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Slow pyrolysis enhances the recovery and reuse of phosphorus and reduces metal leaching from biosolids

David A. Roberts [a,*], Andrew J. Cole [a], Anna Whelan [b], Rocky de Nys [a], Nicholas A. Paul [a,c]

[a] MACRO – the Centre for Macroalgal Resources and Biotechnology, College of Science and Engineering, James Cook University, Townsville, QLD 4811, Australia
[b] Wastewater Operations, Townsville Water and Waste, QLD 4811, Australia
[c] Present address: Faculty of Science, Health, Education and Engineering, University of the Sunshine Coast, Maroochydore, QLD 4558, Australia

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ABSTRACT

In this study, biochar is produced from biosolids with and without alum at a range of temperatures and simulated oxidative aging of the biochars is conducted to quantify the long-term leaching of P and metals. While biosolids containing alum had negligible amounts of plant-available P, after pyrolysis >90% of the P became immediately available for plant growth. When biosolids with no alum were converted into biochar there was a small increase in the availability of P but a larger pool was available after oxidation. Both of the biosolids leached significant amounts of metals after oxidation. In contrast, the biochars had a very low available metal content and this did not increase with oxidation, demonstrating a stable metal content. Pyrolysis is an effective waste management strategy for biosolids that can simultaneously reduce the leaching of metals and increase the efficiency of recycling of P for beneficial re-use.

1. Introduction

Biosolids are a by-product of the conventional treatment of sewage. While biosolids have historically been disposed of at sea or in land-fill, there is now recognition that they could be re-used in a variety of sectors (Roy et al., 2011). In particular, biosolids are rich in P and have strong potential for use as a fertilizer in agriculture or terrestrial rehabilitation (Joo et al., 2015; Kumar, 2013; Waterhouse et al., 2014). However, concerns that contaminants could pose a risk to human health, livestock and plants prevent the widespread re-use of biosolids (Roy et al., 2011). For example, biosolids often contain metals such as Al, Cu, Zn and Fe (Donner et al., 2012; Marchenko et al., 2015). These metals may originate from the waste water or from flocculants used during water treatment. Soils amended with biosolids can therefore have elevated concentrations of metals for decades after application (Cline et al., 2012) and this may have toxic effects on soil biota (Waterhouse et al., 2014). Additionally, there is a risk of pathogens being transferred to livestock and humans, which limits the application of biosolids to land that supports cattle and food crops (EPA, 2000). The re-use of biosolids as fertilizer could be improved by techniques that minimise metal leaching and pathogen transfer, while retaining the available P content that is required for beneficial re-use.

One option to meet both of these aims is to convert biosolids into biochar through slow pyrolysis. Slow pyrolysis involves exposing biomass to high temperatures (300–750 °C) in the absence of oxygen (Lehmann and Joseph, 2009). The oxygen-limited atmosphere prevents combustion of the feedstock and leads to the formation of a solid product known as biochar. Slow pyrolysis has many advantages from the perspective of waste management. The conversion of waste into biochar reduces the mass of waste by up to 50% (Roy et al., 2011). Slow pyrolysis also yields renewable energy in the form of syngas (Wang et al., 2008). Finally, the high temperatures associated with slow pyrolysis can kill pathogens and degrade organic contaminants such as pharmaceuticals and personal care products that are common in biosolids (Ross et al., 2016). Consequently, biosolids that have been stabilised at temperatures >100 °C can be used in a wider variety of applications due to the reduced risk of pathogen transfer (EPA, 2000). While it is less widely recognised, slow pyrolysis can also reduce the risk of metal leaching from wastes. For example, biochar produced via slow pyrolysis of macroalgae (Roberts et al., 2015a,b) and sewage sludge (Méndez et al., 2012) containing metals has an order of magnitude lower water-extractable metal content than the original feedstock. While there are some voluntary biochar certification processes in the northern hemisphere (e.g. the “International Biochar Initiative Certification Program” and the “European Biochar Certificate”), there are currently no mandatory regulatory mechanisms in place for biochar that reflect the greater stability of the material in comparison to un-pyrolysed wastes (Farrell et al.,

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* Corresponding author.
E-mail address: david.roberts1@jcu.edu.au (D.A. Roberts).

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2013). Furthermore, no studies have examined the long-term stability of metals in pyrolysed waste after ageing and this remains an uncertainty in the regulation of biochar containing metals.

In addition to being a waste management technique, slow pyrolysis of biosolids may also enhance opportunities for beneficial re-use. Biochar is a durable charcoal that has a stable C content, a high surface-area to volume ratio and a high cation exchange capacity (CEC) which makes it a useful soil ameliorant (Lehmann and Joseph, 2009). The addition of biochar to soil increases soil organic C (SOC), water holding capacity and nutrient retention, leading to increased crop production across a range of soil types (Jeffery et al., 2013). While there are many possible benefits associated with the pyrolysis of biosolids, there are inevitably trade-offs in any pyrolysis system as the yield, stability and other characteristics of biochar differs depending on the feedstock and production conditions (Jeffery et al., 2013). Indeed, currently published literature has found variable effects of biochar produced from biosolids on plant productivity in biochar-amended soils. While several recent studies have demonstrated positive effects of biosolids-derived biochar on plant growth (Carey et al., 2015; Teranuma and Mori, 2002), a recent meta-analysis found that biochar derived from biosolids can have variable effects on plant productivity and may also decrease plant growth relative to control treatments (Jeffery et al., 2011). In their meta-analysis, Jeffery et al. (2011) note that biochar derived from biosolids has been subject to less experimental investigation than all other biochar feedstocks identified in their review.

Biosolids have a range of characteristics that are dependent on the specific water treatment processes used at different facilities and it is not known how different properties of biosolids influence their suitability for conversion to biochar. Additionally, given the paucity of data with respect to biosolids-derived biochar it is unclear whether slow pyrolysis can stabilise biosolids for re-use while also maintaining the available P content that makes biosolids desirable for re-use. Finally, no studies have specifically considered the long-term stability of biosolids-derived biochar with respect to both P and metal leaching.

This study addresses multiple areas of uncertainty with respect to the production and characteristics of biochar produced from biosolids. First, this study contains the first comparison of the characteristics of biochar produced from biosolids taken from water treatment processes with and without the use of alum as a flocculent. Biochar is produced from biosolids from two waste water treatment plants in Townsville (Queensland, Australia). The main difference between the two biosolids is that one is sourced from a facility that uses alum [$KAl(SO_4)_2{\cdot}12H_2O$] as a flocculent to remove P during water treatment, while the other is sourced from a facility that uses biological treatment processes and does not require alum. Second, this study explicitly considers the effects of pyrolysis temperatures and oxidative ageing of biochars on two aspects that are pertinent to re-use in agriculture; the long-term stability of metals in the biochar, and the availability of P in the biochar. Both of the biosolids are converted into biochar through slow pyrolysis at a range of highest heating temperatures (HHTs) and characterised to determine suitability for use as soil ameliorants. We first consider the effect of HHT on C stability, and the concentration of available P (Colwell P) and metals in biochar. We then examine the effect of HHT on the long-term stability of each biochar through the use of an oxidative accelerated ageing technique.

2. Materials and methods

2.1. Biosolids characterisation

Two types of biosolids were collected for this study from Cleveland Bay Purification Plant (CB) in Townsville (Queensland, Australia; 19.33°S, 146.76°E). CB is a membrane bioreactor filtration plant that services a population of 126,000 and has a maximum treatment capacity of 29 mega litres (ML) per day. Alum is used as a flocculent to remove P at CB, resulting in biosolids with a high Al content. The biosolids are air-dried in a dewatering facility that was upgraded in 2006 to handle 1000 tonnes of biosolids each year (10% moisture content). The CB dewatering facility also handles biosolids from the Mount St John Purification Plant (MSJ), Townsville (Queensland, Australia; 19.25°S, 146.74°E). MSJ uses biological trickling filters to process waste water and has a maximum treatment capacity of 25 ML per day, servicing a catchment of 106,000 people as well as industrial clients. While MSJ has a permit to use alum, the plant does not currently use any chemical flocculants, with lime (CaO) being the only chemical routinely used at MSJ. Three samples (10 L) of the two biosolids were collected from the dewatering facility at CB in September 2015. The biosolids were air-dried to <10% moisture and milled (<4 mm) prior to pyrolysis.

Samples were taken of the milled biosolids for characterisation of the feedstock. The ash content of each sample was measured in triplicate after combustion (~100 mg) in a muffle furnace (SEM Ltd., Adelaide, Australia) at 550 °C until constant weight. The elemental profile of the biosolids (C, H, N, S and P) was determined by an elemental analyser (OEA Laboratories Ltd., United Kingdom). Other trace elements (Al, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Na, Ni, Pb, Se and Zn) were analysed using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at Advanced Analytical Australia (North Ryde, Australia). The availability of trace elements that are regulated in biosolids (Al, As, Cd, Cr, Cu, Ni, Pb and Zn) was determined in deionized (DI) water extractions (Farrell et al., 2013). Briefly, the biosolids were added to DI water (1:10 w/v) and placed in a shaker cabinet for 24 h (25 °C, 100 rpm). The biosolids were filtered (0.45 μm) from the water and the water sample analysed for trace elements as described above.

The stable C content of the biosolids was determined using the Edinburgh method, which uses a rapid oxidation treatment to mimic the loss of C that is expected to occur following 50–200 years of deployment in the field (Crombie et al., 2013; Cross and Sohi, 2013). A sample of the biosolids was weighed into a 15 ml sample tube so that each tube contained 0.1 g total C. The sample was mixed with 7 ml of a 5% H_2O_2 solution, covered with foil and left until bubbling had stopped (2–3 min). The foil was removed and the sample tubes were placed in a shaker cabinet (50 rpm, 80 °C until dry). The samples were re-weighed to calculate the mass of sample lost during oxidation, and the solid residue analysed for total C. The stability of C is expressed as the percentage of the original C remaining after oxidation according to the formula:

$$C\ Stability\ (\%) = \frac{M_f * C_f}{M_i * C_i} * 100$$

where M_i is the initial mass (g) of the sample; M_f is the final mass (g) after oxidation; C_i is the initial C content (%) of the sample; and C_f is the final C content (%) after oxidation.

The availability of macro-nutrients (N and P) in the biosolids was determined through leaching assays. The availability of NO_3-N and NH_3-N was determined in a 2 M KCl solution for 1 h in a shaker cabinet (25 °C, 100 rpm). A 2.5 g sample of each sample was added to 50 ml of the KCl solution. After 1 h the solutions were filtered (0.45 μm) and the liquid fraction analysed for NO_3-N and NH_3-N by TropWater, JCU. The availability of P in the biosolids was determined using the Colwell extraction (Colwell, 1963). Briefly, 1g of biochar was added to 100 ml of a 0.5 M $NaHCO_3$ solution buffered to pH 8.5 and then placed in a shaker cabinet (25 °C, 100 rpm). After 16 h the samples were filtered (0.45 μm) and the liquid fraction analysed for total P by TropWater, JCU.

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