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From waste water treatment to land management: Conversion of aquatic biomass to biochar for soil amelioration and the fortification of crops with essential trace elements

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A B S T R A C T

Macroalgae can be grown in industrial waste water to sequester metals and the resulting biomass used for biotechnological applications. We have previously cultivated the freshwater macroalga *Oedogonium* at a coal-fired power station to treat a metal-contaminated effluent from that facility. We then produced biochar from this biomass and determined the suitability of both the biomass and the biochar for soil amelioration. The dried biomass of *Oedogonium* cultivated in the waste water contained several elements for which there are terrestrial biosolids criteria (As, Cd, Cr, Cu, Pb, Ni, Se and Zn) and leached significant amounts of these elements into solution. Here, we demonstrate that these biomass leachates impair the germination and growth of radishes as a model crop. However, the biochar produced from this same biomass leaches negligible amounts of metal into solution and the leachates support high germination and growth of radishes. Biochar produced at 750 °C leaches the least metal and has the highest recalcitrant C content. When this biochar is added to a low-quality soil it improves the retention of nutrients (N, P, Ca, Mg, K and Mo) from fertilizer in the soil and the growth of radishes by 35–40%. Radishes grown in the soils amended with the biochar have equal or lower metal contents than radishes grown in soil without biochar, but much higher concentrations of essential trace elements (Mo) and macro nutrients (P, K, Ca and Mg). The cultivation of macroalgae is an effective waste water bioremediation technology that also produces biomass that can be used as a feedstock for conversion to biochar for soil amelioration.

1. Introduction

A great and complex challenge facing the world is the need to mitigate climate change while producing food for a growing population. The maintenance of agricultural soil quality will play a critical role in addressing this challenge (Sakschewski et al., 2014). Agricultural soil represents the largest carbon (C) pool on Earth (Sommer and Bossio, 2014), containing 230 times more C than was emitted by anthropogenic activities in 2009 (Sommer and Bossio, 2014). This C pool is critical for agricultural production as soil C and soil quality are intimately linked (Lal, 2008; Sommer and Bossio, 2014). The anthropogenic degradation of soils continues to reduce the global soil C pool and, consequently, the productivity of soils. The application of biochar to soil is one technique that can deliver increased soil C while improving the quality of degraded soils (Lehmann and Joseph, 2009).

Biochar is a C-rich charcoal that is produced through slow pyrolysis of biomass (the combustion of biomass under oxygen-limited conditions) (Lehmann and Joseph, 2009). Biochar can potentially sequester C for millennia and improves the quality of the soils to which it is applied by enhancing nutrient and water retention in soil (Lehmann and Joseph, 2009), and reducing emissions of greenhouse gases (e.g. CO_2 and N_2O) from fertilized soils (Cayuela et al., 2013; Zhang et al., 2010). Most research has focused on ligno-cellulosic ("woody") biomass as a feedstock for biochar. The biochar produced from this feedstock has a high fixed-C content, but low mineral content. An alternative feedstock for biochar production is marine and freshwater macroalgae. While having a lower C content than ligno-cellulosic biochar, algal biochar has high concentrations of macro-nutrients and essential trace elements, particularly N, P, Ca, Mg, K and Mo (Bird et al., 2012, 2011). Consequently, algal biochar can deliver greater improvements in

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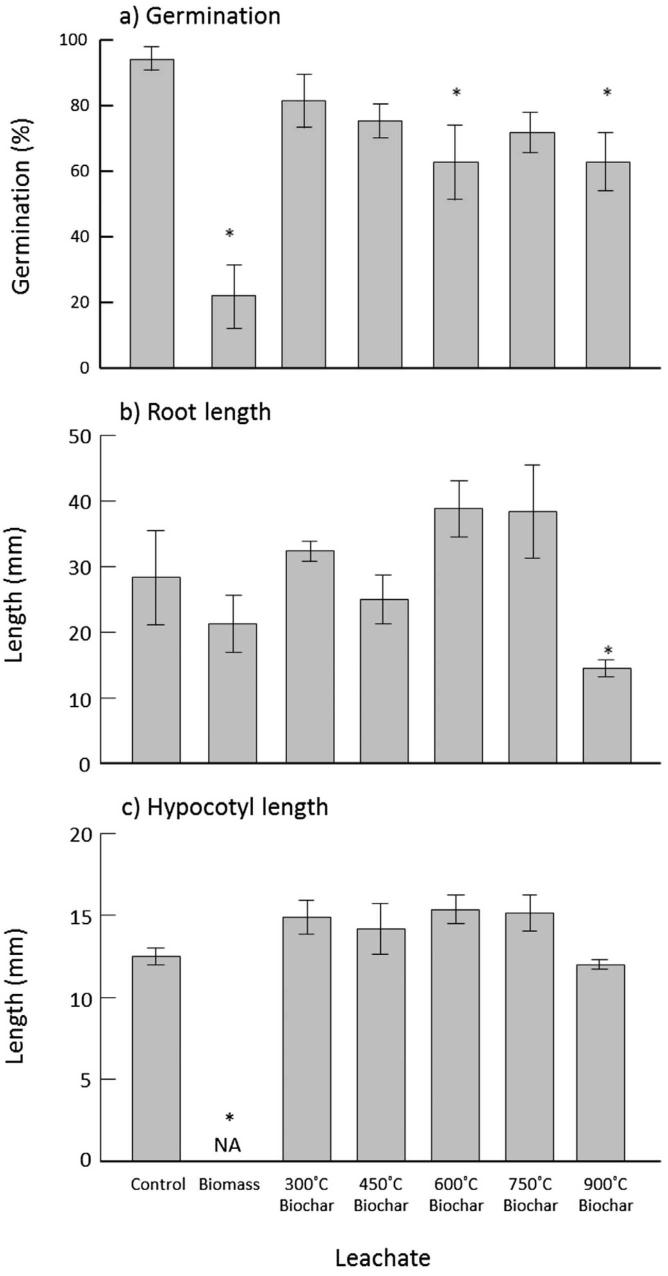

Fig. 1. The germination and growth of radishes in leachates produces from *Oedogonium* biomass and biochar. The panels show a) germination (%) of radish seeds after 72 h exposure to the leachates, and b) root and c) hypocotyl length (mm) after 10 d exposure to the leachates. All data are mean values ± S.E. (n = 4). Bars with an asterisk have a significantly lower germination rate or length than the control treatment (one-sided Dunnett's test, $P < 0.05$).

the quality of some types of soil than ligno-cellulosic biochar through the indirect effects of nutrient retention associated with all types of biochar, and through the direct contribution of macro (N, P, K, Ca and Mg) and micronutrients (e.g. Mo) to soil (Bird et al., 2012).

Table 1
The pH and electrical conductivity (EC) of soil, biochar, and soil-biochar mixtures used in the outdoor pot trial. The percent biochar is provided for context and is expressed as the percent volume of the soil-biochar mixture that was biochar (see Methods section "*Growth of radishes in biochar-amended soils*" for details).

Treatment	pH	EC (μS cm^{-1})
Soil	6.67 ± 0.14	22.5 ± 2.4
Biochar	10.03 ± 0.21	254.0 ± 5.5
0.25 t ha^{-1} (0.0625% biochar)	7.16 ± 0.11*	22.7 ± 1.8
1 t ha^{-1} (0.25% biochar)	7.24 ± 0.02*	21.1 ± 1.9
10 t ha^{-1} (2.5% biochar)	7.35 ± 0.02*	22.1 ± 1.7
50 t ha^{-1} (12.5% biochar)	7.43 ± 0.07*	32.6 ± 0.6*

*Significantly different to the control soil treatment (Dunnett's post-hoc test $P < 0.05$).

One barrier to the production and application of algal biochar is that cultivated algae have established markets as food or as a source of hydrocolloids such as alginate, agar and carrageenan. Alternatively, algal biomass from waste water bioremediation does not compete with these existing markets (Roberts et al., 2015). For example, freshwater macroalgae from the genus *Oedogonium* can be grown at coal-fired power stations in metal-contaminated water to sequester dissolved contaminants from the waste water and recycle a portion of the CO_2 emissions from flue gases into the cultivated biomass (Roberts et al., 2013; Saunders et al., 2012). This bioremediation technology has been validated at a large-scale in bioremediation ponds at an Australian coal-fired station (Roberts et al., 2015). Furthermore, the conversion of this biomass to biochar through slow pyrolysis immobilises the metals into a recalcitrant biochar that may be suitable for value-added applications as a soil ameliorant (Roberts et al., 2015). Given the recalcitrant nature of biochar, it is proposed that the metals accumulated from waste water by the algae (or other metal-laden biomass) will be less bioavailable if applied to soil in the form of biochar rather than as the original biomass feedstock (Farrell et al., 2013; Méndez et al., 2012; Song et al., 2014). To this end, it is critical to understand the effects of pyrolysis conditions on biochar produced from biomass cultivated in bioremediation applications, and the effects of this biochar on soils and plant yields.

In a recent study we cultivated algae (genus *Oedogonium*) in bioremediation ponds at a coal-fired power station to sequester metals from waste water (Roberts et al., 2015). We then produced biochar from the algae at a range of Highest Heating Temperatures (HHT) and characterized the retention of metals by the biochar when placed into solution. Here, for the first time, we examine the suitability of biochar produced from algae cultivated in bioremediation ponds for soil amelioration. First, we test the effects of the leachates from biomass and biochar of *Oedogonium* on the germination and growth of a model plant, the radish *Raphanus sativus*. Second, using the biochar with the best characteristics for soil amelioration, we assess the effects of *Oedogonium* biochar on a low quality soil. We conduct a long-term outdoor experiment to quantify nutrient retention by soils amended with biochar, and the productivity and elemental profile of radishes grown in those soils.

2. Materials and methods

2.1. Biomass and biochar production

The cultivation of *Oedogonium* and the production of biochar from this feedstock are described in a previous study (Roberts et al., 2015). Briefly, *Oedogonium* was grown at Tarong power station in Queensland, Australia in June 2013 (26°46′51″S, 151°54′45″E). Tarong has a 46 000 ML (ML) Ash Dam (AD) containing Ash Water (AW) contaminated with a suite of metals and metalloids (Table S1) (Roberts et al., 2015, 2013). *Oedogonium* was collected from Tarong AD and cultured in 15 000 L bioremediation ponds containing AW that was pumped from the AD. Flue gas containing 20% CO_2 was piped into the ponds to maintain pH between 8.4 and 8.6. *Oedogonium* was harvested twice weekly and sun-dried. A pooled sample of dried biomass was made by mixing equal parts biomass from four successive harvests in June 2013, and converted to