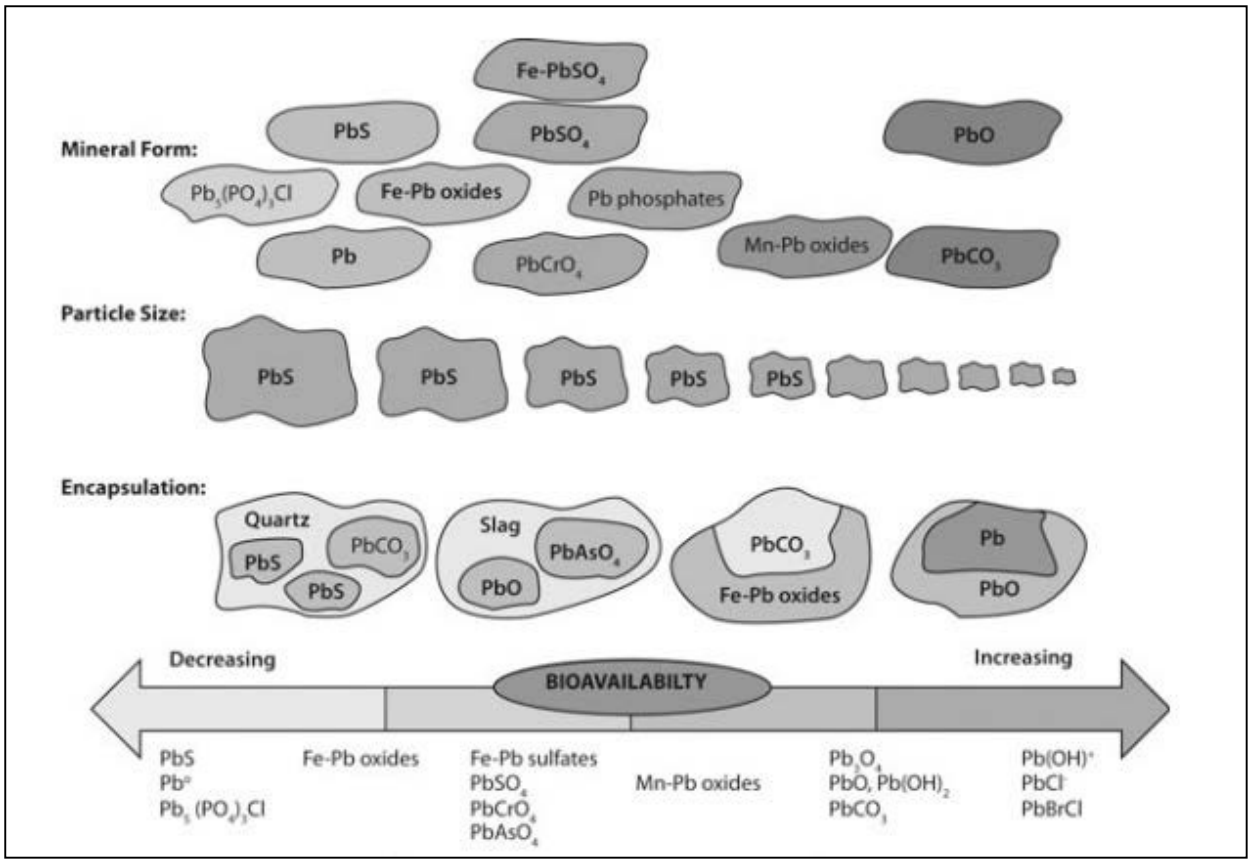
Figure 2 Factors effecting bioavailability of Pb (Ruby et al., 1999)



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2.7 Phosphorus lead chemistry

As discussed above, when Pb is ingested, the amount of Pb available for uptake in to the blood stream is generally governed by the mineral form and stomach pH (Hettiarachchi et al., 2001). Pb phosphates, which form by precipitation between Pb and phosphorus, are insoluble Pb minerals across a wide pH range (Nriagu, 1974). Common products of this reaction include fluropyromorphite, chloropyromorphite and hydroxypyromorphite. This group of Pb phosphate minerals is commonly referred to as pyromorphites. The reaction between Pb and phosphate is commonly used in drinking water distribution systems constructed with Pb pipes i.e the water supply is dosed with phosphate in aim of precipitating any Pb encountered at the point of use (Schock, 1989). Nriagu (1974) first proposed that this reaction could provide utility. Subsequently, a significant body of literature has been generated to demonstrate that this reaction can be used to immobilize Pb in soil (Cotter-Howells, 1996, Cotter-Howells and Caporn, 1996, Hettiarachchi et al., 2001, Moseley et al., 2008, Arnich et al., 2003, Melamed et al., 2003, Scheckel and Ryan, 2004). The primary mechanism of phosphorus-induced Pb immobilization is via precipitation as pyromorphite (Laperche et al., 1996).

Importantly, the form of orthophosphate governs the amount which is available for the pyromorphite reaction. This is the same form of phosphate which is available to for uptake by plants. Broadly, phosphate fertilizers can be grouped as fast release if labile P can be readily solubilised by water and slow release if labile P cannot be readily solubilised by water (Bolan et al., 2003). The solubility of the P and Pb forms along with system pH are the two main factors which govern the kinetics of the precipitation reaction.

There are three phases of P in soils, as per the generalised P cycle:

Soil solution P $\leftrightarrow$ Labile P $\leftrightarrow$ Non-labile P (Scheckel et al., 2013)

The soil solution P is influenced by soil pH; phosphoric acid (H_3PO_4) will dominate at pH < 2.1 dihydrogen phosphate (H_2PO_4) at 2.12 < pH > 7.21; and monohydrogen phosphate (HPO_4) at pH > 7.21 (Brown et al., 2004)

For example, calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$), calcium monohydrogen phosphate ($CaHPO_4$) and tricalcium phosphate ($Ca_3(PO_4)_2$) have solubilities (Log K_{sp}) of -1.14, -6.6 and -24.0 respectively. Of these, $CaHPO_4$ is present in fast release phosphate fertilizers and when added to soil, dissolution occurs to form the less soluble $Ca(H_2PO_4)_2$ where phosphoric acid is released close to the fertilizer granules (Kunhikrishnan et al., 2015). The system pH is lowered as a result. For slow release phosphates, for example, hydroxyapatite ($Ca_{10}(CaPO_4)_6(OH)_2$) acidic conditions are required for dissolution, which occurs according to the equation below. Once in this form, precipitation reactions proceed as per fast release P pathway (Mavropoulos et al., 2004) as shown below.

$Ca_{10}(CaPO_4)_6(OH)_2$ (s) $+14H^+$ (aq) $\rightarrow$ $10Ca^{2+}$ (aq) + $6H_2PO_4$ (aq) $+2H_2O$

The form of Pb is also influenced by soil pH whereby the solubilisation of Pb to Pb^{2+} is increased at low pH. However, Zhang and Ryan (1998) showed that anglesite ($PbSO_4$) solubility was independent of pH (pH 2 – 7) in the presence of hydroxyapatite (HA). Therefore, the solubility of HA could be considered the rate limiting step during precipitation out as pyromorphite. At pH 2 HA was solubilised rapidly, though precipitation as pyromorphite was favoured at pH 4 and 5.

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P amendments can be used for the purpose of in-situ remediation by changing Pb to an insoluble form. By increasing labile and solution P phases in the presence of soluble Pb, the precipitation of pyromorphite minerals (log K_{sp} < -25.75) (Kunhikrishnan et al., 2015) occurs rapidly, being thermodynamically and kinetically favoured. In the case of insoluble phosphate sources, a slightly acidic (pH ~5) is required to optimize the dissolution of Pb minerals and phosphate (Chrysochoou et al., 2007). Following the dissolution of hydroxyapatite, the formation of pyromorphite occurs according as follows (Kunhikrishnan et al., 2015):

$10Pb^{2+}$ (aq) + $6H_2PO_4^-$ (aq) + $2H_2O \rightarrow Pb_{10}(PO_4)_6(OH)_2$ (s)

$Ca_{10}(PO_4)_6(OH)_2$ (s) + $xPb^{2+} \rightarrow (Ca_{10-x}Pb_x)(PO_4)_6(OH)_2$ (s) + xCa^{2+}

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2.8 Managing the risk posed by Pb in soil by reducing bioaccessibility

2.8.1 Suitability of IVBA as a measure of remediation performance

There is a gap in current knowledge as there is no *in vitro* bioaccessibility test which has been validated for use on P amended soils. As an example Ryan et al. (2004) added P at rates of 0.5 and 1% to Pb contaminated soil (2300 mg Pb/kg soil), comparing the results of *in vitro* bioaccessibility tests (Drexler and Brattin, 2007) to results from an *in vivo* study in swine. The treatment reduced the bioavailable Pb available in swine; although the *in vitro* test failed to predict this. A similar discrepancy was observed in Mele et al. (2015) who suggested that low pH used the *in vitro* test could facilitate the formation of pyromorphite which questions the validity of using of *in vitro* tests to measure changes in IVBA Pb following amendment with P based treatments. In contrast, Barnett et al. (2011) tested the formation of pyromorphite during the in vitro test at pH 2.3 and observed negligible precipitation of Pb from solution.

Importantly, whilst recognising the limitations of using IBVA Pb tests in this way, Scheckel et al. (2005) pointed out that the formation of pyromorphite occurs in the stomach and ultimately lowers bioaccessibility. Hence, the outcome of remediation in reality would be similar.

2.8.2 Quantitative Pb speciation using x-ray absorption spectroscopy

The basis of this approach to remediation is in adding an amendment to shift the speciation of Pb to a more insoluble, hence, less bioaccessible form. Commonly available analytical techniques are inadequate in accurately determining, quantitatively, Pb speciation (Scheckel and Ryan, 2004). One analytical technique appropriate for this type of analysis is x-ray absorption spectroscopy (XAS) (Scheckel and Ryan, 2004). XAS can be used to overcome the drawbacks of using *in vitro* tests by attributing reductions in bioaccessibility to the application of a P amendment (Scheckel and Ryan, 2004). It has been used in many instances as an accurate and reliable way of quantitatively measuring Pb speciation in P amendment studies (Moon et al., 2013a, Moseley et al., 2008, Pingitore et al., 2009, Sanderson et al., 2015, Scheckel and Ryan, 2004, Scheckel and Ryan, 2003).

2.9 Using biochar as a way to remediate Pb contaminated soil

Pyrogenic carbon is found in archaeological digs that are hundreds of years old and was used by cultures living in the Amazon area to improve the quality of agricultural lands. These soils are known as "Terra Preta" soils, and they remain stable to the present (Lehmann and Joseph, 2015). The modern counterpart of this approach is to produce biochar, an engineered product of biomass heated in the absence of oxygen (pyrolysis). Biochar has garnered attention as a way to manage waste, sequester carbon, amend soil and control pollution. The intended end use of a biochar governs the choice of feedstock and the heating conditions used.

Biochar has been used in many instances to remediate metal polluted soils (Paz-Ferreiro, 2014), including Pb. Much of the research conducted in Pb polluted soils with biochar has been done at shooting ranges, where co-contamination with other metals, including tin and copper occur (Ahmad et al., 2014, Moon et al., 2013b). As an example, Ahmad et al. (2014) found the organic bound Pb transformed into the more stable Pb-phosphate following amendment with oak biochar. Moon et al. (2013b) applied different concentrations of a soybean stover (forage including stems and leaves) derived biochar to a shooting range soil. They found a reduction of over 90% in Pb leachability at the highest dose of amendment (20% biochar). Pb was immobilized as a consequence of a shift in its speciation. In particular, Pb precipitated as Pb hydroxide as a consequence of an increase in soil pH and was transformed into chloropyromorphite, one of the most stable Pb compounds in soil. Park et al. (2011) compared the performance of two biochars, derived from greenwaste and from manure, on Pb immobilization, monitoring NH_4NO_3 extractable metal concentration. They found chicken-manure biochar to be more effective, with a reduction of 93.5% in the concentration of extractable Pb when compared to the control (polluted soil). The temperature of pyrolysis is one of the main drivers in its ability to immobilize Pb. Uchimiya et al. (2012) found chicken litter biochar prepared at low temperatures to immobilize larger amounts of Pb than biochars prepared at higher temperatures. This was attributed to a change in soluble phosphorus concentration.

In spite of some positive results, and a promising prospect for biochar in the abovementioned contexts, studies are lacking concerning Pb immobilization by biochar in an urban setting. As mentioned before, most of the studies have been conducted in shooting ranges, where Pb is primarily in the form of hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), cerussite ($PbCO_3$) and massicot (PbO) (Hardison Jr et al., 2004).

Considering the important role of phosphorus in Pb immobilization, ash-rich biochars are prime candidates for Pb immobilization in polluted urban landscapes. Ash-rich biochars, as those prepared from manures have moderately high phosphorus contents when compared to other biochars. As an example, Cely et al. (2015) analyzed biochars prepared from different manures and found phosphorus contents ranging from 1.8 to 3.6 g kg^{-1}, an amount of phosphorus comparable to that in the feedstock. Alternatively, biochars prepared from other waste materials could be used to recover phosphorus from wastewater effluent (Shepherd et al., 2016) and then applied to the land. The potential for eutrophication of nearby surface waters from excess phosphorus runoff is another drawback of using traditional phosphates, a risk averted by using ash-rich biochars which act as a slow-release fertilizer (Wang et al., 2014).

As waste streams, poultry litter and biosolids are often problematic to manage. For example the application of raw biosolids to the land can lead to nitrate leaching (Correa et al., 2006), whilst the

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application of raw poultry litter has resulted in eutrophication episodes due to excess P leaching (Kemp et al., 2005). Together with an effective solid waste management strategy, as a means to manage and remediate Pb contaminated soil, biochar would bring further environmental improvements associated with carbon sequestration. On the other hand, biochar can contain PAHs and low concentrations of metals, but with thoughtful choice of feedstock this issue can be minimized or avoided. Moreover, the availability of metals tends to be less than in the feedstock (Paz-Ferreiro et al., 2014b).

2.10 Effects on soil quality

2.10.1 Soil enzymes

The application of biochar to the land has been shown to improve soil health in many instances (Paz-Ferreiro and Fu, 2016). The use of biological indices to evaluate soil quality is an approach is being used more commonly in recent years (Paz-Ferreiro and Fu, 2016), one such index involves the measurement of the activitiy of soil enzymes which respond rapidly to changes in land management, for example the addition of an amendment. In terms of contamination remediation, there is a lack of previous studies aiming to assess the effect on soil quality of adding conventional phosphorus amendments compared with P rich biochars.

2.10.2 Excess P leaching

Studies highlighting the drawbacks of using phosphorus to immobilise Pb in contaminated soil cite the runoff or leaching of excess P as a poor environmental outcome associated with this remediation method (Chrysochoou et al. 2007). It is important to examine the potential for excess P leaching following the addition of biochar to remediate Pb contaminated soils as this will impact the feasibility of deploying this approach in the field.

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2.11 Research overview

In this study biochars were produced from poultry litter and biosolids across a range of pyrolysis temperatures. The biochars were characterised before being tested for their ability to reduce IVBA Pb compared with two conventional phosphorus options. XAS was used to quantitatively reveal the pre-treatment form of Pb in soil and also to reveal any changes in Pb speciation following treatment with the biochars and conventional phosphorus options. Finally the activity of various soil enzymes was measured to calculate a soil quality index following treatment and Olsen P was measured to understand if any of the treatments had the potential to result in excess P, which would be a poor environmental outcome.

2.11.1 Research questions

- Can P rich biochar be used as a source of phosphorus to immobilise Pb in soil?
    - How does the performance of biochar for this purpose compare to conventional amendments?
    - What are the potential negative side effects of the use of biochar for remediation in terms of soil quality impacts using two indicators: Soil enzymatic activity?
    - Olsen P?

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2.11 References

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3.0 Phosphorus-rich biochars can transform lead in an urban contaminated soil

This chapter was written in the form of a manuscript which has been submitted to the Journal of Quality and at the time of writing this thesis was under review following revisions. A copy of the submitted manuscript is attached as Appendix A.

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3.1 Abstract

Transformation of soil lead to pyromorphites and phosphates has the potential to be an effective strategy to immobilize this contaminant *in situ*. Soil treatment using monocalcium phosphate, NTS Softrock and biochars prepared from poultry litter and from biosolids at three different temperatures (300, 400 and 500 C) and two doses (1% and 3%) were evaluated. Lead bioaccesibility, mobility and solid speciation were measured. Leachable lead (Toxicity Characterised Leaching Procedure) was not significantly ($P>0.05$) changed after biochar addition, but a significant decrease in bioaccesible lead was found for several treatments ($P<0.05$). This was particularly notable for treatments receiving biosolids prepared at 400 and at 500 °C or monocalcium phosphate at the 3% dose. Decrease in bioaccesible lead concentration in the biochar treatments were similar to in traditional phosphate amendments. Our research found transformation of lead species to the more stable pyromorphite and Pb-phosphate to be partially responsible for the observed changes, although other mechanisms, including pH changes might also play an important role. Overall, pyrolysis was an effective method to upgrade waste streams and facilitate lead immobilization in contaminated soils, although key pyrolysis parameters need to be selected carefully.

Keywords: Lead; immobilization; biochar; poultry litter; biosolids

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3.2 Introduction

Lead (Pb) contamination is almost ubiquitous amongst urban soils around the world. This is due to historical use of Pb in car batteries, ammunition, special glass, radiation protection, construction elements or as additives petrol and paint, as well as from point source industrial activities. Legacy contamination remains and soil Pb persists as a threat to human health (Mushak, 2011), particularly children, as they are more likely to ingest soil. Once ingested, Pb travels down the gastrointestinal tract and, if solubilised, may be absorbed in to the blood stream. Recently (in 2012), the US Centers for Disease Control and Prevention declared that there is no safe concentration of Pb in blood, abandoning the previously designated "level of concern". To this end, continued and concerted effort is required to address the issue of urban soils that are historically contaminated with Pb.

Currently there are a wide range of solutions available for remediating soils contaminated with Pb. These solutions aim at risk-based remediation; comprising dig-and-dump, in-situ chemical immobilisation, phytocapping and soil/asphalt capping amongst others (Laidlaw et al., 2017). Excavating a soil in dense urban communities is expensive and technically challenging. In recent years, in-situ chemical immobilisation of Pb in soil has been suggested as the best management practice to remediate shooting range soils which are often heavily impacted by Pb (Chrysochoou et al., 2007). The process involves applying a phosphate-based amendment to the soil with the aim of shifting Pb to a more insoluble, less bioaccessible, and hence, lower risk form (Henry et al., 2015). The goal of remediating soils using in-situ chemical immobilisation is to transform Pb in to pyromorphite, which is an insoluble form of Pb across a wide range of environmental conditions. Previously, many different sources of phosphate have been tested as candidates for Pb remediation and a number of authors have consolidated these options in the form of review articles (Hettiarachchi and Pierzynski, 2004, Miretzky and Fernandez-Cirelli, 2008, Scheckel et al., 2013, Henry et al., 2015). Broadly, these phosphate sources can be grouped as fast release (if labile P can be readily solubilised by water) or slow release (if labile P cannot be readily solubilised by water) (Bolan et al., 2003).

There are some concerns surrounding the long-term feasibility of phosphate amendments for Pb remediation of soil (Laidlaw et al., 2017, Henry et al., 2015, Chrysochoou et al., 2007). Phosphorus is a valuable element for agriculture and peak phosphorus has been predicted to occur as soon as 2030 (Cordell et al., 2009). Thus, several authors (see for example Chrysochoou et al. (2007)) have advocated for the use of phosphorus containing wastes as a promising solution compared to mined or manufactured phosphates. In many cases though, excess phosphorus leaching has been cited as a poor environmental outcome in Pb immobilisation studies (Chrysochoou et al., 2007, Dermatas et al., 2008), which could be avoided by using slow release P. .Biochar is the solid product of biomass pyrolysis, which involves heating biomass in an environment with little to no oxygen. The characteristics of a biochar mostly depend upon the heating regime and the properties of the feedstock biomass (Basu, 2010). With this in mind, biochars can be engineered for a specific application or end-use. Biochars could provide some other ecosystem services when applied in land remediation, including carbon sequestration (Gascó et al., 2016) and an improvement in soil microbial activity (Benavente et al., 2018), which could pose an advantage over phosphate-based amendments. An increasing number of studies have highlighted biochar as a way to capture and recycle phosphorus from biogenic wastes (Roberts et al., 2017, Wang et al., 2014, Cely et al., 2015, Shepherd et al., 2016) and to remediate heavy metal polluted soils (Kosolsaksakul et al., 2018;

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Shahbaz et al., 2018). However, biochar has only been used in few instances in the remediation of Pb contaminated soils (Yang et al., 2016, Rajapaksha et al., 2015, Moon et al., 2013b, Uchimiya et al., 2012, Cao et al., 2011), though none of these studies have tackled the challenge of remediating urban soils, instead focussing on shooting range soils that tend to be much more polluted than urban soils. For example, in shooting range soils Pb has been detected at concentrations exceeding 15000 mg kg^{-1} (Rajapaksha et al., 2015, Hashimoto et al., 2009), whilst in contaminated urban soils, Pb tends to be lower than 4000 mg kg^{-1} (Brown et al., 2003, Smith et al., 2011, Yang and Mosby, 2006). Moreover, there is a lack of studies that have tested the efficacy of phosphorus-rich biochars, which is surprising given the important role of P in the immobilisation of Pb. For example, Moon et al. (2004) tested a soybean stover biochar, while Rizwan et al. (2016) utilised a rice straw biochar for Pb remediation. Phosphorus contained within biochar tends to behave as a slow release fertilizer (Wang et al., 2014), an important characteristic with consideration to its long term feasibility for use in remediation of Pb contaminated soils (Laidlaw et al., 2017).

Most biochars have an alkaline pH (Dai et al., 2018), which is one of the factors underlying the ability of biochar to immobilise heavy metals. However, it is possible to produce acidic and neutral biochars. The former have usually been neglected in remediation studies even though recent work has demonstrated that acidic biochars are effective in the immobilisation of Cd, particularly in soils with a low adsorption capacity (Qi et al., 2018). To our knowledge, equivalent studies for Pb are not available in the literature. Moreover, Pb-P reaction kinetics are promoted under acidic soil conditions (Dermatas et al., 2008) and therefore applying an acidic biochar could favour the formation of phosphates and pyromorphites.

Taking into account the abovementioned considerations, in this study we prepared P-rich biochars from two different feedstocks and at three different temperatures, with the aim of testing biochar´s and conventional P sources (slow and fast release P) ability to immobilise Pb. We hypothesized that pyrolysis would result in the production of cost-effective biochars that would be suitable substitutes for the phosphate-based materials typically used in the remediation of urban contaminated Pb. We also hypothesized that acidic biosolids biochar would outperform alkaline poultry litter biochar due to intrinsic differences in pH.

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3.3 Materials and methods

3.3.1 Soil

This study used a soil from an anonymous contaminated site in urban Victoria. Historically the site was used for blacksmithing with uncontrolled filling at the site known to have occurred. The site was underlain by fluvial sediments comprising silt, sand and gravel. Mean annual temperature and rainfall at the site are 20ºC and 800 mm, respectively. Moist soil was disaggregated and sieved to 2 mm before being mixed thoroughly. A subsample of the bulk soil (2kg) was collected and dried for soil characterisation purposes as follows. pH and EC were measured in 1:25 soil:H_2O extract after shaking for 1 hour. Soil texture was determined by laser diffraction using a Malvern Mastersizer 3000. Soil organic matter was estimated by the loss on ignition method based on sample weight loss upon heating to 375°C. For pseudo-total metals, the soil was digested with 3:1 HCl:HNO_3 before dilution and analysis by ICP-MS for Al, As, Cd, Cu, Sb, Se, Pb and Zn. Whilst Ca, Fe, K, Mg and Mn was determined by MP-AES (USEPA, 1994). The cation exchange capacity was determined by extraction with NH_4OAc/HOAc at pH 7.0, following the method of Sumner and Miller (1996). The moisture content of the soil was determined gravimetrically. For maximum water holding capacity, a subsample of the oven dried soil was saturated with water and allowed to drain. Maximum water holding capacity (WHC) was calculated as the ratio of water in the saturated soil to the dry soil weight.

3.3.2 Biochar

Poultry litter (PL) (approximately 12 kg) was collected from a stockpile after one week of stockpiling at poultry farm in Anakie, Victoria (37°57'18.36"S and 144°18'8.09"E). The feedstock was dried in an oven at 70°C for 48 hours, ground using a mortar and pestle and then sieved to <2mm. Biosolids (BS) were produced from Pakenham Water Treatment Plant (38°07’46”, 145°29’15”) where they have been stockpiled for three years before being transferred to Bald Hill Farm (38° 6'3.61"S and 145°30'3.10"E). From there around 3kg of biosolids were collected for the purposes of this study. Later, the BS were dried and crushed before sieving to <2mm. Biochar was produced by packing the feedstock into an air tight vessel. The vessel was placed in to a muffle furnace and heated at 10°C min^{-1} to pre-determined pyrolysis temperatures of 300, 400 and 500°C. Once reached, the target temperature was held for 2hours, after which the heating ceased and the vessel was removed and allowed to cool to room temperature. Six different biochars were produced using two feedstocks and three pyrolysis temperatures: PL300, PL400, PL500, BS300, BS400 and BS500.

Later, each biochar was characterised as follows. pH and EC were measured in 1:25 soil:H_2O extract after shaking for 1 hour. For heavy metals, biochars were digested with 3:1 HCl:HNO_3 before dilution and analysis by ICP for Al, As, Cd, Cu, Sb, Se, Pb and Zn. Whilst Ca, Fe, K, Mg and Mn were determined by MP-AES (USEPA, 1994). P was determined as per Hanson (1950). The cation exchange capacity was determined by extraction with NH_4OAc/HOAc at pH 7.0 (Sumner and Miller, 1996). Thermogravimetric analysis (PerkinElmer TGA 4000) was used to determine moisture, ash and volatile matter content. Samples were heated at 20°C min^{-1} to 600°C in an N_2 atmosphere which was purged at a rate of 40 mL min^{-1} At 600°C. The purge gas was switched to air, purging at 20 mL min^{-1}, until a constant weight was reached. Moisture was determined by the weight loss at 105°C, volatile

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matter at 600°C and ash as the constant weight remaining at the end. Fixed C was calculated by subtracting the sum of moisture, volatile matter and ash from 100%. BET surface area BET SA) was measured by nitrogen adsorption using an ASAP 2400 (Micrometrics) at 77K after degassing at 200°C. C, H and N content in the biochars were determined by dry combustion using a Perkin Elmer 2400 Series II Elemental Analyser.

3.3.3 Incubation experiment

The sieved soil was separated in to 250mL polyethylene jars with each jar containing 300g of soil. The control was the polluted, untreated soil. The treatments (PL300, PL400, PL500, BS300, BS400, BS500, monocalcium phosphate (MCP)(Sigma-Aldrich) and NTS Softrock™ (NTS) (nutri-tech.com.au) were added to the jars at two treatment rates (1 and 3% w/w). The higher dose was selected to ensure that the P to Pb ratio satisfied the pyromorphite stoichiometry (0.6) for all treatments, while the lower dose represented a P to Pb ratio lower than 0.6 for the biochars (see Table 3). Monocalcium phosphate [$Ca(H_2PO_4)_2$] addition to soil can effectively transform various Pb minerals into insoluble chloropyromorphite, although the process is greatly dependent on pH (Cao et al., 2008). NTS softrock is a dicalcium phosphate [$CaHPO_4$] based material. Dicalcium phosphate has been successfully used in the immobilization of Pb in soil (Theodoratos et al., 2002). The jars were made up to 60%WHC using ultrapure water (18 MΩ.cm) and this moisture was reinstated every two days by the addition of ultrapure water.

Treatments were coded according to the material added to the soil (PL, BS, MCP or NTS), followed by the temperature of preparation (for biochars only, 300, 400 or 500 °C) and the dose (1 or 3). For example, PL500-3 would indicate a 3 % addition of poultry litter biochar prepared at 500°C. Each of the seventeen was replicated four times. After three months of incubation, a subsample (around 10g) was collected from each jar and air dried at 40° for 72 hours.

3.3.4 In vitro bioaccessibility

In vitro bioaccessible Pb testing was carried out according to USEPA (2008). The dried subsample was sieved to 250µm. This is the fraction considered to represent an exposure pathway to children (USEPA, 2008). The extracting solution consisted of 0.4 M glycine ($C_2H_5NO_2$). The glycine solution was heated to 37°C and adjusted to pH 1.5 using concentrated, trace metal grade HCl. The solution was made up to 1.0L and the pH was again adjusted to pH 1.5 with commercial HCl.

The heated extracting solution (100±1.0mL) was added to 1g of <250µm soil in a 125mL High Density Polyethylene (HDPE) bottle and shaken for 1 hour, end-over-end at 37±2°C. A 40mL aliquot of supernatant was withdrawn from the bottle using a luerlock syringe and filtered through a 0.45µm cellulose acetate filter. Pb in the filtered extract was determined using MP-AES (Agilent Technologies) and the bioaccessibility was calculated using the following equation:

$$In\ vitro\ bioaccessibility\ (\%) = \frac{in\ vitro\ bioaccessible\ Pb\ (mg\ kg^{-1})}{Pb\ in\ soil\ (mg\ kg^{-1})} \times 100$$

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3.3.5 Toxicity Characteristic Leaching Procedure (TCLP)

TCLP was carried out by a NATA accredited commercial laboratory according to USEPA (1992). The extractant used (pH 5.0) was selected based on the pH of the untreated control soil post incubation. One gram of soil was extracted with 20 mL of extractant (prepared by adding 5.7 mL of glacial acetic acid into 1 L of milli-Q water) for 18 hours. Following extraction, the solution was tested for Pb by ICP-AES.

3.3.6 X-Ray absorption near edge structure (XANES)

XANES spectroscopy was conducted in order to investigate the speciation of Pb in the control and the treatments. Data were collected on the X-ray Absorption Spectroscopy (XAS) beamline at the Australian Synchrotron, ANSTO, Clayton Victoria. The crushed and sieved (<250μm) soils were mounted on to Poly(methyl methacrylate) sample holders and sealed with Kapton tape.

Pyromorphite (produced as per (Ryan et al., 2001), PbO (Sigma-Aldrich) and $PbHPO_4$ (Sigma-Aldrich) were included as Pb mineral standards collected at the XAS beamline. Additional Pb mineral standards utilized for linear combination fitting (LCF) are described in Obrycki et al. (2016). The experiment was conducted at room temperature in fluorescence mode with beam energy of 3 GeV and current 200 mA. Once tuned to the Pb (13,035 eV) L_{III}, fluorescence was detected using a 100-element detector. Data analysis was conducted using Athena software (Ravel and Newville, 2005). Triplicate scans for each sample were merged, normalized, and converted into k-space. Linear combination fitting was used to identify Pb speciation in the samples. Linear combination fits (−30 to +70 eV relative to the calibration energy) were performed using XAS normalized and derivative □(Ⓔ) spectra from reference standards to identify Pb phases in the soil samples. During the LCF, components were only allowed to contribute to the model if the sum-square error was reduced by 20% (Manceau et al., 2002). The □ is a measure of the mean square sum of misfit at each data point and describes the degree of uncertainty in the fitting process (Ravel, 2009). Linear combination fits are provided in Figure 3.

3.3.7 Statistical analysis

Statistical differences between treatments were calculated using SPSS version 18.0. A one-way ANOVA was conducted in order to see the various treatment effects. Means were considered to be significantly different when $P < 0.05$ using Tukey's test.

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3.4 Results and discussion

3.4.1 Soil characterisation

The soil was classified as a sandy loam, with 70 % sand, 28 % silt and 2 % clay content (see Table 4). The soil pH was 4.9±0.1 and the CEC value 16.1±0.1 cmol/kg. The soil was polluted with a total concentration of 3192±45 mg/kg Pb, which is 10 times over the human health investigation level set in the National Environmental Protection Measure for managing contaminated sites in Australia (300 mg/kg) (NEPC, 2013). Cd, As and Sb were not found at detectable levels in the soil whilst Zn and Cu were present well below the respective health investigation levels, specifically 117 ±1 and 385±2 mg/kg respectively. As such, Pb was identified as the only contaminant of concern within the group of contaminants analysed for. The absence of co-contamination is an important factor when assessing phosphate immobilisation as a remediation strategy. Whilst the concentrations of Zn and Cu were not identified as contamination, these metals can also precipitate with P and so may compete with Pb for P and impede the formation of Pb phosphates (Ma et al., 1994).

3.4.2 Biochar characterisation

The PL biochars had an alkaline pH, that increased as the temperature of production increased in agreement with similar research by Song and Guo (2012). In comparison, the BS biochars were acidic but followed a similar trend of increasing pH with pyrolysis temperature. In both cases, cation exchange capacity was maximised at 400 °C production temperature. The BET surface area of PL300 was low (7.73 m^2 g^{-1}) compared to PL400 and PL500 (29.94 and 33.64 m^2 g^{-1} respectively). This could be due to the positioning of mineral rich ash within the pores of the biochar (Song and Guo, 2012), which may have been displaced as cellulose and hemicellulose decomposed between 300 and 400°C (Kim and Agblevor, 2007). A similar trend was observed in the work of Yuan et al. (2015) whereby the surface area of biochar from sewage sludge increased from 14.4 to 22.7 m^2 g^{-1} as the temperature increased from 300 to 400 °C before reaching a maximum of 26.70 m^2 g^{-1} at 700°C. The biosolids biochar BET surface area was less affected by pyrolysis temperature compared to the poultry litter biochar, specifically increasing from 21.6 m^2 g^{-1} to 25.3 m^2 g^{-1} as the temperature increased from 300 to 500°C.

Ash content was highest in BS500 (93.4±0.1 %) and decreased at lower pyrolysis temperatures (92.7±0.5 % and 91.1±0.8 % for BS400 and BS300 respectively). These results are similar compared to previous studies. For example, Chen et al. (2014) produced biochar from biosolids across a range of temperatures (500-900°C) and reported maximum ash content of 88.1±0.6% at 900 °C. Similarly in Oh et al. (2012) ash content was 90.7% in biochar produced from biosolids at 900 °C. In our study, the biosolids had been stored stockpiled for three years prior to being converted to biochar, and given the relatively low volatile matter content in the biochars, volatiles may have evaporated during stockpiling resulting in high ash content. The PL biochars had ash contents of 58.7±0.8 %, 62.1±0.5 % and 66.5 ± 4.2 % for PL300, PL400 and PL500 respectively. These results are in agreement with Song and Guo (2012) who reported ash contents of 47.8±0.1 %, 56.6±0.3 % and 60.6±0.1 % for biochars produced from PL at 300, 400 and 500°C respectively. In all cases, volatile matter content was reduced as the temperature of production increased which coincided with a decrease in yield, indicating that more volatile compounds were driven off at higher temperatures.

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Results for C, H and N are shown in Table 4. As the temperature of production increased from 300 to 500 °C, C content decreased from 32.3±4.4% to 19.1±3.0% in the case of the PL biochars. The C content in the BS biochars was similarly affected, specifically decreasing from 4.4±1.6 % to 2.7± 0.1% for PL300 and PL500 respectively. In agreement with Zhang et al. (2015), this trend was common to the H and N contents.

The PL500 treatment had the highest total P content amongst the biochars, which decreased at lower pyrolysis temperatures. This trend was also observed in the BS biochars, though there was around half as much P compared to the PL biochars. As expected, for both feedstocks, biochar yield decreased as temperature increased. This is because more organic matter is volatilised at higher temperatures and so less volatile material i.e. minerals and most metals are increasingly enriched. Here the data showed that all minerals (P, Ca, K, Mg and Na) became enriched as the pyrolysis temperature increased. This was also the case for heavy metals (As, Cd, Cu, Pb, Sb, Zn) in all of the biochars. The raw biosolids were previously precluded from unrestricted use due to the presence of Zn and Cu at concentrations above contaminant class one (C1) grade (EPA Victoria, 2004). Importantly, this classification was maintained after pyrolysis i.e. enrichment of heavy metals did not degrade the quality of the biosolids with respect to land application.

3.4.3 Bioaccesibility test

The Pb in the untreated control soil had an *in vitro* bioaccessibility of 86.9±10.6 %, which is at the upper end of values reported in previous Pb bioaccessibility studies involving urban soils. For example, Smith et al. (2011) tested peri-urban soils contaminated from a range of different sources (n=31) and found that on average Pb was 66.0 ± 24.3% bioaccessible. This varied according to the source of contamination, for example, Pb in soils contaminated from shooting range activities was 89.0±18.3% (n=9) bioaccessible, compared to those contaminated from mining/smelting activities, which were less bioaccessible (54.8±29.1 %, n=13), although two of the mining impacted soils had bioaccessibilities of >90%.

Several treatments (MCP-3, BS500-3, BS400-3, PL300-1, BS400-1, BS300-1, PL400-1, PL500-3) had a decreased IVBA Pb relative to the control; in the remaining treatments IVBA was not different to the control ($P<0.05$) (Figure 4). At the lower P application rate (1 %), most biochars treatments outperformed the MCP and NTS softrock treatments in decreasing IVBA Pb. The amount of IVBA Pb in soils receiving the phosphate treatments at a 1% dose did not differ from the control. For the lower (1%) P application rate, PL300 was the most effective, decreasing the IVBA to 62.7±5.7% compared to the untreated control (IVBA Pb 86.9±10.6%). As the temperature of pyrolysis increased, this decreasing effect on IVBA Pb was reduced, specifically in the PL400-1 treatment IVBA was 68.7±4.8%.

Given that pyrolysis temperature had a marginal effect on the characteristics of the BS biochars, it was expected that the effect of temperature on ability of these biochars to decrease IVBA Pb would be similarly marginal. As such, BS300-1 and BS400-1 had a similar effect on IVBA Pb, specifically decreasing it to 66.6±0.1% and 66.1±1.67%, respectively, compared to the control (Figure 4).

At the higher application rate, PL500-3 decreased IVBA Pb to 68.8 ± 11.3 %. The addition of poultry litter biochar increased soil pH by 0.8 pH units. Soluble P can be increased by the raise in pH observed after biochar addition (Lehmann et al. (2003). This effect can be attributed to a weakening

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of the ionic interactions in Al and Fe phosphates, which are insoluble forms of P. Furthermore, (DeLuca et al. (2012)) suggested that biochar could also influence available phosphate by inducing sorption of chelating organic molecules. By reducing soluble chelates, the effects of chelates on soluble phosphate could be diminished. In contrast to the lower application rate, pyrolysis temperature had an effect on the ability of BS biochars to reduce IVBA Pb when these biochars were applied at the higher application rate. Specifically, BS400-3 and BS500-3 decreased IVBA Pb to 62.1±8.0 % and 57.8±5.2%, respectively. Here soil pH was not expected to have had a notable impact on IVBA Pb, as post treatment soil pH was decreased by 0.2 pH units compared to the control in the case of both treatments ($p<0.05$).

At the higher application rate, MCP was most effective in decreasing IVBA, specifically to 45.8±7.6% compared to the untreated control. This value was not statistically significantly different from the one achieved by treatment BS500-3 ($P>0.05$). A similar treatment effect was observed by Brown et al. (2005) who applied MCP (2% w/w) to a soil contaminated by mine waste (Pb 5022 mg kg^{-1}), Pb bioaccessibility was lowered from 84.9 % pre-treatment to 31.6 % post-treatment. Dissolution of soil minerals is likely to occur within the acidic in vitro test, releasing sorbed Pb and P for subsequent precipitation to insoluble Pb phosphates. Further dissolution of soil minerals could be restricted as Pb phosphates are chemically stable at conditions within the in vitro test (Hettiarachchi et al., 2000).

Uchimiya et al. (2012) prepared P rich biochars from broiler litter at 350 and 750 °C and added them to a shooting range soil contaminated by Pb (19906 mg kg^{-1}) at treatment rates of 2, 5, 10 and 20 % (w/w). In their study, there was no decrease in IVBA Pb after treatment by biochar. However, the amount of Pb in their soil was more than one order of magnitude higher than in the present study thus the capacity of the biochar to immobilise Pb might have been exceeded in their work. Failure to reduce bioaccesible Pb was also found in studies using phosphorus-poor biochars (see for example, Rizwan et al., 2016).

3.4.4 Lead XANES

Our analyses indicate a transformation in Pb phosphorus species due to the addition of amendments containing P (Table 5). In the control soil, the amount of Pb adsorbed to soil minerals accounted for 57 % of Pb, while 35 % was adsorbed to organic matter and 8 % as PbO. Pyromorphyte formation, one of the most stable Pb species in soils, was only observed for the treatments NTS-3 and PL500-3. Pb-phosphate formation was observed following all treatments except BS400-1. Pb-phosphate formation was particularly high (23 %) for the treatment PL500-3. There was a clear trend to higher Pb-phosphate formation with higher temperature for PL, but not for BS. The amounts of Pb adsorbed to organic matter, a readily bioaccessible Pb form (Farshadirad et al., 2017), was reduced in several biochar treatments compared to the control. Specifically, the maximum reduction was achieved by the treatment PL500-3, where a readily bioaccessible Pb fraction constituted 17 % of the total Pb, compared to 35 % in the control.

The transformation of Pb to insoluble species under the BS treatments could be attributed to an increase in acidity in soils receiving this treatment (pH 4.9 ± 0.1) compared to the control soils (pH 5.2 ± <0.1) ($p<0.05$) whereby both more Pb and P were solubilised from the soil and biochar respectively. Once in solution, the creation of this new phase of Pb phosphate could have occurred by way of a precipitation reaction between Pb and P.

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Noticeably, BS400-1 did not induce the creation of any new Pb phases (Table 5), though a reduction in bioaccesible Pb was observed (Table 5). Possibly, a shift in speciation could have occurred in the in vitro extraction. Under this scenario insoluble P from the biochar may have been solubilised at the low pH used in the vitro test. In the presence of solution Pb, precipitation to an insoluble form is favourable (Geebelen et al., 2003). Here Juhasz et al. (2014) found that *in vivo* processes would have a similar effect to *in vitro* processes suggesting that the transformation to insoluble Pb species is not required to occur in situ and that ultimately the remediation outcome would not change

The amounts of phosphate-Pb formed in our study were substantial. For example, Moon et al. (2013) found no Pb-phosphate formation after addition of a biochar derived from soybean stover at a dose of 1 %. In their study, chloropyromorphyte only started forming at a dose of 5 %, higher than the one used in our study, while Pb-phosphate was only detected when a dose of 10 % biochar was added. These differences are most likely attributed to the higher P content in the biochars used in the present study, coupled with differences in the pH of the biochars.

3.3.5 Leachability

TCLP leachable Pb in the untreated control was 1.23 ± 0.32 mg/L (Table 6) which indicates that the pH of the extractant was only able to solubilise a small fraction of the total Pb in the soil. This is in contrast to the IVBA extractant which solubilised over 85% of total Pb in the soil. This is not surprising given the acidic pH of the control soil and thus in the field infiltration of rainfall in to the subsurface may have displaced leachable Pb further down the soil profile. Adding biochar and NTS treatments to the soil did not affect TCLP-Pb compared to the control ($P>0.05$). The treatment MCP-1 (fast release phosphate fertiliser) was able to decrease TCLP-Pb compared to the control ($P<0.05$) whereby leachable Pb was 0.20 ± 0.08 mg/L and less than the laboratory limit of reporting (0.01 mg/L) following treatment at a dose of 1 % and 3 %, respectively. Overall, the values of TCLP-Pb were below the critical value of 5 mg/L. Differences within treatments might have been mitigated by the strong buffer effect of the extracting solution used in the TCLP-test.

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3.5 Implications of our study and conclusions

Previous studies on Pb remediation using biochar have trialled a limited number of biochars, usually only one individual biochar (Ahmad et al., 2014; Rizwan et al., 2016). Moreover, these materials did not possess elevated amounts of phosphorus, which limited the formation of insoluble Pb species. For the first time, we synthesized a large number of biochars from two feedstocks and at three temperatures and compared them to traditional phosphate-based amendments for Pb remediation. Our initial hypothesis of phosphorus-rich biochars offering a potential to substitute phosphate-based amendments was confirmed. A diminishing of bioaccesible Pb, with an efficiency comparable to monocalcium phosphate, was quantified in various biochar treatments. This lower bioaccessible Pb was linked to the formation of pyromorphites and phosphates, which was verified by LCF-XANES for all treatments besides BS400-1.

Our hypothesis regarding a better performance of acidic biochars, due to the need of phosphorus and Pb to be in solution in order to react, was confirmed. Thus, the best performing biochars were acidic (BS400-3 and BS500-3). The amounts of Pb transformed to pyromorphite or phosphates tended to increase with temperature, a result which could be associated to higher phosphorus content in the biochars prepared at higher temperatures.

Phosphorus concentration in our biochars ranged from 1 % to 2.5 %. This was much lower than the 20 % P in monocalcium phosphate or the 9 % P in NTS Softrock. Thus, although not within the scope of the current study, it seems plausible that the significant secondary pollution caused by P leaching, which has been sometimes associated with Pb remediation using phosphate-based amendments (Dermatas et al., 2008), could be diminished by remediation of Pb contaminated soils using biochar.

Overall, our research has identified two waste streams that could be valorised towards the remediation of Pb contaminated soils. More importantly, it signals acidic biochars, a product which to date has found less applications than their alkaline counterparts, as more suitable for Pb remediation.

In spite of the significance of our results, important questions prevail, which could open an avenue for further research. A limitation of our study is that only one soil was considered. Initial Pb concentration and speciation, soil characteristics (pH, texture, mineralogy) and the presence of co-contaminants might limit the validity of our approach in other situations. Translation to the field might also be impacted by intrinsic differences between laboratory studies, with an optimal moisture content, and field studies where the diffusion of P and Pb into solution may be limited by soil moisture. More work should also be done to identify the mechanisms explaining the different interactions observed between the biochars and Pb. Thus, besides precipitation as insoluble phosphate forms, differences in cation exchange and intra-particle diffusion could contribute to explain the differences found among all biochars tested.

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Table 3 Amount of P added per treatment and molar P to Pb ratio

Sample	P added per treatment (mg)	P/Pb ratio (molar)
Control	0	0
PL300-1	60	0.42
PL400-1	79	0.49
PL500-1	75	0.53
BS300-1	32	0.22
BS400-1	34	0.23
BS500-1	34	0.24
NTS-1	255	1.8
MCP-1	765	5.3
PL300-3	180	1.25
PL400-3	211	1.47
PL500-3	227	1.58
BS300-3	95	0.66
BS400-3	101	0.70
BS500-3	103	0.71
NTS-3	765	13.3
MCP-3	1233	39.8

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Table 4 Soil and Biochar Characteristics

	Soil	PL300	PL400	PL500	BS300	BS400	BS500
Yield (%)		67.3±0.1	60.4±0.1	48.6±0.1	91.9±0.1	89.8±0.1	87.7±0.1
pH	4.9±0.1	8.4±0.1	9.7 ±0.1	10.3 ±0.1	5.4±0.1	5.2 ± 0.1	5.2 ±0.1
Moisture (%)		1.0±0.7	1.2±1.2	1.2±1.2	0.1±0.1	0.1 ±0.1	0.2±0.7
Volatile Matter (%)		23.2±0.7	13.4±0.1	7.2±0.3	5.7±0.5	4.3±0.1	3.4±0.1
Ash (%)		58.7±0.8	62.1±0.5	66.5 ± 4.2	91.1±0.8	92.7±0.5	93.4±0.1
Fixed C (%)		17.1±2.1	23.3±0.4	25.1±0.8	3.1±0.3	2.9±0.5	3.0±0.9
CEC (cmol/kg)	16.1±0.1	46.4±0.5	55.8± 0.1	54.1±0.7	34.5± 0.8	38.3±0.6	36.6± 0.5
BET ($m^2\ g^{-1}$)		7.73	29.94	33.64	21.63	24.61	25.32
C%		32.3±4.4	26.6±1.1	19.1±3.0	4.4±1.6	3.1± 0.4	2.7±0.1
H%		2.91±0.35	2.18±0.28	0.98±0.12	0.80±0.23	0.67±0.28	0.37±0.17
N%		2.93±0.27	2.40±0.06	1.62±0.24	2.40±0.06	1.96±0.61	1.66±0.32
P ($g\ kg^{-1}$)		19.99±0.65	23.40±0.28	25.18±0.57	10.56±0.44	11.18±0.18	11.39±0.12
Pb ($mg\ kg^{-1}$)	3192±45	5±1	6± 1	6±1	27±1	29±1	29±1
Cd ($mg\ kg^{-1}$)	<0.10	<0.10	<0.10	<0.10	0.49 ± 0.00	0.50±0.01	0.52±0.01
Sb ($mg\ kg^{-1}$)	0.03±0.02	0.11±0.02	0.15±0.03	0.21±0.01	0.36±0.01	0.39±0.01	0.41±0.01
As ($mg\ kg^{-1}$)	<0.10	6.0±0.4	6.6±0.4	8.0±1.8	3.4±0.1	3.8±0.1	4.0±0.1
Zn ($mg\ kg^{-1}$)	13± 2	473±11	512±6	589±20	356±4	359±4	371±8
Cu ($mg\ kg^{-1}$)	36±4	118±11	133±8	144± 8	165±11	167±20	169± 10
Fe ($g\ kg^{-1}$)	45.1±8.5	39.4±1.7	48.1±0.5	54.8± 3.0	43.0±0.4	43.4± 1.5	46.7± 1.0
Ca ($g\ kg^{-1}$)	7.3±0.6	5.2±0.2	5.4±0.4	6.2±0.1	4.5±0.1	5.1±0.1	5.6±0.3
K ($g\ kg^{-1}$)	19.3±2.8	15.3±0.1	16.4±0.1	18.1±0.2	1.3±0.1	1.3±0.1	1.7±0.1
Mg ($g\ kg^{-1}$)	3.0±0.7	7.8±0.3	9.7±0.2	10.3±0.2	2.9±0.1	3.0 ± 0.1	3.1±0.1
Na ($g\ kg^{-1}$)		7.2±0.1	7.7±0.1	8.9±0.1	1.9±0.1	2.0±0.1	2.2±0.1

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Figure 3 Results of linear combination fitting

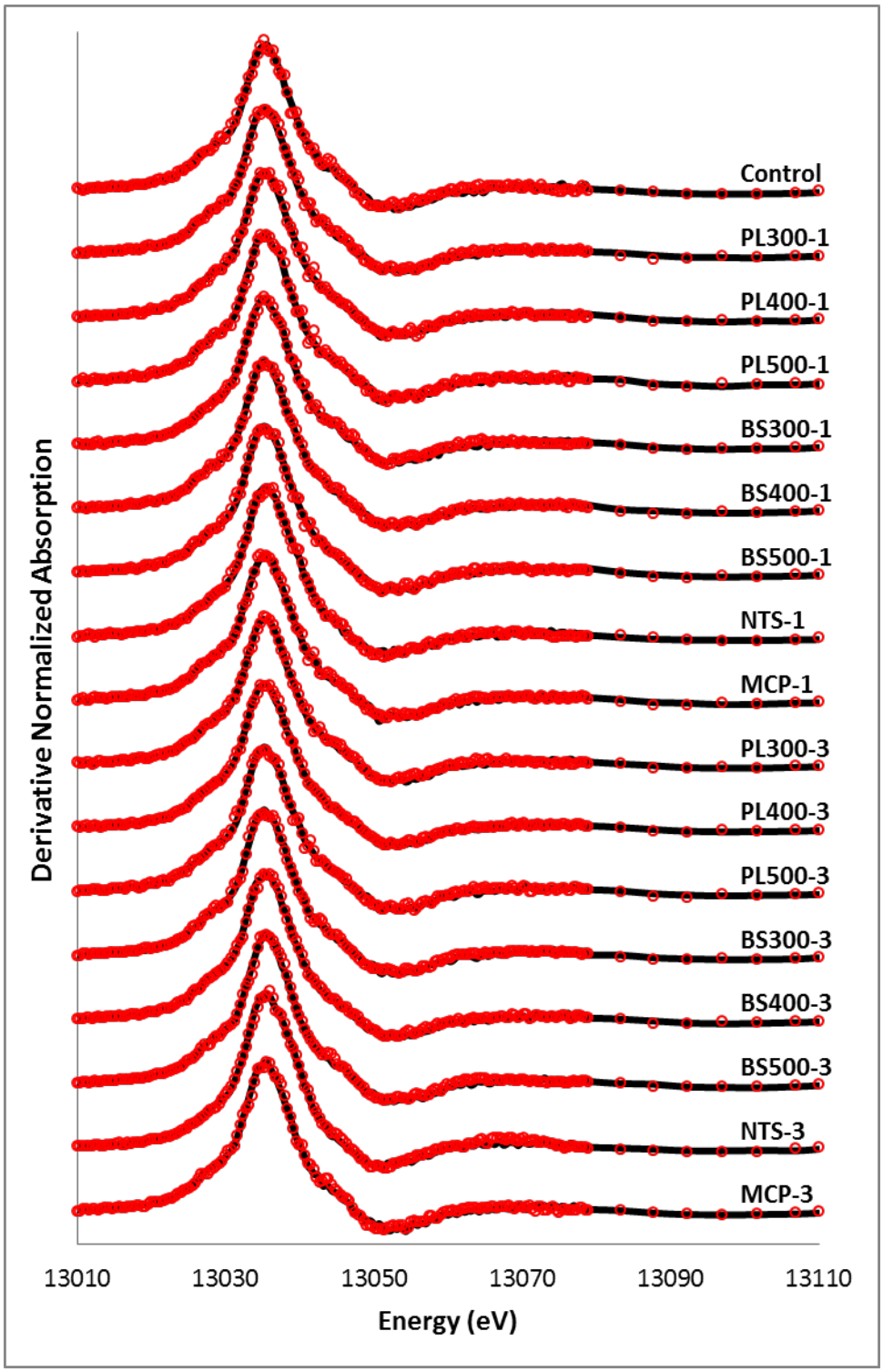

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Table 5 Proportions of Pb species treated and untreated soil as determined by linear combination fittings (LCF) on XANES

Sample	Pb Adsorbed Soil Minerals (%)	Pb Adsorbed Organic Matter (%)	PbO (%)	Pyromorphite (%)	Pb Phosphate (%)	$\square^2$
Control	57	35	8	0	0	0.0009
PL300-1	53	35	6	0	5	0.0009
PL400-1	62	27	4	0	7	0.0015
PL500-1	51	32	7	0	10	0.002
BS300-1	52	33	4	0	10	0.0016
BS400-1	53	39	8	0	0	0.0015
BS500-1	51	37	6	0	6	0.0009
NTS-1	65	33	0	0	3	0.0031
MCP-1	55	35	4	0	6	0.001
PL300-3	57	31	3	0	9	0.0011
PL400-3	60	26	3	0	11	0.0011
PL500-3	52	17	0	8	23	0.0009
BS300-3	56	29	8	0	7	0.0019
BS400-3	61	30	2	0	7	0.0014
BS500-3	60	22	9	0	10	0.0014
NTS-3	52	33	7	5	3	0.0007
MCP-3	57	25	0	0	18	0.0031

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Table 6 Results for the toxicity characteristics leaching procedure in the samples

Sample	TCLP (mg/L)
Control	1.23±0.32 a
PL300-1	0.93±0.10 a
PL400-1	0.95±0.06 a
PL500-1	1.10±0.12 a
BS300-1	1.08±0.14 a
BS400-1	1.05±0.10 a
BS500-1	1.20±0.22 a
NTS-1	1.23±0.26 a
MCP-1	0.20±0.08 b
PL300-3	0.93±0.05 a
PL400-3	0.95±0.24 a
PL500-3	1.10±0.36 a
BS300-3	1.20±0.14 a
BS400-3	1.30±0.42 a
BS500-3	1.05±0.19 a
NTS-3	1.20±0.29 a
MCP-3	0.10±0.01 b

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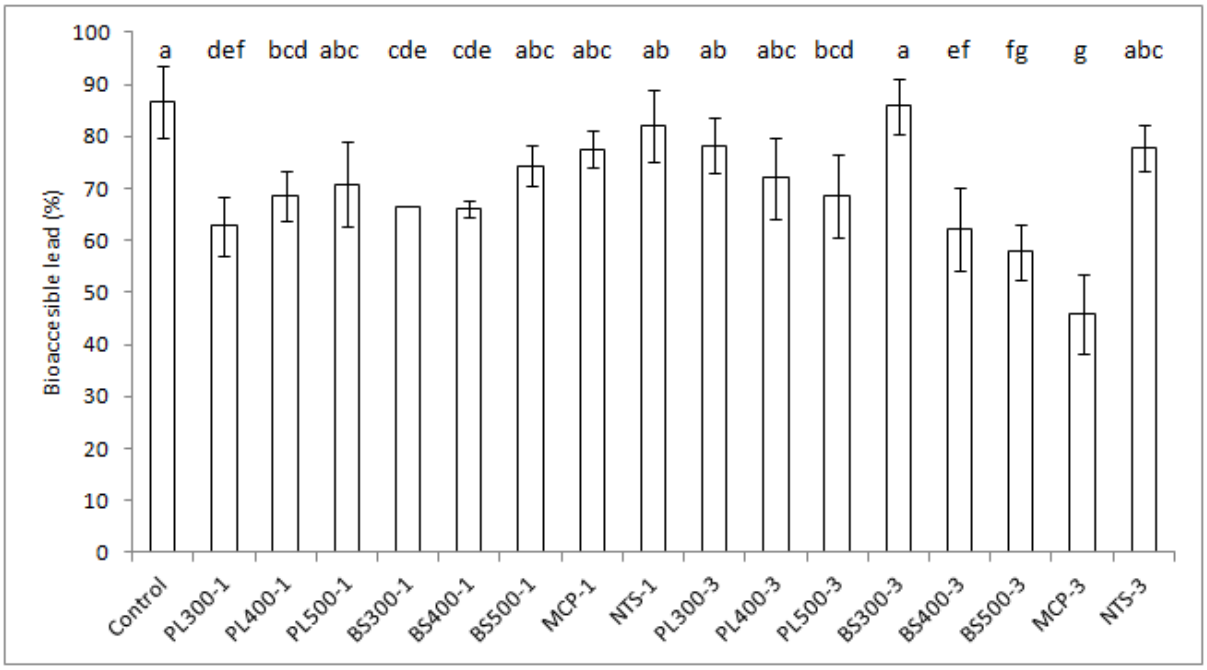
Figure 4 In vitro bioaccessibility (IVBA) of biochars produced from poultry litter and biosolids



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4.0 Using phosphorus rich biochars to remediate lead contaminated soil: influence on soil enzymes and extractable P

4.1 Introduction

The release and build-up of lead (Pb) in soil affects urban communities all over the world. Humans can be exposed to Pb by; eating food grown in impacted soils, inhaling Pb containing dust or by ingesting of impacted soils. The risks of Pb to human health have been well documented and the need to manage these risks remains ever present. Broadly, contamination risk mitigation strategies aim at breaking a source-pathway-receptor linkage. For example, dig and dump is a common approach involving the removal of the source of contamination by excavation and disposal at a landfill (Aschengrau et al., 1994, Goulet et al., 1996). The pathway linkage can be broken by introducing a barrier between contamination and the receptor, for example by capping the area with clean soil or geotextile (Aschengrau et al., 1997, Yang and Cattle, 2017). Finally, at the receptor, management controls can be introduced, for example by limiting urban agriculture in contaminated areas (Pelfrêne et al., 2018).

With the recent release of the International Standard for Soil Quality – Sustainable Remediation (ISO, 2017), a universal framework has been set out to guide the holistic remediation of contaminated soils to encompass economic, social and environmental dimensions. With respect to the remediation of Pb contaminated urban soils, dig and dump is unlikely to be viewed favourably. Moreover, the poor social outcomes of depriving residents from interacting with soils engaging in urban agriculture is apparent with Brown et al. (2016) suggesting that the positives far outweigh the negatives when it comes to gardening in contaminated urban environments. As such, the in-situ chemical immobilisation of Pb in soils is emerging as an attractive alternative (Henry et al., 2015). This approach involves treating the soil with amendments, usually phosphorus based, in aim of transforming the Pb into a less soluble form (Cao et al., 2003). That is, when ingested with soil the Pb may not be available for uptake in to the blood stream therefore the exposure pathway is limited.

Previously deployed amendments are generally mined or manufactured phosphorus, though in recent times the environmental drawbacks of using manufactured fertilisers relating to excess P leaching and soil acidification have been recognised (Kilgour et al., 2008, Dermatas et al., 2008, Chrysochoou et al., 2007). To this end, the use of biochar from biogenic waste sources of phosphorus is emerging as a promising alternative (refer to Chapter 3 of this thesis).

In view of the International Standard for Soil Quality – Sustainable Remediation (ISO, 2017) the effect of remediation on soil health is highlighted as an important metric of remediation performance. One indicator of soil health is the activity of soil enzymes involved in important soil processes, for example nutrient cycling and the mineralisation of organic matter. In this study, we measured the activity of soil enzymes following incubation with a range of phosphorus rich biochars and manufactured phosphorus amendments (both slow and fast release) added to a Pb contaminated soil. In a previous study it was shown that these biochars performed comparably with the conventional phosphorus amendments in reducing Pb bioaccessibility. In this study we examine the effects of these amendments on soil enzymes and available phosphorus. The activity of soil enzymes provides an early indication of the effects of management changes in soil quality (García-

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Ruiz et al., 2008). The use of biological indices to evaluate soil quality is an approach is being used more commonly in recent years (Paz-Ferreiro and Fu, 2016), in particular Gmea has been used in several instances as an early indication of changes in soil quality following the addition of an amendment (Paz-Ferreiro et al., 2012, García-Ruiz et al., 2008, Paz-Ferreiro et al., 2014a). The application of biochar to the land has been shown to improve soil health in many instances (Paz-Ferreiro and Fu, 2016). Consequently, we hypothesised that the feasibility of using biochar over manufactured amendments could be enhanced in view of ancillary environmental improvements.

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4.2 Materials and methods

4.2.1 Soil and biochar characterisation

The methods used to characterise the soil and biochar used in this experiment and a comprehensive discussion of the biochars' properties are described in Chapter 3 Section 3.3 and 3.4.

4.2.2 Incubation experiment

The sieved soil was separated in to 250mL polyethylene jars with each jar containing 300g of soil. The control was the polluted, untreated soil. The treatments (PL300, PL400, PL500, BS300, BS400, BS500, monocalcium phosphate (MCP)(Sigma-Aldrich) and NTS Softrock™ (NTS) (nutri-tech.com.au) were added to the jars at 1 w/w and the jars were made up to 60%WHC using ultrapure water (18 MΩ.cm); this moisture was reinstated every two days by the addition of ultrapure water. Each of the eight treatments plus the untreated control were replicated four times.

4.2.3 Soil enzyme assays

After three months of incubation, a subsample was collected and the activity of three soil enzymes were measured according to the same methods used by (Paz-Ferreiro et al., 2015). Briefly, the activity of these enzymes was determined by measuring the amount of p-nitrophenol released during enzymatic hydrolysis after incubation at 37°C. Acid phosphomonoesterase was determined according the method of Saá et al. (1993), using 16 mM p-nitrophenyl phosphate as substrate. β-Glucosidase activity was determined in the same was as phosphomonoesterase activity, though 25 mM p-nitrophenyl-β-d-glucopyranoside was used as the substrate (Eivazi and Tabatabai 1988). Arylsulphatase activity was determined after incubating the samples with 5 mM p-nitrophenyl sulphate (Tabatabai and Bremner 1970). The p-nitrophenol released during enzymatic hydrolysis was determined using a spectrophotometer at a wavelength of 400 nm.

The amount of p-nitrophenol released during enzymatic hydrolysis was determined colorimetrically using a spectrophotometer at a wavelength of 400 nm. Paz-Ferreiro et al. (2012) found that the product of the hydrolysis reaction can adsorb to the surfaces of biochars and organic matter. To account for these amounts of adsorbed p-nitrophenol, a standard curve was prepared for each of the treatments as suggested by Swaine et al. (2013). The activity of each of these three enzymes was expressed as µmol p-nitrophenol g^{-1} h^{-1}.

The geometric mean of enzyme activity (Gmea) has been used in several instances as an indicator of soil quality in response to the addition of amendments as it has been shown to be sensitive to land use changes (Paz-Ferreiro et al., 2012, Lu et al., 2015, Paz-Ferreiro and Fu, 2016, García-Ruiz et al., 2008, García-Ruiz et al., 2012). Gmea was calculated as follows:

$$\boldsymbol{Gmea} = (\boldsymbol{Glu} \times \boldsymbol{Phos} \times \boldsymbol{Aryl})^{\boldsymbol{1/3}}$$

Where, Glu, Phos and Aryl are β-Glucosidase, phosphomonoesterase and Arylsulphatase, respectively.

4.2.4 Olsen extractable P

Analysis for Olsen-P was completed by ALS Laboratories (NATA Accredited) according to the method of Rayment and Higginson (1992)

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4.2.5 Statistical analysis

Statistical differences between treatments were calculated using SPSS version 18.0. A one-way ANOVA was conducted in order to see the various treatment effects. Means were considered to be significantly different when $P < 0.05$ using Tukeys test.

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4.3 Results and discussion

4.3.1 Soil enzyme activity

Phosphomonesterase activity increased following the addition of PL500, BS300, BS400, BS500 and NTS whereas it was inhibited following the addition of PL300 and MCP and was unaffected by the addition of PL400. Notably MCP decreased the activity of phosphomoesterase by more than 50% compared to the control, whereas NTS led to a 50% increase in the activity of this enzyme. The activity of β-glucosidase was either unaffected or decreased following the addition of the amendments with the largest decrease observed in soil treated with MCP. The activity of arysulfatase was relatively unaffected following incubation with the amendments, except for MCP which led to a 50% decrease in the activity of this enzyme. The results of the enzyme assays are presented in table 7 with the enzyme activity expressed as μmoles p-nitrophenol g^{-1} h^{-1}. Phosphomonesterase is involved the cycling of P from inorganic to plant available organic P. Paz-Ferreiro et al. (2012) suggested that the activity of this enzyme should increase in response to a shortage of P and vice-a-versa. In this study the addition of MCP (readily available P) reduced the activity of phosphomonoesterase by more than 50% compared to the control soil. The application of PL300 led to similar decrease and whilst PL400 had no effect, likely reflecting the availability of P in these treatments, specifically in increase in pyrolysis temperature has been shown to decrease the availability of P (see for example: (Wang et al., 2012)). The activity of β-glucosidase was reduced or unaffected following treatment, notably the largest decrease was observed in MCP, followed by NTS and BS400. This is consistent with previous studies. Interestingly, biochars prepared at 400°C led to a larger decrease in β-glucosidase compared to those prepared at 300 and 500°C which could be due to the fact that cation exchange capacity was maximised at this pyrolysis temperature resulting in more adsorption of the enzyme to exchange sites on the biochar. Other inherent differences in the biochars, for example hydrophobicity, surface area and pore size could also be involved in this effect (Foster et al., 2018, Kinney et al., 2012), although these mechanisms are poorly understood. Contrary to previous studies, the application of biochar to soil affected the activity of arylsulfatase, an enzyme involved in the catalysis of ester sulfate bonds. BS500 and PL500 increased the activity of this enzyme compared to the control which could be due to the depletion of organic carbon in the biochars produced at 500°C whereby the activity of this enzyme is known to be inhibited by the addition of organic amendments (Dick, 1992). The remaining amendments decreased the activity of arylsulfatase compared to the control, which agrees with previous studies (Swaine et al., 2013). The largest decrease was observed following treatment by MCP which decreased arylsulfatase activity by 50% compared to the control.

In our study the addition of MCP led to a 53% reduction in Gmea whilst PL300, PL400, BS400 and NTS also led to a decrease in Gmea, though to a lesser effect ranging from 13 – 25%. Notably the biochars prepared at 500°C (PL500 and BS500) led to an increase in Gmea by 10 and 13% respectively which is relatively consistent with previous studies, for example in Paz-Ferreiro et al. (2012) biochar produced from biochar at 600°C led to a 19% increase in Gmea compared to the control. To our knowledge, in terms of contamination remediation, this is the first study to assess the effect on soil quality of adding conventional phosphorus amendments compared with P rich biochars. This is important given that these biochars have been shown to perform comparably to conventional options for the purposes of immobilising Pb in soil (Chapter 3 Section 5).

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Table 7 Soil enzyme assay results

Sample	Phosphomonoesterase	β-glucosidase	arylsulfatase	Gmea
Control	4.56±0.09c	1.21±0.10e	0.17±0.02de	0.99±0.03ef
PL300	2.87±0.10b	1.03±0.05cd	0.13±0.02bc	0.74±0.05b
PL400	4.53±0.44c	0.94±0.09bc	0.11±0.01b	0.76±0.04bc
PL500	5.66±0.15de	1.15±0.11cde	0.21±0.01f	1.12±0.03g
BS300	5.24±0.16d	1.16±0.05cde	0.15±0.01cd	0.97±0.01de
BS400	5.92±0.14ef	0.83±0.08b	0.12±0.01b	0.84±0.05bc
BS500	6.47±0.28e	1.09±0.01cde	0.19±0.02ef	1.09±0.05fg
MCP	2.02±0.10a	0.65±0.04a	0.08±0.01a	0.46±0.02a
NTS	7.23±0.51f	0.83±0.04b	0.12±0.01b	0.86±0.10cd

4.3.2 Olsen P

Chemical immobilisation of Pb in soil by adding phosphorus based amendments is an accepted approach remediating this contaminant in-situ. In recent times the addition of waste containing phosphorus has emerged as a promising alternative to conventional mined or manufactured phosphates. The technique is not without critique, for example Chrysochoou et al. (2007) cited the runoff or leaching of excess P as a poor environmental outcome associated with the use of fast release P fertilizer, like the MCP treatment examined in this study. Here MCP led to an order of magnitude increase in the amount of Olsen P compared to the untreated control and the remaining treatments. This has a number of implications for the wider ecology. For example, large amounts of available P can be toxic to plants, for example those in the Proteaceae family (Hawkins et al., 2008, Kariman et al., 2016) and according to Handreck (1997), an Olsen-extractable P concentration of around 20 mg/kg can be lethal to the seedlings of P-sensitive Australian native species. When undertaking a remediation options assessment, a holistic approach should consider potential impacts to the wider ecology, in this way, for example, the deployment of MCP to immobilize Pb in an urban parkland in Australia could present a risk to native plant species. With respect to leaching and runoff of excess P, (Pizzeghello et al. (2016)) found that when Olsen P concentration exceeded 54 mg/kg the amount of phosphorus released into water increased markedly from 4.0 mg/kg to 28 mg/kg. Whilst assessing a change point was not within the scope of this study, the potential for the addition of MCP, which increased Olsen P from 14 ± 2 to 170 ± 23 mg/kg, to have resulted in this threshold Olsen P being exceeded, should be considered. With respect to the biochars and NTS amendments, the treatments did not Pb to a statistically significant change in Olsen P, which aligns with previous studies reporting that P rich biochars tend to act as a slow release source of P.

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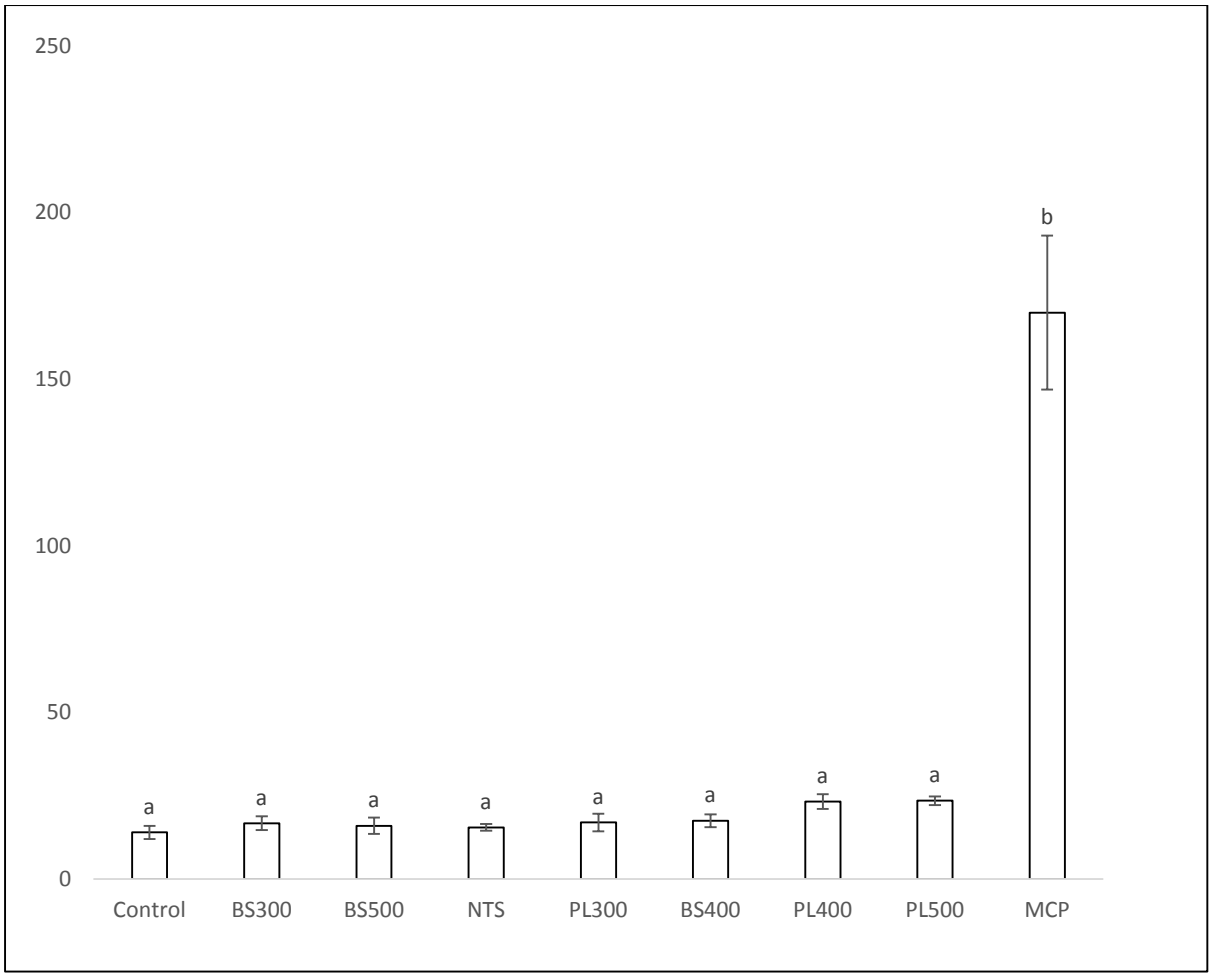
Figure 5 Olsen-P results



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4.4 Conclusion

The application of an amendment for the purposes of immobilizing heavy metals in soil should consider wider environmental outcomes to ensure that a net environmental benefit is achieved. Under a holistic approach to assessing remediation options, these wider environmental outcomes will help to equip researchers and industry alike in their endeavour to reduce the burden posed by contaminated soils. In this study we found that the application of MCP, a conventional amendment used to remediate Pb contaminated soils, reduced the activity of soil enzymes involved in important soil processes. Secondly, we observed that the application of MCP has the potential to result in excess P being released in to the environment, a concern which has been echoed by several previous authors. Along with the potential for this type of amendment to result in a net loss in soil quality, the need to develop alternative options avoiding these risks is a pressing area of research. To this end, our hypotheses were that biochars produced from poultry litter and biosolids could present as a better alternative. The results indicate that the application of biochars produced from these feedstocks at 500°C increased the activity of soil enzymes, signaling an increase in soil quality. Consistent with previous authors, our results indicate that phosphorus-rich biochars act as a slow release source of P, whereby the availability of P in the receiving soil was not affected following treatment with biochar, indicating that the release of excess P in to the environment could be avoided using biochars for this purpose.

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4.5 References

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5.0 Conclusions and future Work

This research examines phosphorus rich biochars as candidates towards the in-situ remediation of Pb contaminated soil. Whilst the results indicate that biochar performs comparably to conventional treatment options for this purpose, important questions prevail which future research should aim at addressing. Specifically,

- Influences of soil chemistry on remediation performance. A limitation of our study is that only one soil was considered. Initial Pb concentration and speciation, soil characteristics (pH, texture, mineralogy) and the presence of co-contaminants might limit the remedial effect in other situations.
- Translation to the field might also be impacted by intrinsic differences between laboratory studies, whereby the diffusion of P and Pb into solution may be limited by soil moisture. Work should be done to conduct field trials to further the understanding of these important factors.
- More work should also be done to identify the mechanisms explaining the different interactions observed between the biochars and Pb. Thus, besides precipitation as insoluble phosphate forms, differences in cation exchange and intra-particle diffusion could contribute to explain the differences found among all biochars tested.
- This experiment was conducted at a single data point. The long-term fate of Pb after remediation with different phosphate amendments remains unexplored.
- Effects on the wider environment and ecology. The assessment of new and emerging in-situ remediation options by researchers should continue to take a more holistic approach in considering wider effects on the environment, considering the potential for poor incidential outcomes.

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Appendices

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Appendix A – Manuscript submitted to Journal of Environmental Quality

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JOURNAL OF ENVIRONMENTAL QUALITY

Phosphorus-rich biochars can transform lead in an urban contaminated soil

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Phosphorus-rich biochars can transform lead in an urban contaminated soil

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Abstract

Transformation of soil lead to pyromorphites and phosphates has the potential to be an effective strategy to immobilize this contaminant *in situ*. Soil treatment using monocalcium phosphate, NTS Softrock and biochars prepared from poultry litter and from biosolids at three different temperatures (300, 400 and 500°C) and two doses (1% and 3%) were evaluated. Lead bioaccesibility, mobility and solid speciation were measured. Leachable lead (Toxicity Characterised Leaching Procedure) was not significantly ($P>0.05$) changed after biochar addition, but a significant decrease in bioaccesible lead was found for several treatments ($P<0.05$). This was particularly notable for treatments receiving biosolids prepared at 400 and at 500 °C or monocalcium phosphate at the 3% dose. Decrease in bioaccesible

lead concentration in the biochar treatments were similar to traditional phosphate amendments. Our research found transformation of lead species to the more stable pyromorphite and Pb-phosphate to be partially responsible for the observed changes, although other mechanisms, including pH changes might also play an important role. Overall, pyrolysis was an effective method to upgrade waste streams and facilitate lead immobilization, although key pyrolysis parameters need to be selected carefully.

Keywords: Lead; immobilization; biochar; poultry litter; biosolids

Introduction

Lead contamination is almost ubiquitous amongst urban soils around the world. This is due to historical use of Pb in car batteries, ammunition, special glass, radiation protection, construction elements or as additives petrol and paint, as well as from point source industrial activities. Legacy contamination remains and soil Pb persists as a threat to human health (Mushak, 2011), particularly children, as they are more likely to ingest soil. Once ingested, Pb travels down the gastrointestinal tract and, if solubilised, may be absorbed in to the blood stream. Recently (in 2012), the US Centers for Disease Control and Prevention declared that there is no safe concentration of Pb in blood, abandoning the previously designated "level of concern". To this end, continued and concerted effort is required to address the issue of urban soils that are historically contaminated with Pb.

Currently there are a wide range of solutions available for remediating soils contaminated with Pb. These solutions aim at risk-based remediation; comprising dig-and-dump, in-situ chemical immobilisation, phytocapping and soil/asphalt capping amongst others (Laidlaw et al., 2017). Excavating a soil in dense urban communities is expensive and technically challenging. In recent years, in-situ chemical immobilisation of Pb in soil has been suggested as the best management practice to remediate shooting range soils which are often heavily

impacted by Pb (Chrysochoou et al., 2007). The process involves applying a phosphate-based amendment to the soil with the aim of shifting Pb to a more insoluble, less bioaccessible, and hence, lower risk form (Henry et al., 2015). The goal of remediating soils using in-situ chemical immobilisation is to transform Pb in to pyromorphite, which is an insoluble form of Pb across a wide range of environmental conditions. Previously, many different sources of phosphate have been tested as candidates for Pb remediation and a number of authors have consolidated these options in the form of review articles (Hettiarachchi and Pierzynski, 2004, Miretzky and Fernandez-Cirelli, 2008, Scheckel et al., 2013, Henry et al., 2015). Broadly, these phosphate sources can be grouped as fast release (if labile P can be readily solubilised by water) or slow release (if labile P cannot be readily solubilised by water) (Bolan et al., 2003).

There are some concerns surrounding the long-term feasibility of phosphate amendments for Pb remediation of soil (Laidlaw et al., 2017; Henry et al., 2015; Chrysochoou et al., 2007). Phosphorus is a valuable element for agriculture and peak phosphorus has been predicted to occur as soon as 2030 (Cordell et al., 2009). Thus, several authors (see for example Chrysochoou et al. (2007)) have advocated for the use of phosphorus containing wastes as a promising solution compared to mined or manufactured phosphates. In many cases though, excess phosphorus leaching has been cited as a poor environmental outcome in Pb immobilisation studies (Chrysochoou et al., 2007, Dermatas et al., 2008), which could be avoided by using slow release P.

Biochar is the solid product of biomass pyrolysis, which involves heating biomass in an environment with little to no oxygen. The characteristics of a biochar mostly depend upon the heating regime and the properties of the feedstock biomass (Basu, 2010). With this in mind, biochars can be engineered for a specific application or end-use. Biochars could provide some other ecosystem services when applied in land remediation, including carbon

sequestration (Gascó et al., 2016) and an improvement in soil microbial activity (Benavente et al., 2018), which could pose an advantage over phosphate-based amendments. An increasing number of studies have highlighted biochar as a way to capture and recycle phosphorus from biogenic wastes (Roberts et al., 2017; Wang et al., 2014; Cely et al., 2015; Shepherd et al., 2016) and to remediate heavy metal polluted soils (Kosolsaksakul et al., 2018; Shahbaz et al., 2018). However, biochar has only been used in few instances in the remediation of Pb contaminated soils (Yang et al., 2016, Rajapaksha et al., 2015, Moon et al., 2013, Uchimiya et al., 2012, Cao et al., 2011), though none of these studies have tackled the challenge of remediating urban soils, instead focussing on shooting range soils that tend to be much more polluted than urban soils. For example, in shooting range soils Pb has been detected at concentrations exceeding 15000 mg kg^{-1} (Rajapaksha et al., 2015, Hashimoto et al., 2009), whilst in contaminated urban soils, Pb tends to be lower than 4000 mg kg^{-1} (Brown et al., 2003, Smith et al., 2011, Yang and Mosby, 2006). Moreover, there is a lack of studies that have tested the efficacy of phosphorus-rich biochars, which is surprising given the important role of P in the immobilisation of Pb. For example, Moon et al. (2004) tested a soybean stover biochar, while Rizwan et al. (2016) utilised a rice straw biochar for Pb remediation. Phosphorus contained within biochar tends to behave as a slow release fertilizer (Wang et al., 2014), an important characteristic with consideration to its long term feasibility for use in remediation of Pb contaminated soils (Laidlaw et al., 2017).

Most biochars have an alkaline pH (Dai et al., 2018), which is one of the factors underlying the ability of biochar to immobilise heavy metals. However, it is possible to produce acidic and neutral biochars. The former have usually been neglected in remediation studies even though recent work has demonstrated that acidic biochars are effective in the immobilisation of Cd, particularly in soils with a low adsorption capacity (Qi et al., 2018). To our knowledge, equivalent studies for Pb are not available in the literature. Moreover, Pb-P

reaction kinetics are promoted under acidic soil conditions (Dermatas et al., 2008) and therefore applying an acidic biochar could favour the formation of phosphates and pyromorphites.

Taking into account the abovementioned considerations, in this study we prepared P-rich biochars from two different feedstocks and at three different temperatures, with the aim of testing biochar´s and conventional P sources (slow and fast release P) ability to immobilise lead. We hypothesized that pyrolysis would result in the production of cost-effective biochars that would be suitable substitutes for the phosphate-based materials typically used in the remediation of urban contaminated Pb. We also hypothesized that acidic biosolids biochar would outperform alkaline poultry litter biochar due to intrinsic differences in pH.

Materials and methods

Soil

This study used a soil from an anonymous contaminated site in urban Victoria. Historically the site was used for blacksmithing with uncontrolled filling at the site known to have occurred. The site was underlain by fluvial sediments comprising silt, sand and gravel. Mean annual temperature and rainfall at the site are 20ºC and 800 mm, respectively. Moist soil was disaggregated and sieved to 2 mm before being mixed thoroughly. A subsample of the bulk soil (2kg) was collected and dried for soil characterisation purposes as follows. pH and EC were measured in 1:25 soil:H_2O extract after shaking for 1 hour. Soil texture was determined by laser diffraction using a Malvern Mastersizer 3000. Soil organic matter was estimated by the loss on ignition method based on sample weight loss upon heating to 375°C. For pseudo-total metals, the soil was digested with 3:1 HCl:HNO_3 before dilution and analysis by ICP-MS for Al, As, Cd, Cu, Sb, Se, Pb and Zn. Whilst Ca, Fe, K, Mg and Mn was determined by MP-AES (USEPA, 1994). The cation exchange capacity was determined by extraction with

124 NH_4OAc/HOAc at pH 7.0, following the method of Sumner and Miller (1996). The moisture
125 content of the soil was determined gravimetrically. For maximum water holding capacity, a
126 subsample of the oven dried soil was saturated with water and allowed to drain. Maximum
127 water holding capacity (WHC) was calculated as the ratio of water in the saturated soil to the
128 dry soil weight.

129

130 **Biochar**

131 Poultry litter (PL) (approximately 12 kg) was collected from a stockpile after one week of
132 stockpiling at poultry farm in Anakie, Victoria (37°57'18.36"S and 144°18'8.09"E). The
133 feedstock was dried in an oven at 70°C for 48 hours, ground using a mortar and pestle and
134 then sieved to <2mm. Biosolids (BS) were produced from Pakenham Water Treatment Plant
135 (38°07'46", 145°29'15") where they have been stockpiled for three years before being
136 transferred to Bald Hill Farm (38° 6'3.61"S and 145°30'3.10"E). From there around 3 kg of
137 biosolids were collected for the purposes of this study. Later, the BS were dried and crushed
138 before sieving to <2mm. Biochar was produced by packing the feedstock into an air tight
139 vessel. The vessel was placed in to a muffle furnace and heated at 10°C min^{-1} to pre-
140 determined pyrolysis temperatures of 300, 400 and 500°C. Once reached, the target
141 temperature was held for 2hours, after which the heating ceased and the vessel was removed
142 and allowed to cool to room temperature. Six different biochars were produced using two
143 feedstocks and three pyrolysis temperatures: PL300, PL400, PL500, BS300, BS400 and
144 BS500.

145 Later, each biochar was characterised as follows. pH and EC were measured in 1:25 soil:H_2O
146 extract after shaking for 1 hour. For heavy metals, biochars were digested with 3:1
147 HCl:HNO_3 before dilution and analysis by ICP for Al, As, Cd, Cu, Sb, Se, Pb and Zn. Whilst

Ca, Fe, K, Mg and Mn were determined by MP-AES (USEPA, 1994). P was determined as per Hanson (1950). The cation exchange capacity was determined by extraction with NH_4OAc/HOAc at pH 7.0 (Sumner and Miller, 1996). Thermogravimetric analysis (PerkinElmer TGA 4000) was used to determine moisture, ash and volatile matter content. Samples were heated at 20°C min^{-1} to 600°C in an N_2 atmosphere which was purged at a rate of 40 mL min^{-1}. At 600°C the purge gas was switched to air, purging at 20 mL min^{-1}, until a constant weight was reached. Moisture was determined by the weight loss at 105°C, volatile matter at 600°C and ash as the constant weight remaining at the end. Fixed C was calculated by subtracting the sum of moisture, volatile matter and ash from 100%. BET surface area BET SA) was measured by nitrogen adsorption using an ASAP 2400 (Micrometrics) at 77 K after degassing at 200°C. Elemental C, H and N content in the biochars were determined by dry combustion using a Perkin Elmer 2400 Series II Elemental Analyser.

Incubation experiment

The sieved soil was separated in to 250 mL polyethylene jars with each jar containing 300 g of soil. The control was the polluted, untreated soil. The treatments (PL300, PL400, PL500, BS300, BS400, BS500, monocalcium phosphate (MCP)(Sigma-Aldrich) and NTS Softrock™ (NTS) (nutri-tech.com.au) were added to the jars at two treatment rates (1 and 3% w/w). The higher dose was selected to ensure that the P to Pb ratio satisfied the pyromorphite stoichiometry (0.6) for all treatments, while the lower dose represented a P to Pb ratio lower than 0.6 for the biochars (see Table 1). Monocalcium phosphate [$Ca(H_2PO_4)_2$] addition to soil can effectively transform various Pb minerals into insoluble chloropyromorphite, although the process is greatly dependent on pH (Cao et al., 2008). NTS softrock is a dicalcium phosphate [$CaHPO_4$] based material. Dicalcium phosphate has been successfully used in the immobilization of Pb in soil (Theodoratos et al., 2002). The jars were made up to 60% WHC

using ultrapure water (18 MΩ.cm) and this moisture was reinstated every two days by the addition of ultrapure water.

Treatments were coded according to the material added to the soil (PL, BS, MCP or NTS), followed by the temperature of preparation (for biochars only, 300, 400 or 500) and the dose (1 or 3). For example, PL500-3 would indicate a 3 % addition of poultry litter biochar prepared at 500°C. Each of the seventeen treatments (control, BS300-1, BS400-1. BS500-1, PL300-1, PL400-1, PL500-1, BS300-3, BS400-3. BS500-3, PL300-3, PL400-3, PL500-3, MCP-1, MPC-3, NTS-1 and NTS-3) was replicated four times. After three months of incubation, a subsample (around 10 g) was collected from each jar and air dried at 40°C for 72 hours.

In vitro bioaccessibility

In vitro bioaccessible Pb testing was carried out according to USEPA (2008). The dried subsample was sieved to 250 µm. This is the fraction considered to represent an exposure pathway to children (USEPA, 2008). The extracting solution consisted of 0.4 M glycine ($C_2H_5NO_2$). The glycine solution was heated to 37°C and adjusted to pH 1.5 using concentrated, trace metal grade HCl. The solution was made up to 1.0 L and the pH was again adjusted to pH 1.5 with commercial HCl.

The heated extracting solution (100±1.0mL) was added to 1 g of <250µm soil in a 125 mL High Density Polyethylene (HDPE) bottle and shaken for 1 hour, end-over-end at 37±2°C. A 40mL aliquot of supernatant was withdrawn from the bottle using a luerlock syringe and filtered through a 0.45 µm cellulose acetate filter. Lead in the filtered extract was determined using MP-AES (Agilent Technologies) and the bioaccessibility was calculated using the following equation:

$$In\ vitro\ bioaccessibility\ (\%) = \frac{in\ vitro\ bioaccessible\ Pb\ (mg\ kg^{-1})}{Pb\ in\ soil\ (mg\ kg^{-1})} \times 100$$

195

196 **Toxicity Characterised Leaching Procedure (TCLP)**

197 TCLP was carried out by a NATA accredited commercial laboratory according to USEPA
198 (1992). The extractant used (pH 5.0) was selected based on the pH of the untreated control
199 soil post incubation. One gram of soil was extracted with 20 mL of extractant (prepared by
200 adding 5.7 mL of glacial acetic acid into 1 L of milli-Q water) for 18 hours. Following
201 extraction, the solution was tested for Pb by ICP-AES.

202 **X-Ray absorption near edge structure (XANES)**

203 XANES spectroscopy was conducted in order to investigate the speciation of Pb in the
204 control and the treatments. Data were collected on the X-ray Absorption Spectroscopy (XAS)
205 beamline at the Australian Synchrotron, ANSTO, Clayton Victoria. The crushed and sieved
206 (<250 μm) soils were mounted on to Poly(methyl methacrylate) sample holders and sealed
207 with Kapton tape.

208 Pyromorphite (produced as per (Ryan et al., 2001), PbO (Sigma-Aldrich) and $PbHPO_4$
209 (Sigma-Aldrich) were included as Pb mineral standards collected at the XAS beamline.
210 Additional Pb mineral standards utilized for linear combination fitting (LCF) are described in
211 Obrycki et al. (2016). The experiment was conducted at room temperature in fluorescence
212 mode with beam energy of 3 GeV and current 200 mA. Once tuned to the Pb (13,035 eV)
213 L_{III}, fluorescence was detected using a 100-element detector. Data analysis was conducted
214 using Athena software (Ravel and Newville, 2005). Triplicate scans for each sample were
215 merged, normalized, and converted into k-space. Linear combination fitting was used to
216 identify Pb speciation in the samples. Linear combination fits (−30 to +70 eV relative to the

calibration energy) were performed using XAS normalized and derivative μ(E) spectra from reference standards to identify Pb phases in the soil samples. During the LCF, components were only allowed to contribute to the model if the sum-square error was reduced by 20% (Manceau et al., 2002). The χ^2 is a measure of the mean square sum of misfit at each data point and describes the degree of uncertainty in the fitting process (Ravel, 2009). Linear combination fits are provided in Supplementary Figure 1.

Statistical analysis

Statistical differences between treatments were calculated using SPSS version 18.0. A one-way ANOVA was conducted in order to see the various treatment effects. Means were considered to be significantly different when $P < 0.05$ using Tukey's test.

Results and discussion

Soil characterisation

The soil was classified as a sandy loam, with 70 % sand, 28 % silt and 2 % clay content (see Table 1). The soil pH was 4.9±0.1 and the CEC value 16.1±0.1 $cmol_c\ kg^{-1}$ (see Table 2). The soil was polluted with a total concentration of 3192±45 mg kg^{-1} Pb, which is 10 times over the human health investigation level set in the National Environmental Protection Measure for managing contaminated sites in Australia (300 mg kg^{-1}) (NEPC, 2013). Cd, As and Sb were not found at detectable levels in the soil whilst Zn and Cu were present well below the respective health investigation levels, specifically 117±1 and 385±2 mg kg^{-1} respectively. As such, Pb was identified as the only contaminant of concern within the group of contaminants analysed for. The absence of co-contamination is an important factor when assessing phosphate immobilisation as a remediation strategy. **Biochar characterisation**

The PL biochars had an alkaline pH, that increased as the temperature of production increased in agreement with similar research by Song and Guo (2012). In comparison, the BS biochars were acidic but followed a similar trend of increasing pH with pyrolysis temperature. In both cases, cation exchange capacity was maximised at 400 °C production temperature. The BET surface area of PL300 was low (7.73 m^2 g^{-1}) compared to PL400 and PL500 (29.94 and 33.64 m^2 g^{-1} respectively). This could be due to the positioning of mineral rich ash within the pores of the biochar (Song and Guo, 2012), which may have been displaced as cellulose and hemicellulose decomposed between 300 and 400°C (Kim and Agblevor, 2007). A similar trend was observed in the work of Yuan et al. (2015) whereby the surface area of biochar from sewage sludge increased from 14.4 to 22.7 m^2 g^{-1} as the temperature increased from 300 to 400 °C before reaching a maximum of 26.70 m^2 g^{-1} at 700°C. The biosolids biochar BET surface area was less affected by pyrolysis temperature compared to the poultry litter biochar, specifically increasing from 21.6 m^2 g^{-1} to 25.3 m^2 g^{-1} as the temperature increased from 300 to 500°C.

Ash content was highest in BS500 (93.4±0.1%) and decreased at lower pyrolysis temperatures (92.7±0.5% and 91.1±0.8% for BS400 and BS300 respectively). These results are similar compared to previous studies. For example, Chen et al. (2014) produced biochar from biosolids across a range of temperatures (500-900°C) and reported maximum ash content of 88.1±0.6% at 900 °C. Similarly in Oh et al. (2012) ash content was 90.7% in biochar produced from biosolids at 900 °C. In our study, the biosolids had been stored stockpiled for three years prior to being converted to biochar, and given the relatively low volatile matter content in the biochars, volatiles may have evaporated during stockpiling resulting in high ash content. The PL biochars had ash contents of 58.7±0.8 %, 62.1±0.5 % and 66.5 ± 4.2 % for PL300, PL400 and PL500 respectively. These results are in agreement with Song and Guo (2012) who reported ash contents of 47.8±0.1%, 56.6±0.3% and

60.6±0.1% for biochars produced from PL at 300, 400 and 500°C respectively. In all cases, volatile matter content was reduced as the temperature of production increased which coincided with a decrease in yield, indicating that more volatile compounds were driven off at higher temperatures.

Results for C, H and N are shown in Table 2. As the temperature of production increased from 300 to 500 °C, C content decreased from 32.3±4.4% to 19.1±3.0% in the case of the PL biochars. The C content in the BS biochars was similarly affected, specifically decreasing from 4.4±1.6 % to 2.7± 0.1% for PL300 and PL500 respectively. In agreement with Zhang et al. (2015), this trend was common to the H and N contents.

The PL500 treatment had the highest total P content amongst the biochars, which decreased at lower pyrolysis temperatures. This trend was also observed in the BS biochars, though there was around half as much P compared to the PL biochars. As expected, for both feedstocks, biochar yield decreased as temperature increased. This is because more organic matter is volatilised at higher temperatures and so less volatile material i.e. minerals and most metals are increasingly enriched. Here the data showed that all minerals (P, Ca, K, Mg and Na) became enriched as the pyrolysis temperature increased. This was also the case for heavy metals (As, Cd, Cu, Pb, Sb, Zn) in all of the biochars. The raw biosolids were previously precluded from unrestricted use due to the presence of Zn and Cu at concentrations above contaminant class one (C1) grade (EPA Victoria, 2004). Importantly, this classification was maintained after pyrolysis i.e. enrichment of heavy metals did not degrade the quality of the biosolids with respect to land application.

Bioaccesibility test

The Pb in the untreated control soil had an *in vitro* bioaccessibility of 86.9±10.6%, which is at the upper end of values reported in previous Pb bioaccessibility studies involving urban

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soils. For example, Smith et al. (2011) tested peri-urban soils contaminated from a range of different sources (n=31) and found that on average Pb was 66.0 ± 24.3% bioaccessible. This varied according to the source of contamination, for example, Pb in soils contaminated from shooting range activities was 89.0±18.3% (n=9) bioaccessible, compared to those contaminated from mining/smelting activities, which were less bioaccessible (54.8±29.1%, n=13), although two of the mining impacted soils had bioaccessibilities of >90%.

Several treatments (MCP-3, BS500-3, BS400-3, PL300-1, BS400-1, BS300-1, PL400-1, PL500-3) had a decreased IVBA Pb relative to the control; in the remaining treatments IVBA was not different to the control ($P<0.05$) (Figure 1). At the lower P application rate (1%), most biochars treatments outperformed the MCP and NTS softrock treatments in decreasing IVBA Pb. The amount of IVBA Pb in soils receiving the phosphate treatments at a 1% dose did not differ from the control. For the lower (1%) P application rate, PL300 was the most effective, decreasing the IVBA to 62.7±5.7% compared to the untreated control (IVBA Pb 86.9±10.6%). As the temperature of pyrolysis increased, this decreasing effect on IVBA Pb was reduced, specifically in the PL400-1 treatment IVBA was 68.7±4.8%.

Given that pyrolysis temperature had a marginal effect on the characteristics of the BS biochars, it was expected that the effect of temperature on ability of these biochars to decrease IVBA Pb would be similarly marginal. As such, BS300-1 and BS400-1 had a similar effect on IVBA Pb, specifically decreasing it to 66.6±0.1% and 66.1±1.67%, respectively, compared to the control (Figure 1).

At the higher application rate, PL500-3 decreased IVBA Pb to 68.8 ± 11.3%. The addition of poultry litter biochar increased soil pH by 0.8 pH units. Soluble P can be increased by the raise in pH observed after biochar addition (Lehmann et al., 2003). This effect can be attributed to a weakening of the ionic interactions in Al and Fe phosphates, which are

312 insoluble forms of P. Furthermore, DeLuca et al. (2012) suggested that biochar could also
313 influence available phosphate by inducing sorption of chelating organic molecules. By
314 reducing soluble chelates, the effects of chelates on soluble phosphate could be diminished.
315 In contrast to the lower application rate, pyrolysis temperature had an effect on the ability of
316 BS biochars to reduce IVBA Pb when these biochars were applied at the higher application
317 rate. Specifically, BS400-3 and BS500-3 decreased IVBA Pb to 62.1±8.0 % and 57.8±5.2%,
318 respectively. Here soil pH was not expected to have had a notable impact on IVBA Pb, as
319 post treatment soil pH was decreased by 0.2 pH units compared to the control in the case of
320 both treatments ($p<0.05$).

321 At the higher application rate, MCP was most effective in decreasing IVBA, specifically to
322 45.8±7.6% compared to the untreated control. This value was not statistically significantly
323 different from the one achieved by treatment BS500-3 ($P>0.05$). A similar treatment effect
324 was observed by Brown et al. (2005) who applied MCP (2% w/w) to a soil contaminated by
325 mine waste (Pb 5022 mg kg^{-1}), Pb bioaccessibility was lowered from 84.9% pre-treatment to
326 31.6% post-treatment. Dissolution of soil minerals is likely to occur within the acidic in vitro
327 test, releasing sorbed Pb and P for subsequent precipitation to insoluble Pb phosphates.
328 Further dissolution of soil minerals could be restricted as Pb phosphates are chemically stable
329 at conditions within the in vitro test (Hettiarachchi et al., 2000).

330 Uchimiya et al. (2012) prepared P rich biochars from broiler litter at 350 and 750°C and
331 added them to a shooting range soil contaminated by Pb (19906 mg kg^{-1}) at treatment rates of
332 2, 5, 10 and 20 % (w/w). In their study, there was no decrease in IVBA Pb after treatment by
333 biochar. However, the amount of lead in their soil was more than one order of magnitude
334 higher than in the present study thus the capacity of the biochar to immobilise lead might
335 have been exceeded in their work. Failure to reduce bioaccesible lead was also found in
336 studies using phosphorus-poor biochars (see for example, Rizwan et al., 2016).

337

338 **Lead XAFS Spectroscopy**

339 Our analyses indicate a transformation in Pb phosphorus species due to the addition of
340 amendments containing P (Table 3). In the control soil, the amount of Pb adsorbed to soil
341 minerals accounted for 57% of Pb, while 35% was adsorbed to organic matter and 8% as
342 PbO. Pyromorphyte formation, one of the most stable Pb species in soils, was only observed
343 for the treatments NTS-3 and PL500-3. Pb-phosphate formation was observed following all
344 treatments except BS400-1. Pb-phosphate formation was particularly high (23 %) for the
345 treatment PL500-3. There was a clear trend to higher Pb-phosphate formation with higher
346 temperature for PL, but not for BS. The amounts of Pb adsorbed to organic matter, a readily
347 bioaccessible Pb form (Farshadirad et al., 2018), was reduced in several biochar treatments
348 compared to the control. Specifically, the maximum reduction was achieved by the treatment
349 PL500-3, where a readily bioaccessible Pb fraction constituted 17% of the total lead,
350 compared to 35% in the control.

351 The transformation of lead to insoluble species under the BS treatments could be attributed to
352 an increase in acidity in soils receiving this treatment (pH 4.9±0.1) compared to the control
353 soils (pH 5.2±0.1) ($p<0.05$) whereby both more Pb and P were solubilised from the soil and
354 biochar respectively. Once in solution, the creation of this new phase of Pb phosphate could
355 have occurred by way of a precipitation reaction between Pb and P.

356 Noticeably, BS400-1 did not induce the creation of any new Pb phases (Table 3), though a
357 reduction in bioaccesible lead was observed (Table 3). Possibly, a shift in speciation could
358 have occurred in the in vitro extraction. Under this scenario insoluble P from the biochar may
359 have been solubilised at the low pH used in the vitro test. In the presence of solution Pb,
360 precipitation to an insoluble form is favourable (Geebelen et al., 2003). Here Juhasz et al.

(2014) found that *in vivo* processes would have a similar effect to *in vitro* processes suggesting that the transformation to insoluble Pb species is not required to occur in situ and that ultimately the remediation outcome would not change

The amounts of phosphate-Pb formed in our study were substantial. For example, Moon et al. (2013) found no Pb-phosphate formation after addition of a biochar derived from soybean stover at a dose of 1 %. In their study, chloropyromorphyte only started forming at a dose of 5 %, higher than the one used in our study, while Pb-phosphate was only detected when a dose of 10 % biochar was added. These differences are most likely attributed to the higher P content in the biochars used in the present study, coupled with differences in the pH of the biochars.

Leachability

TCLP leachable Pb in the untreated control was 1.23±0.32 mg/L (Table 4) which indicates that the pH of the extractant was only able to solubilise a small fraction of the total Pb in the soil. This is in contrast to the IVBA extractant which solubilised over 85% of total Pb in the soil. This is not surprising given the acidic pH of the control soil and thus in the field infiltration of rainfall in to the subsurface may have displaced leachable Pb further down the soil profile. Adding biochar and NTS treatments to the soil did not affect TCLP-Pb compared to the control ($P>0.05$). The treatment MCP-1 (fast release phosphate fertiliser) was able to decrease TCLP-Pb compared to the control ($P<0.05$) whereby leachable Pb was 0.20 ± 0.08 mg/L and less than the laboratory limit of reporting (0.01 mg/L) following treatment at a dose of 1 % and 3 %, respectively. Overall, the values of TCLP-Pb were below the critical value of 5 mg/L. Differences within treatments might have been mitigated by the strong buffer effect of the extracting solution used in the TCLP-test.

385

386 **Implications of our study and conclusions**

387 Previous studies on lead remediation using biochar have trialled a limited number of
388 biochars, usually only one individual biochar (Ahmad et al., 2014; Rizwan et al., 2016).
389 Moreover, these materials did not possess elevated amounts of phosphorus, which limited the
390 formation of insoluble Pb species. For the first time, we synthesized a large number of
391 biochars from two feedstocks and at three temperatures and compared them to traditional
392 phosphate-based amendments for Pb remediation. Our initial hypothesis of phosphorus-rich
393 biochars offering a potential to substitute phosphate-based amendments was confirmed. A
394 diminishing of bioaccesible lead, with an efficiency comparable to monocalcium phosphate,
395 was quantified in various biochar treatments. This lower bioaccessible lead was linked to the
396 formation of pyromorphites and phosphates, which was verified by LCF-XANES for all
397 treatments besides BS400-1.

398 Our hypothesis regarding a better performance of acidic biochars, due to the need of
399 phosphorus and lead to be in solution in order to react, was confirmed. Thus, the best
400 performing biochars were acidic (BS400-3 and BS500-3). The amounts of lead transformed
401 to pyromorphite or phosphates tended to increase with temperature, a result which could be
402 associated to higher phosphorus content in the biochars prepared at higher temperatures.

403 Phosphorus concentration in our biochars ranged from 1 % to 2.5 %. This was much lower
404 than the 20 % P in monocalcium phosphate or the 9 % P in NTS Softrock. Thus, although not
405 within the scope of the current study, it seems plausible that the significant secondary
406 pollution caused by P leaching, which has been sometimes associated with lead remediation
407 using phosphate-based amendments (Dermatas et al., 2008), could be diminished by
408 remediation of Pb contaminated soils using biochar.

Overall, our research has identified two waste streams that could be valorised towards the remediation of lead contaminated soils. More importantly, it signals acidic biochars, a product which to date has found less applications than their alkaline counterparts, as more suitable for lead remediation.

In spite of the significance of our results, important questions prevail, which could open an avenue for further research. A limitation of our study is that only one soil was considered. Initial lead concentration and speciation, soil characteristics (pH, texture, mineralogy) and the presence of co-contaminants might limit the validity of our approach in other situations. Translation to the field might also be impacted by intrinsic differences between laboratory studies, with an optimal moisture content, and field studies where the diffusion of P and Pb into solution may be limited by soil moisture. More work should also be done to identify the mechanisms explaining the different interactions observed between the biochars and lead. Thus, besides precipitation as insoluble phosphate forms, differences in cation exchange and intra-particle diffusion could contribute to explain the differences found among all biochars tested.

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603 Table 1: Amount of P added per treatment and molar P to Pb ratio.

Sample	P added per treatment (mg)	P/Pb ratio (molar)
Control	0	0
PL300-1	60	0.42
PL400-1	79	0.49
PL500-1	75	0.53
BS300-1	32	0.22
BS400-1	34	0.23
BS500-1	34	0.24
NTS-1	255	1.8
MCP-1	765	5.3
PL300-3	180	1.25
PL400-3	211	1.47
PL500-3	227	1.58
BS300-3	95	0.66
BS400-3	101	0.70
BS500-3	103	0.71
NTS-3	765	13.3
MCP-3	1233	39.8

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613 Table 2: Soil and biochar characteristics

	Soil	PL300	PL400	PL500	BS300	BS400	BS500
Yield (%)		67.3±0.1	60.4±0.1	48.6±0.1	91.9±0.1	89.8±0.1	87.7±0.1
pH	4.9±0.1	8.4±0.1	9.7 ±0.1	10.3 ±0.1	5.4±0.1	5.2 ± 0.1	5.2 ±0.1
Moisture (%)		1.0±0.7	1.2±1.2	1.2±1.2	0.1±0.1	0.1 ±0.1	0.2±0.7
Volatile Matter (%)		23.2±0.7	13.4±0.1	7.2±0.3	5.7±0.5	4.3±0.1	3.4±0.1
Ash (%)		58.7±0.8	62.1±0.5	66.5 ± 4.2	91.1±0.8	92.7±0.5	93.4±0.1
Fixed C (%)		17.1±2.1	23.3±0.4	25.1±0.8	3.1±0.3	2.9±0.5	3.0±0.9
CEC (cmol/kg)	16.1±0.1	46.4±0.5	55.8± 0.1	54.1±0.7	34.5± 0.8	38.3±0.6	36.6± 0.5
BET (m^2 g^{-1})		7.73	29.94	33.64	21.63	24.61	25.32
C%		32.3±4.4	26.6±1.1	19.1±3.0	4.4±1.6	3.1± 0.4	2.7±0.1
H%		2.91±0.35	2.18±0.28	0.98±0.12	0.80±0.23	0.67±0.28	0.37±0.17
N%		2.93±0.27	2.40±0.06	1.62±0.24	2.40±0.06	1.96±0.61	1.66±0.32
P (g kg^{-1})		19.99±0.65	23.40±0.28	25.18±0.57	10.56±0.44	11.18±0.18	11.39±0.12
Pb (mg kg^{-1})	3192±45	5±1	6± 1	6±1	27±1	29±1	29±1
Cd (mg kg^{-1})	<0.10	<0.10	<0.10	<0.10	0.49 ± 0.00	0.50±0.01	0.52±0.01
Sb (mg kg^{-1})	0.03±0.02	0.11±0.02	0.15±0.03	0.21±0.01	0.36±0.01	0.39±0.01	0.41±0.01
As (mg kg^{-1})	<0.10	6.0±0.4	6.6±0.4	8.0±1.8	3.4±0.1	3.8±0.1	4.0±0.1
Zn (mg kg^{-1})	13± 2	473±11	512±6	589±20	356±4	359±4	371±8
Cu (mg kg^{-1})	36±4	118±11	133±8	144± 8	165±11	167±20	169± 10
Fe (g kg^{-1})	45.1±8.5	39.4±1.7	48.1±0.5	54.8± 3.0	43.0±0.4	43.4± 1.5	46.7± 1.0
Ca (g kg^{-1})	7.3±0.6	5.2±0.2	5.4±0.4	6.2±0.1	4.5±0.1	5.1±0.1	5.6±0.3
K (g kg^{-1})	19.3±2.8	15.3±0.1	16.4±0.1	18.1±0.2	1.3±0.1	1.3±0.1	1.7±0.1
Mg (g kg^{-1})	3.0±0.7	7.8±0.3	9.7±0.2	10.3±0.2	2.9±0.1	3.0 ± 0.1	3.1±0.1
Na (g kg^{-1})		7.2±0.1	7.7±0.1	8.9±0.1	1.9±0.1	2.0±0.1	2.2±0.1

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618 Table 3: Proportions of Pb species treated and untreated soil as determined by linear
619 combination fittings (LCF) on XANES

Sample	Pb Adsorbed Soil Minerals (%)	Pb Adsorbed Organic Matter (%)	PbO (%)	Pyromorphite (%)	Pb Phosphate (%)	χ^2
Control	57	35	8	0	0	0.0009
PL300-1	53	35	6	0	5	0.0009
PL400-1	62	27	4	0	7	0.0015
PL500-1	51	32	7	0	10	0.002
BS300-1	52	33	4	0	10	0.0016
BS400-1	53	39	8	0	0	0.0015
BS500-1	51	37	6	0	6	0.0009
NTS-1	65	33	0	0	3	0.0031
MCP-1	55	35	4	0	6	0.001
PL300-3	57	31	3	0	9	0.0011
PL400-3	60	26	3	0	11	0.0011
PL500-3	52	17	0	8	23	0.0009
BS300-3	56	29	8	0	7	0.0019
BS400-3	61	30	2	0	7	0.0014
BS500-3	60	22	9	0	10	0.0014
NTS-3	52	33	7	5	3	0.0007
MCP-3	57	25	0	0	18	0.0031

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629 Table 4. Results for the toxicity characteristics leaching procedure in the samples

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Sample	TCLP (mg/L)
Control	1.23±0.32 a
PL300-1	0.93±0.10 a
PL400-1	0.95±0.06 a
PL500-1	1.10±0.12 a
BS300-1	1.08±0.14 a
BS400-1	1.05±0.10 a
BS500-1	1.20±0.22 a
NTS-1	1.23±0.26 a
MCP-1	0.20±0.08 b
PL300-3	0.93±0.05 a
PL400-3	0.95±0.24 a
PL500-3	1.10±0.36 a
BS300-3	1.20±0.14 a
BS400-3	1.30±0.42 a
BS500-3	1.05±0.19 a
NTS-3	1.20±0.29 a
MCP-3	0.10±0.01 b

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641 Figure captions

642 Figure 1: In vitro bioaccessibility (IVBA) of biochars produced from poultry litter and
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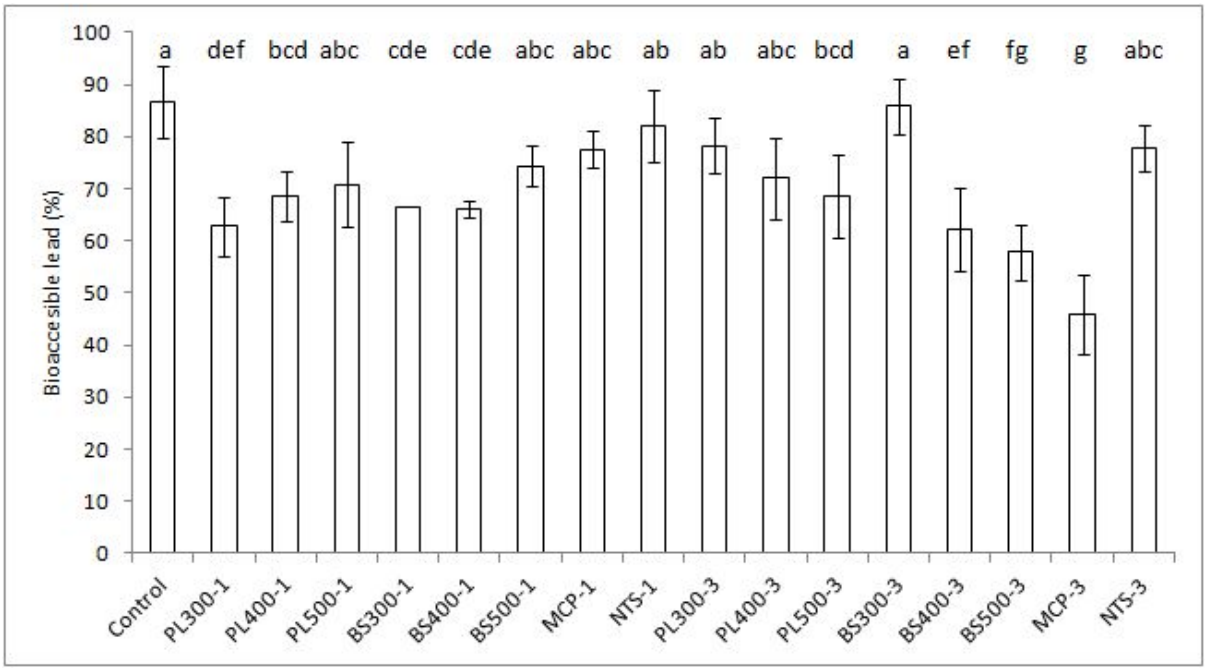
Figure 1



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Supplementary Figure 1. Linear combination fits for XANES spectra