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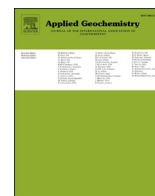
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# Amendments of waste ochre from former coal mines can potentially be used to increase soil carbon persistence

Mark E Hodson<sup>\*</sup>, Mahmuda Islam, Matty Metcalf, Amy CM Wright<sup>1</sup>

Department of Environment and Geography, University of York, Wentworth Way, York, YO10 5NG, UK

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## ABSTRACT

There is an increasingly urgent need to remove CO<sub>2</sub> from the atmosphere. Increasing C storage in soils has been discussed as a possible method of achieving this. Regardless of whether increasing soil C would result in reduced atmospheric C or not, increasing the amount of organic carbon (OC) stored as organic matter in soils is widely regarded as leading to agronomic benefits such as increased water retention and resistance to erosion. Fe oxides adsorb OC in soil, protecting it from degradation. In this study we investigated the use of waste ochre (Fe oxyhydroxide) that precipitates from the drainage of former coal mines as a soil amendment to increase C storage in soils via reduced C lability. In preliminary batch experiments, ochres reduced the release of OC from soils into solution. In plant growth experiments with wheat (var. Skyfall, RAGT) 5 wt% amendments of ochre to soils significantly reduced the concentration of hot water extractable OC by approximately 16% and OC lost from the soils in leachate by approximately 43%. Above ground plant biomass was significantly reduced by approximately 50% in the amended soils. There was no evidence for increased uptake of potentially toxic elements in the plants from the ochre-amended soils compared to the study controls but Olsen P extractable phosphate was decreased by the ochre amendments. In subsequent experiments with agronomically realistic additions of KH<sub>2</sub>PO<sub>4</sub> there was no difference in plant biomass between the study controls and the ochre-treated soils suggesting that reduced plant growth was due to reduced P availability; C lability was still significantly reduced. Furthermore, the ochre amendments helped retain th added phosphate in the soil. These results indicate that Fe oxide amendments to soil may be a viable way of changing soil chemistry in order to increase the amount of OC retained in soils. Further experiments investigating the impacts of the ochre amendments on greenhouse gas emissions and soil biology are required followed by field trials where the impact of more variable soil moisture and temperature effects can be assessed and crops grown to harvest. A full Life Cycle Analysis could then be performed. Given the relatively limited quantities of former coal mine ochres available in the UK and the carbon footprint of transporting materials prior to adding them to soils, similar experiments to those reported here, taking into account chemical and mineralogical variations, are warranted to determine the global stock pile of Fe-rich wastes that could potentially be used to reduce C lability in soils.

## 1. Introduction

Increasing levels of CO<sub>2</sub> in the atmosphere are driving climate change (IPCC, 2021). Soils are one of the largest global pools of C, containing an estimated 2–3 times as much C as the atmosphere and vegetation combined (IPCC, 2014; Shepherd et al., 2009). Small increases in the proportion of C held in soils could significantly reduce atmospheric CO<sub>2</sub> concentrations, an idea that has given rise to the 4 per mille initiative (Wiesmeier et al., 2019; Rumpel et al., 2020).

Investigating possible methods of increasing the concentration of C in soils is of clear importance with regards to the current climate crisis (Sommer and Bossio, 2014). Various soil management practices to achieve this have been, and are, explored in the current literature including the addition of biochar to soils (e.g. reviews by Lorenz and Lal, 2014 and Vijay et al., 2021) and limited/conservation tillage, cover cropping, crop rotation, the application of manure and compost and rotational grazing (often referred to in combination as regenerative agriculture, e.g. Wiltshire and Beckage, 2022). In addition to suggested

<sup>\*</sup> Corresponding author.

E-mail addresses: [mark.hodson@york.ac.uk](mailto:mark.hodson@york.ac.uk) (M.E. Hodson), [mahmudaislam48@gmail.com](mailto:mahmudaislam48@gmail.com) (M. Islam), [matty.metcalf@hotmail.co.uk](mailto:matty.metcalf@hotmail.co.uk) (M. Metcalf), [aw1154@pgr.aru.ac.uk](mailto:aw1154@pgr.aru.ac.uk) (A.C. Wright).

<sup>1</sup> Current address: School of Life Sciences, Anglia Ruskin University, East Road, Cambridge, Cambridgeshire, CB1 1PT

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impacts on atmospheric CO<sub>2</sub> levels, increasing the amount of organic carbon (OC) in soils has a variety of other benefits such as almost always leading to increases in soil fertility, water holding capacity and resistance to erosion (e.g. Quastel, 1952; Tiessen et al., 1994; Rawls et al., 2003; Schmidt et al., 2011) such that increasing soil organic matter content is usually considered a worthwhile endeavour regardless of the impact on the climate (Moinet et al., 2023). However, increasing C sequestration in soil is not a simple process of just adding organic matter to the soil (Powelson et al., 2011; Moinet et al., 2023); a decrease in the lability of the OC is instead required. This may be most readily achieved by altering the soil composition and properties responsible for the structure of the soil (Bruce et al., 1999).

The importance of Fe oxides in protecting organic matter from degradation in soils has long been recognised (Kaiser and Guggenberger, 2000; Evans and Wilson, 1985; Tisdall and Oades, 1982). Various studies have investigated the relationship between Fe oxides and OC in soils, with particular focus on the roles of adsorption and aggregation. Direct adsorption of OC onto Fe oxides is relatively well documented and understood (Honghai et al., 2008; Adams and Kassim, 1984). In particular, Wagai and Mayer (2007) demonstrated correlations between total soil OC and the sorption capacity of Fe oxides. Fe oxides also bind OC to other particles to form microaggregates (e.g. Wen et al., 2019; Krause et al., 2020; Wagai et al., 2020). OC that is adsorbed to Fe-oxides and/or incorporated into microaggregates is protected from degradation by micro-organisms and can accumulate in soil (Balesdent et al., 2000; Lehmann et al., 2007; Sollins et al., 1996; Kaiser and Guggenberger, 2000). Silva et al. (2015) observed increases in soil C following addition of Fe-rich biosolids at a mine restoration site in Brazil; their research showed that the increases resulted from the formation of organo-Fe complexes leading to increased aggregation. More recently, Button et al. (2022) added synthetic Fe(OH)<sub>3</sub> to soil in a laboratory incubation experiment and observed small decreases in CO<sub>2</sub> release from soil together with reductions in the dissolved organic carbon (DOC) and phosphate in the soil solution. The studies of Silva et al. (2015) and Button et al. (2022) suggest that Fe amendments to soils could lead to an increase in C retention in soil.

Ochres are Fe-rich materials commonly precipitated from mine water draining from Fe-rich rocks. In the UK, thousands of tonnes of ochre are deposited from water draining former coal mines each year (Sapsford et al., 2015; Kusun et al., 2012). The vast majority of this ochre is currently landfilled, but it has also shown potential for immobilizing trace elements such as As and nutrients, particularly P within soils (Fenton et al., 2009, 2012; Doi et al., 2005; Dobbie et al., 2009; Sapsford et al., 2015). Furthermore, globally approximately 100 million tonnes of Fe-rich sludge are produced during waste water treatment and are largely disposed of as a waste material (Chen et al., 2015).

The aim of this study was to determine whether ochre amendments to soil have the potential to increase C retention in the soil. We hypothesised that ochre amendments to soils would adsorb OC and increase the abundance and C content of microaggregates, in turn reducing the C released into solution and decreasing the availability of OC for degradation. However, because of its ability to adsorb P (Fenton et al., 2009, 2012; Dobbie et al., 2009; Sapsford et al., 2015), and because P is a key plant nutrient (e.g. Haygarth et al., 2013), we also hypothesised that the ochre amendments would reduce both plant growth, due to nutrient limitation, and P leaching from soil which, if unchecked can lead to eutrophication (Djordjic et al., 2004; Ulén et al., 2007). To investigate our hypotheses we carried out three experiments. In a batch experiment, soil and ochre were mixed and the release of OC and P into solution was determined. This was an initial experiment designed to determine whether or not ochre amendments had the capacity to lower C lability by reducing its release into solution. Although ochres are predominately Fe oxides, as natural materials they can contain a range of trace elements including potentially toxic elements such as As (e.g. Fenton et al., 2009, 2015; Olimah et al., 2015) and a range of metals (e.g. Cu, Cd, Cr, Ni, Pb, Zn Fenton et al., 2009; 2012).

Therefore, in addition to measuring C release we also measured the release of metals and P into solution in order to check for additional potential positive or negative consequences of ochre amendments to soil. Having demonstrated the ochres' ability to reduce C release into solution from two different soils we then conducted two longer time-scale plant growth experiments to determine whether this reduced C lability was still seen in more realistic scenarios, namely those in which soil was not in suspension but was kept moist, and in which plants were growing. Only a single soil was used in the plant growth experiments due to cost and time constraints. In the first plant growth experiment, winter wheat plants (var. Skyfall, RAGT) were grown in ochre-amended soils and various indicators of C lability were measured, together with Olsen (plant available) P, plant biomass and plant metal uptake. In the second plant growth experiment winter wheat was grown in ochre amended soil with additions of phosphate fertiliser; plant biomass, Olsen P and C and P export in leachate were measured.

## 2. Materials and methods

### 2.1. Soils and ochres

Two soils were used, a sandy clay loam Agricultural soil from a local arable field (SE 62635 49583) and a sandy clay Woodland soil from a local deciduous woodland (SE 62084 50860). Texture classes were determined by hand texturing (Thien, 1979). Samples were taken from the top 20 cm of the soil after removal of any litter layer. The soils were air-dried, sieved to ≤2 mm (to homogenise the soil and remove unreactive larger particles and coarse grained, undegraded organic material), and stored prior to characterisation and use in experiments. Ochre samples were provided by Mr Jon Aumonier of the UK's Coal Authority and were collected from the former coalmines of Morlais (SN 57225 02234), Saltburn (NZ 67260 19783), Ynysarwed (SN 80857 01749), Lynemouth (NZ 28372 91616), Blenkinsop (NY 67006 64317), Polkemmet (NS 93550 64050) and Whitworth (SS 79810 96870). Production rates of ochres from these sites are up to approximately 1000 tonnes per year (J. Aumonier, The Coal Authority, UK, Pers. Comm., 2020). The Saltburn, Ynysarwed, Blenkinsop, Polkemmet and Whitworth ochres were supplied moist in sealed, plastic containers; the Morlais and Lynemouth ochres were supplied dry. All ochres were freeze dried and crushed to ≤2 mm prior to characterisation. Soil and ochre properties were determined as part of this study and are summarised in Table 1. pH was determined in water (Rowell, 1994). Rather than measuring organic carbon in our samples, mass loss on ignition at 350 °C was used as a proxy for organic matter content (Ayub and Boyd, 1994); the temperature of 350 °C is used to avoid the breakdown of carbonate minerals and loss of structural water from clay minerals artificially increasing the estimate of organic matter, however lignin may not be combusted at these temperatures and ochres have been shown to lose adsorbed water between 105 °C and this temperature (Perera-Solis et al., 2019) so these measurement must be treated as approximations. Particle size distribution of the ochres was determined using a Malvern Instruments MasterSizer 2000 laser granulometer. Pseudo-total elemental composition was measured by aqua regia digest (British Standard, 1995) and subsequent analysis by inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo iCAP 7000). Extractable Fe was determined using sodium pyrophosphate (SP, assumed to extract organically complexed Fe), acid ammonium oxalate (AO, assumed to extract organically complexed and amorphous inorganic Fe) and dithionite-citrate (DC, assumed to extract organically complexed, amorphous inorganic and fine crystalline Fe) (Courchesne and Turmel, 2007). Plant available inorganic P as PO<sub>4</sub> was measured by the Olsen P extraction (Olsen et al., 1954) and analysis on an autoanalyser (Seal AA3 Autoanalyser). Quantitative mineralogy of ochres was determined by X-ray diffraction using a Philips PW1050 with Philips X40 software under contract at the University of Leeds; semi-quantitative mineralogy of soils was determined using a Bruker D8 Advance with a scintillation

**Table 1**

Mean soil and ochre physical and chemical properties (n = 3 ± std dev). Different letters represent a significant difference in a parameter between the soils and ochres (p ≤ 0.05, Analysis of Variance (ANOVA) and Tukey test).

	Agricultural soil	Woodland soil	Morlais	Saltburn	Ynysarwed	Lynemouth	Whitworth	Blenkinsop 1	Blenkinsop 2	Polkemmet	
pH	6.86 ± 0.030 <sup>a</sup>	6.69 ± 0.010 <sup>b</sup>	7.92 ± 0.020 <sup>c</sup>	8.23 ± 0.030 <sup>d</sup>	8.34 ± 0.040 <sup>e</sup>	8.07 ± 0.020 <sup>f</sup>	4.45 ± 0.050 <sup>g</sup>	7.83 ± 0.010 <sup>h</sup>	9.36 ± 0.050 <sup>i</sup>	8.02 ± 0.020 <sup>f</sup>	
Loss on ignition for organic matter/%	3.69 ± 0.090 <sup>a</sup>	5.63 ± 0.12 <sup>b</sup>	8.41 ± 0.19 <sup>c</sup>	11.24 ± 0.060 <sup>d</sup>	7.52 ± 0.12 <sup>e</sup>	12.38 ± 0.20 <sup>f</sup>	14.31 ± 0.10 <sup>g</sup>	10.68 ± 0.090 <sup>h</sup>	6.67 ± 0.13 <sup>i</sup>	12.45 ± 0.15 <sup>f</sup>	
BET surface area/m <sup>2</sup> g <sup>-1</sup>	ND	ND	71.3	163	273	133	105	177	38.8	139	
Particle size	ND	ND	<2 µm 1.70% 2–20 µm 34.1% 20–2000 µm 64.2%	<2 µm 2.60% 2–20 µm 23.0% 20–2000 µm 74.4%	<2 µm 16.5% 2–20 µm 32.7% 20–2000 µm 50.8%	<2 µm 15.1% 2–20 µm 60.8% 20–2000 µm 24.1%	<2 µm 3.99% 2–20 µm 38.9% 20–2000 µm 57.1%	<2 µm 7.45% 2–20 µm 25.9% 20–2000 µm 66.7%	<2 µm 7.67% 2–20 µm 44.5% 20–2000 µm 46.8%	<2 µm 6.06% 2–20 µm 36.5% 20–2000 µm 57.4%	
Ca/mg kg <sup>-1</sup>	720 ± 2.6 <sup>ab</sup>	690 ± 82 <sup>a</sup>	1500 ± 14 <sup>b</sup>	5000 ± 130 <sup>c</sup>	10000 ± 300 <sup>d</sup>	3900 ± 460 <sup>e</sup>	210 ± 63 <sup>a</sup>	2900 ± 27 <sup>g</sup>	29000 ± 630 <sup>h</sup>	2000 ± 16 <sup>b</sup>	
Mg/mg kg <sup>-1</sup>	420 ± 0.93 <sup>a</sup>	380 ± 3.2 <sup>b</sup>	210 ± 3.7 <sup>c</sup>	340 ± 8.5 <sup>d</sup>	400 ± 5.4 <sup>ab</sup>	810 ± 25 <sup>e</sup>	61 ± 7.7 <sup>f</sup>	300 ± 3.0 <sup>g</sup>	ND	290 ± 1.5 <sup>g</sup>	
K/mg kg <sup>-1</sup>	290 ± 3.0 <sup>a</sup>	210 ± 6.2 <sup>b</sup>	75 ± 21 <sup>c</sup>	6.2 ± 1.4 <sup>d</sup>	16 ± 0.71 <sup>d</sup>	61 ± 7.6 <sup>ce</sup>	63 ± 1.8 <sup>ce</sup>	11 ± 0.97 <sup>d</sup>	7.9 ± 1.3 <sup>d</sup>	52 ± 1.0 <sup>e</sup>	
Na/mg kg <sup>-1</sup>	8.1 ± 16 <sup>a</sup>	120 ± 110 <sup>ac</sup>	45 ± 24 <sup>ac</sup>	340 ± 160 <sup>ac</sup>	240 ± 170 <sup>ac</sup>	850 ± 42 <sup>b</sup>	120 ± 96 <sup>ac</sup>	140 ± 150 <sup>ac</sup>	380 ± 150 <sup>c</sup>	100 ± 130 <sup>ac</sup>	
Al/mg kg <sup>-1</sup>	2700 ± 19 <sup>a</sup>	1300 ± 7.0 <sup>b</sup>	400 ± 6.9 <sup>c</sup>	23.2 ± 0.98 <sup>d</sup>	370 ± 5.6 <sup>e</sup>	55 ± 2.1 <sup>f</sup>	330 ± 4.9 <sup>g</sup>	260 ± 2.0 <sup>h</sup>	74 ± 1.0 <sup>f</sup>	290 ± 2.6 <sup>i</sup>	
Fe/mg kg <sup>-1</sup>	4000 ± 50 <sup>a</sup>	2500 ± 16 <sup>b</sup>	31000 ± 170 <sup>c</sup>	39000 ± 710 <sup>d</sup>	33000 ± 350 <sup>e</sup>	39000 ± 1400 <sup>d</sup>	36000 ± 58 <sup>f</sup>	39000 ± 240 <sup>d</sup>	22000 ± 320 <sup>g</sup>	39000 ± 140 <sup>d</sup>	
Mn/mg kg <sup>-1</sup>	110 ± 0.52 <sup>a</sup>	69 ± 0.51 <sup>b</sup>	390 ± 7.1 <sup>c</sup>	82 ± 2.1 <sup>b</sup>	310 ± 4.9 <sup>d</sup>	100 ± 3.1 <sup>a</sup>	17 ± 0.30 <sup>e</sup>	130 ± 0.81 <sup>f</sup>	930 ± 12 <sup>g</sup>	240 ± 0.88 <sup>h</sup>	
B/mg kg <sup>-1</sup>	53 ± 0.13 <sup>a</sup>	31 ± 0.24 <sup>a</sup>	520 ± 6.5 <sup>b</sup>	780 ± 18 <sup>c</sup>	600 ± 6.2 <sup>d</sup>	840 ± 23 <sup>e</sup>	720 ± 11 <sup>f</sup>	850 ± 6.7 <sup>e</sup>	340 ± 3.6 <sup>g</sup>	850 ± 2.9 <sup>e</sup>	
Ba/mg kg <sup>-1</sup>	51 ± 0.055 <sup>a</sup>	27 ± 0.10 <sup>b</sup>	26 ± 0.72 <sup>c</sup>	6.2 ± 0.40 <sup>d</sup>	6.3 ± 0.69 <sup>d</sup>	11 ± 0.42 <sup>e</sup>	12 ± 0.38 <sup>e</sup>	6.2 ± 0.70 <sup>d</sup>	3.3 ± 0.60 <sup>f</sup>	29 ± 0.19 <sup>g</sup>	
Co/mg kg <sup>-1</sup>	1.50 ± 0.0079 <sup>a</sup>	0.83 ± 0.0069 <sup>b</sup>	0.86 ± 0.035 <sup>b</sup>	2.9 ± 0.080 <sup>c</sup>	3.5 ± 0.040 <sup>d</sup>	1.3 ± 0.080 <sup>e</sup>	0.48 ± 0.012 <sup>f</sup>	1.9 ± 0.011 <sup>g</sup>	5.9 ± 0.073 <sup>h</sup>	0.45 ± 0.029 <sup>i</sup>	
Li/mg kg <sup>-1</sup>	5.60 ± 0.039 <sup>a</sup>	2.4 ± 0.052 <sup>b</sup>	1.2 ± 0.031 <sup>c</sup>	0.28 ± 0.0087 <sup>d</sup>	0.13 ± 0.0032 <sup>e</sup>	1.0 ± 0.030 <sup>f</sup>	0.54 ± 0.019 <sup>g</sup>	0.37 ± 0.010 <sup>h</sup>	1.5 ± 0.019 <sup>i</sup>	0.63 ± 0.022 <sup>j</sup>	
Zn/mg kg <sup>-1</sup>	15 ± 0.31 <sup>a</sup>	13 ± 0.12 <sup>b</sup>	11 ± 0.18 <sup>b</sup>	26 ± 0.97 <sup>c</sup>	18 ± 0.35 <sup>d</sup>	18 ± 0.25 <sup>d</sup>	18 ± 1.7 <sup>d</sup>	23 ± 0.82 <sup>g</sup>	13 ± 0.33 <sup>b</sup>	17 ± 0.51 <sup>ad</sup>	
Pb/mg kg <sup>-1</sup>	7.5 ± 0.11 <sup>a</sup>	7.9 ± 0.077 <sup>b</sup>	2.9 ± 0.085 <sup>c</sup>	2.2 ± 0.12 <sup>d</sup>	1.7 ± 0.059 <sup>e</sup>	2.5 ± 0.045 <sup>f</sup>	3.7 ± 0.036 <sup>g</sup>	2.4 ± 0.092 <sup>df</sup>	1.0 ± 0.035 <sup>h</sup>	3.2 ± 0.018 <sup>i</sup>	
Sr/mg kg <sup>-1</sup>	3.5 ± 0.084 <sup>a</sup>	2.2 ± 0.22 <sup>a</sup>	19 ± 0.37 <sup>b</sup>	100 ± 3.1 <sup>c</sup>	61 ± 0.78 <sup>d</sup>	120 ± 4.9 <sup>f</sup>	2.5 ± 0.25 <sup>a</sup>	64 ± 0.15 <sup>d</sup>	240 ± 5.5 <sup>g</sup>	56 ± 0.47 <sup>e</sup>	
SP Fe/mg kg <sup>-1</sup>	3240 ± 326 <sup>ab</sup>	4170 ± 5170 <sup>ab</sup>	701 ± 503 <sup>a</sup>	1770 ± 1450 <sup>ab</sup>	6920 ± 2170 <sup>b</sup>	1330 ± 643 <sup>ab</sup>	3180 ± 640 <sup>ab</sup>	3880 ± 2290 <sup>ab</sup>	396 ± 493 <sup>a</sup>	445 ± 347 <sup>a</sup>	
AO Fe/mg kg <sup>-1</sup>	5190 ± 203 <sup>a</sup>	2650 ± 225 <sup>b</sup>	50900 ± 8690 <sup>c</sup>	49600 ± 1210 <sup>g</sup>	67300 ± 1660 <sup>cd</sup>	84600 ± 15700 <sup>def</sup>	86199 ± 15700 <sup>ef</sup>	97000 ± 3480 <sup>f</sup>	38600 ± 2580 <sup>g</sup>	60600 ± 6650 <sup>c</sup>	
DC Fe/mg kg <sup>-1</sup>	7630 ± 378 <sup>a</sup>	6140 ± 1780 <sup>a</sup>	144000 ± 13900 <sup>d</sup>	128000 ± 25200 <sup>b</sup>	153000 ± 7700 <sup>bd</sup>	190000 ± 4860 <sup>eg</sup>	171000 ± 1330 <sup>cd</sup>	191000 ± 10700 <sup>eg</sup>	88700 ± 8520 <sup>f</sup>	213000 ± 8590 <sup>g</sup>	
Olsen P/mg kg <sup>-1</sup>	34.6 ± 4.7 <sup>a</sup>	18.6 ± 0.83 <sup>b</sup>	ND	ND	ND	ND	ND	ND	ND	ND	
Mineralogy	Quartz 83% Muscovite 8% Alkali feldspar 3% Plagioclase 4% Kaolinite 2% Chlorite 1%	Quartz 84% Muscovite 7% Alkali feldspar 2% Plagioclase 5% Kaolinite 2% Chlorite 1%	Goethite 67% Quartz 30% Calcite 3%	Goethite 95% Calcite 4% Quartz 1%	Amorphous 100%	Goethite 98% Calcite 3%	Goethite 84% Quartz 16%	Goethite 97% Calcite 3%	Calcite 30% Goethite 27% Aragonite 23% Brushite 12% Magnetite 8% Quartz 1%	Goethite 97% Quartz 2% Calcite 1%	Goethite 97% Quartz 2% Calcite 1%

detector and Siroquant software at the University of Edinburgh.

## 2.2. Batch experiment

A batch experiment, based on well established methodologies (e.g. Doi et al., 2005) was carried out to determine whether the ochres had the capacity to reduce C release from soil into solution. One gram of ≤2 mm air-dried soil was shaken with 0.05 or 0.1 g dry ochre in 20 mL of 0.01 M CaCl<sub>2</sub> at 20 °C in an end over end shaker at 30 rpm for 24 h; controls had no added ochre. These ratios were chosen as a compromise between having sufficient ochre to detect adsorption and ensuring that our mixture was predominantly soil. The experiment was run for 24 h as many experiments of this nature show that the majority of adsorption and desorption occurs within 24 h (e.g. Hodson et al., 2017; Doi et al.,

2005). More specifically kinetic experiments that investigated the adsorption of P onto ochres show that the majority of adsorption occurs within minutes (Heal et al., 2003; Fenton et al., 2009). Experiments were performed in triplicate. After 24 h, the pH of each suspension was measured using a Thermo Orion Star A111 pH meter calibrated with pH 4.01, 7 and 10.01 buffers. Subsequently, samples were centrifuged at 3000 rpm for 10 min; the supernatant was filtered (Whatman 40 filter paper) into separate vials and frozen at -20 °C to preserve samples until analysis of DOC, metals and phosphorus. Unpublished work in our laboratory has shown that this does not affect analyte concentrations. DOC was analysed using an elemental analyser (Elementar varioTOC Select) and dissolved elemental concentration (metals and phosphorus) by inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo iCAP 7000). Concentrations of elements released into solution

were compared between the control and the treatments. Quality control information is in [Table S1](#).

### 2.3. Plant growth experiment 1

Air-dried <2 mm Woodland soil was amended with dry Morlais, Lynemouth or Polkemmet ochre in an amount equal to 5% of the soil mass. This level of amendment was chosen as it was the lower of the two ochre amendment levels tested in our batch experiment and is similar to levels of biochar and basalt amendment that are currently being explored in the scientific literature for improving soil nutrient status and increasing soil C (e.g. [Kelland et al., 2020](#); [Lorenz and Lal, 2014](#); [Strefler et al., 2018](#); [Vijay et al., 2021](#)). The mixtures, and unamended soil, were moistened with deionised water equal to 25% of their dry mass. The moist mixtures were added to approximately 1 cm below the rim of pots with a diameter of 10 cm and a height of 9 cm giving a volume of material in each pot equal to approximately 650 cm<sup>3</sup>. Masses of material ranged from 258 to 332 g due to the differing densities of the ochres ([Table S2](#)). A 4-day old pre-germinated Skyfall wheat seedling (*Triticum aestivum*) was added to each pot. Five replicates were established per treatment. Four experimental blocks were established; each block contained each treatment. Pots were randomly rearranged within their blocks weekly.

The plants were grown under natural light conditions on a window sill in a laboratory that has a temperature of 16–19 °C. The plants were watered twice weekly with a total of 110 mL deionised water per week. On days 3, 14, 21, 28, 35 and 42 after the start of the experiment the water that had drained from the pots was collected, weighed, filtered (Whatman 2 filter paper) and stored at –20 °C for DOC analysis using an elemental analyser (Elementar varioTOC Select). After 6 weeks plant biomass was determined; plants were harvested 0.5 cm above the soil surface, weighed then dried to constant mass at 60 °C before being weighed again. The biomass was then ground to a fine powder using a Retsch MM200 ball mill. 0.05–0.1 g of ground plant material was digested in 5 mL of 65% HNO<sub>3</sub> overnight. The mixture was then heated to 60 °C, left for 3 h then heated to 110 °C and left for 6 h. The solutions were allowed to cool, filtered, diluted by a factor of 10 and analysed for metals by ICP-OES. Soil from each pot was homogenised and air-dried for later analysis. Cold and hot water extractable carbon (CWEC and HWEC) was extracted following the method of [Ghani et al. \(2003\)](#) and analysed using an elemental analyser (Elementar varioTOC Select). Subsamples of soil were separated into water stable aggregate (WSA) fractions of varying sizes (>2 mm, 1–2 mm, 250–1000 µm, 53–250 µm and <53 µm) following a wet sieving method adapted from [Cambardella and Elliott \(1993\)](#). A 70 g subsample was placed on a 2000 µm sieve and left, submerged in water to a depth of 15 mm for 5 min. The sieve was then moved vertically up and down over a distance of 5 cm fifty times over 1.5 min. Any floating material was removed and material retained on the sieve was transferred to an aluminium tin for drying. The remaining water and soil were poured onto a 1000 µm sieve and, again for a depth of water 15 mm above the sieve mesh, the sieve was moved up and down over a distance of 5 cm but for forty times over a period of 1 min and 10 s. The process was repeated using a 250 µm sieve (with thirty up and down movements over 1 min and 20 s) and a 53 µm sieve (with ten up and down movements and sufficient time to allow all the water to drain through the sieve on each occasion). The remaining suspension was transferred to a 2000 mL beaker and allowed to settle for 24 h. The clear water was then poured away and the remaining suspension transferred to an aluminium tin. The fractions were air-dried, weighed and oven-dried at 105 °C to constant mass. It should be noted that whilst this method produces an internally consistent set of measurements, the original aggregate distribution of the soils will have been disrupted when they were air dried and sieved prior to the experiment. Furthermore, drying the soil post experiment prior to determining the WSA distribution may also have had an effect, for example [Bullock et al. \(1988\)](#) show that air-drying can increase

aggregate stability. Thus this method may not be sensitive enough to differentiate subtle differences in WSA distributions. The oven-dried samples were weighed then ground in a ball mill (Retsch MM200) at 1500 rpm for 3 min. Samples were stored in air-tight bags prior to C analysis by elemental analyser (Elementar vario MACRO cube). Plant available inorganic P as PO<sub>4</sub> concentrations in the soil were determined through an Olsen P extraction ([Olsen et al., 1954](#)) and analysis by autoanalyser (SEAL AA500). pH was measured in solution (1:2.5 soil to water ratio, shaken for 15 min) using a portable probe (Fisher Scientific Accumet AP72 pH Meter) calibrated with pH 4.00, 7.00 and 10.00 buffers. Quality control information is in [Table S3](#).

### 2.4. Plant growth experiment 2

This followed the same methodology as the first plant growth experiment with the following changes. Only the Morlais ochre was used due to time and cost constraints as all three ochres had shown broadly similar results in both the batch and first plant growth experiment. In addition to the ochre, the soils were also amended with KH<sub>2</sub>PO<sub>4</sub> which was mixed throughout the soil as a dry powder at two levels, 50 mg and 150 mg, indicative of UK Agriculture and Horticulture Development Board ([AHDB 2017](#)) recommended P fertiliser loads for soil with Olsen P in the range 1–9 mg L<sup>-1</sup>, i.e. levels of P fertilisation currently being used in agriculture. Thus, treatments comprised an ochre- and KH<sub>2</sub>PO<sub>4</sub>- free control, soil plus ochre, soil plus two levels of KH<sub>2</sub>PO<sub>4</sub> and, soil plus ochre and two levels of KH<sub>2</sub>PO<sub>4</sub> (referred to as Control, Morlais, 50P, 150P, M50P and M150P respectively). Masses of moist soil in each treatment are reported in [Table S4](#). The pre-germinated wheat seedlings were 7 days old when added to the soils. Watering and leachate collection occurred on days 6, 13, 19, 26, 34 and 41. Leachate volume, leachate DOC (by an elemental analyser, Elementar varioTOC Select) leachate inorganic P as PO<sub>4</sub> (by autoanalyser, SEAL AA500), plant available P in the soil (Olsen P as PO<sub>4</sub> by autoanalyser, SEAL AA500) and plant biomass were measured. Quality control information is in [Table S5](#).

### 2.5. Statistics

Statistical analysis was carried out in SigmaPlot 14.5 for Windows. Values below detection were set at the detection limit divided by the square root of 2 ([Croghan and Egeghy, 2003](#)). For each experiment, analysis of variance (ANOVA) was used to compare treatments including the controls except for the comparisons between measured and predicted WSA distributions which used one-sample t tests. Holm Sidak and Dunn's post hoc comparisons were used for pairwise comparisons. A p value ≤ 0.05 was set for significance for all tests. Further detail of specific ANOVAs used to analyse individual data sets are given in the Supplementary information.

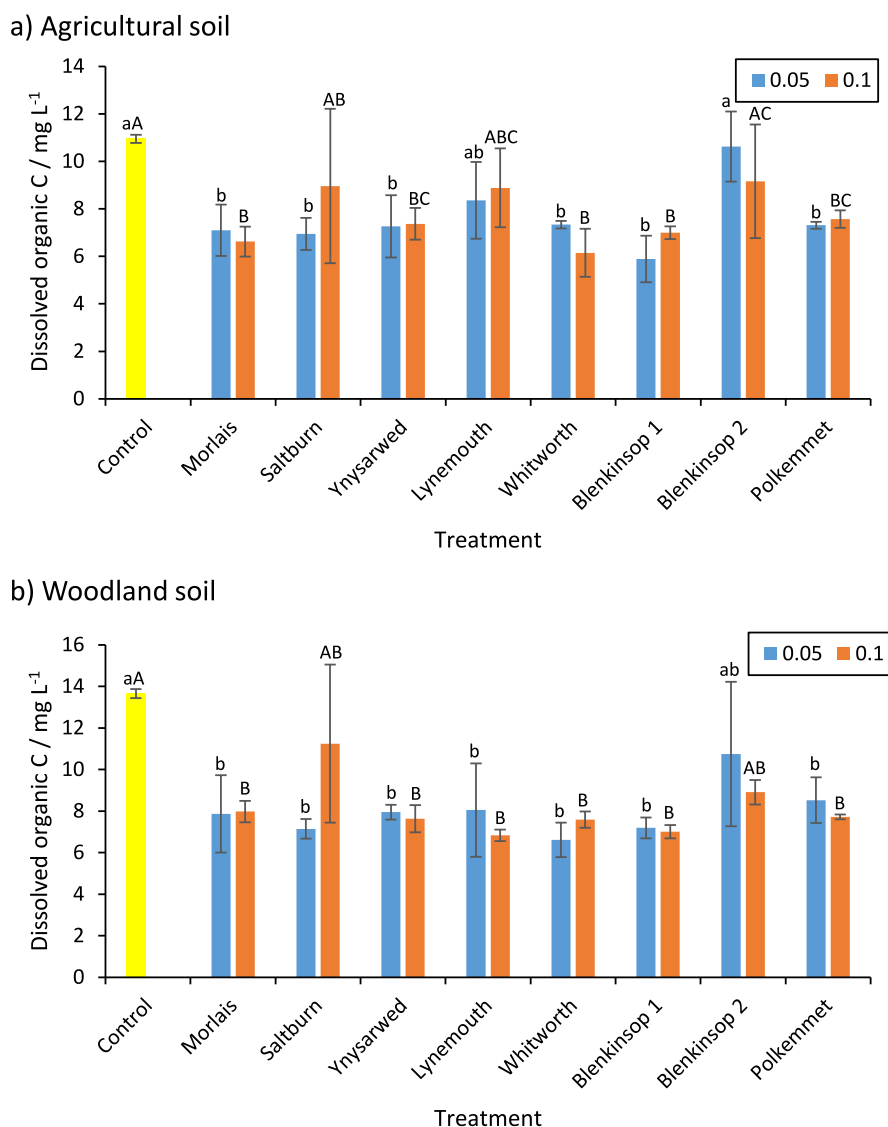
## 3. Results and discussion

### 3.1. Batch experiment

Ochre amendments typically reduced OC release into solution; generally the mass of ochre added made no significant difference to the C release ([Fig. 1](#)).

Two-way ANOVA of the soil types and ochre treatment indicated that the Woodland soil released more OC into solution than the Agricultural soil, consistent with its higher organic matter content and that the Control soils released more OC into solution than the ochre-amended soils, consistent with sorption of OC to the ochre amendments ([Fig. 1](#)). There was little difference in the performance of the ochres both in terms of the type of ochre and the mass of ochre added. One-way ANOVA on each soil individually indicated that the Controls for both soils released more C into solution than all the 0.05 g ochre treatments except for the Blenkinsop 2 treatment and, for the Agricultural soil, the Lynemouth





**Fig. 1.** Mean OC released into solution ( $\text{mg L}^{-1}$ ) from 1 g of a) the Agricultural soil and b) the Woodland soil for unamended Control soil and soil amended with 0.05 g or 0.1 g of ochre. Error bars are standard deviations,  $n = 3$ . For each soil, lower case letters represent significant differences in DOC between the 0.05 g ochre treatments (and Control); upper case letters represent significant differences between the 0.1 g ochre treatments (and Control).

treatment; there were no significant differences in the amount of C released by the different ochre treatments except for the Blenkinsop 2 treated Agricultural soil which released more C.

One-way ANOVA on the 0.1 g ochre treatments indicated no significant difference in the C released from the Control and the Saltburn, Lynemouth and Blenkinsop 2 treated Agricultural soils and no significant difference in C released from the Control and Saltburn and Blenkinsop 2 treated Woodland soils. The Blenkinsop 2 treated Agricultural soil released more C into solution than some of the other treatments but there were no differences in C release between the Woodland 0.1 g ochre treated soils. Three-way ANOVA indicated that there was no significant difference in C released from the Agricultural and Woodland ochre treated soils and no significant difference between the 0.05 g and 0.1 g amendments. However, more C was released from the Saltburn 0.1 than the 0.05 g treatment. For the 0.05 g treatments more C was released from the Blenkinsop 2 treatments than the Blenkinsop 1, Whitworth, Saltburn, Morlais, Ynysarwed and Polkemmet treatments. For the 0.1 g treatments more C was released from the Saltburn treatment than from the Whitworth, Blenkinsop 1 and Morlais treatment.

The reduction in DOC in the ochre treated experiments is consistent with experiments that show that Fe oxides adsorb OC (e.g. Adams and Kassim, 1984; Honghai et al., 2008; Wagai and Mayer, 2007; Zhao et al., 2016; Zhao et al., 2022). The general lack of a significant difference between the 0.05 g and 0.1 g treatments most likely reflects differences in adsorption of different organic compounds. Dissolved organic matter is a complex mixture of different compounds and studies have shown that Fe oxides, including goethite, adsorb different organic compounds to differing extents (e.g. Gu et al., 1995; Sowers et al., 2019; Han et al., 2021). Thus the lack of a difference in the reduction in DOC between the 0.05 g and 0.1 g treatments is most readily explained by the 0.05 g treatment being sufficient to adsorb all the DOC that is preferentially adsorbed by the ochre; no further decrease in DOC is seen in the 0.1 g treatment as the remaining DOC represents organic molecules that are not readily adsorbed by the ochre. Further work characterising the DOC that remains in solution would be required to confirm this.

The Blenkinsop 2 ochre performed least well at immobilizing OC; for both soil types and ochre levels DOC was the same as in the Controls. The Saltburn and Lynemouth ochres also performed less well with some

combinations of soil type and ochre level failing to reduce DOC to below Control levels. The Blenkinsop ochre had a lower surface area and the lowest goethite, ammonium oxalate and dithionite citrate extractable Fe levels (Table 1) suggesting that on a per mass basis the Blenkinsop 2 treatments would contain less Fe oxide surface for C adsorption than in the other treatments. Furthermore, these three ochres also had higher Na contents than the other ochres (Table 1) and the Saltburn and Lynemouth treatments released more Na into solution (Table S1) though not always at significantly different values. Increases in Na in solution can lead to dispersion of soil and desorption of organic C (e.g. Rashad et al., 2010; Setia et al., 2013; Wong et al., 2010; Zhang et al., 2021). This is consistent with the more Na-rich ochre amendments resulting in less of a reduction in C release into solution and, for Saltburn, the 0.1 g ochre amendment leading to a greater release of C into solution than the 0.05 g amendment.

The pH and concentration of other elements released into solution are reported in Tables S6–S9 in the Supplementary information. Concentrations of released P were significantly greater for the Controls of both soils ( $0.57 \pm 0.29 \text{ mg L}^{-1}$  for the Agricultural soil and  $0.26 \pm 0.08 \text{ mg L}^{-1}$  for the Woodland soil;  $n = 3$ ) than for the ochre treatments ( $0.05 \pm 0.05 \text{ mg L}^{-1}$  for the Agricultural soil,  $0.04 \pm 0.04 \text{ mg L}^{-1}$  for the Woodland soil;  $n = 48$ ); there were no significant differences between the different ochre treatments for either soil. Previous studies have demonstrated P adsorption by ochres (e.g. Dobbie et al., 2009; Fenton et al., 2009) with maximum adsorption capacities in the range 16–30.5  $\text{g kg}^{-1}$  (Fenton et al., 2009; Heal et al., 2003). If the difference in P concentration in our experiment between Controls and ochre treatments was due entirely to adsorption onto the ochres, adsorption would have been in the range 0.1–0.2  $\text{g kg}^{-1}$  for the Agricultural soil and 0.04–0.09  $\text{g kg}^{-1}$  for the Woodland soil. Thus the decrease in P observed in our experiments is consistent with adsorption by the ochres.

### 3.2. Plant growth experiment 1

The ochre amendments reduced the lability of the OC in the ochre treated soils consistent with sorption of the OC onto the Fe oxides present in the ochre (Honghai et al., 2008; Adams and Kassim, 1984; Wagai and Mayer, 2007). The concentration of OC exported from the treatments is shown in Fig. 2 and was greater in the Controls than the ochre-treated soils. The weekly leachate volumes and DOC concentrations are presented in Tables S10 and S11.

There were significant differences in leachate DOC concentrations between treatments, between sampling times and significant interactions between the two. Leachate DOC concentration was constant

over time for the ochre-amended soils. Leachate DOC concentration varied over time for the Controls with concentrations on Days 21 and 28 being particularly high. Initially (Days 3 and 14) there was no significant difference in leachate DOC between the Control and the treatments. However, on Days 21, 28 and 42 leachate DOC concentration was significantly greater for the Control than the ochre treated soils and on Day 35 leachate DOC concentration was significantly greater for the Control than for the Morlais and Polkemmet treated soils. Throughout the duration of the experiment there was no significant difference in leachate DOC concentration at each time point between the different ochre treatments. In total, significantly more OC was exported from the Control than the ochre treated soils; there was no significant difference in the total OC exported from the different ochre treatments.

The Morlais and Lynemouth amended soils contained significantly less CWEC and HWEC than the Control and Polkemmet treatments (Table 2). CWEC represents readily soluble C that is highly labile whilst HWEC represents labile C that is readily available for microbial decomposition (Ghani et al., 2003). Although values of CWEC and HWEC were also lower than the Control for Polkemmet, the difference was not statistically significant. The Polkemmet ochre has a higher surface area and goethite content than the Morlais ochre and very similar properties to the Lynemouth ochre; the pH of the three ochres and the pH at the end of the plant growth experiment are almost identical. As goethite adsorbs organic matter on its surface (e.g. Han et al., 2021) Polkemmet's goethite content and surface area would be expected to result in similar reductions in CWEC and HWEC to Lynemouth and greater reductions than observed for Morlais. The reasons that this is not the case are not obvious. It is possible that the goethite in the Polkemmet ochre is concentrated in the coarser fraction so that despite the higher surface area of the ochre as a whole, there is actually a lower surface area of goethite available for adsorption. Following pre-experiment treatment there was no visual difference between the three ochres but Heal et al. (2003) do describe Polkemmet as a coarse grained ochre. To confirm this hypothesis the different size fractions of the Polkemmet ochre would have to be separated and characterised which was beyond the scope of this study.

Although the ochre amendments reduced OC export and OC lability in the soils, we were unable to detect significant impacts on soil structure and aggregation. The drying of our samples prior to determination of the WSA distribution, which tends to increase aggregate stability (e.g. Bullock et al., 1988), may have obscured any subtle differences between treatments. There were significant differences between the measured distribution of WSA and those predicted on the basis of the Controls' WSA distribution and the particle size distribution of the ochres (Table 1). The Morlais treated soil contained a significant lower mass of <53  $\mu\text{m}$  and 250  $\mu\text{m}$ –1 mm sized aggregates but a greater mass of 53–250  $\mu\text{m}$  sized aggregates (Fig. 3). The Lynemouth treatment had a significantly greater mass of <53  $\mu\text{m}$  and 53–250  $\mu\text{m}$  sized aggregates but again a lower mass of 250  $\mu\text{m}$ –1 mm sized aggregates. In contrast the Polkemmet treatment contained a significant greater mass of 1–2 mm

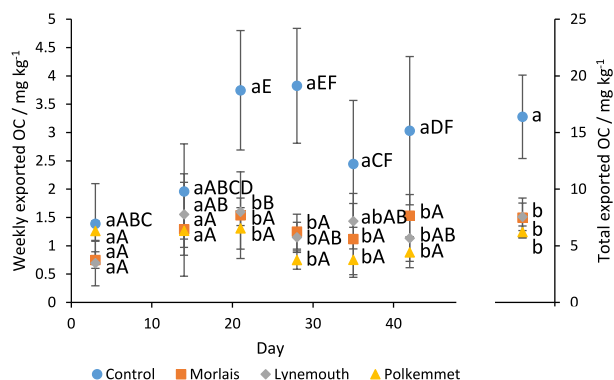


Fig. 2. Mean ( $n = 5$ ,  $\pm$  std dev) OC exported over the course of the first plant growth experiment from the Control and the different treatments. Different lower case letters indicate significant differences between treatments for a particular sample time, upper case letters indicate significant differences between sample times for individual treatments.

Table 2

Mean ( $\pm$ std. dev.,  $n = 5$ ) values for CWEC, HWEC, oven-dried plant biomass, Olsen P (P as  $\text{PO}_4$ ) and pH for the Control and the different treatments at the end of the first plant growth experiment. Values with different superscript letters are significantly different.

	CWEC/mg $\text{kg}^{-1}$	HWEC/mg $\text{kg}^{-1}$	Plant biomass/g	Olsen P/ $\text{mg kg}^{-1}$	pH
Control	$255 \pm 28^a$	$1407 \pm 116^a$	$0.09 \pm 0.02^a$	$7.98 \pm 0.75^a$	$6.60 \pm 0.05^a$
Morlais	$162 \pm 24^b$	$1126 \pm 55^b$	$0.05 \pm 0.01^b$	$5.17 \pm 0.67^b$	$6.66 \pm 0.16^{ab}$
Lynemouth	$141 \pm 20^b$	$1104 \pm 39^b$	$0.04 \pm 0.00^b$	$3.96 \pm 1.07^c$	$6.99 \pm 0.22^b$
Polkemmet	$224 \pm 29^a$	$1291 \pm 94^a$	$0.05 \pm 0.01^b$	$6.76 \pm 0.98^a$	$6.77 \pm 0.22^{ab}$

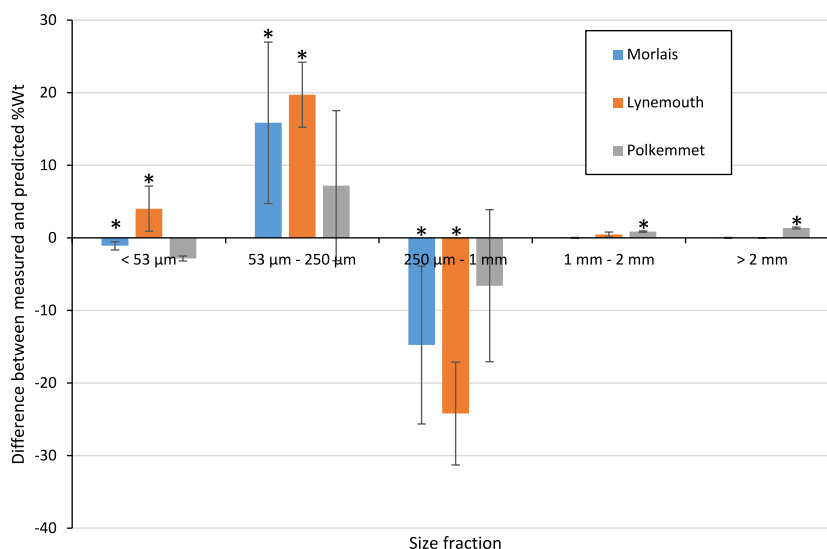


Fig. 3. The difference between measured and predicted Wt% of WSA (±std. dev., n = 5) based on the measured WSA distributions of the Control and treated soils and the particle size distribution of the ochres. Negative values indicate a lower Wt% than predicted. \* indicates a value that is significantly different to 0.

and >2 mm sized aggregates than would be predicted. The relatively Na-rich nature of the Lynemouth ochre relative to the Morlais and Polkemmet ochres (Table 1) could explain the greater than predicted fraction of <53 μm aggregates with the Na causing dispersion of soil particles (Rashad et al., 2010; Setia et al., 2013; Wong et al., 2010; Zhang et al., 2021). The lower than predicted fraction of <53 μm aggregates in the Morlais treated soil perhaps suggests enhanced aggregation. However, for both the Lynemouth and Morlais treated soils, greater than predicted masses of the 53–250 μm size fraction were balanced by lower than predicted masses of the 250 μm–1 mm fraction.

Regardless of the differences between predicted and measured distributions of the soil aggregates the mass proportion of the 53–250 μm and 250 μm–1 mm size fractions varied between treatments (Fig. 4). However, these size fractions always represented the majority of the aggregates.

The mass of >2 mm aggregates recovered was too little for C analysis. The concentration of C in the aggregates decreased in the order

<53 μm > 1 mm–2 mm > 53–250 μm > 250 μm–1 mm but the only significant variation between treatments was in the <53 μm fraction where the Control and Lynemouth treatments had a higher concentration than the Morlais and Polkemmet treatments (Fig. 5). As with the mass distribution of the WSAs, the C content of each size fraction expressed as a % of the total C was greatest in the 53–250 μm fraction and lowest in the <53 μm and 1–2 mm fractions (Fig. S1a). Within a given size fraction, only the <53 μm fraction of the Lynemouth treatment showed a significant difference to the Control. This was most likely related to dispersion due to Na levels as discussed above.

Plant growth and loss through leaching caused a reduction in the concentration of Olsen P in all the soils relative to their initial composition (Tables 1 and 2). Plant biomass was significantly reduced by the ochre treatments relative to the Control as was Olsen P suggesting that the majority of Olsen P was lost via leaching rather than plant uptake (Table 2). The reduction in plant biomass is likely due to either a negative impact of trace elements present in ochres (Table 1) on plant growth (e.g. Kabata-Pendias 2010) or P adsorption to the ochre (Parfitt and Atkinson, 1976; Luengo et al., 2006; Heal et al., 2003; Fenton et al.,

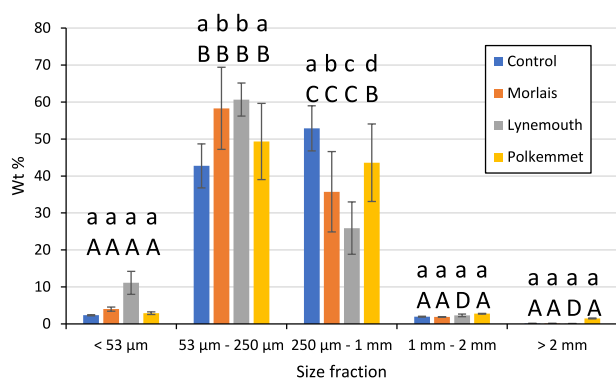


Fig. 4. Mean (±std. dev., n = 5) relative abundance of WSAs. Different lower case letters indicate significant differences between treatments for individual size fractions, e.g. between Control, Morlais, Lynemouth and Polkemmet <53 μm fractions, different upper case letters indicate significant differences between size fractions for individual treatments, e.g. the different size fractions within the Control.

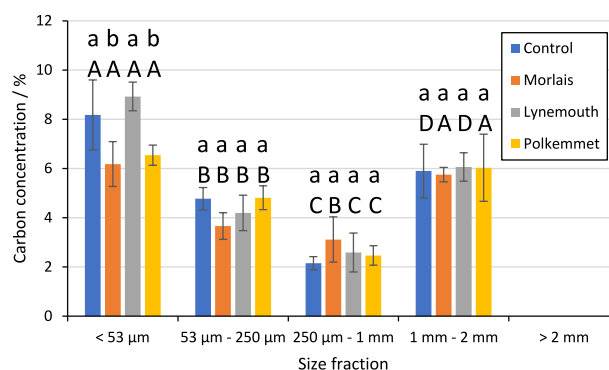


Fig. 5. Mean (±std. dev., n = 5) C concentration in the individual size fractions. Different lower case letters indicate significant differences between treatments for individual size fractions, different upper case letters indicate significant differences between size fractions for individual treatments.



2009, 2012; Button et al., 2022) leading to limited availability of this key plant growth nutrient (Haygarth et al., 2013). As natural materials, ochres contain variable amounts of trace elements including arsenic and potentially toxic metals. In our batch experiments there was relatively little release of metals into solution by the ochre treatments relative to the Controls (Tables S7 and S8). Similarly ochres used to remove P from waste water effluent in a 3 year field experiment did not lead to increases in the concentration of potentially toxic elements in the treated water (Dobbie et al., 2009) but adsorption experiments testing the removal of P from waste water with other ochres have documented the significant release of potentially toxic metals, e.g. Fenton et al. (2009), highlighting the need to characterise specific ochres when considering their use as soil amendments. The only elements that were consistently enriched in the plant tissues of the ochre-treatment plants relative to the Control in our experiments were Mn and Sr (Table S12). Mn toxicity can occur in plants that are deficient in phosphorus (El-Jaoual and Cox, 1998), which would be consistent with the ochres reducing plant available P. However, typical symptoms on Mn toxicity are brown spots surrounded by chlorotic zones (Bould et al., 1983), which were not observed in our plants. Furthermore, the measured Mn concentrations are below those reported as critical toxicity levels for a range of plants (El-Jaoual and Cox, 1998) and specifically for wheat (Fales and Okhi, 1982). Qi et al. (2015) report Sr concentrations in a range of wheat cultivars at concentrations one to two orders of magnitude greater than those measured in the current experiment with no impact on biomass production. Thus, Mn or Sr toxicity seem unlikely to explain the reduced plant biomass in the ochre treatments. Although Olsen P was significantly reduced by the Morlais and Lynemouth treatments, but not the Polkemmet treatment (Table 2), in the batch experiments P release from the soils was significantly reduced by all the ochres (Table S9). Thus, there is good evidence that reduced availability of P but not metal toxicity played a substantial role in the reduction in biomass. However, it remains possible that other, currently unknown, factors, also played a role.

### 3.3. Plant growth experiment 2

The concentration of P in solution in the presence of ochres was significantly reduced in the batch experiments (Table S9). The concentration of Olsen P was reduced in the Morlais and Lynemouth treatments relative to the Control in the first experiment (Table 2). Both these results are consistent with sorption of P to the ochre amendments (Parfitt and Atkinson, 1976; Luengo et al., 2006; Heal et al., 2003; Fenton et al., 2009, 2012; Button et al., 2022) reducing P availability which, in turn, could limit growth. When considering soil amendments to achieve increased C storage it is important that this environmental goal is not achieved at the expense of agronomic goals such as food production. For that reason we carried out the second plant growth experiment in which we combined ochre amendments with additions of P at a level consistent with current agronomic practise, to test whether increased C storage could be achieved without impacting plant growth. The second plant experiment showed that agronomically realistic levels of P addition to the soils removed the negative impact of the ochre amendments on plant growth.

Total OC and inorganic P as  $\text{PO}_4$  exported from the treatments in the leachate, Olsen P as  $\text{PO}_4$  in the soil at the end of the experiment and oven-dried plant biomass are reported in Table 3; leachate volumes, DOC and P as  $\text{PO}_4$  concentrations in the leachate are listed in Tables S13–15. As in the first plant growth experiment and consistent with sorption of OC to the ochres, significantly more OC was exported from the Control than the Morlais treatments. More OC was also exported from the 150P than from the 50P and no P treatments; there were no significant interactions. The greater OC export from the 150P treatments could be due to competitive adsorption of P over OC on other soil components (Guppy et al., 2005; Hiemstra et al., 2010).

As in the first plant growth experiment Olsen P was reduced in all the

**Table 3**

Mean ( $n = 5$ ,  $\pm$  std dev) OC and P as  $\text{PO}_4$  exported over the duration of the second plant experiment and plant dry biomass. For exported OC, values with different superscript letters are significantly different. For exported P, Olsen P and plant biomass values with different lower case superscript letters are significantly different within the ochre-free or ochre-amended soil groups; values with different upper case superscript letters are significantly different between the same phosphate loading of the ochre-free and ochre-amended soils.

	Total exported OC/mg kg <sup>-1</sup>	Total exported P/mg kg <sup>-1</sup>	Olsen P mg kg <sup>-1</sup>	Plant biomass/g
Control	27.8 $\pm$ 2.1 <sup>a</sup>	0.13 $\pm$ 0.14 <sup>aA</sup>	3.58 $\pm$ 0.70 <sup>aA</sup>	0.211 $\pm$ 0.068 <sup>aA</sup>
50P	27.2 $\pm$ 3.6 <sup>a</sup>	0.50 $\pm$ 0.07 <sup>bA</sup>	13.09 $\pm$ 1.25 <sup>bA</sup>	0.349 $\pm$ 0.041 <sup>bA</sup>
150P	37.2 $\pm$ 5.3 <sup>b</sup>	2.97 $\pm$ 0.57 <sup>cA</sup>	15.26 $\pm$ 2.06 <sup>bA</sup>	0.319 $\pm$ 0.051 <sup>bA</sup>
Morlais	14.1 $\pm$ 2.0 <sup>c</sup>	0.06 $\pm$ 0.00 <sup>aA</sup>	2.03 $\pm$ 0.61 <sup>aA</sup>	0.092 $\pm$ 0.030 <sup>aB</sup>
M50P	14.0 $\pm$ 1.5 <sup>c</sup>	0.05 $\pm$ 0.01 <sup>aB</sup>	8.85 $\pm$ 4.69 <sup>bB</sup>	0.302 $\pm$ 0.083 <sup>bA</sup>
M150P	20.8 $\pm$ 3.0 <sup>d</sup>	0.36 $\pm$ 0.19 <sup>bB</sup>	18.38 $\pm$ 3.12 <sup>cA</sup>	0.291 $\pm$ 0.070 <sup>bA</sup>

soils by plant growth and leaching. Similarly, plant biomass was reduced in the Morlais treatment relative to the Control though in this case although Olsen P was also reduced, the reduction was not significant (Table 3). Olsen P increased with the P amendments and was lower in the M50P than the 50P treatment. Biomass also increased with the P amendments and there was no significant difference in plant biomass between the P treated ochre-free and ochre-amended treatments. Despite the lack of significant differences in the Olsen P extractions, this is consistent with P limitation due to sorption of P to the ochre being the main cause of the reduced plant biomass in the ochre treated soils in the absence of the P amendments. P leaching from soils can lead to eutrophication (Djordjic et al., 2004; Ulén et al., 2007). However, leaching of P was significantly reduced in the ochre treated soils. Total P exported from the treatments varied significantly with ochre and P treatments and there were significant interactions. Total P exported increased significantly with P loading in the ochre-free soils; P export was significantly greater from the 150P ochre amended soil than the Control and 50P ochre amended soil. Significantly more P was exported from the 50P and 150 P treated ochre-free soils than from the equivalent ochre-amended soils. Thus, it seems that P amendments at typical agronomic levels are sufficient to overcome any impacts of ochres on plant growth without increasing eutrophication risk.

### 3.4. Considerations for using ochre as a soil amendment to increase soil C

The results of these experiments demonstrate the ability of additions of the waste ochre tested in this experiment to soil to reduce the lability of OC and are consistent with the findings of Silva et al. (2015) and Button et al. (2022). Silva et al. (2015) reported increased soil OC following addition of Fe-rich sludge at a mine-remediation site. Button et al. (2022) reported reductions in soil pore water dissolved OC following addition of  $\text{Fe}(\text{OH})_3$  to soil. Button et al. (2022) also observed a small reduction of  $\text{CO}_2$  release from the  $\text{Fe}(\text{OH})_3$  amended soils but concluded that reductions in  $\text{CO}_2$  release were insufficient to support the addition of synthetic  $\text{Fe}(\text{OH})_3$  as a C sequestration method. If the reduction in HWEC in the ochre treated soils represents OC that is no longer labile, the ochre amendments have helped retain approximately 300 mg kg<sup>-1</sup> OC. This would represent an approximate 0.5% increase in OC held in the soil. Whilst we did not measure  $\text{CO}_2$  release in this experiment, we suggest that this increase in OC retention at least merits further investigation of the method. We also note that until the pool of readily available C is depleted, a reduction in  $\text{CO}_2$  release would not necessarily be expected and the experiments of Button et al. (2015) may not have reached this point; reductions in  $\text{CO}_2$  release may have

increased with time. Reductions in plant growth in the presence of the ochres appear to be linked to sorption of P to the ochres and, if unaddressed would result in the environmentally desirable goal of increasing soil C content only being achieved at the expense of the agronomic goal of crop production if ochres were applied to arable land. However, the reduced plant growth can be avoided by the application of P fertiliser at agronomically realistic levels thus avoiding conflicts between environmental and agronomic goals. Furthermore, this added P is less mobile in the presence of ochres suggesting that at field scale the ochres might reduce eutrophication risks due to P fertilisers. Ochres contain trace concentrations of potentially toxic metals, but these were not taken up in significant quantities by plants growing in the ochre-amended soil. It is also noteworthy that Dobbie et al. (2005) found that P-loaded ochre acted as an effective slow-release P fertiliser and did not release significant quantities of potentially toxic elements into the soil in both laboratory plant pot and field trials. Thus, the addition of ochres to soils may be a viable approach to altering soil chemistry to encourage the retention of OC, reducing CO<sub>2</sub> levels in the atmosphere with potential additional benefits in reducing the amount of P leached out of soils. Nonetheless questions remain regarding the viability of ochre amendments to aid C sequestration.

Whilst Fe oxides are highly stable in oxidising environments, they can dissolve in reducing environments. Increased frequency of flooding is already happening due to climate change (Hirabayashi and Kanae, 2009; Kundzewicz et al., 2014). Flooded soils rapidly become anoxic and the dissolution of C-bearing Fe oxides could lead to an increase in DOC, albeit in a reducing environment where the OC would not be oxidised. Drainage and reoxidation of the soil might lead to reprecipitation of the Fe oxide and resorption of the OC or oxidation of the OC and loss of the C to the atmosphere. More generally, different soils have different chemical, physical and biological properties which will impact on adsorption and Fe oxide stability so experiments on a range of soil types are required. Additions of Fe oxide to soils could alter the soil microbiome with unforeseen greenhouse gas relevant biogeochemical consequences. For example, in the current experiments although changes in OC lability were measured, respiration rates, and CO<sub>2</sub> release were not. These issues require further research including longer term field-based experiments to determine whether OC does accumulate in ochre-amended soils and at what, if any, consequence to soil quality. Interactions with other amendments are also of interest. As global production of P uses non-renewable geological resources there is increased interest in the use of waste materials, designed to remove P from waste water, as a source of agronomically useful P (e.g. Johnston and Richards, 2003; Arenas-Montaña et al., 2021); indeed ochres have been proposed as a way of removing P from waste water with subsequent use as a slow release fertiliser (Dobbie et al., 2005). Experiments investigating whether amendments of P-saturated ochre lead to increase C storage and how ochre interacts with the P release from other P-rich waste materials would be of interest. In Western agriculture there is a growing adoption of “regenerative agricultural” methods. These are loosely defined but many involve the addition of fresh organic residues or manures to soil (Newton et al., 2020; Wiltshire and Beckage, 2022). Much of this inputted C will be highly labile so experiments investigating the interaction of ochre and these carbon sources are also merited.

Regardless of any science case for ochre amendments to aid soil C sequestration, ethical and practical issues also exist. Decisions would need to be made as to whether to apply ochres only to unproductive land or to include agricultural land which would greatly increase the land available for amendment. The C footprint of applying ochres to soil would need to be determined to ensure that any increased C storage in soils was not cancelled out by the act of transporting and adding ochres to soil. Life cycle analysis (LCA) approaches have been applied to other soil amendment based C storage approaches, in particular enhanced mineral weathering which involves the amendment of soil with ground rock (e.g. Lefebvre et al., 2019; Moorsdorf et al., 2014). These studies showed that a key control on whether such approaches have a net

positive or negative C footprint are the transport distances between the source of the amendment and its site of application. A full LCA for ochre amendments is beyond the scope of this study and the C footprint of amending soils with ochres is likely to be far different to that of amending soils with ground basalt. However, Lefebvre et al. (2019) calculate a carbon footprint of 0.011 t CO<sub>2</sub> eq per tonne of rock applied to soil for a transport distance of 65 km whilst Moorsdorf et al. (2014) estimate transportation emissions of 0.007–0.022 t CO<sub>2</sub> eq per tonne of rock. If we assume that the C footprint of ochre amendments due to transport is similar to that of rock amendments and that our 5 wt% ochre treatment resulted in soils retaining 300 mg kg<sup>-1</sup> OC in the top 15 cm of a soil with a density of 1.2 g cm<sup>-3</sup> then the ochre amendments would have a net positive effect (i.e. a reduction) on C emissions up to the higher, pessimistic (their term), estimates of the CO<sub>2</sub> emissions associated with the transport of rock produced by Moorsdorf et al. (2014). This suggests that for ochre amendments to be a useful method of increasing soil C storage the amendments should be applied locally and that an accurate LCA of ochre amendments is required to determine the net impact on C storage. As well as these environmental costs, financial costs should also be considered.

The global availability of Fe-rich wastes also needs to be considered. In addition to forming from former coal mine drainage, Fe-rich sludges, typically containing either goethite or ferrihydrite which can be a precursor to goethite (e.g. Cornell et al., 1987; Cudennec and Lecerf, 2006; Das et al., 2011) are a common waste product of a variety of industries and industrial processes such as the treatment of drinking and waste water and steel processing (e.g. Georgaki et al., 2004; Chen et al., 2012; Turner et al., 2019; Yang et al., 2021). Chen et al. (2015) estimate that approximately 100 million tonnes of Fe-rich waste is produced globally and in the UK it is estimated that there are c. 6.7 million tonnes of zinc or iron rich sludge currently stockpiled, with 90 000 tonnes being produced annually (BEIS, 2022). In the UK current production rates of ochre from disused coal mines are approximately 5000 tonnes per year. If ochres were incorporated into the top 15 cm of a soil with a density of 1.2 g cm<sup>-3</sup> at a rate of 5 wt% and helped retain c. 300 mg C kg<sup>-1</sup> soil this would represent retention of c. 3.96 t CO<sub>2</sub>eq ha<sup>-1</sup>. Whilst this is a similar rate of C retention to those estimated for enhanced mineral weathering (e.g. Kelland et al., 2020; Lewis et al., 2021) 5000 tonnes of ochre is only sufficient to treat 0.5 km<sup>2</sup> of land per year. If other Fe-rich sludges are also able to retain C in soil, the amount of land it would be possible to treat would be greatly increased. Further research would be required to characterise these sludges and determine their suitability as soil amendments but if, for example, only 10% of the 100 million tonnes of Fe-rich waste were suitable, and were applied as above (and similarly helped retain 300 mg kg<sup>-1</sup> C in soil) this would allow treatment of 1000 km<sup>2</sup> of land annually and retain 396 kt CO<sub>2</sub>eq. Compared to global C emissions and estimates of the land area that enhanced mineral weathering using crushed basalt could be applied to, e.g. Beerling et al. (2018), these values are relatively small. Nonetheless, all efforts to both reduce C emissions and increase the C content of soils are worth consideration and additions of Fe-rich wastes may represent a useful method of industry off-settings its C footprint locally and boosting soil organic matter content. However, continuous additions of ochres to soils are probably not sustainable as the ochre does not degrade but remains in the soil; repeated additions would ultimately convert a soil to an ochre deposit, impacting on the functioning of soil as a plant growth medium. So any increase in soil OC may represent a single, one off, benefit. Finally, although ochre amendments may lead to increases in the OC content of soils, the only sustainable way to reduce CO<sub>2</sub> levels in the atmosphere and slow or reverse climate change is to reduce humanity's C footprint; C sequestration technologies should not be seen as an alternative solution to the climate crisis.

#### Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data is proved in the paper and supplementary materials

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## Appendix A. Supplementary data

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