Research article

A circular economy approach to drinking water treatment residue management in a catchment impacted by historic metal mines

Benjamin Nunn [a,*], Richard Lord [a], Christine M. Davidson [b]

[a] *Department of Civil and Environmental Engineering, University of Strathclyde, 73 Montrose Street, Glasgow, G1 1XJ, United Kingdom*
[b] *Department of Pure and Applied Chemistry, University of Strathclyde 295 Cathedral Street, Glasgow, G1 1XL, United Kingdom*

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ABSTRACT

Drinking water treatment residues (DWTR) from mining areas which remove and contain potentially toxic elements (PTE) could still potentially be used as a soil amendment to restore contaminated sites in the same catchment, thus eliminating waste and reducing the chemical and physical mobility of the pollutants. To assess this restorative and regenerative approach to DWTR management, field and pot trials were established with soils from a historic Pb–Zn mine site in the North East of England, amended with either local DWTR or the nearest available municipal green waste compost (GWC). Soils from the mine site were found to have very low levels of nutrients and very high levels of PTE (Pb and Zn > 13, 000 mg/kg). The perennial grass species *Phalaris arundinacea,* known for many ecosystem service benefits including soil stabilization, was used throughout this study. The application of the BCR sequential extraction to soils amended with the DWTR in the pot trials found a significant decrease in the bioavailability of Pb and Cu ($p < 0.05$) after plant growth when compared with an unamended control. The field trial involved 648 pre-grown grass plants planted-out into mine soils amended with either DWTR, GWC or a mixture (MIX) of the two, all at rates of 25–30% w/w. Both amendments and the MIX had significant positive effects on biomass production compared to the unamended control in the following order GWC > MIX > DWTR ($p < 0.05$). Results of the elemental analysis of biomass from the field trial were generally ambiguous and did not reflect the decreased bioavailability noted in the pot trials using the BCR procedure. Pot trials, however, showed increases in plant growth and decreases in concentrations of Cr, Cu, Pb and Zn in above ground biomass following the application of both amendments. Further work should involve the testing of a mixture of DWTR and other soil amendments to enhance plant growth. The success of these trials should provide confidence for those working in drinking water treatment and catchment management to reuse the waste residues in a circular economy and a sustainable way that could improve water quality over time.

1. Introduction

A combination of more sustainable thinking and a rise in the cost of landfill disposal of wastes has led to an increasing interest in a 'circular economy' approach to solid waste management by re-using organic wastes (Maina et al., 2017). The three principles of a circular economy are, by design, to eliminate waste and pollution, circulate products and materials at their highest value, and to regenerate nature (ellenmacarthurfoundation.org, 2023). Organic waste soil amendments (OWSA) represent a group of solid waste materials that are the result of an industrial/commercial process and contain enough organic matter to make them suitable for soil conditioning. The OWSA typically fall into one of the following categories: animal manure; biosolids from municipal waste water treatment works; green manure and crop residues; food residues and waste; waste from manufacturing processes and composts (Gómez-Sagasti et al., 2018; Goss et al., 2013), to which drinking water treatment residues (DWTR), generated in the process of drinking water clarification, may be similar. The application of OWSA to soil has been found to have a positive effect on organic matter content, structure, water holding capacity and nutrient content, whilst also reducing dependence on agrochemicals (Angin and Yaghanoglu, 2011; de León-González et al., 2000; Goss et al., 2013). Many OWSA have been found to reduce the chemical mobility of contaminants, such as potentially toxic elements (PTE) (e.g. Cu, Pb and Zn), at relatively low amendment rates (compared with top soil or clay capping), resulting in further interest and great potential for their use on contaminated land

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* Corresponding author.

E-mail addresses: benjamin.nunn@strath.ac.uk (B. Nunn), richard.lord@strath.ac.uk (R. Lord), c.m.davidson@strath.ac.uk (C.M. Davidson).

(Brown and Chaney, 2016). Despite recent interest, there have been few field trials that demonstrate the value of amendment-based PTE immobilization, leading to a lack of evidence on the impact of the application of OWSA on contaminated land, such as the effect on co-contaminants (Bolan et al., 2014).

This study aims to evaluate the use of DWTR in the phytostabilisation of eroding C19th-20th Pb–Zn–F mines in the catchment of a drinking water supply reservoir containing the water treatment works in which the DWTR is produced. The primary objective was to compare the effectiveness of DWTR against green waste compost (GWC) (PAS 100) for contaminated land restoration and revegetation. Validation of this approach would allow the recovery for reuse of this potential resource, thus eliminating waste. In turn, restoration of mine sites using DWTR might reduce erosion, Zn and Pb loadings in water courses, in the reservoir sediments, in major rivers downstream (Jarvis et al., 2019) or in the DWTR generated, which would otherwise potentially limit its future suitability for conventional recovery and beneficial use by application to agricultural land.

2. Materials and methods

2.1. Studied area

The Whiteheaps Mine and subsequent processing complex is situated in the Northern Pennines on the boundary between the counties of Northumberland and Durham. It lies on the banks of Bolts Burn (NGR: NY946465) within the Derwent Valley (Pickin, 1992). The Northern Pennines are well-known as an area of Pb–Zn–Ag–Ba–F mineralisation and historic mining activity (Dunham, 1948). Mining for Pb took place at Whiteheaps from at least 1690 and ceased in 1989, by which time the site was predominantly used for the production of fluorspar (CaF_2), when the processing wastes were regraded across the site and the buildings were removed (Pickin, 1992). Whiteheaps Mine site is located within the catchment of the Derwent drinking water reservoir which lies to its east (as shown in the graphical abstract). Bolts Burn is one of the head waters, and the largest tributary, of the River Derwent which feeds the reservoir and also flows through the southern end of the Whiteheaps Mine site. A comprehensive study of contamination levels in sediment within the Derwent Reservoir showed that 70% of Zn, 97% of Cd and 89% of Pb in the total loads entering the reservoir was retained in bottom sediments (Harding and Whitton, 1978). Harding and Whitton also refer to unpublished work which showed that metal pollution originated mainly from Bolts Burn and suggested that the origin of Zn and Cd was their dissolution in mine water pumped from an adit to drain the mine workings, whereas Pb was mainly in particulate forms associated with discharge from the fluorspar processing plant located at Whiteheaps, which was still operational at the time. Mosswood water treatment works (WTW) treats the water supplied by the Derwent reservoir.

2.2. Sampling of materials used in pot and field trials

50 L bulk samples were collected in August 2018 from two plots identified following preliminary investigation of six areas at Whiteheaps Mine site (Nunn, 2022). These were named WH3 and WH5. At both plots 10 × 5 L vessels were filled with equal amounts of material taken to 10 cm depth of soil from 10 places using a clean trowel. Samples from each vessel were then added to two 25 L containers by trowel in turn so as to provide an initial homogenisation of the bulk sample. Soil amendments were collected on site during August 2018 in 2 × 25 L containers. Dewatered DWTR was collected from Mosswood (WTW) (Northumbrian Water Ltd.). Here the coagulant, ferric sulfate is added to screened water to encourage flocculation of suspended colloids. Sodium hydroxide is then added and the resulting waste flocs are removed as a ferric hydroxide sludge which is stored on site for dewatering and then taken from the site as a waste by-product (Johnson et al., 2018). The GWC (BSI PAS100: 2018) was processed at Codlaw Hill (DJ and SJ Recycling)

using the windrow composting system, which involves the piling of green waste in long narrow rows or piles followed by maturation and screening of the material (Maheshwari et al., 2014). Both amendments were collected from stockpiles of processed material. Small amounts of soil amendment were added to 25 L containers from different parts of the stockpiles to provide a representative sample. Bulk amendments were then refrigerated at 4 °C in sealed containers. The chemical analysis of the contaminated soils and the two OWSA (all by NRM, Bracknell UK) are presented in Table 1. When compared to the average characteristics of Fe-based DWTR reported in a review paper for DWTR application (Ippolito et al., 2011), the DWTR used in this study has a much lower pH, similar total N and P but much lower available nutrient content, much greater concentrations of Zn but similar concentrations of Cu and Pb (Agyin-Birikorang et al., 2007; Leader et al., 2008; Sarkar et al., 2007; Sotero-Santos et al., 2005). The greater than average concentrations of Zn but average concentrations of Pb in the DWTR used in this study when compared to those reported by Ippolito et al. support the findings of the study regarding the differential behavior of Pb and Zn in the Derwent reservoir as it found that greater concentrations of Pb were retained in bottom sediments than Zn (Harding and Whitton, 1978).

3. Experimental designs

3.1. Pot trial

Pot trials following the British Standard (BS ISO 11269–2, 2005) were implemented in 2019 with three replicates using soils from the bulk samples of both WH3 and WH5 planted with the perennial grass species reed canary grass (RCG) (*Phalaris arundinacea*). As a control, a set of plants were grown in commercial compost to provide an indication that the growing conditions of the pot trial were appropriate. John Innes No.1 young plant compost (produced by Arthur Bowyer) was selected as an ideal growing media (Bunt, 1976). The 9 cm diameter plastic pots were filled with dried unamended mine soils and then either 20% or 30% of the mass of dried soil was removed from the pot and replaced with the equivalent mass of 'as received' amendment, which was then homogenised with the mine soil in batches of 3 using the cone and quartering method, a common method for homonogising soils, to divide again for the 3 replicates (Schumacher et al., 1990). The two OWSA were found to have a marked difference in moisture content (GWC – 38% and DWTR – 76%) thus affecting the dry mass of the target amendment application rates (0, 20 and 30% amendment as received weight equivalent/soil dry weight). The 33 experimental units were arranged in four electric propagators (Stewart variable temperature control 52 cm unit); each propagator had at least one replicate of each treatment so as to minimise variability due to treatment arrangement. The average room temperature was 20 °C. Water holding capacity

Table 1
Chemical characteristics of mine 'soils' and amendments used in this study.

Sample	Unit	WH3	WH5	GWC	DWTR
pH (Value)	#	6.7	7.1	8.2	5.2
Cd	mg/kg	5.07	6.3	0.55	1.5
Cu	mg/kg	545	890	72.1	27.8
Pb	mg/kg	13, 873	9112	159	50.5
Zn	mg/kg	1852	5150	293	595
Oven Dry Matter	%	77.7	83.9	62.7	24
Nitrate Nitrogen	mg/kg	<1	<1	<10	<10
Ammonium Nitrogen	mg/kg	<1	<1	23.8	<10
Total Nitrogen	%	0.09	0.14	1.23	1.07
Available Phosphorus	mg/l	<2.5	<2.5	65.2	<0.01
Available Potassium	mg/l	30	34	2630	194
Available Magnesium	mg/l	69	58	96.2	88.1
Organic C (Dumas)	%	5.1	1.3	15.3	17.7
Organic Matter (Calculated)	%	8.7	2.2	26.4	30.5
Conductivity	uS/cm	945	266	1260	192
Total Phosphorus	mg/kg	135	233	2174	887

(WHC) of growing media for each factor was determined by adapting the method found in Annex C of BS EN ISO 11269–2:2013. To compensate for non-germinating seeds, a higher number of seeds (10) were planted in each pot than plants required for the test. Following first emergence, the germination rate of 10 seeds was recorded at 5 and 13 days. Seedlings were then thinned out to the five largest and evenly spaced specimens of the plants in each pot. Following a 10-week growth period pot trials were completed.

3.2. Field trial

The field trial was planted over two weeks in late July 2019 and involved two 9 × 9 m areas fully enclosed with rabbit-proof fencing (plots WH3 and WH5) both divided into nine 3 m × 3 m sections which each contained 36 individual RCG plants (plants) on a 0.5 × 0.5 m grid, grown in one of four 1.5 m × 1.5 m blocks of 9 with the same experimental soil amendment factors (Un-amended soil, +GWC, +DWTR and a mixture of both amendments (MIX) with half as much of each). Two simple methods of soil amendment were compared, using approaches which might be adopted for future scale-up. On plot WH3 the soils were amended volumetrically i.e. 1 L was removed from each planting space in a set of nine, giving 9 L of mine soil to which 3 L of amendment were added. The amended soils were then homogenised for approximately 5 min in an electric 46 L cement mixer (300 W 230 V SIP Loughborough, UK) powered by a four-stroke petrol generator (EX650 240 V, Honda, Shizuoka, Japan). One litre of the amended soil was then returned to each planting space and firmed in. The same homogenisation procedure was used on the unamended sets. This gave a 3:1 soil:amendment ratio (or 25% amendment) by volume. Due to the soil compaction, the lower density of the compost compared to soil, and unknown field moisture contents, this simple method gave a lower dry mass ratio than was originally intended when calculated retrospectively. On plot WH5 a more complex amendment method was used with the approximate rates determined gravimetrically in the field. One kg of soil removed from each of the nine planting spaces using a spade was weighed into a plastic vessel on a spring balance connected to an A frame, giving 9 kg in total. The amendment was then added to the soil at a rate of 3.7 kg to provide a mixture of 12.7 kg. This gave a soil:amendment (wet) mass ratio of 3:1.33, equal to 30% amendment by weight (on a wet basis). The soil and amendment mixture was again homogenised in a cement mixture using the aforementioned method. Approximately 1.4 kg of the amended soil mixture was returned to each planting space and firmed in, so all amended soil was used in this case. The amended area for each of the nine plants was approximately 10 cm × 10 cm (the spade width and hole

dimensions) giving a total amended area within one plot of 0.9 m^2 from which the mass/area amendment rate can be estimated (Table 2). The same homogenisation procedure was used on the unamended plots. Amended soils were then left to naturally hydrate and equilibrate prior to planting for 14 days for WH3 and two days for WH5. A total of 648 seed tray spaces were planted with three seeds in each space to allow for germination failure. Seeds were planted in approximately 10 g of commercial compost (John Innes No 1). All 648 plant plugs were planted out using the following method. A seedling dibber was used to make a hole in the amended soil approximately 10 cm deep with a diameter of 5 cm. The plug containing three germinated seeds was then placed in the hole and firmed in. The experimental design of different treatments and their dry weight application rates for both the pot and field trials are shown Table 2. In both experiments amendment rates were guided by previous successes growing RCG with GWC. Lord found that an application of 500 t/ha was optimum for brownfield land (Lord, 2015). Textural characteristics for the two mine soils used in the pot and field trials are shown in Table 3.

3.3. Analytical methods

In situ bulk density determinations were made using the excavation method (BS EN ISO 11272:2017, 2017) but substituting water and a plastic sheet) for sand as the replacement material. The key physical and textural properties of the mine soil and amendment samples (<2 mm fraction) were characterized by a commercial laboratory (NRM, Bracknell, UK) using laser-scanning particle size analysis. Digestion of the plant material obtained following the 10-week pot trials was carried out using a microwave digestion system using the manufacturer

Table 3
Physical and soil textural characteristics of the two mine soils taken from Whiteheaps historic mine complex.

Sample	Textural Classification	Sand (2.00–0.063 mm)	Silt (0.063–0.002 mm)	Clay (<0.002 mm)	In situ bulk density (dry)
Unit	%	%	%	%	g/cm^3
WH3	Sandy Silt Loam	45	41	14	1.84 ± 0.003 (n = 2)
WH5	Silty Clay Loam	14	61	25	1.40 ± 0.001 (n = 2)

Table 2
Treatment combinations for pot and field trials.

Pot trial			Field trial		
Treatment combinations	Treatment code	Dry weight of OWSA applied to each pot (0.008 m2), t/ha	Treatment combinations	Treatment code	Dry weight of OWSA applied to each plant (0.01m2), t/ha
WH3 Unamended (control)	WH3U	–	WH3 Unamended	WH3U	–
WH3 + GWC 20%	WH3GWC20%	60	WH3 + GWC 25% v/v	WH3GWC	132
WH3 + GWC 30%	WH3GWC30%	105	WH3 + DWTR 25% v/v	WH3DWTR	69.3
WH3 + DWTR 20%	WH3DWTR20%	24	WH3 + MIX 25% v/v	WH3MIX	109
WH3 + DWTR 30%	WH3DWTR30%	41	WH5 Unamended	WH5U	–
WH5 Unamended (control)	WH5U	–	WH5 + GWC 30% (by wet mass)	WH5GWC	258
WH5 + GWC 20%	WH5GWC20%	51	WH5 + DWTR 30% (by wet mass)	WH5DWTR	98.7
WH5 + GWC 30%	WH5GWC30%	92	WH5 + MIX 15% + 15% (by wet mass)	WH5MIX	178
WH5 + GWC 20%	WH5DWTR20%	20	–	–	–
WH5 + DWTR 30%	WH5DWTR30%	36	–	–	–
Commercial compost (John Innes No.1)	Compost	–	–	–	–

Note: GWC, green waste compost; DWTR, drinking water treatment residue; OWSA Organic waste soil amendment; MIX, equal amounts of each OWSA by volume or wet mass; WH, Whiteheaps.

recommended conditions for "plant material" (MARS Xpress, obtained from CEM Microwave Technology Ltd., Buckingham, UK). All plant material above 5 cm from the soil surface was cut using scissors, washed in ultra-pure deionized water (UPDI) and oven dried at 40 °C for 72 h followed by desiccation to a constant dry weight (DW) which was recorded. Plant material (ranging from 0.1 to 1 g depending on quantity available analysis) was then digested in nitric acid (10 mL) (Primar-Plus-Trace analysis grade, >68% HNO_3, Fisher Scientific, Loughborough, UK). The digestates were analysed using ICP-MS (Model 7700x, Agilent Technology, Cheshire, UK) alongside ERM-CD281 (rye grass). Replicate analysis was not possible due to the limited sample mass following drying.

The soil from the pots was air dried in a fume cupboard for 3 weeks at approximately 20 °C. Soils were then sieved with a 2 mm sieve which removed organic debris including roots, placed in sample bags and refrigerated at 4 °C. The pH of soil samples following the completion of the pot trial were found using a pH meter (Mettler Toledo MPC 227, Schwerzenbach, Switzerland), following a method adapted from a British Standard (BS ISO 13652:2001, 2001) with a solid to liquid (water) ratio of 1:5. In October 2020 all biomass was harvested from both field plots at Whiteheaps (WH3 and WH5) over the course of one week. Individual plants were cut with scissors at approximately 5 cm above ground and placed separately in labelled zip lock bags. Bagged plants were returned to the laboratory and any visible dirt and debris was removed. Plants were removed from bags and washed in UP DI water three times. Plants were then dried in their cleaned bags in an oven at 40°C to constant weight. Once the dry mass was recorded the plants were then bulked separately by their variety, amendment and field trial plot before analysis. For example, WH3GWCSWRF5004 contained the 3 groups of 9 plants with that amendment and species grown across three blocks. The bulking of the biomass in this way provided 12 biomass samples from each plot, including four bulk samples per amendment factor per plot. Biomass analysis was completed commercially by ACME labs (BV minerals, Canada) using sample digests and ICP-MS.

3.4. BCR sequential extraction method

The 'modified' BCR sequential extraction procedure was applied in order to determine the effect of the OSSA and plant growth on the mobility of PTE during the pot trial process. This method is described in detail elsewhere (Rauret et al., 1999) and consists of three successive extraction steps and a residual digestion for quality control, which aims to find the 'operational speciation' of an element within a sediment or soil sample. It is summarised in Table 4. The reagent volume and the sample mass were halved to allow extraction to be carried out in 50 mL centrifuge tubes rather than 100 mL. Miniaturisation of the procedure to this extent has previously been demonstrated to have little effect on the accuracy of the results obtained (Sagagi et al., 2021). Following addition of the reagent to ground pot trial soils an end-over-end shaker (RS12 C. Gerhardt GmbH and Co. KG, Königswinter, Germany) was used to

perform extraction for 16 h at a speed of 20 rpm and temperature of 22 ± 5 °C. The extracts were separated from the solid sample residue using a centrifuge (PK130 Thermo Fisher Scientific Waltham, East Grinsted, UK) at 3000 g for 20 min. The supernatant liquid was decanted into a 50 mL centrifuge tube and stored at 4 °C prior to analysis. During step three a graphite digestion block (Digi prep, SCP Science, Montreal, Canada) was used to heat solutions to a temperature of 85 °C. The microwave digestion system was used to assist digestion in aqua regia during step four. Digestates were made up to volume in 50 mL volumetric flasks following digestion and filtered (to < 0.45 μm).

The determinations of levels of Cd, Cu, Pb and Zn in the extracts were performed by ICP-OES (iCAP 6000 Series, Thermo Scientific, East Grinstead, UK). The certified reference material (CRM) BCR 701 (lake sediment) was analysed alongside as a check. Reagent blanks, calibration with matrix matched standard solutions for each of the steps and extraction in triplicate per sample were implemented throughout. A recovery test was conducted by comparing the sum of analyte released in step 1–4 of the BCR procedure with the pseudo total values from analysis of the CRM using Equation 1. The results obtained (Cd 87%, Cu 96%, Pb 104% and Zn 99%) suggest that the procedure was carried out correctly and little of the sample was lost during the four extraction steps.

$$\frac{sum\ of\ results\ from\ step\ 1 - 4}{Pseudo\ total\ value\ (PT)} \times 100$$

Equation 1Mass balance recovery equation used for CRM analysis.

In order to show that an effect has taken place on the mobility of elements following soil amendment due to a change caused by the properties of the amendment and not simply a dilution and introduction of elements bound in different way, a calculated amended soil is presented alongside the measured sequential extraction results. The equation for this is shown in Equation 2.

$$c = (u * (1 - r)) + (a * r)$$

Where;

c is the calculated sample value, u is the value measured in the unamended soil, a is the value measured in the pure amendment r is the amendment addition rate % as a decimal e.g. 30% = 0.3.

Equation 2mass balance equation for the calculated sample value used in the presentation of sequential extraction results.
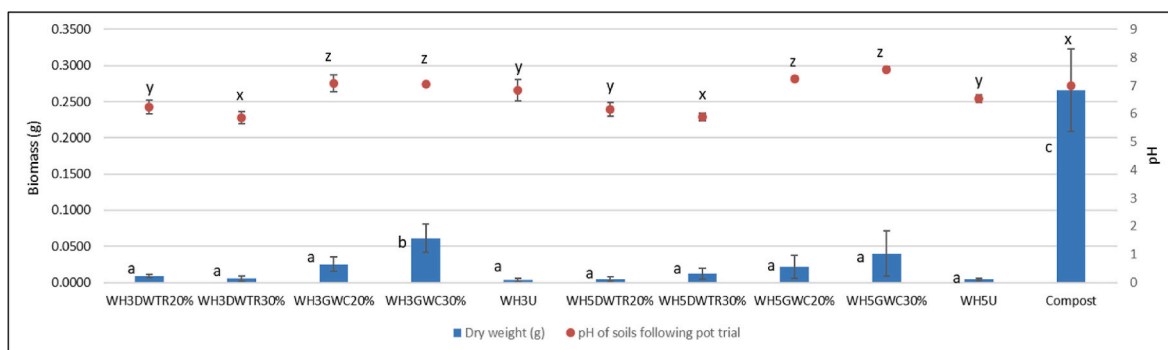
Consistently low variability between triplicate results were obtained for each step of the sequential extraction, which provides further confidence in the results. The Statistical Package for the Social Sciences (SPSS) (IBM, Armonk, New York) was used for all statistical analysis.

4. Results

4.1. Above ground dry weight and PTE concentration of pot trial plants

The above ground biomass production and the pH of the soils following the pot trial are shown in Fig. 1.

The mean dry weight (DW) of the grass produced for each factor (n = 3 pots) is greater in the plants grown on soils amended with DWTR and GWC than in the unamended mine soils. Only the biomass produced by the WH3 mine soil amended with 30% GWC was significantly greater than the unamended control according to a one-way ANOVA with a Bonferroni post hoc test (p < 0.05). This is likely due to the low sample number (n = 3 pots, each containing 5 plants) and large standard deviation within results. The pH of the soils following the pot trial (Fig. 1) was found to be influenced by the pH of their respective amendment (see Table 1). The pH was lower in those amended with DWTR and in proportion to the amendment rate, while it was higher in those amended with GWC, but independently of the application rate. The optimal pH for the growth of RCG has been found to be in the range of 7.7–8.2 (Usťak et al., 2019). Due to the low quantity of dry biomass obtained (<0.05 g) from the pot trial repeat analysis could not be conducted and thus

Table 4
Modified BCR sequential extraction procedure (Rauret et al., 1999).

| Extraction Steps	Reagent/concentration/pH	Soil phase targeted for PTE release
1	Acetic acid CH_3COOH (0.11 mol l^{-1})	Exchangeable, water and acid-soluble (e.g. carbonates, etc.)
2	Hydroxyl ammonium chloride NH_2OH_sHCl (0.5 mol l^{-1})	Reducible (e.g. iron/manganese oxides)
3	Hydrogen peroxide H_2O_2 (8.8 mol l^{-1}) & then ammonium acetate CH_3COONH_4 (1 mol l^{-1}), pH 2	Oxidisable (e.g. organic matter and sulphides)
4	HNO_3 HCl 1:3 ratio	Residual (non-silicate bound metals)

Fig. 1. Above ground mean dry reed canary grass biomass (bars) and final soil pH (circles) mean values (n = 3), following a 10-week pot trial comparing mine soils amended with drinking water treatment residue (DWTR) and green waste compost (GWC) A commercial compost (compost) and the unamended mine soils (U) were used as controls. Letters show statistically different results (p < 0.05), tested separately for biomass and for pH by simple (one-way) ANOVA and a Bonferroni post hoc test, indicating the effect of the soil characteristics (in 11 groups of 3 pots), on biomass or on pH.

statistical significance could not be obtained. The results of the analysis are therefore only mentioned briefly here. The analysis of biomass sample WH3DWTR20% returned unreliable data so has been omitted from the following results and discussion. Otherwise, RCG grown in soils amended with GWC have relatively lower Cd content than the control or those with DWTR. In general, the concentrations of the PTE were lower in the grass grown in soils amendment with GWC than in soils amended with DWTR. However, in every case biomass produced in soils amended with both OWSA had concentrations of PTE that where far lower than those produced in the unamended soils. At each location the highest concentration of Cu was found in biomass produced in unamended mine soils (79.3–107 mg/kg). The lowest concentrations of Cu were all found in soils amended with GWC (11.1–24.1 mg/kg). The grass grown in unamended soils contained the greatest concentrations of Pb (869–958 mg/kg). The lowest concentrations of Pb were found in the biomass grown in soils amended with GWC (113–190 mg/kg). The addition of DWTR also had an impact on the biomass concentrations of Pb

(277–520 mg/kg). Reed canary grass grown in the unamended soils contained the most Zn (5940–11, 400 mg/kg) with the lowest concentrations of Zn found in the plant material grown in soils amended with GWC (670–1300 mg/kg). The addition of DWTR had less of an observable impact on the Zn biomass concentrations (3230–5000 mg/kg).

4.2. Sequential extraction of pot trial soils

The results from the analysis of the pot trial WH5 soils amended at 30% following the BCR procedure are shown in Fig. 2. In the unamended WH5 (WH5U) pot trial soil the PTE studied were all found to be mostly in the more available fractions. Cd was found to be predominantly in the exchangeable fraction (65%) and Cu was found to be relatively evenly distributed, with the majority in the exchangeable (35%) and oxidisable fractions (33%). The high concentrations of Pb found in the exchangeable fraction (64%) of the WH5U mine soil made Pb the most mobile of all the PTE studied in this work. The majority of the Zn found in the
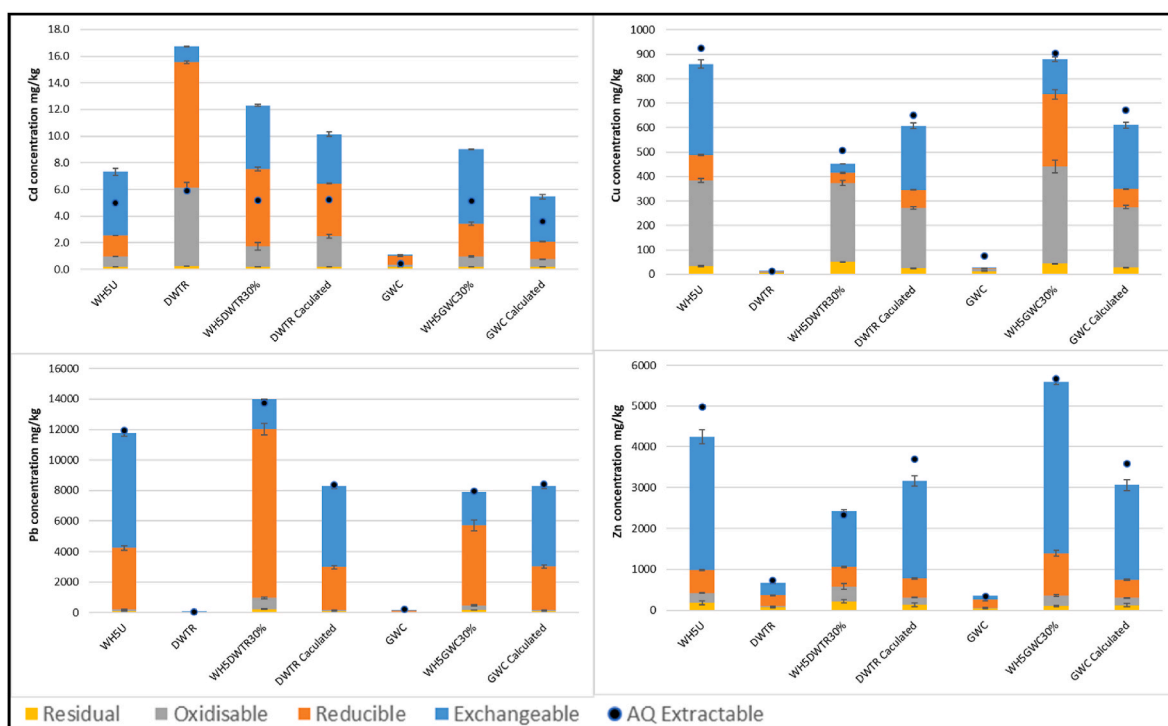
Fig. 2. Results of modified BCR sequential extraction on soils amended with green waste compost (GWC) and drinking water treatment residue (DWTR) after plant growth. Analysis of the organic waste soil amendments and a mass balance calculation for the anticipated concentration in the amended soil mixtures are also presented along with the results of a separate aqua regia pseudo-total digestion (AQ extractable). All concentrations are in mg/kg.

unamended mine soil was in the exchangeable fraction (77%). Absolute levels of contaminants found in the pure amendments were low compared to those in the mine spoils. The exception was Cd in the DWTR which was found to be predominantly in the reducible (56%) and oxidisable fractions (35%).

Following amendment and plant growth the following effects were observed which cannot be explained simply by mixing the two end-members in the proportions used: Firstly, the soils amended with GWC show significantly greater concentrations of Pb and Cu in the reducible fraction, and lower concentrations in the exchangeable fractions, when compared to the unamended soils and mass balance concentrations ($p < 0.05$), indicating a reducing overall mobility of the analytes; Secondly, the pot trial mine soil amended with 30% DWTR (WH5DWTR30%) was observed to contained significantly greater concentrations of Cd in the reducible and oxidisable fractions when compared to the unamended pot soil. Conversely, the pot trial mine soil amended with 30% GWC (WH5GWC30%) exhibited significantly greater observed concentrations of Cd and Zn in the more labile fractions, particularly the reducible, when compared with the fractionation patterns found in the unamended soil and that of the mass balance concentrations ($p < 0.05$). Furthermore, concentrations of Cu in the DWTR amended mine soil are significantly reduced when compared to WH5U and mass balance, except for the oxidisable fraction, which is significantly increased in the amended soil when compared to the mass balance calculations ($p < 0.05$). These results are described further in Nunn (2022).

4.3. Field trial

The OWSA also all had a positive effect on plant survival at both sites (Fig. 3) where differences in total plant survival rates were connected to site conditions:WH3 was affected by both a time-limited grazing event by herbivores and by more regular sheet flooding, resulting in the loss of 58 plants; WH5 was fed water by an adit, meaning the plot never fully dried out in the summer months, resulting in the loss of only 27 plants. The field trial results showed high variability in plant survival rate and dry weight (DW) on both sites and between all amendment factors. This is a common issue with field trials as there are many aspects that cannot wholly be controlled or eliminated e.g. differences between individual plants, heterogeneity in soil characteristics, and differences in environmental/climatic conditions experienced during growth. (French et al., 2006; Meers et al., 2005). At both WH3 and WH5 plants grown in soils amendment with the DWTR, GWC and the mixture of the two amendments (MIX) had a greater mean DW than those grown in the unamended soils. At plot WH3 the soils amended with GWC and the MIX produced significantly more ($p < 0.05$) dry mass when compared to the unamended control. The DWTR amended soils produced more DW biomass although not significantly compared to the unamended soils ($p = 0.08$) according to the Mann-Whitney U test. At plot WH5 the soils amended with GWC, DWTR and the MIX produced significantly more ($p < 0.05$) dry mass when compared to the unamended soils. The soils amended with GWC and the MIX also produced significantly more ($p < 0.05$) dry mass when compared to the DWTR.

No consistent result for concentrations of PTE in biomass from the two sites and each OWSA option could be found (Fig. 4). This reflects the heterogeneity of the soils between the replicate plots with the same treatment. Soil heterogeneity of PTE is typical of historic mine sites and analysis of plants grown on contaminated land in general (Boente et al., 2022; Fang et al., 2021; French et al., 2006). However, concentrations of Pb and Cd were found to be significantly greater in the total biomass produced on site WH3 when compared to that produced at WH5 according to the Mann-Whitney U test ($p < 0.05$). This difference is most pronounced for Pb, echoing the underlying differences in soil concentrations, where the mean concentrations ($n = 12$) found in the WH3 (4450 ± 1230 mg/kg) biomass is greater by almost a factor of 10 compared to WH5 (578 ± 143 mg/kg). On plot WH5 the plants grown in soils amended with GWC and the MIX were found to have significantly lower Pb compared to the plants grown in the in soils amended with DWTR ($p < 0.05$), which mimicked the result of the pot trials. In general, the field trial biomass analysis results do not consistently follow those from the pot trial or the implications for metal mobility from the BCR sequential extraction tests.
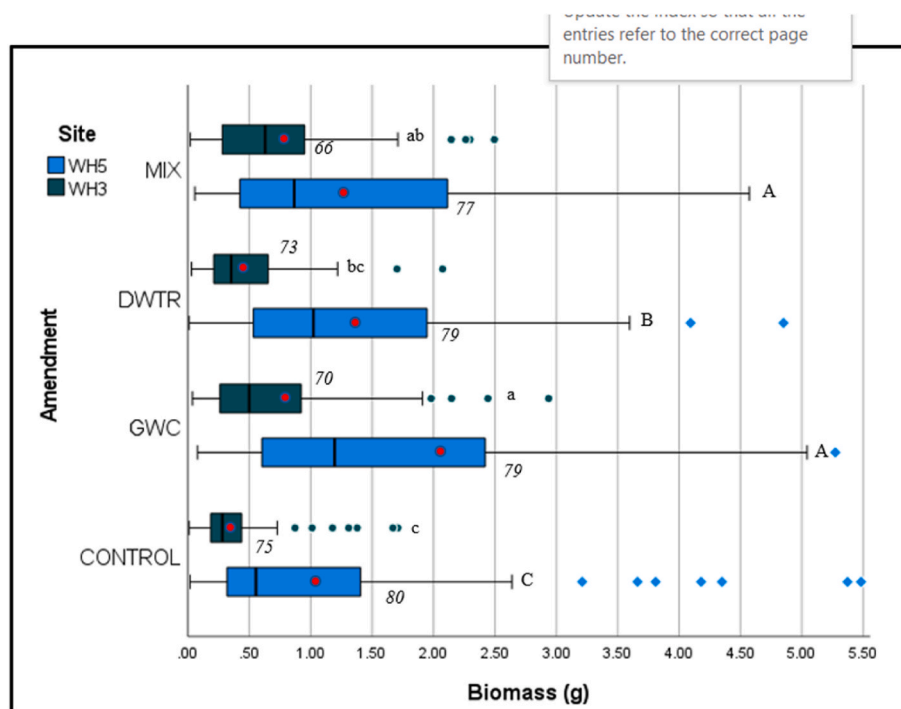

Fig. 3. Dry mass box plots with survival rate (n out of 85 at start, italicised) of RCG plants harvested from Whiteheaps field trial in October 2021. Dry mass marked with the same letter (from the same trial i.e. WH3 or WH5) have mean concentrations that do not differ significantly according to the Mann-Whitney u test ($p < 0.05$). Means of dry mass are marked with red dots.
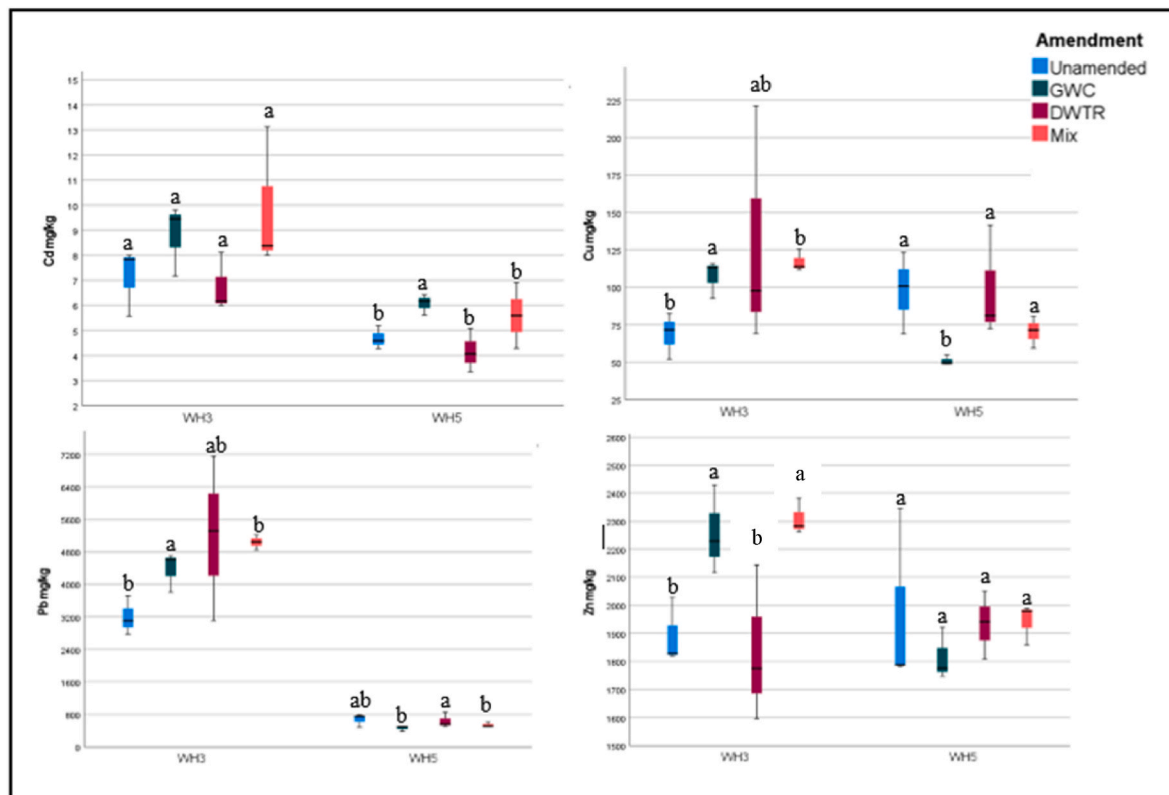
Fig. 4. Box plot of concentrations of PTE found in RCG plants harvested from Whiteheaps field trial in October 2021. Amendment factors marked with the same letter have mean concentrations that do not differ significantly from those at the same site (WH3 or WH5) according to the Mann-Whitney *U* test (p < 0.05).

5. Discussion

5.1. Drinking water treatment residue

The high bound water content of DWTR makes dewatering and transport difficult and expensive, while the occasional high concentrations of PTE limit the suitability for its application to land (Babatunde and Zhao, 2007). The production of DWTR is currently increasing in the UK and globally, due to population growth, regulatory changes and increasingly variable raw water quality associated with climatic changes (Delpla et al., 2009; Keeley et al., 2014). This provides a clear incentive to find suitable reuse options and a sustainable circular economy approach to the management of this non-hazardous by-product of the coagulation-flocculation process used in the treatment of drinking water.

5.2. Use of DWTR in the historic mine impacted catchment

Whiteheaps is typical of historic metal mine soils with very little of the nutrients required for plant growth. As is typically the case the contaminated material is finely crushed due to the ore refinement process, remains unvegetated and so is highly mobile, allowing for easy distribution of PTE. Local waterways are often impacted, either by mine water or erosion of mine waste, the sites are normally very large, combining point and diffuse sources of contamination and also are often open to the public (Davies and White, 1981; Gutiérrez et al., 2016; Johnston et al., 2008). The majority of research conducted into DWTR as a remediation material has focused on the control of phosphorus (P) in waterways to prevent eutrophication as DWTR has high P adsorption potential (Wang and Jiang, 2016). This is due to the effect of P binding to oxides in the DWTR thus also potentially limiting nutrient plant availability. Several studies have shown that there is great potential for

DWTR to be used in PTE remediation at a chemical level as the large, active surface areas and amphoteric nature of the metal hydroxides (in this case $Fe(OH)_3$) used to precipitate colloidal particles from raw water make them suitable for sorption and immobilization of a wide range of soil contaminants (Alvarenga et al., 2018; Ippolito et al., 2011; Johnson et al., 2018; Kerr, 2019; McCann et al., 2015; Turner et al., 2019). However, very few studies have applied their findings to trials in the field as has been done in the present study (Bolan et al., 2014).

5.3. Mobility of PTE in DWTR

The sequential extraction analysis of the DWTR, showed that most PTE, were either at lower concentrations or in less mobile forms than they were in the unamended mine material. The higher levels of Cd in the DWTR were found to be predominantly in the reducible (56%) and oxidisable fractions (35%). This finding is supported by a study that found that DWTR is an efficient adsorbent for Cd^{+2} (Abo-El-Enein et al., 2017). Low concentrations of Cu and Pb found in the DWTR were in the less labile fractions with the greatest amount found in the residual fraction (40–43%). This indicates that the majority of Cd, Cu and Pb in this catchment has a geogenic source. In contrast, the majority of the Zn found in the DWTR was in the two most labile fractions, with the majority exchangeable (45%). Zn feeding into the Mosswood WTW has been found to be largely dissolved, entering the reservoir sediments the least rapidly of other PTE studied in the area (Harding and Whitton, 1978). BCR sequential extractions of the pot trial mine soils amended with 30% DWTR amendment showed similar results to the DWTR on its own, suggesting that the far greater concentrations of elements in the mine soils interacted with the DWTR in the same way. Although higher concentrations of Cd were found after amendment with DWTR these were in the reducible and oxidisable fractions, however, when compared to the unamended mine soil. Here Cd was found to be predominantly in

the exchangeable fraction (65%). This is of general concern given the toxicity of the analyte, adding to the argument for remediation, and comparable with similar studies of soils taken from historic mine sites which have been identified as one of the most significant pollution threats in the UK affecting more than 5000 km of rivers, including many important drinking water supply aquifers (Ahmadipour et al., 2014; Johnston et al., 2008; Medyńska-Juraszek et al., 2020). Concentrations of Cu were found to be significantly increased in the oxidisable fraction of the DWTR amended soil when compared to the mass balance calculations and the unamended soil ($p < 0.05$), with the exchangeable fraction now far lower. Addition of DWTR also reduced the biomass Cu concentrations from 100 mg/kg in the WH5 unamended soil to 50 mg/kg in that amended with 30%. These findings suggest that the DWTR is reducing the mobility of the Cu. A study, using similar extraction procedures has also confirmed the ability of DWTR to reduce the mobility and plant availability of Cu (Mahdy and Fathi, 2008; Moharem et al., 2013). Pb was found to be predominantly in the reducible fraction of the DWTR amended soil - indicating that it is occurring in a form bound to Fe oxides - and in the exchangeable fraction in the unamended mine soil – consistent with a carbonate bound form and the observed mineralogy (cerussite ($PbCO_3$). Mass balance suggests that there should have been a drop in the total concentrations of Pb, rather than an increase, with limited changes in form. However, significant changes ($p < 0.05$) in the fractionation of the amended soil were found when compared to the unamended and calculated concentrations, suggesting that a process has taken place that alters the fractionation of Pb to a less mobile form, following the addition of DWTR. The high complexation and sorption potential of Pb in the presence of Fe oxides is well reported in the literature (Finlay, 2015; Yiacoumi and Tien, 1995). A reduction in the mobility of Pb through the addition of DWTR is a key finding of the current study and one that suggests a need for further study on the reuse of this material for remediation purposes. Pb is both a highly toxic element and found at many of the approximately 5000 UK historic metal mine sites where its presence affects important drinking water supply aquifers (Johnston et al., 2008; Sinnett and Sardo, 2020). The addition of 30% DWTR however, does not seem to have any effect on the availability of Zn, although, 57% was lost in the amended soil, presumably through leaching.

5.4. DWTR effect on plant growth

Throughout this study soils amended with DWTR have outperformed the unamended control mine soils as a substrate for plant growth. For this study a suitable phyto stabilising plant was required, with a tolerance to the biogeochemical site conditions typically found in historic mining areas of the UK and the ability to quickly establish a fine binding network of rootlets capable of stabilising gravelly soil. Reed canary grass (RCG) a perennial rhizomatous C3 grass species native to the UK, has been shown to exhibit all of these traits and also has some secondary benefits such as improving ecosystem services and providing a biofuel feedstock (Jensen et al., 2018; R. A. Lord, 2015). In the pot trials the addition of a relatively small amount of DWTR provided an increased mean average dry weight by a factor of approximately 1.5–3. This was in spite of the high to moderate levels of organic matter calculated from the baseline organic carbon content measured for WH3 and WH5 soils respectively. Whilst this may seem a relatively small increase in growth, it is not insubstantial if applied to a whole site or growth season, especially as DWTR is typically put into landfill leading to financial and environmental costs (Hidalgo et al., 2016). In the field trials the application of DWTR was also successful in terms of encouraging plant growth resulting in statistically significant yield increases when compared to the unamended RCG at site WH5. A key reason for the increases in yield following DWTR application is likely to be the increase in nutrients.

5.5. DWTR effect on plant concentrations of PTE

The sequential extraction results were reflected in the elemental analysis of the biomass grown in the pot trials for Cu, Pb and Zn. For example, the biomass grown in the DWTR amended soils had concentrations of Cu, Pb and Zn that were approximately lower by a factor of 2–3 when compared to that grown on the unamended soil. The pot trial biomass analysis results for Cd showed consistent increases in concentrations in the biomass grown in DWTR amended soils, when compared to that of the unamended, despite the sequential extraction results showing a reduced mobility following DWTR application. However, as Cd was the only PTE studied that was found in similar concentrations in the DWTR and the unamended mine soil this may have been a mass loading effect from more Cd available for absorption into biomass. No significant differences were found in the concentrations of the PTE studied found in the biomass grown in either unamended mine soils or the soils amended with DWTR. Mean average biomass elemental concentration results did not correlate with results of the sequential extraction tests.

5.6. Green waste compost

The DWTR in this study has been evaluated as a growth medium and soil amendment, alongside the more commonly used PAS 100 green waste compost (GWC) (PAS100:2018 Specification for Composted Materials, 2018). Green waste compost is the product of composting operations that treat and stabilise biological wastes such as grass clippings, leaves or other plant material and certain food waste streams. This material is typically collected by local authorities and composted using the open windrow method, followed by the maturation and screening of the material.

In the UK the production of source-segregated GWC has considerably increased over the last 20 years, making GWC a widely available waste product that has been widely evaluated (Badmos et al., 2015; Eades et al., 2020; Karami et al., 2011; Kulikowska et al., 2015; Longhurst et al., 2019; R. A. Lord, 2015; R. Lord and Sakrabani, 2019; Montoneri et al., 2009). Application rates as high as 500 t ha^{-1} were found to be the optimum for one-off applications to restore brownfield land to productive use for energy crops (Lord, 2015; Lord and Sakrabani, 2019). The application of GWC to the mine soils consistently increased RCG yield when compared to both the unamended and DWTR amended soils in both the pot and field trials. For example, plants grown on site WH5 in GWC amended soil had a significantly greater ($p < 0.05$) dry weight by a factor of 2 when compared to plants grown in the unamended and DWTR amended soils. Again this effect of adding OWSA was seen in soils that might otherwise be viewed as having acceptable baseline levels of organic matter or carbon. The lower pH of the pot trial soils amended with DWTR may have been a factor contributing to the lower RCG biomass production, compared to plants grown in soils amended with GWC, for which the amended soils all fell into the optimal pH range (7.7–8.2) (Usťak et al., 2019). Plants grown in pots containing WH3 soils amended with GWC at 30% had a significantly greater DW when compared to all other experimental factors. Generally, the application of GWC had a similar but less profound effect on the mobility of the PTE following the sequential extraction procedure due to the reduction of Cu and Pb in the exchangeable fraction, which also includes carbonates. Whilst Pb in 'fresh' mine tailings can often be found in sulfide bound mineralogy (e.g. galena PbS), mine tailings that have been weathered over time often contain high concentrations of carbonate bound Pb (e.g. cerussite $PbCO_3$). A recent study of historic mine tailings in Belgium found that dissolution of cerussite was a controlling factor in the release of Pb in acidic, alkaline and neutral soil conditions (Helser and Cappuyns, 2021). The application of GWC to contaminated soils has been found to reduce the concentrations of plant available PTE, an effect that is attributed to increasing pH and complexation of mobile Cu with humic acids and organic matter found within the GWC (Li et al., 2021; Oorts, 2013).

5.7. Combining GWC with DWTR

A combination of the two OWSA (MIX) was evaluated as part of this field trial to find out if mixing DWTR with GWC could provide a means to reduce PTE mobility alongside providing nutrients and organic matter. As the WTW producing this DWTR is local to the Whiteheaps mine complex, this presented a potential holistic solution and circular economy opportunity wherein application of the DWTR to land could reduce the overall impact of the mine sites on water quality over time. Although GWC and DWTR have occasionally been compared as growth amendments for RCG on contaminated land (Badmos et al., 2015) the combination of the two amendments is a novel approach. The MIX outperformed the DWTR amended and unamended soils in terms of DW of RCG produced during the field trial with significant improvements on site WH5. In terms of bioavailability of PTE, the biomass produced in soils amended with the MIX had concentrations of PTE similar to that of those produced in soils amended with the GWC with no clearly disenable pattern. A study on the impact of applying mixtures made with different ratios of DWTR and GWC would develop this research further.

5.8. Summary of key results and further work

It is clear that even at relatively low concentrations DWTR is able to affect the chemical and physical characteristics of mine soils allowing for changes that promote revegetation and the reduction in availability of PTE in certain cases. Both the OSWA resulted in significant increases in RCG yield. Whilst GWC outperformed DWTR in many cases, DWTR is currently a low value waste material and so therefore may provide a very competitive alternative if locally available. Due to the different physical characteristics of the OWSA, it was practically difficult to amend the soils equally in trials and thus provide directly comparable results. For example, the addition of the same mass of each OWSA potentially led to different nutrient addition/PTE dilution as a result of the differences in bulk density and moisture content. This discrepancy led to an amendment rate of 258 t/ha of GWC and 99 t/ha DWTR being applied to plants at plot WH5 when recalculated on a dry basis. This is a clear limitation of comparing OWSA which are often very different in their physical composition. Further work should be undertaken with a standardised process that allows for adequate comparison of these amendments, perhaps focusing on a single characteristic of the amendment e.g. concentration of N, P, K or dry mass. With this adjustment it may be that the DWTR could have had a similar effect on increasing grass yield if it were applied at a similar dry weight. A very clear result from the sequential extraction procedure on the WH5 pot trial soils is the effect that the addition of DWTR has had on the availability of Pb. Here a significant portion of the Pb found in the mine soil was extracted in the reducible fraction with increases also found in the oxidisable and residual when compared to the unamended pot trial WH5 soil. This effect was by far the most pronounced and remarkable - given the toxicity and quantity of the element - of the sequential extraction results for both OWSA. Further work should be conducted on the presence of Fe oxides in the DWTR and their effect on PTE mobility. A significant finding of the biomass analysis of the plant material grown as part of the pot trials, was that the greatest concentrations of most of the PTE tested (Cr, Cu, Pb and Zn) were generally found in the biomass produced in the unamended soils. This provided an indication that the OWSA may have reduced the mobility of some PTE in the amended soils resulting in the lower biomass concentrations. However, it might have also been an artefact of a breakdown in normal physiological processes due to phytotoxic PTE, or that the PTE loadings were absorbed in equal quantities at the beginning of growth and thus the concentrations were diluted in the plants that achieved greater biomass production, as they did in the amended soils. The pH of the mine soils was also altered considerably through the application of the amendments (reduced by the DWTR and increased by the GWC) and this is a likely factor in any changes in the PTE bioavailability. Further work should focus on confirming the effects on the availability of PTE following DWTR application to contaminated soil and discovering whether combining other OWSA with DWTR (such as the MIX) could hold the key to the sustainable reuse of this undervalued solid waste by-product of water treatment.

6. Conclusion

This study demonstrated the following findings:

1) The application of DWTR to historically contaminated soil can result in significant improvements in the growth of plants capable of providing a vegetative cover and stabilising soils.
2) Following a 10-week pot trial Pb, Cd & Cu in the mine soils amended with DWTR were found to be significantly less mobile compared to unamended soils suggesting a reduction in bioavailability
3) These two findings above for DWTR compare well to those of the more commonly applied soil amendment GWC: This suggests that DWTR could provide a more sustainable alternative when it is available locally, especially when produced in a metal mine impacted drinking water catchments, where a circular economy approach can be applied to reduce future PTE loadings.

Credit author statement

Benjamin Nunn – Writing – original draft, Data curation, Investigation, Richard Lord – Conceptualisation, Writing – review & editing, Supervision, Funding acquisition, Christine M Davidson - Methodology, Supervision

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interestsBenjamin Nunn reports financial support was provided by Northumbrian Water Ltd.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2023.118809.

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