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### **Research article**

## The effects of feedstock pre-treatment and pyrolysis temperature on the production of biochar from the green seaweed *Ulva*

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#### ABSTRACT

Green seaweeds from the genus Ulva are a promising feedstock for the production of biochar for carbon (C) sequestration and soil amelioration. Ulva can be cultivated in waste water from land-based aquaculture and Ulva blooms ("green tides") strand millions of tons of biomass on coastal areas of Europe and China each year. The conversion of Ulva into biochar could recycle C and nutrients from eutrophic water into agricultural production. We produce biochar from Ulva ohnoi, cultivated in waste water from an aquaculture facility, and characterize its suitability for C sequestration and soil amelioration through biochemical analyses and plant growth experiments. Two biomass pre-treatments (fresh water rinsing to reduce salt, and pelletisation to increase density) were crossed with four pyrolysis temperatures (300 -750 °C). Biomass rinsing decreased the ash and increased the C content of the resulting biochar. However, biochar produced from un-rinsed biomass had a higher proportion of fixed C and a higher vield. C sequestration decreased with increasing pyrolysis temperatures due to the combination of lower yield and lower total C content of biochar produced at high temperatures. Biochar produced from unrinsed biomass at 300  $^{\circ}$ C had the greatest gravimetric C sequestration (110–120 g stable C kg<sup>-1</sup> seaweed). Biochar produced from un-pelletised Ulva enhanced plant growth three-fold in low fertility soils when the temperature of pyrolysis was less than 450 °C. The reduced effectiveness of the hightemperature biochars (>450 °C) was due to a lower N and higher salt content. Soil ameliorated with biochar produced from pelletised biomass had suppressed plant germination and growth. The most effective biochar for C sequestration and soil amelioration was produced from un-rinsed and unpelletised Ulva at 300 °C. The green tide that occurs annually along the Shandong coastline in China generates sufficient biomass (200,000 tons dry weight) to ameliorate 12,500 ha of soil, sequester 15,000 t C and recycle 5500 t N into agriculture. We provide clear parameters for biochar production to enable the beneficial use of this biomass.

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#### 1. Introduction

Biochar is a charcoal-like material that is produced through the combustion of biomass in a low oxygen atmosphere — a technique known as slow pyrolysis (Lehmann and Joseph, 2009). Biochar has a high C content that can be resistant to degradation, and so is considered to be "stable" for centuries to millennia, thus providing a form of C sequestration (Lehmann and Joseph, 2009). In addition, biochar can improve the fertility of soils by altering soil properties such as water holding capacity and through the retention of

\* Corresponding author. E-mail address: david.roberts1@jcu.edu.au (D.A. Roberts). nutrients on the surface of the biochar particles (Lehmann and Joseph, 2009). Consequently, the amelioration of soils with biochar can greatly improve the efficiency of fertilizer use, the yield of crops, and the re-vegetation of soils for landscape rehabilitation, while also increasing the C content of soils (reviewed in Beesley et al., 2011; Jeffery et al., 2011; Spokas, 2010).

While biochar has recognized roles in C sequestration and the amelioration of soil, both the stability of biochar C and the agronomic utility of biochar are strongly influenced by the properties of the feedstock and the conditions under which the biochar is produced (Bird et al., 2015). It is possible that not all of the benefits of biochar application can be maximized simultaneously (Jeffery et al., 2013). For example, if the feedstock has a high ash content this can alter the rate of decomposition of the biomass during pyrolysis and







the chemical pathways by which biochar is formed, with concomitant effects on C sequestration (White et al., 2011). Additionally, high pyrolysis temperatures are typically predicted to yield biochar with a higher fixed C content (McBeath et al., 2015) but this can be at the expense of its agronomic benefits (Zhao et al., 2013). The production of biochar must therefore be conducted with the intended application in mind and it is important to quantify tradeoffs between C sequestration and agronomic utility for a range of feedstock and production conditions (Abiven et al., 2013).

Seaweeds are a novel feedstock for biochar production (Bird et al., 2011; Roberts et al., 2015a) that can be sourced from ocean farms (Roberts et al., 2015b), land-based cultivation (De Paula Silva et al., 2008), or from seaweed blooms that occur in eutrophic waters (Merceron et al., 2007). Biochar produced from seaweed has a lower C content (~30-35%) than those produced from lignocellulosic ("woody") biomass (typically >70%), but high concentrations of exchangeable trace elements and macro-nutrients (N, P, Ca, Mg, K, Zn and Mo) that are essential for plant production (Roberts et al., 2015b). Consequently, seaweed biochar can outperform ligno-cellulosic biochars, particularly in low fertility soil (Bird et al., 2012). Green seaweeds from the genus Ulva are particularly promising as they can be cultivated in waste water from land-based aquaculture and so sequester and recycle nutrients for terrestrial crop production (Lawton et al., 2013). Ulva is also a bloom forming ("green tide") seaweed that is an issue in eutrophic water bodies, most famously along the Shandong coast in China (Wang et al., 2015), and in Brittany, France (Merceron et al., 2007). The annual *Ulva* bloom along the Shandong coastline alone can result in millions of tons of Ulva being beached (Liu et al., 2013). The annual production of cultivated seaweeds is in the vicinity of 20 million tons (FAO, 2012), so this green tide represents a significant resource. The conversion of green tide biomass into biochar would serve the dual purposes of reducing the volume of material to be removed from coastal areas and would valorize a nuisance biomass.

While seaweed biochar improves the growth of crops in low fertility soils (Bird et al., 2012) it does have limitations. Seaweed biochar has a high exchangeable Na content which may have negative effects on soil microbes in anything other than sandy soils (Bird et al., 2012; Domene et al., 2015; Rajkovich et al., 2012). The availability of Na can be controlled by manipulating the conditions under which the biochar is produced. Na can volatilize from biomass at high temperatures (Lane et al., 2015), or the Na content of seaweed can be reduced through a fresh water rinse of the biomass before pyrolysis (Neveux et al., 2014). By removing salts, fresh water rinsing can also increase the C, N and P content of the feedstock, potentially making it a more suitable material for C sequestration and soil amelioration. Finally, the fact that seaweed is a brittle feedstock may result in losses of surface-supplied biochar in agronomic settings, and is a barrier to the use of biochar in plant nurseries where bulky materials are required for soil aeration (Dumroese et al., 2011). Pelletisation of biomass prior to pyrolysis can improve the pyrolysis of low density and brittle feedstock and reduce the loss of biochar when applied to soil (Kim et al., 2014). Biochar produced from pelletised biomass may also be more recalcitrant and sequester C more effectively (Manyà, 2012; Sigua et al., 2014).

In this study we examine how biomass pre-treatment (fresh water rinsing and pelletisation) interact with pyrolysis temperatures to influence the properties and utility of biochar produced from seaweed. We consider how these factors alter the composition of seaweed biochar, and its ability to sequester C and improve the production of plants in soils. We do so through a combination of biochar characterisation and plant growth experiments in a low fertility soil ameliorated with biochar.

#### 2. Methods

#### 2.1. Biomass cultivation and biochar production

The green seaweed *Ulva ohnoi* was grown in 50 m High Rate Algal Ponds (HRAPs) at the MBD Energy seaweed cultivation facility within the Pacific Reef Fisheries Ltd. prawn farm in northern Queensland, Australia (19°28′46″ S, 147°29′18″ E). The HRAPs are operated with discharge water from the prawn farm via two sand filters that convert dissolved organic nitrogen (DON) into the dissolved inorganic N (DIN) required for the seaweed. The water and biomass are circulated in the HRAPs with a paddle wheel and the biomass is harvested by draining the water through coarse mesh baskets. The *U. ohnoi* was cultivated between February–April, 2015.

Four feedstocks for biochar production were prepared from U. ohnoi – un-manipulated seaweed, fresh water rinsed seaweed, pelletized seaweed and pelletized fresh water rinsed seaweed. To make the fresh water rinsed seaweed, a subset of the drained U. ohnoi was washed in fresh water following the methods of Neveux et al. (2014). Briefly, U. ohnoi was loosely packed into a 60 L plastic tub (~100 g biomass  $L^{-1}$ ). The tub was filled with fresh water and stirred for 60 s, then removed and drained and the process repeated two more times with new water. This technique reduces the ash content of the seaweed by approximately 50% (Neveux et al., 2014). The rinsed and un-rinsed biomass were spread on plastic trays and dried overnight in a solar kiln at 60 °C. Half of the rinsed and un-rinsed dried biomass was then converted into pellets using a Nova N-Micro Pellet Mill. The pellet mill pulverizes dried U. ohnoi with a hammer mill then sieves the biomass (<3 mm). The sieved biomass is mixed with a small amount of water to attain 10% moisture content. This biomass is then extruded through a rotating pellet die to produce pellets with a diameter of 6 mm and an average length of 25 mm. The pelletizing process increased the bulk density of the dried seaweed from 0.033  $\pm$  0.001 g cm<sup>-3</sup> to  $0.707 \pm 0.004$  g cm<sup>-3</sup>. The remaining biomass was left in its natural "flake" morphology.

The four feedstocks were converted into biochar at one of four temperatures (300, 450, 600 and 750 °C). The flakes or pellets were placed in a sealed stainless steel retort inside a muffle furnace that was pre-heated to the target temperature. The retort was purged with N<sub>2</sub> gas at 4 L min<sup>-1</sup> during pyrolysis. The biomass was left at the target temperature for 60 min and the retort was removed from the furnace and cooled under continued N<sub>2</sub> flow. The biochar was weighed to calculate yield (% of original feedstock). Three independent samples were produced for each combination of biomass pre-treatment and pyrolysis temperature. A constant mass of feedstock (80 g) was included in the biomass and pellet treatments to ensure the biochar yield from a constant feedstock mass could be compared across the treatments.

#### 2.2. Biochar characterisation

The yield of biochar (%) was recorded for each sample. The elemental profile (C, H, O, N, and S) of the biomass and biochar were analysed with an elemental analyser (OEA Laboratory Ltd, United Kingdom). The stability of C in each biochar sample was determined through the Edinburgh method (Crombie et al., 2013; Cross and Sohi, 2013). Briefly, once the C content of each sample had been determined, a sufficient quantity of each sample was weighed into a 15 ml sample tube to give a biochar sample containing 0.1 g C. Each sample was then mixed with 7 ml of a 5% H<sub>2</sub>O<sub>2</sub> solution and capped with aluminium foil until bubbling stopped (2–3 min). The foil covering was removed and the sample tubes were placed in a

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