Assessment of biochar and iron filing amendments for the remediation of a metal, arsenic and phenanthrene co-contaminated spoil

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ABSTRACT

Sites contaminated with mixtures of metals, metalloids and organics are difficult to remediate as each contaminant type may require a different treatment. Biochar, with high metal sorption capacity, used singly and in combination with iron filings, is investigated in microcosm trials to immobilise metal(loid)s within a contaminated spoil, thereby enabling revegetation and degradation of organic pollutants. A mine spoil, contaminated with heavy metals, arsenic and spiked with phenanthrene was treated with either 1%w/w biochar, 5%w/w iron or their combination, enhancing phenanthrene degradation by 44−65%. Biochar treatment reduced Cu leaching and enabled sunflower growth, but had no significant effect on As mobility. Iron treatment reduced Cu and As leaching but negatively impacted soil structure and released high levels of Fe causing sunflower plant mortality. The combined treatment reduced both Cu and As leaching and enabled sunflower growth suggesting this could be a useful approach for treating co-contaminated sites.

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1. Introduction

Sites contaminated with mixtures of metals, metalloids and organic compounds can pose complex remediation problems since metal(loid) toxicity can inhibit the biodegradation of organic contaminants (Lee et al., 2012; Riis et al., 2002; Sokhn et al., 2001). Relatively few laboratory or field studies address both contaminant types, usually focussing on either metals or organics individually. Metal immobilisation using soil amendments aims to reduce metal leaching and bioavailability through processes such as ion exchange, surface precipitation and sorption to mineral surfaces (Kumpiene et al., 2008). Where metal toxicity is the main limiting factor to biodegradation, this kind of approach could restore the microbial activity and functionality of a metal contaminated soil. As a result, organic contaminants can be degraded providing they are bioavailable. In situations containing complex mixtures of contaminants, such as a range of heavy metals, arsenic and hydrocarbons, a careful selection of amendments could be used to immobilise non-degradable contaminants in order to enhance the bioremediation of organic ones. Since different amendments often have specific actions, a blend of materials may be required to immobilise both metal cations and arsenic anions but it is important to consider the effects of an amendment on all the contaminants that might be present in the soil. For example, immobilisation of metal cations requires either an increase in pH or the addition of materials with cation binding capacity. Conversely, arsenic exists predominantly in anionic forms whose mobility increases with increasing pH.

A soil amendment that is increasingly under investigation for land remediation is charcoal or biochar (Beesley and Marmiroli, 2011; Beesley et al., 2011; Carcamo et al., 2012; Fellet et al., 2011; Karami et al., 2011; Uchimiya et al., 2011). In a trial using soil taken from a tin mine spoil heap in the Tamar Valley (Great Console, Cornwall, UK) containing >1600 mg/kg Cu, >800 mg/kg Cd, >180 mg/kg Pb and >30 000 mg/kg As, treatments of between 0.2% w/w and 4%w/w biochar produced from stinging nettles (Urtica dioica L.) reduced Cu leaching to below detectable levels, increased soil pH, increased aerobic bacterial counts and enhanced plant growth and thus stabilisation of the soil (Wingate, 2008). However, the increased pH, particularly at high biochar amendment rates, led to increased As mobility and plant uptake, highlighting the need to co-amend with materials that bind As species.

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Iron amendments have been investigated for the stabilisation of metal(loid)s in soils (Bes and Mench, 2008; Koo et al., 2012; McBride and Martinez, 2000; Cundy et al., 2008; Hartley and Lepp, 2008a,b; Kumpiene et al., 2006). Zero valent iron, Fe(0), usually in the form of iron grit (approx 97% Fe), oxidises within the soil to poorly crystalline iron oxides and hydroxides that bind both arsenic and heavy metal ions. The use of Fe(0) avoids the acidification of soil as caused by Fe(II) and Fe(III) sulphate additions which can potentially mobilise cations. However, it has been reported that application rates of higher than 5%w/w Fe can cause soil structure problems such as aggregate cementation and reduced soil porosity (Kumpiene et al., 2008). Iron amendments have also been noted to reduce the concentrations of soluble macronutrients such as Mg, P, Ca and S (McBride and Martinez, 2000).

Here we report on the use of a mixture of amendments to address the remediation of soils with mixed contamination problems of heavy metals, arsenic and polyaromatic hydrocarbons. The following treatments were used singly and in combination; biochar derived from stinging nettles (*U. dioica* L.) was selected for its metal sorption capacity and ability to raise soil pH while iron filings, Fe(0), were selected for their ability to reduce metal and As mobility. The efficacies of the treatments were measured in two microcosm trials using the same co-contaminated spoil for each. Firstly, in terms of leachable Cu, Fe and As and the extent of phenanthrene degradation and secondly in terms of phytotoxicity and foliar element concentration using a sunflower (*Helianthus annus* L.) growth trial.

2. Materials and methods

2.1. Soil and microcosm preparation

Solvents and reagents were obtained from Fisher Scientific, UK, unless otherwise stated. A metal and As contaminated spoil was collected from an abandoned tin mine spoil heap in the Tamar Valley (Great Console, Cornwall, UK), sieved to <4 mm and spiked with 1000 mg/kg phenanthrene as a model organic contaminant. 1000 mg/kg was chosen based on previous trials using this spoil as a concentration expected to show clear differences in the efficacy of the amendments. Table 1 gives spoil properties before spiking with phenanthrene. Moisture content was determined gravimetrically by measuring mass loss after drying the spoil at 105 °C for 24 h. All following measurements were calculated on a dry weight basis. Spoil was spiked in 5 kg batches to enable thorough mixing in stainless steel containers using a stainless steel trowel. To protect microbial life in the spoil from the spiking solvent, only half the total required amount of soil was spiked with double the final required concentration of phenanthrene. As such, for 10 kg total soil containing 1000 mg/kg phenanthrene, 5 kg was mixed with 10 g phenanthrene dissolved in 500 ml acetone. After spiking the acetone was allowed to evaporate for 2 days at room temperature with daily mixing. The spiked spoil was then mixed with a further 5 kg non-spiked spoil to give a final phenanthrene concentration of 1000 mg/kg.

Biochar was prepared from stinging nettles (*U. dioica* L.) harvested from the countryside surrounding Guildford, UK, which were dried overnight at 105 °C. Dried nettles were wrapped in several layers of aluminium foil to exclude air and then charred at 450 °C for 6hr in a Carbolite LMF 4 furnace. Once cooled, the biochar was ground and sieved to a particle size of <500 μm. Table 2 gives properties of the biochar. Iron filings (technical grade) were purchased from Fisher Scientific, UK, and used as received. Microcosm trials were carried out in 10 cm diameter plastic plant pots with an approximate volume of 400 ml. Spoils were mixed with 25%v/v perlite (J Arthur Bowers, B&Q, UK) to improve aeration and water holding capacity before amendments were added. Each pot contained 450 g spoil and 10 g perlite, based on the apparent density of the two materials. Treatments were applied on a dry weight basis; thus a 1%w/w biochar treatment was equivalent to 4.6 g biochar per pot. Treated and non-treated soils were mixed together with 2 g slow release fertiliser (Miracle Gro Slow Release Fertiliser, B&Q, UK) and moistened to 60% water holding capacity with tap water. Eight microcosms were prepared for each treatment using the phenanthrene spiked spoil. Treatments consisted of; 1%w/w biochar (B), 5%w/w iron filings (Z) and a combination of 1%w/w biochar and 5%w/w iron filings (BZ).

Table 2
Characteristics of biochar produced from stinging nettles (*Urtica dioica* L.).

C (%)	H (%)	N (%)	Ash content (%)	N_2 BET surface area (m^2/g)
52.11	1.21	2.12	50.54	3.48

Untreated soils were prepared to act as controls (C). Amendment rates were chosen based on previous experiments using biochar in this spoil and with consideration to the very high As concentrations present. Previous experiments using this spoil had shown little microbial life naturally present due to the high metalloid concentrations; therefore 24 h after treatment, 1%w/w freshly collected garden soil (collected from the University of Surrey campus, Guildford, UK) was added to all microcosms to act as a source of non-specific soil microbes to reduce the lag time before phenanthrene degradation began.

2.2. Metal leaching and phenanthrene degradation microcosms

Four microcosm replicates of each treatment were used to assess metal(loid) leaching and phenanthrene degradation. Microcosms were incubated in a randomised experimental design at 25 °C for 56 days and maintained at a 60% water holding capacity by daily weight adjustment with tap water. The 56 day trial period was deemed sufficient time to establish differences between treatments in terms of plant growth and phenanthrene degradation without the sunflower plants outgrowing the pots. Samples were taken every 3 or 4 days and measured for leachable Cu, Fe and As, soil pH and bacterial phenanthrene degrading population. Approximately 20 g spoil was taken from each pot on days 1 and 56 for the determination of phenanthrene concentrations and stored at −18 °C until analysis.

Spoil pH was determined from a 1:2.5 suspension of air dried soil in RO (reverse osmosis) water shaken for 30 min using a Hanna Instruments pH 210 meter. As the metal(loid) contaminants occurring at the highest concentration in the soil, leachable Cu and As were monitored along with Fe leaching to determine the time required for iron filings to corrode. Leachable concentrations were determined in batch tests using BS EN 12457-2:2002 (BSI, 2002). In brief, 2 g air dried soil and 20 ml RO water were shaken on an orbital shaker at 200 rev/min at 20 °C for 24 h in a glass screw top vial. After 15 min settlement time, samples were filtered through a 0.45 μm syringe filter. Cu and Fe concentrations were determined directly by flame atomic absorption using a Perkin Elmer Analyst 400 Absorption Spectrometer at 324.7 nm and 248.3 nm respectively. As was determined using hydride-generation flame atomic absorption (HG-FAAS) at 193.7 nm using a Thermo SP Atomic Absorption Analyser with a Perkin Elmer MHS 10 Hydride System, using 9M HCl and 3% m/v $NaBH_4$ to give total As without the need for a pre-reduction step (Anthemidis et al., 2005). Calibration standards were prepared using Trace Cert Analytical Standards (Sigma Aldrich, UK). Since leaching was measured using batch tests, results were calculated in mg/kg on a dry soil weight basis rather than mg/l.

Populations of degrading micro-organisms were quantified using spray plate counts (Kiyohara et al., 1982). One gram soil was mixed with 10 ml, ¼ strength Ringer's solution then serially diluted. Subsequently, a 0.1 ml sample was spread plated onto basal salt medium and incubated overnight at 25 °C to dry (Bogardt and Hemmingsen, 1992; Juhasz and Naidu, 2000). Plates were sprayed with a solution of phenanthrene in diethyl ether (5 g in 500 ml) using a Preval sprayer unit (Rigby Taylor Ltd, UK) to give an opaque coating of phenanthrene using a spraying distance of >50 cm to allow evaporation of the diethyl ether before it reached the plate. Plates were incubated at 25 °C for 10 days until zones of clearance were visible within the phenanthrene layer indicating a colony of bacteria capable of phenanthrene degradation. Phenanthrene degrading populations were calculated on a dry soil weight basis.

Phenanthrene was extracted from the soil with DCM/Acetone (1:1 v/v) using accelerated solvent extraction and quantified by GC−MS using a method developed from US EPA methods 3545A, 8000B and 8270C (US EPA, 1996a,b, 1998). Phenanthrene concentrations were measured relative to *o*-terphenyl as an internal standard and analyte recovery was determined relative to chloro-octadecane as a recovery standard. Extractions were carried out using a Dionex ASE 200 in an 11 ml extraction cell using the following system parameters; system pressure 10 MPa (1500 psi), oven temperature 100 °C, 5 min oven heat up, 5 min static time, 100% flush volume, 10 MPa (1500 psi) nitrogen purge for 60 s. Two static cycles were found to be necessary to give optimal recovery rates. After drying the extracts over anhydrous sodium sulphate, phenanthrene concentrations were determined by GC−MS using a Thermo Finnigan Voyager GC−MS. Components were separated on

Table 1
Characteristics of Tamar Valley mine spoil before spiking with phenanthrene.

pH	Sand (%)	Silt (%)	Clay (%)	Textural Class	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	As (mg/kg)
3.2	92	4	4	Sand	1641	47	189	813	34	34,470