

Remediation and Restoration

Trialling Water-Treatment Residuals in the Remediation of Former Mine Site Soils: Investigating Improvements Achieved for Plants, Earthworms, and Soil Solution

Karrar A.H. Arab,^{a,b} David F. Thompson,^c and Ian W. Oliver^{a,*}^aSchool of Geography, Geology and the Environment, Keele University, Keele, United Kingdom^bDepartment of Ecology, College of Science, University of Kufa, Najaf, Iraq^cSchool of Chemical and Physical Sciences, Keele University, Keele, United Kingdom

Abstract: During clarification processes of raw water, a vast amount of by-product known as “drinking water-treatment residuals” (WTRs) are produced, being principally composed of hydroxides of the Al or Fe salts added during water treatment plus the impurities they remove. Aluminum-based (Al-WTR) and iron-based (Fe-WTR) materials were applied at 10% w/w to degraded, bare (unvegetated) soils from a restored coal mining site in central England (pH <3.9) to study their potential amelioration effects on earthworm mortality, biomass yield of seedling plants, and element concentrations in plant tissues, earthworm tissues, and soil solutions. A separate treatment with agricultural lime was also conducted for comparison to evaluate whether any observed improvements were attributable to the liming capacity of the WTRs. After completion of the trials, all samples were subjected to a wet–dry cycle, and the experiments were repeated (i.e., simulating longer-term effects in the field). Both types of WTRs significantly increased the biomass of plants, and in some treatments, survival of earthworms was also enhanced compared to nonamended soils. Excess plant tissue element concentrations and element concentrations in soil solutions were reduced in amended soils. The implications are that adding WTRs to mining-impacted soils is a potentially viable, sustainable, and low-cost remediation method that could be used globally to improve the soil condition. *Environ Toxicol Chem* 2020;39:1277–1291. © 2020 The Authors. *Environmental Toxicology and Chemistry* published by Wiley Periodicals LLC on behalf of SETAC.

Keywords: Soil remediation; Water-treatment residuals; Mine restoration; Earthworms; Soil contamination; Soil ecotoxicology

INTRODUCTION

Resource extraction (mining) and use of the obtained materials has been a fundamental part of human history and a crucial process in the development of nations and technologies. The extraction of coal, for example, largely powered what is thought of as the Industrial Revolution (Reed 2002) and provided economic stimulus and employment for vast numbers of people. For example, at the peak of coal mining activity in the United Kingdom (ca. 1913), 1 million people were directly employed across 1600 active mines, producing approximately 300 million

tonnes of coal per year (Johnston et al. 2008). However, despite its importance and contributions, coal mining has left a legacy of pollution in many parts of the world that continues to cause environmental concerns. This can particularly be the case at old or abandoned mines that predate modern effective environmental controls. Mine spoil, waste rock, and other solid and liquid wastes are generated during coal extraction and processing; and all can become future sources of soil and water pollution in the surrounding environment. Thus, acid or neutral mine drainage, aerial or fluvial movement, and deposition of spoil materials and other mechanisms can all result in wider contamination of former mine areas. Often, this contamination arises because sulfide minerals in the solid phases react with oxygen and water to produce sulfuric acid and, in turn, dissolve potential toxic elements (PTEs) from the solid phase of minerals and soil. The pH of any receiving soil and water can also be impacted, affecting the mobility and toxicity of PTEs. Indeed, PTEs at elevated concentrations arising from mining activities can adversely affect soil and aquatic biota

This article includes online-only Supplemental Data.

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* Address correspondence to i.Oliver@keele.ac.uk

Published online 5 March 2020 in Wiley Online Library (wileyonlinelibrary.com).

DOI: 10.1002/etc.4706

communities, habitat, and ecosystems (e.g., Anawar 2015; Kostarelos et al. 2015).

Remediation and restoration of mining impacted areas have become major undertakings, with many different approaches and options available. The cost, long-term effectiveness/permanence, and commercial availability of remediating materials must be considered when planning a remediation effort, as must the general public acceptance of them and their capacity to deal with potentially high metal concentrations that may have considerable toxicity and mobility. The remediation approach adopted must therefore consider all such points and strike a balance (Abdullahi 2015). The need for plentiful, effective, low-cost materials for use in mine site remediation has therefore stimulated interest in finding additional uses for readily available by-products that might otherwise simply be discarded; in the present study, we tested the utility of using water-treatment residuals (WTRs) in the remediation of mining-impacted soils.

The most common method of clarifying raw water sources for drinking is to add metal salts (usually aluminum- or iron-based) to coagulate and flocculate impurities and remove them via settling and sedimentation. This process generates a sludge or residue material (WTRs) that comprises the removed impurities and the reaction/precipitation products of the added metal salts (Howe et al. 2012).

When aluminum or iron coagulant is added to the water, it reacts with the natural or supplemented alkalinity of the water, producing aluminum or iron hydroxides, respectively. Typical constituents and properties of partially dried WTRs are shown in Table 1.

Millions of tons of WTRs are produced every year all over the world (Basibuyuk and Kalat 2004). According to Henderson et al. (2009), the United Kingdom uses 138 000 tonnes of aluminum-based salts (generating what can be referred to as Al-WTR) and 181 000 tonnes from ferric-based salts (Fe-WTR) annually, whereas the United States generates more than 2 million tons of WTRs every day (Prakash and SenGupta 2003). As cited in Keeley et al. (2014), WTRs are considered inert waste under European Union Council Directive 99/31/EC (1999) and can be used as construction materials in, for example, ceramics and bricks (Goldbold et al. 2003) and geotechnical work materials (Carvalho and Antas 2005). Another use that has been proven successful is as the main substrate in constructed reedbeds for wastewater filtration (Zhao et al. 2011). A portion of the generated WTRs can also be recycled as coagulant (Keeley et al. 2014).

Other studies have demonstrated that WTRs can be used as an inexpensive adsorbent for the removal of As, Co, Hg, and perchlorate from water and wastewater (Makris et al. 2006; Hovsepyan and Bonzongo 2009; Ociński et al. 2016; Jiao et al. 2017) and

to remove Cr, Cd, and Pb from landfill leachate (Mohammed et al. 2016). Chiang et al. (2012) found that adsorption of Cd, Co, Ni, Pb, and Zn in contaminated sediments using WTRs was significantly better than that of goethite. Disposal of WTRs via application to soil has also become more common, and Zhao et al. (2015) found that WTRs can be used as a suitable soil amendment to avoid glyphosate contamination of marine ecosystems by improving the glyphosate retention capacity in soils. The most common soil application of WTRs reported in the literature to date has been as a general amendment and as a means to limit P mobility in overfertilized or otherwise overenriched soils (Oliver et al. 2011).

Beneficial use of WTRs is therefore an attractive option that offers financial advantages and facilitates development of a more circular economy with greater levels of material recycling. The use of WTRs in the remediation of mining and metal-contaminated soils has yet to be comprehensively investigated. Moreover, although a number of studies have investigated their effects on soil microbes following soil amendment with WTRs (e.g., Garau et al. 2014), very few, if any, have examined the influence of WTR application on plants, earthworms, and soil solution chemistry in mining-affected soils. This is a gap in the current understanding of the risks and benefits of using these materials in mining-affected soils, especially considering that plants and earthworms are widely recognized as essential ecosystem factors in a soil under restoration.

The specific aims of the present study, therefore, were to assess the remediation of mining-contaminated soils using 2 types of WTRs from central England, examining improvements in soil and soil porewater chemical properties as well as improvements in plant growth and earthworm survival following amendment with WTRs.

METHODS

Water treatment residuals and soils—Source and preparation

Water-treatment residuals from 2 water-treatment plants in Staffordshire, England, were provided by Severn Trent Water. One plant primarily uses Al salts and the other Fe-based salts, generating what is designated here as Al-WTRs and Fe-WTRs, respectively. According to the results from a previous project carried out on the same materials (Howells et al. 2018), the properties of Al-WTRs once dry were pH 7.34 ± 0.06 , Al content $11.64 \pm 1.08\%$ w/w, organic matter content $28.0 \pm 0.1\%$ w/w, and Fe $0.91 \pm 0.08\%$ w/w; and those of Fe-WTRs were pH 7.37 ± 0.01 , Fe $17.69 \pm 0.19\%$ w/w, organic matter $25.9 \pm 0.2\%$ w/w, and Al $0.71 \pm 0.12\%$ w/w. The WTRs were dried at 30 °C until stable mass and ground to pass a 2-mm sieve.

Soil samples were collected from a restored coal mining site in Staffordshire, England (Figure 1), that is now used partly as a nature reserve and partly for cattle grazing. The site is in the heart of the coal mining area of the English Midlands, a region in which hundreds of small mines and several large ones had been worked over the centuries. At various points around the site there are large patches of bare soil where no, or very little,

TABLE 1: Typical constituents and properties of partially dried water treatment residuals^a

Al (%)	Fe (%)	Ca (%)	Mn (%)	Pb (mg/kg)	Zn (mg/kg)	Organic matter (%)	pH
4–18	1–10	0.4–2	0.04–1	3–16	5–60	20–30	6.5–8.0

^aData from Babatunde and Zhao (2007), Castaldi et al. (2014), Lombi et al. (2010), Ulén et al. (2012), and Wang et al. (2012).



FIGURE 1: Soil sample collection general location in Staffordshire, England (inset maps), and example of the bare soil “seep” points (main image).

vegetation grows (Figure 1), suggesting that the mining legacy at the site still impacts the soil either through remaining contamination hot spots or through upwelling or percolation of mining-affected near-surface groundwater. Soil samples from the top 15 cm depth (~8 kg total) were collected from each of 3 such bare points (or “seeps”) that were approximately 200 to 300 m apart. The samples were stored in sealed plastic containers and transported to the laboratory, where they were air-dried and ground to pass a 2-mm sieve. Samples collected from within a particular seep point were bulked and homogenized for use in the experiments.

Loss on ignition (≥ 4 h at 450°C) was used to determine organic matter content (Nelson and Sommers 1996), and pH was determined in 0.001 M CaCl_2 extracts (1:5 solid:solution) using a Jenway 3510 pH meter and probe. Total element contents were determined via microwave-assisted digestion of oven-dried soils in reverse aqua regia (see Supplemental Data, Table S1, for procedures, quality control measures, and determined values).

Remediation of contaminated soils using WTRs

Plant growth trial. Soil from each of the 3 seep collection points was amended separately with either 10% Al-WTR w/w, 10% Fe-WTR w/w, or 10% agricultural lime w/w (total solid mass 250 g/replicate). Controls (i.e., with no amendment) were also established. All treatments and controls were prepared in triplicate ($n = 3$). Every individual replicate was prepared separately (as opposed to large batch mixing and splitting) to ensure that a consistent addition rate was achieved across treatments and replicates. Once prepared, each soil sample was placed into a separate plastic plant pot (~0.25 L). The addition rate of 10% w/w was selected because it was thought to represent the upper limit of what might realistically be used in a remediation scenario but could still avoid the worst of the reductions in available soil phosphorus reported at rates of WTR

application above this level (Dayton and Basta 2001). The agricultural lime treatment was included to allow an assessment as to whether any improvements observed were mainly attributable to pH increases anticipated to be brought about by WTR addition. Ultrapure water was added (60% of water holding capacity; determined by soaking, allowing to drain, and calculating water retained) to all samples, and moisture was maintained every day by watering to mass using ultrapure water. Perennial ryegrass (*Lolium perenne*; 1.5 g) seeds that had been moistened were added to the top of the soil, followed by adding vermiculite (1 g) to decrease loss from evaporation. To allow full access to natural light, the pots were placed in an unheated incubator next to a large window. The 2 growth periods were 4 wk (28 d) in each of November and January in the United Kingdom. The humidity inside the incubator was maintained by placing 100 mL of ultrapure water in a glass beaker inside the incubator. At 28 d after sowing, shoots were removed by cutting at the surface with scissors and dried at 65 to 70°C in an oven for 48 h, followed by recording the mass of dry weight.

Once dry mass was recorded, samples were cut into small pieces with scissors and digested in nitric acid (Yilmaz 2007). In this method approximately 0.4 g of dry plant material is placed in the digestion vessel, then 10 mL of high-purity, concentrated (16 M) HNO_3 is added, and the digestion is carried out using a CEM-MARS 6 microwave. This procedure achieved complete digestion and dissolution of the plant samples (i.e., no visible residue). The digest solutions were transferred to centrifuge tubes, made up to 20 mL with 0.1% HNO_3 , and filtered through a $0.45\text{-}\mu\text{m}$ syringe filter into plastic vials. Nutrients and heavy metal concentrations were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-MS/OES). In each batch of analyses, a blank sample was carried out for quality control, and certified reference solutions were used for calibration standards. All acids used were of high purity grade (i.e., Primar Plus trace analysis).

Earthworm survival trial. The earthworm survival assay was conducted in accordance with Organisation for Economic Co-operation and Development (OECD) protocol 222 (2016). Treatments and controls (i.e., 0 and 10% Al-WTR, 10% Fe-WTR, or 10% lime; $n = 3$; replicates mixed individually) were prepared separately but in an identical manner to those described for the plant test. Once prepared, control or treatment soils were placed in plastic containers (~0.35 L) for the earthworm assay. Four “procedural controls” were also prepared from a pristine soil collected from pasture land on the campus of Keele University (Staffordshire, England) to verify that the earthworm assay design and conditions met the validity criteria of the OECD 222 protocol (i.e., adult mortality $\leq 10\%$ in negative controls; this criterion was achieved and, thus, the assay was validated). Ultrapure water was added (60% of water holding capacity) to all samples and maintained every day (using ultrapure water). Then, 5 adult *Eisenia fetida* earthworms were weighed and added to each container. Oatmeal, approximately 2 g, was added as a food source. Cling film was used to cover the containers to prevent escape and pierced to facilitate air flow. Oatmeal was added every week. After 4 wk, survival was determined, and living worms were allowed to depurate for 1 d, then rinsed with ultrapure water, patted dry, weighed, and frozen. To determine element contents, the worms were dried at 70 to 100 °C for 48 h in borosilicate glass beakers, weighed, and then digested in 10 mL of HNO₃ (Primar Plus trace analysis) on a hot plate. The digest solutions then were transferred to a centrifuge tube and made up to 20 mL with 0.1% HNO₃. The solutions were filtered through a 0.45- μm syringe filter into a plastic vial. Nutrient and heavy metal concentrations were analyzed using ICP-MS/OES.

Simulated soil solution investigation. After the earthworm survival experiment, the soils were saturated with ultrapure water and allowed to stand for approximately 3 d to generate simulated soil porewater (Ma et al. 2006; Ardestani and van Gestel 2013). Soil solution was then extracted from each pot by centrifugation for 20 min at 3500 rpm. The resulting extracted solutions were filtered using 0.45- μm syringe filters, then acidified with 0.1 mL concentrated HNO₃ and kept cold at 4 °C until they were analyzed using ICP-MS/OES.

Examinations of the effects of a wetting–drying cycle on plant yield, earthworm survival, and element uptake in amended and

nonamended soils were also carried out. After completion of the plant and earthworm trials and the simulated soil solution generation, all of the samples were subjected to a wet–dry cycle (i.e., simulating longer-term effects in the field). Each individual replicate was dried at 25 °C in an oven for 1 wk, followed by regrinding, homogenization, and determination of remaining water content (a small subsample was also removed for determination of soil pH following treatments). Ultrapure water was added to reestablish moisture content at 60% of water holding capacity, and samples were allowed to equilibrate for a few days before the plant and earthworm trials were repeated following the same protocols.

Statistical analyses

Statistical assessment of differences among treatments and controls were conducted via *t* tests and analysis of variance (ANOVA), when underlying assumptions of the tests were met (i.e., normality of distribution) or via Mann-Whitney tests if necessary. All statistical assessments were conducted using GraphPad Prism software.

RESULTS

Soil pH and organic matter effects

Despite the high organic matter content of the WTRs (typically 28% in Al-WTR and 26% in Fe-WTR), their addition at 10% w/w had a negligible impact on the total organic matter percentage of the soils determined by loss on ignition, as shown in Table 2. This is likely due to the mining-impacted soils still having the presence of small coal fragments that were combusted during the organic matter content measurement. Addition of lime did decrease the overall organic matter content of the soil because the lime contained no organic matter. However, WTR treatment had a profound effect on soil pH (Table 2), with statistically significant increases from pH <4 in the untreated controls to generally pH >4 in treated soils. Both Al-WTRs and Fe-WTRs significantly increased the pH, with no consistent pattern as to which raised the pH more. The pH buffering capacity of the soils, calculated based on response to lime addition, were shown to vary (Table 2), whereas the 2 WTRs were each found to have 45 to 50% lime effect

TABLE 2: Organic matter content and pH of untreated and treated soils, plus buffering capacity of the soils calculated from response to lime addition: Uncertainties (\pm values) indicate standard deviation

Soil	Nonamended (control)	Al-WTR amended	Fe-WTR amended	Lime amended	Buffering capacity ^a
Organic matter (%)					
Seep 1	32.09 \pm 0.31	32.88 \pm 0.18	32.18 \pm 0.26	8.17 \pm 0.19*	n/a
Seep 2	27.92 \pm 0.23	26.62 \pm 0.27*	24.95 \pm 0.88	22.48 \pm 0.4*	n/a
Seep 3	8.11 \pm 0.3	8.99 \pm 0.1	8.23 \pm 0.09	5.14 \pm 0.06*	n/a
pH					
Seep 1	3.28 \pm 0.02*	4.38 \pm 0.06*	3.80 \pm 0.02*	6.36 \pm 0.04*	21 400 \pm 0.00
Seep 2	3.83 \pm 0.06*	5.67 \pm 0.10*	6.01 \pm 0.05*	6.88 \pm 0.03*	32 700 \pm 0.00
Seep 3	3.40 \pm 0.01*	5.23 \pm 0.06*	5.42 \pm 0.02*	7.15 \pm 0.06*	26 600 \pm 0.00

*Significantly different from nonamended ($p < 0.05$).

^aBased on lime addition and measured pH, in milligrams of CaCO₃ per kilogram of soil per pH unit.

n/a = not applicable; WTR = water treatment residual.

equivalent value on average in terms of capacity to raise pH in the soils (Supplemental Data, Table S2).

Plant yield and element concentrations

The increase in dry mass of plant growth in all amended soils was statistically significant in comparison with that of non-amended control soil in both the initial plant growth trial and the trial following a wet–dry cycle (Table 3). In the initial trial the highest masses were found in Fe-WTR-amended soils, which were 238, 136, and 215% of that in nonamended control soils in seep 1, seep 2, and seep 3, respectively. The increase in dry mass of plant growth in Al-WTR- and lime-amended soils was almost as high. Following the wet–dry cycle, the yield increases achieved with Al-WTR, Fe-WTR, and lime treatments were similar (Table 3).

Plant tissue element concentrations from the initial plant growth trial are shown in Table 4, whereas those from the trial following the wet–dry cycle are presented in Supplemental Data, Table S3; there was a significant decrease in Al assimilation in all seeps brought about by every treatment (Fe-WTR, Al-WTR, and lime), while Pb assimilation was decreased by WTR treatments in almost every case. There were also modest yet significant decreases in As assimilation in all treated soils in the post-wetting–drying trial and for seep 3 (for all amendments) in the initial plant trial. The treatments also increased the tissue concentrations of the macro- and micronutrients Ca, Cu, Mg, and K in almost every case across the 2 plant trials.

The effects on Fe assimilation were more variable, with some large and significant decreases observed following treatments. The Ni concentrations were also generally decreased by the treatments. Assimilation of Mn was rather variable, with some significant increases following WTR treatments that were not observed in lime treatments, indicating that WTRs can act as a source of plant available Mn in some situations. However, in some cases WTR treatments decreased Mn assimilation. Plant Zn concentrations were generally decreased by treatments in the initial plant trial, but this effect was much less apparent in the second trial following the wet–dry cycle, in which some WTR treatments modestly increased plant Zn relative to untreated controls.

TABLE 3: Mean aboveground dry plant mass per pot (grams, \pm standard deviation) in the original plant trial and following a wet–dry cycle

Site	Nonamended	Al-WTR	Fe-WTR	Lime
Original plant trial yield				
Seep 1	0.18 \pm 0.02	0.34 \pm 0.01*	0.43 \pm 0.01*	0.35 \pm 0.02*
Seep 2	0.36 \pm 0.03	0.47 \pm 0.02*	0.49 \pm 0.01*	0.42 \pm 0.01*
Seep 3	0.20 \pm 0.01	0.35 \pm 0.02*	0.43 \pm 0.02*	0.36 \pm 0.02*
Yield following wet–dry cycle				
Seep 1	0.35 \pm 0.03	0.45 \pm 0.02*	0.48 \pm 0.02*	0.58 \pm 0.03*
Seep 2	0.38 \pm 0.01	0.46 \pm 0.03*	0.51 \pm 0.03*	0.47 \pm 0.01*
Seep 3	0.32 \pm 0.02	0.42 \pm 0.03*	0.43 \pm 0.01*	0.43 \pm 0.02*

*Significantly different from nonamended ($p < 0.05$).
WTR = water treatment residual.

Earthworm trial (survival and element uptake)

Survival percentages of earthworms were high in procedural control soil samples (91 \pm 4%), meeting the validity criteria of the protocol. In the initial earthworm trial, there was no survival (100% mortality) of earthworms in the nonamended seep soils (Table 5). The highest survival percentages (100%) were observed in lime treatments in all seep soils, but survival rates were also significantly increased in Al-WTR and Fe-WTR treatments of seep 1 soil (to 80 and 40%, respectively). In seep 2, survival also increased significantly following both Al-WTR and Fe-WTR addition, to 53 \pm 29% and 20 \pm 11.5%, respectively. A significantly increased survival rate (85 \pm 9.5%) was achieved in seep 3 following Fe-WTR treatment, but no such significant improvement was found in that soil with addition of Al-WTRs. In the second earthworm trial (i.e., following the wet–dry cycle), lime, Al-WTR, and Fe-WTR treatments all had significantly increased survival in seep 2 and 3 soils, with Fe-WTR and lime achieving the highest rates (Table 5). However, all worms died in seep 1 soil regardless of treatment.

Elemental analysis of earthworms was, by definition, restricted to those treatments from which earthworms were recovered. There were no surviving earthworms in the non-amended seep soils, and therefore, there are no values for the measured elements from those samples. Table 6 (initial trial) and Supplemental Data, Table S4 (post-wetting–drying cycle), therefore show element concentrations in earthworms recovered from the amended samples only. Element concentrations were rather variable across treatments and among replicates within treatments, with ANOVA revealing few significant differences. Nevertheless, some patterns appeared; in both trials (i.e., before and after a wetting–drying cycle) the addition of Al-WTRs resulted in higher mean Al concentrations than were observed in the other treatments (where data are available to directly compare), indicating that a portion of the Al in the WTRs was bioavailable. The increase in Fe in Fe-WTR-amended samples was much less distinct and only apparent in the tissues of earthworms from the trial post-wetting–drying (Supplemental Data, Table S4). Unsurprisingly, in both trials, the addition of lime increased the Ca concentrations in earthworms. The mean water contents (percent w/w) of earthworms recovered from soils in the first trial, determined during the preparation for sample digestion, were 85.0 \pm 2.0, 83.2 \pm 6.2, and 86.4 \pm 1.4% for Al-WTR, Fe-WTR, and lime treatments, respectively, indicating a very consistent and healthy level.

Simulated soil solutions—Element concentrations

All treatments significantly reduced the soil solution Al concentration, with Fe-WTRs and lime being the most effective (Table 7). The As concentrations were marginally increased in seep 1 soil following Al-WTR and Fe-WTR amendment but more substantially increased by lime treatment. The other seep soils did not have any significant alterations to soil solution As concentrations following treatment. The WTR treatments significantly reduced Cd concentrations in seep 3 solutions, from

TABLE 4: Mean element content in aboveground plant tissue (milligrams per kilogram \pm standard deviation or percentage of w/w where indicated) from the initial plant growth trial

Element	Soil	Nonamended control	Al-WTR	Fe-WTR	Lime
Al	Seep 1	176.02 \pm 6.64	44.02 \pm 1.38*	51.81 \pm 5.98*	78.85 \pm 1.22*
	Seep 2	67.79 \pm 7.02	38.52 \pm 3.23**	33.23 \pm 0.58**	35.42 \pm 1.39**
	Seep 3	602.69 \pm 24.15	30.05 \pm 0.07*	32.49 \pm 0.06*	37.03 \pm 4.13*
As	Seep 1	0.14 \pm 0	1.31 \pm 1.12	0.98 \pm 0.65	0.28 \pm 0.05
	Seep 2	0.34 \pm 0.05	0.32 \pm 0.04	0.29 \pm 0.03	0.28 \pm 0.07
	Seep 3	0.27 \pm 0.09	0.10 \pm 0.01*	0.08 \pm 0.00*	0.09 \pm 0.01*
Ca%	Seep 1	0.15 \pm 0.00	0.78 \pm 0.02*	1.17 \pm 0.01*	0.89 \pm 0.00*
	Seep 2	0.3 \pm 0.00	0.55 \pm 0.00*	0.67 \pm 0.01*	0.64 \pm 0.05*
	Seep 3	0.27 \pm 0.00	0.85 \pm 0.00*	1.31 \pm 0.06*	1.26 \pm 0.09*
Cd	Seep 1	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00
	Seep 2	0.06 \pm 0.05	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00
	Seep 3	0.07 \pm 0.05	0.00 \pm 0.00	0.00 \pm 0.00	0.01 \pm 0.01
Co	Seep 1	0.55 \pm 0.01	0.20 \pm 0.00*	0.51 \pm 0.02	0.1 \pm 0.00*
	Seep 2	9.2 \pm 0.33	1.02 \pm 0.00*	1.3 \pm 0.09*	1.19 \pm 0.08*
	Seep 3	9.54 \pm 0.43	0.45 \pm 0.00*	0.63 \pm 0.01*	0.74 \pm 0.00*
Cr	Seep 1	1.37 \pm 0.24	1.4 \pm 0.13	1.32 \pm 0.15	3.87 \pm 2.7
	Seep 2	1.03 \pm 0.14	1.2 \pm 0.10	1.2 \pm 0.00	1.03 \pm 0.17
	Seep 3	2.47 \pm 0.30	1.31 \pm 0.12*	1.03 \pm 0.15*	0.75 \pm 0.06*
Cu	Seep 1	11.61 \pm 0.67	15.62 \pm 0.11*	13.5 \pm 0.42*	14.15 \pm 0.11*
	Seep 2	11.85 \pm 0.2	15.85 \pm 0.32*	14.54 \pm 0.09*	13.57 \pm 0.53*
	Seep 3	10.81 \pm 0.41	13.05 \pm 0.36*	12.41 \pm 0.61*	13.11 \pm 0.16*
Fe	Seep 1	522.19 \pm 37.11	179.24 \pm 22.02*	402.85 \pm 62.03	230.48 \pm 12.76*
	Seep 2	205.91 \pm 29.87	135.75 \pm 2.97	132.07 \pm 3.75	102.17 \pm 3.29
	Seep 3	1446.76 \pm 59.51	112.64 \pm 1.82*	112.82 \pm 1.39*	104.5 \pm 4.34*
K%	Seep 1	0.56 \pm 0.03	0.79 \pm 0.02*	0.94 \pm 0.02*	1.57 \pm 0.35*
	Seep 2	2.39 \pm 0.03	3.52 \pm 0.01*	3.13 \pm 0.01*	3.68 \pm 0.01*
	Seep 3	1.44 \pm 0.00	2.04 \pm 0.05*	2.31 \pm 0.14*	2.95 \pm 0.15*
Mg%	Seep 1	0.16 \pm 0.00	0.3 \pm 0.01*	0.32 \pm 0.00*	0.2 \pm 0.00*
	Seep 2	0.34 \pm 0.00	0.38 \pm 0.00*	0.36 \pm 0.00*	0.24 \pm 0.00*
	Seep 3	0.32 \pm 0.01	0.36 \pm 0.00	0.42 \pm 0.00**	0.24 \pm 0.01
Mn	Seep 1	45.3 \pm 0.43	339.45 \pm 8.32*	286.02 \pm 11.36*	60.17 \pm 3.26*
	Seep 2	372.05 \pm 0.51	283.03 \pm 3.45*	190.21 \pm 5.69*	101.89 \pm 2.05*
	Seep 3	298.41 \pm 4.85	342.4 \pm 4.48*	247.23 \pm 1.92*	125.34 \pm 7.93*
Ni	Seep 1	9.59 \pm 0.82	7.1 \pm 0.31	7.24 \pm 0.16	5.33 \pm 0.1
	Seep 2	37.33 \pm 2.17	28.24 \pm 1.66*	13.71 \pm 1.13*	6.59 \pm 0.17*
	Seep 3	28.98 \pm 5.54	14.92 \pm 2.5	7.55 \pm 0.35*	7.09 \pm 0.34*
P%	Seep 1	0.80 \pm 0.05	1.14 \pm 0.01*	0.95 \pm 0.01**	0.99 \pm 0.03
	Seep 2	0.97 \pm 0.01	0.79 \pm 0.01*	0.72 \pm 0.01*	0.74 \pm 0.01*
	Seep 3	0.61 \pm 0.03	0.88 \pm 0.02*	0.77 \pm 0.04*	0.82 \pm 0.00*
Pb	Seep 1	0.71 \pm 0.08	0.65 \pm 0.20*	0.58 \pm 0.03*	1.33 \pm 0.48
	Seep 2	0.65 \pm 0.17	0.26 \pm 0.02*	0.27 \pm 0.03*	0.32 \pm 0.05
	Seep 3	0.39 \pm 0.06	0.09 \pm 0.02*	0.09 \pm 0.01*	0.35 \pm 0.23
S%	Seep 1	2.61 \pm 0.03	3.65 \pm 0.06*	2.39 \pm 0.03*	4.12 \pm 0.13*
	Seep 2	4.82 \pm 0.13	5.89 \pm 0.05*	2.73 \pm 0.15*	5.17 \pm 0.09*
	Seep 3	4.44 \pm 0.09	4.57 \pm 0.23	2.71 \pm 0.05*	4.97 \pm 0.07**
Zn	Seep 1	74.22 \pm 4.89	65.05 \pm 4.79	53.6 \pm 1.28	45.91 \pm 0.24**
	Seep 2	72 \pm 1.09	59.99 \pm 0.31*	53.9 \pm 1.24*	61.88 \pm 0.58*
	Seep 3	79.54 \pm 1.67	52.66 \pm 0.40*	48.12 \pm 1.55*	49.42 \pm 0.31*

*Significantly different from nonamended ($p < 0.05$).**Almost significantly different from nonamended ($p \sim 0.06$).

WTR = water treatment residual.

approximately 11 to $<0.25 \mu\text{g/L}$, but had negligible influence on the other seeps (which had much lower initial Cd concentrations). The concentrations of Co were generally greatly reduced by all amendments, except in the case of seep 1 amended with Fe-WTRs, which had a significant increase from approximately 100 to $330 \mu\text{g/L}$. Concentrations of Fe, Ni, and Zn were generally reduced by each of the treatments, whereas K was increased in every case, with the degree of change rather variable among the treatments and among the various seep soils (Table 7). Addition of the amendments generally decreased the concentration of Pb or had no effect, except for the lime

treatment in seep 1, which resulted in a much higher concentration than in the untreated sample (i.e., ~ 161 vs $<1 \mu\text{g/L}$).

DISCUSSION

Effects of WTR addition on soil characteristics

Addition of the WTR amendments resulted in negligible or marginal differences in total organic matter content of the tested soils as determined by loss on ignition. However, the loss-on-ignition method does not indicate the relative ecological importance of the organic matter determined and does not

TABLE 5: Earthworm survival percentage in treated and control soils (mean \pm standard error)

Site	Nonamended	Al-WTR	Fe-WTR	Lime
Survival percentages of earthworms in original trial				
Seep 1	0.00 \pm 0.00	80 \pm 8.16*	40 \pm 8.16*	100 \pm 0.00
Seep 2	0.00 \pm 0.00	53.33 \pm 29.05	20 \pm 11.54	100 \pm 0.00
Seep 3	0.00 \pm 0.00	0.00 \pm 0.00	85 \pm 9.57*	100 \pm 0.00
Survival percentages of earthworms in the trial after wet–dry cycle				
Seep 1	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00
Seep 2	13.33 \pm 13.33	80 \pm 20.00**	100 \pm 0.00*	93.33 \pm 6.66*
Seep 3	0.00 \pm 0.00	60 \pm 20.00	100 \pm 0.00*	100 \pm 0.00*

*Significantly different from nonamended ($p < 0.05$).**Almost significantly different from nonamended ($p \sim 0.06$).

WTR = water treatment residual.

distinguish ecologically active organic matter from combustible materials left behind from a coal mining history. Therefore, total organic matter is not the only consideration; for example, humic acids can immobilize Cr, Pb, Cd, and Cu by binding them (Song and Greenway 2004; Walker et al. 2004; O'Dell et al. 2007;

Alvarenga et al. 2009), whereas other organic forms may mobilize them. Therefore, alteration of the distribution and availability of metal(loid)s in soil can result from addition of organic amendments directly or indirectly. This can depend on the type of soil, metal(loid), or amendment properties, for example, pH, cation

TABLE 6: Mean element concentrations in earthworm tissue (milligrams per kilogram or micrograms per kilogram, as indicated, \pm standard error) following the initial trial

Element	Site	Al-WTR	Fe-WTR	Lime
Al (mg/kg)	Seep 1	290.20 \pm 181.381	33.55 \pm 8.5	121.18 \pm 27.44
	Seep 2	603.78 \pm 178.56	380.14 \pm 350.26	207.64 \pm 34.56
	Seep 3	N.R.	431.02 \pm 60.62*	227.96 \pm 75.37
As (μ g/kg)	Seep 1	B.D.	3.69 \pm 3.69	4.16 \pm 2.2
	Seep 2	11.14 \pm 3.84	B.D.	B.D.
	Seep 3	N.R.	B.D.	4.24 \pm 3.03
Ca (mg/kg)	Seep 1	1693.03 \pm 144.99	1890.22 \pm 258.86	6166.19 \pm 698.69
	Seep 2	1989.83 \pm 231.28	10148.77 \pm 9234.85	8106.78 \pm 1048.33
	Seep 3	N.R.	2796.43 \pm 386.15	6776.81 \pm 2625.36
Co (μ g/kg)	Seep 1	6.19 \pm 1.49	18.63 \pm 7.85	1.92
	Seep 2	1.24	2.01 \pm 0.42	2.86 \pm 1.75
	Seep 3	N.R.	4.16 \pm 1.41	1.11 \pm 0.49
Cr (μ g/kg)	Seep 1	4.79 \pm 2.88	27.19 \pm 8.36	B.D.
	Seep 2	B.D.	B.D.	4.29
	Seep 3	N.R.	2.77 \pm 1.18	B.D.
Cu (μ g/kg)	Seep 1	19.9 \pm 1.87	40.22 \pm 12.45	15.23 \pm 2.96
	Seep 2	12.15 \pm 2.29	6.12 \pm 2.62	10.27 \pm 0.27
	Seep 3	N.R.	9.59 \pm 1.64	4.53 \pm 1.14
Fe (mg/kg)	Seep 1	6585.79 \pm 4833.78	1252.11 \pm 274.93	10250.5 \pm 2544.85
	Seep 2	3722.8 \pm 722.61	7767.2 \pm N.R.	6317.71 \pm 714.82
	Seep 3	N.R.	8657.76 \pm 779*	3387.83 \pm 461.58
K (mg/kg)	Seep 1	7045.24 \pm 111.77	7283.72 \pm 651.26	6417.23 \pm 389.89
	Seep 2	6613.93 \pm 583.44	9074.32 \pm 4198.43	6364.92 \pm 449.61
	Seep 3	N.R.	6087.23 \pm 614.85	4995.38 \pm 1066.11
Mg (mg/kg)	Seep 1	462.09 \pm 55.9	319.04 \pm 83.49	402.33 \pm 7.96
	Seep 2	427.44 \pm 18.73	797.64 \pm 651.12	613.38 \pm 48.3
	Seep 3	N.R.	663.44 \pm 56.87	499 \pm 125.48
Mn (mg/kg)	Seep 1	28.78 \pm 10.11	31.59 \pm 7.48	5.55 \pm 1.68
	Seep 2	17.56 \pm 3.5	19.16 \pm 9.05	21.13 \pm 1.98
	Seep 3	N.R.	40.69 \pm 4.46*	13.94 \pm 0.46
Ni (μ g/kg)	Seep 1	1.91 \pm 0.88	8.3 \pm 4.18	1.55 \pm 0.92
	Seep 2	0.93 \pm 0.93	B.D.	2.99 \pm 0.97
	Seep 3	N.R.	3.22 \pm 1.37	0.64 \pm 0.34
Pb (μ g/kg)	Seep 1	4.26 \pm 1.6	2.86 \pm 1.95	4.16 \pm 0.5
	Seep 2	1.21 \pm 0.33	9.4 \pm 3.45	10.64 \pm 2.88
	Seep 3	N.R.	4.71 \pm 1.33	3.68 \pm 1.88
Zn (μ g/kg)	Seep 1	75.63 \pm 6.54	105.7 \pm 29.35	55.77 \pm 5.33
	Seep 2	56.79 \pm 9.2	133.67 \pm 9.3	66.95 \pm 6.22
	Seep 3	N.R.	72.51 \pm 10.84	49.04 \pm 7.46

*Significantly different ($p < 0.05$) from Al-WTR.

B.D. = below detection; N.R. = not reported because no earthworms survived, hence element analysis was not possible; WTR = water treatment residual.

TABLE 7: Mean element concentrations ($\mu\text{g/L}$ or mg/L , \pm standard error) in simulated soil solutions

Element	Site	Nonamended	Al-WTR	Fe-WTR	Lime
Al (mg/L)	Seep 1	154.39 \pm 44.36	54.07 \pm 8.32	6.96 \pm 2.93*	1.05 \pm 0.21*
	Seep 2	3.38 \pm 1.6	0.3 \pm 0.20**	0.07 \pm 0.00**	0.06 \pm 0.00**
	Seep 3	34.85 \pm 11.27	0.22 \pm 0.05**	0.07 \pm 0.00**	N.R.
As ($\mu\text{g/L}$)	Seep 1	2.86 \pm 0.21	3.54 \pm 0.38*	4.09 \pm 0.2*	12.2 \pm 0.44*
	Seep 2	19.68 \pm 5.82	12.61 \pm 1.95	7.5 \pm 2.61	6.52 \pm 0.87
	Seep 3	12.24 \pm 1.56	23.63 \pm 6.94	9.98 \pm 2.1	N.R.
Ca (mg/L)	Seep 1	201.21 \pm 12.5	240.54 \pm 3.86	236.57 \pm 1.16	231.88 \pm 0.25
	Seep 2	247.4 \pm 0.44	253.53 \pm 1.78*	252.09 \pm 1.78*	268.72 \pm 0.94*
	Seep 3	251.37 \pm 1.27	249.96 \pm 8.46	269.41 \pm 0.25*	N.R.
Cd ($\mu\text{g/L}$)	Seep 1	5.89 \pm 2.61	2.78 \pm 0.28	7.35 \pm 3.87	0.02 \pm 0.15
	Seep 2	1.57 \pm 0.98	0.00 \pm 0.00	0.00 \pm 0.00	0 \pm 0
	Seep 3	11.21 \pm 3.98	0.22 \pm 0.16*	0.00 \pm 0.00*	N.R.
Co ($\mu\text{g/L}$)	Seep 1	99.76 \pm 7.68	48.45 \pm 4.03*	331.76 \pm 58.07*	0.36 \pm 0.17*
	Seep 2	550.27 \pm 66.48	10.07 \pm 2.04*	40.37 \pm 9.32*	0.02 \pm 0.01*
	Seep 3	538.89 \pm 63.46	4.39 \pm 0.9*	47.7 \pm 2.36*	N.R.
Cr ($\mu\text{g/L}$)	Seep 1	3.54 \pm 0.67	4.99 \pm 0.91	7.37 \pm 1.82	0.29 \pm 0.16
	Seep 2	1.24 \pm 0.07	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00
	Seep 3	17.19 \pm 2.89	2.18 \pm 0.41	0.58 \pm 0.02	N.R.
Cu ($\mu\text{g/L}$)	Seep 1	48.52 \pm 16.21	28.31 \pm 2.04	39.23 \pm 11.73	81.42 \pm 21.19
	Seep 2	8.48 \pm 2.49	3.47 \pm 0.92	2.85 \pm 0.61	1.44 \pm 0.37*
	Seep 3	24.58 \pm 11.12	3.01 \pm 0.79	1.94 \pm 0.5*	N.R.
Fe (mg/L)	Seep 1	913.32 \pm 170.23	96.87 \pm 16.85*	670.15 \pm 289.76	205.83 \pm 76.54**
	Seep 2	327.42 \pm 53.91	61.15 \pm 10.27*	65.79 \pm 2.67*	0.00 \pm 0.00*
	Seep 3	395.29 \pm 77.6	42.92 \pm 15.15*	95.95 \pm 12.85*	N.R.
K (mg/L)	Seep 1	8.32 \pm 1.68	555.48 \pm 45.13*	156.91 \pm 43.92*	5546.4 \pm 131.3*
	Seep 2	254.96 \pm 18.65	446.62 \pm 41.31*	408.81 \pm 21.69*	327.97 \pm 14.73*
	Seep 3	51.57 \pm 2.42	151.84 \pm 21.42*	142.12 \pm 9.94*	N.R.
Mg (mg/L)	Seep 1	93.96 \pm 5.07	135.79 \pm 2.51*	159.31 \pm 6.54*	98.81 \pm 8.98
	Seep 2	261.17 \pm 1.73	198.12 \pm 12.67*	209.06 \pm 13.46*	124.05 \pm 5.09*
	Seep 3	231.68 \pm 0.92	140.76 \pm 14.93*	158.72 \pm 1.56*	N.R.
Mn (mg/L)	Seep 1	9.99 \pm 0.76	60.7 \pm 2.85	114.25 \pm 16.69	0.23 \pm 0.04
	Seep 2	68.9 \pm 2.61	17.97 \pm 2.98*	27.66 \pm 4.21*	0.17 \pm 0.01*
	Seep 3	45.49 \pm 1.75	18.18 \pm 7*	32.43 \pm 0.62*	N.R.
Ni ($\mu\text{g/L}$)	Seep 1	962.35 \pm 73.95	124.46 \pm 13.33*	501.59 \pm 176.86*	6.06 \pm 1.65*
	Seep 2	2425.22 \pm 248.02	22.03 \pm 2.79*	53.76 \pm 10*	11.06 \pm 0.29*
	Seep 3	2289.93 \pm 261.57	36.55 \pm 6.7*	76.06 \pm 6.44*	N.R.
Pb ($\mu\text{g/L}$)	Seep 1	0.54 \pm 0.2	0.83 \pm 0.57	0.79 \pm 0.35	161.05 \pm 89.51
	Seep 2	4.86 \pm 1.01	2.67 \pm 1.59	0.47 \pm 0.14*	0.8 \pm 0.32*
	Seep 3	5.69 \pm 1.03	1.09 \pm 0.34*	0.31 \pm 0.13*	N.R.
Zn ($\mu\text{g/L}$)	Seep 1	1182.15 \pm 133.4	415.46 \pm 43.32*	1128.03 \pm 342.36	26.76 \pm 1.57*
	Seep 2	1453.84 \pm 341.3	25.2 \pm 2.19*	50.12 \pm 12.78*	6.19 \pm 0.9*
	Seep 3	2420.86 \pm 471.37	27.39 \pm 2.48*	46.97 \pm 3.62*	N.R.

* $p < 0.05$ (indicating significant difference from nonamended control).

** $p < 0.06$.

N.R. = not reported because of sample loss; WTR = water treatment residual.

exchange capacity (CEC), electrical conductivity, and moisture content (Shuman 1999; Walker et al. 2004; Bernal et al. 2007).

Addition of WTRs raised soil pH by 0.5 to >2 units, indicating that the materials have substantial but variable liming capacities, perhaps arising from varying carbonate concentration, hydroxide content, surface reactivity, and CEC. Differences in buffering capacity/liming effect of different WTRs have been noted elsewhere (Heil and Barbarick 1989; Howells et al. 2018), and the liming potential of WTRs has also been effectively utilized as a neutralizing agent for acid-generating mine waste (Van Rensburg and Morgenthal 2003).

Plant yield and element concentrations

The WTRs and the lime raised soil pH and consequently would have increased the phytoavailability of certain

essential macronutrients (Üçer et al. 2006) as well as decreased the bioavailable amounts of potentially toxic elements such as Al. Together, such effects account for all amendments having raised plant yields, with a fair degree of consistency. Interestingly, the yields in the nontreated control samples were higher in the second trial (after wet–dry cycle) than in the first, raising the possibility that the wet–dry step may have leached out some contaminant or acidic components and made the seep soils more acceptable for plant growth. Such a process has itself been used in some commercial remediation efforts, where it is referred to as “soil washing.” This is more widely done for soils contaminated with industrial solvents, petroleum products, and other organic chemicals rather than for soils contaminated with metals; and it involves using water and various additives (depending on the main contaminants present) to scrub,

wash, and sieve excavated soil before returning it, often after removal of the fine fraction where much of the contaminants is retained. Of course, this remediation strategy requires soil excavation and treatment and so is very expensive, and the removal of the fine fraction can also change the texture of the soil, which may limit some future uses. It also leaves the removed, contaminated fine fraction as a waste material, which then requires secure disposal. These aspects often limit its appeal as a remediation method. Nevertheless, a good review of cases in which metal-contaminated soils were treated with soil washing in this way has been published (Dermont et al. 2008).

A comparison of the plant growth increases observed in the present study with those reported in the literature for a mining soil remediation trial using sewage sludge, municipal solid waste compost, and garden waste compost on a very comparable, highly acidic, pH 3.7 to 4.1, sandy loam soil (Alvarenga et al. 2009) indicates that the WTRs used in the present study achieved better plant yield increases than those from sewage sludge and garden waste compost at all sites except seep 2, while almost but not quite achieving as high an increase as that achieved by municipal solid waste compost with the exception of Fe-WTR at seep 1. This indicates that WTRs are essentially as good as, and in some cases even more effective than, these other readily available recovered wastes/resources in terms of restoring soils to a condition where plant growth is possible and enhanced.

It is useful to compare the measured tissue element concentrations with those generally considered indicative of deficient and toxic levels for the tested species, perennial ryegrass (*Lolium perenne*; Reuter and Robinson 1997). The critical value of P for ryegrass is 0.34% w/w, and all treatments and nonamended controls had P concentrations above this; hence, P deficiency would not likely have been a problem in any of the plants. However WTR treatment did not universally increase plant P and in some cases decreased it marginally, which is in agreement with what has been reported on occasion elsewhere (and what has sometimes been the main aim in some field application situations) following application of WTRs, that is, immobilization of excess P in overfertilized soils (Makris et al. 2004). Such immobilization has caused excessive restriction of P availability in some studies (e.g., Elliott and Dempsey 1991; Lucas et al. 1994; Lombi et al. 2010) but has not been observed universally. This inconsistency of effect on soil P is likely intertwined with the effects WTRs have on soil pH because altering soil pH itself has an impact on P availability, with maximum plant available P usually occurring within the pH range of approximately 6.3 to 7.5 (Brady and Weil 2016). Added to this, the chemistry of mining-affected soil might be different from that which has been studied previously (i.e., mostly agricultural soils); and therefore, the increase in the P assimilation noticed at seeps 1 and 3 might be related to other aspects associated with mining soils. There is a need for further examination of the P assimilation in plants grown in mining-affected soil.

All amendments increased plant concentrations of K, a key macronutrient; but even so the plants in seep 1 still had

K levels within the deficiency range of <1.7% w/w (Reuter and Robinson 1997), indicating that further supplements may be required to reach optimum plant growth. For seep 3, all amendments resulted in plants moving from within the K-deficient range into the K-sufficient range, whereas all seep 2 plants were also in the sufficient range (including controls). The Cu concentration in plant tissues generally increased by a modest amount following all treatments, which suggests that the pH increases resulting from the amendments were primarily responsible because, although Cu^{2+} ions are more mobile at lower pH (Cavallaro and McBride 1980; Sauv   et al. 1997), it is known that organic matter-induced mobilization of Cu is maximized at more neutral pH. However, a number of the samples showed greater increases in plant Cu following WTR treatments than lime treatments, which suggests that the WTRs might act as a source of this micronutrient. Supporting this idea, previous research (Shahin et al. 2019) has shown that Cu associated with low-molecular weight organic components in WTRs can be released during decay of biota residues, so that process may increase the availability of Cu to plants. Greater than 21 mg/kg of Cu is reported as being the toxic threshold value for ryegrass (Reuter and Robinson 1997), so even with the increases observed in the treatments, Cu toxicity is not likely to arise when WTRs are used to treat soils in this way.

The results indicate the possibility that WTRs can be a source of plant available Mn but that this effect is inconsistent. This inconsistency of Mn supply is likely intertwined with interactions between Mn and other trace metals, for example, antagonism interaction between Mn and iron (Alvarez-Tinaut et al. 1980) and antagonism between Mn and Ca, K, Mg, Na, N, and P (Kabata-Pendias 2010). Added to this, other factors such as redox processes (Marschner 1988) and interactions between roots and microorganisms (Marschner and Rengel 2005) might also impact Mn phytoavailability in WTR-treated soils. Greater than 1110 mg/kg of Mn is noted as a toxic value in grasses, which is a value far above the concentrations observed here, so Mn toxicity is not expected in these soils following WTR application.

The reduced amounts of plant-assimilated Zn observed in the second (i.e., post-wetting-drying) trial (particularly in the control soils) raises the possibility that the wet-dry step may have leached out plant available Zn from the control soils. A similar trend of decreased Zn assimilations was also observed in lime-amended treatments in the second trial. Meanwhile, although treatments generally reduced plant Zn in the first trial, in the second trial Zn assimilations were increased relative to controls in the majority of WTR-amended soils, suggesting that WTRs contain Zn that would still be plant available after a wet-dry cycle. Importantly, the plants were all above the 10 mg/kg Zn deficiency threshold.

The small but significant decreases in Pb assimilation by plants observed for WTR treatments in almost all cases, in contrast with the no effect and even increases observed in some lime treatments, confirm the Pb sorbing capacity of WTRs and the associated potential environmental benefits from their

field applications that have been discussed in the literature (Turner et al. 2019). In both trials, the treatments decreased As assimilation relative to control in seep 3, in agreement with a previously published study (Sarkar et al. 2007) that showed the effectiveness of WTRs at immobilizing As in As-contaminated soils. In the present study, the differences were not significant in seep 1 and 2 soils following treatment in the first trial; however, after the wet–dry process, the decreases were significant in all seeps for all amendments, suggesting that the wet–dry process and the regrinding might have exposed fresh surfaces on the WTRs or that the lime that could better sorb As. It should be borne in mind, however, that the plant As concentrations were very low in the present study.

Although Ni immobilization by WTRs has been reported (Chiang et al. 2012), it is likely that the pH increases brought about by the treatments were the main reason for the across-the-board decrease in plant Ni assimilation observed in the present study in both plant trials.

Earthworm survival and element uptake

Survival of earthworms in nonamended control soils was zero in all seeps across both trials (pre- and post-wetting–drying cycle), with the exception of 13% survival in seep 2 control soil in the second test. This shows that the seep soils were very hostile to earthworms, with the low pH (~3.3–3.8) and likely associated Al toxicity being important factors. Other studies have shown that *E. fetida* can survive at pH 4 and are content at pH 5 if other soil factors are favorable (Spurgeon and Hopkin 1996; Dominguez and Edwards 2011), but in the present study the soil was too acidic without amendment. It may also be that the soil had toxic components that needed neutralization for earthworms to survive. The amendments, in general, greatly increased survival, and this is likely to be primarily linked to the pH increase they brought about. A similar finding was reported previously for acidic forest soils (Homan et al. 2016) in which soils at pH 3.1 had zero survival of the species *Lumbricus terrestris* in laboratory tests, but when the pH was raised with lime, an increase in survival was achieved even with a modest increase to pH 3.7. The same study also reported field observations that included zero earthworms in the soil at pH 3.6 but an abundance of them in areas that had been limed so that the soil pH had reached 4.4. One investigation that examined remediation of Zn–Pb smelter–contaminated soil found that only when biosolid amendments were mixed with lime did earthworm survival occur (100% mortality in nonamended and biosolids only–amended soil but <10% mortality in biosolids+lime–amended soil; Conder et al. 2001). This illustrates the importance of pH and liming effect (either from lime or with amendments that have liming capacity) when remediating acidic soils. However, in the present study, despite good improvements in survival in treated seep 1 soil in the first trial, all seep 1 soils in the post-wet–dry cycle test had zero survival. This raises the possibility that, with the chance of experimental artifacts or errors aside, the wet–dry cycle (and possibly the regrinding that followed) triggered the release of a toxic component in this seep

soil and/or otherwise altered the conditions, rendering them too hostile again for the earthworms. It is unlikely that the amendments caused the toxicity because it was not observed in the other seep soils and it has been shown that *E. fetida* are not affected by WTR application even at up to 20% w/w addition (Howells et al. 2018).

The treatments enabled earthworm survival in most cases, and the water contents of the surviving earthworms were within the $82 \pm 7.7\%$ reported as typical for the *E. fetida* species (Hartenstein et al. 1980). This suggests that the treatments not only facilitated survival but also allowed the earthworms to be in a healthy condition in terms of moisture retention.

Element contents of earthworms were highly variable between treatments and trials and, in some instances, among replicates. This makes interpretation challenging, as does the 100% mortality in the nontreated seep soils, which prevents evaluation of whether the treatments reduced the assimilation of potentially toxic elements (i.e., with no values for nontreated seep soils, there is no baseline to compare with). However, the concentrations observed can be evaluated using the wider literature. The Al concentrations determined in the surviving earthworms in the first trial in the present study were, in all cases except one, at or below 437 mg/kg, which was the concentration reported previously (Hartenstein et al. 1980) for *E. fetida* maintained in uncontaminated soils. The second trial, following the wet–dry cycle, generated higher earthworm Al concentrations in the Al-WTR and the Fe-WTR treatments (~500–1330 mg/kg; Supplemental Data, Table S4), suggesting that the wet–dry and regrinding process may have brought more Al into the bioavailable pool. However, although these values are above those reported as typical (Hartenstein et al. 1980), even these values are below the approximately 1600 mg/kg reported elsewhere for *E. fetida* maintained in a clean garden soil (a latosol) with a comparable pH of 4.3 (Zhang et al. 2013). This would indicate that the Al concentrations observed in the present study in the earthworms from treated soils were not too far removed from what might be expected in a normal soil with low pH.

The greatest As concentration observed was ~11 µg/kg, having occurred in the first trial in earthworms from the seep 2 soil amended with Al-WTRs; however, even this value is much lower than the 35 to 40 mg/kg reported as the level at which cocoon production was decreased by 10% in *E. fetida* (Bustos et al. 2015). The As concentrations in the present study are also all lower than those reported for *E. fetida* earthworms subjected to experiments using contaminated soils from an old gas works (i.e., ~20 mg/kg; Gomez-Eyles et al. 2011). It would therefore seem that As is not at high toxicity levels in the surviving earthworms from the treated soils of the present study.

For Cu, there was variation from near zero to 40 µg/kg in the first experiment but little evident pattern. In the second (post-wetting–drying) experiment the earthworm tissues had generally lower Cu levels, but again there was no clear pattern. The concentrations were within or below the typical Cu concentrations reported for compost-bred *E. fetida* (i.e., 22–812 mg/kg; Gunya et al. 2016), and therefore, no toxicity from Cu is likely to

have occurred. The Fe concentrations in earthworm tissues varied very widely, across treatments and across seep soils. Concentrations were equally high in lime and Fe-WTR treatments in the first experiment (up to 10 000 and 8600 mg/kg, respectively) but differed in the second experiment, where the highest concentrations were noted in the Fe-WTR treatment (19 534 mg/kg for seep 2 soil). The concentrations in earthworms from all treatments were high compared to typical Fe values reported elsewhere for clean soils or composts (i.e., <1500 mg/kg; Hartenstein et al. 1980; Gunya et al. 2016), but it is difficult to determine whether the measured body burdens would have any negative effects; therefore, this could be a direction for future research. The Mg, Mn, Ni, and Pb concentrations were all within typical ranges observed in earthworms from clean environments (Langdon et al. 2005; Gunya et al. 2016; Howells et al. 2018), with, for example, typical Pb concentrations reported at up to 16.4 mg/kg for a related *Eisenia* species (Langdon et al. 2005). This indicates that the treatments did not facilitate assimilation of these metals to unusual or dangerous levels. The concentrations of Zn, where measured, were also consistent with values reported for control soils (e.g., 80 mg/kg; Howells et al. 2018); and thus, excessive Zn uptake was not a problem experienced by the earthworms.

The earthworm results were useful and allow evaluation of general earthworm and wider ecosystem health if these amendments were used for remediation of mining-impacted soils, but the wide variability across the results does limit how definitive conclusions can be. This possibly reflects the variability of element uptake generally for earthworms and may indicate effects of other factors on the element uptake in earthworms such as their digestion of soil and the effectiveness of depuration.

Simulated soil solutions

Raising the soil pH and providing surfaces for sorption via the treatments would be expected to decrease the concentrations of cationic elements in soil solution. All treatments greatly reduced the soil solution Al concentration, often by orders of magnitude; and this was indeed likely due to the increases in pH the amendments brought about. These decreases also matched up with the decreases in plant tissue Al observed in the treated seep soils, indicating that the amendments did reduce both mobility and bioavailability, as was the aim. The soil solution Al concentrations observed in the untreated seeps was highest (154 mg/L) in seep 1, with the values being similar to those observed in the subsoil of acid sulfate soils (pH 3.8–4.2) in Finland (e.g., 113–159 mg/L; Virtanen et al. 2014). The successful reduction of the soil solution Al concentrations observed following treatment, particularly with Fe-WTRs, might suggest that acid sulfate soil remediation measures could also benefit from incorporating addition of Fe-WTRs.

Reduced root length of *Lolium perenne* (ryegrass) has been observed at 25 mg/L Al at pH 3.5 (Hackett 1965), whereas slight injuries on roots of coffee plants have been observed at Al concentrations of 1 mg/L and medium or severe injuries at

4 mg/L (Pavan and Bingham 1982). Comparing the Al concentrations in the soil solutions of the untreated seep soils in the present study (i.e., ~3.4–154 mg/L) with those determined by Pavan and Bingham would therefore lead to a conclusion that injuries to plant roots would likely occur to some degree in all the seeps (confirming the plant yield results), whereas seep 2 and seep 3 soils, once treated, would have Al concentrations in their soil solutions that were below the levels causing injury. Whereas seep 1 soil did have a drastic reduction in soil solution Al concentrations following all types of treatment imposed, the levels appear to still be near or above those that could start to cause plant root injury. This suggests that the treatments were only partially successful in seep 1 soil in relation to completely lowering the Al in the soil solution to ecologically unimportant levels.

One estimate for an average natural abundance of As in soil solution is 0.75 µg/L (Wolt 1994), whereas effect concentrations reported to cause a 10% inhibition (EC10) in growth of cucumber (*Cucumis sativus*) ranged from 2.2 to 697 µg/L across a selection of soils from Australia (Lamb et al. 2016). An example of increased As in porewater of As-contaminated soil is 430 µg/L from land impacted by mining activities at Mina Mónica (Madrid, Spain; Beesley et al. 2013). Applications of Fe-WTRs (2.5% w/w) were found to decrease As in the porewaters of an As-contaminated soil in Denmark (Nielsen et al. 2011); however, in the present study, concentrations were only reduced by the treatments in seep 2 and were actually increased in seep 1 (from 2.9 to 12.2 µg/L). A similar increase in porewater As was reported for soils amended with biochar, with the effect attributed to mobilization by increases in dissolved organic carbon and pH (Beesley et al. 2010). Because As occurs as an oxyanion in the porewater environment (i.e., typically as arsenate or arsenite), its solubility can increase when the pH is brought up from acidic conditions to more neutral conditions, as was the case when the treatments were added. Desorption (mobilization) of As can also occur in the presence of nutrient anions such as PO_4^{2-} , CO_3^{2-} , SO_4^{2-} , and Cl^- (Violante et al. 2008) because of competition for binding places and displacement, so a similar case might be in effect here as the treatments can contribute nutrients to the soil. Nevertheless, the porewater As concentrations observed in the treated soils were very much at the lower end of the EC10 thresholds noted by Lamb et al. (2016).

The increases in Ca in all treatments in all seeps suggest that the amendments provide Ca to the soil. The increases were within typical Ca levels in soil solution in acid soils, which have been reported to range from 15.2 to 372 mg/L (Kamprath 1978). The increase in soil solution Mg in both WTR treatments in seep 1 suggests that the WTR amendments can provide or release soluble Mg to the soil. Contrastingly, decreases in soil solution Mg were noted in all treatments in seeps 2 and 3, showing that the effects on Mg are variable. Plant available Mg concentrations in the soil solutions have been reported to vary between 3 and 204 mg/L even in non-contaminated soils (Barber 1995), so the Mg contents observed in the present study do not appear to present an environmental problem.

Large increases in K in the soil solutions following all treatments in all seeps suggest that the amendments provide readily mobile K to the soil. The increase in soil solution K had a corresponding increase in the plants in all seeps in both trials. Considering that K is a very important element that is often added as a fertilizer component, this is likely to be viewed as another positive associated with these treatments.

Generally in soils, Co is only slowly mobilized and low concentrations are expected in soil solution, with the concentration ranges typically between 0.3 and 87 $\mu\text{g/L}$ (Kabata-Pendias 2010). In the present study, soil solution Co in non-treated seeps 2 and 3 was much elevated above this typical range, with both having $>500 \mu\text{g/L}$. All treatments reduced the solution Co concentrations in seep 2 and seep 3 soils to $<50 \mu\text{g/L}$. Seep 1 soil had approximately 100 $\mu\text{g/L}$ in the untreated state, and this decreased to $<50 \mu\text{g/L}$ following Al-WTR and lime treatments but increased to 331 $\mu\text{g/L}$ following Fe-WTR treatment. The results of the 2 plant growth trials discussed showed a related pattern. The reason for the difference in Co mobility in this seep soil + Fe-WTR combination is unclear, and it is difficult to provide a speculative explanation for other than perhaps something linked to a possibly different organic matter component present in the Fe-WTRs that is released when mixed with the seep 1 soil because organic matter differences have been reported to have the potential to mobilize soil Co (Lange et al. 2016). This warrants further investigation on the mechanisms involved because it would be anticipated that Co in solution would be decreased following treatment and that the amendments would immobilize Co in the soil solution because WTRs have been shown to have the ability to adsorb Co (Chiang et al. 2012). Nevertheless, in all cases in the present study, the soil solution Co concentration was well below the no-observed-effect concentration (i.e., the highest concentration imposed in a toxicity test that shows no negative effect) reported previously for the springtail species *Folsomia candida*, which was reported to be 62 200 and 9440 $\mu\text{g/L}$, respectively, in the 2 soils in which it was determined (Lock et al. 2004).

The average natural abundance of Cr in soil solution has been estimated as 0.52 $\mu\text{g/L}$ (Wolt 1994), and all of the untreated seep soils had concentrations above this typical amount. All treatments produced substantial decreases in seeps 2 and 3, in agreement with high Cr sorption capacity previously noted for WTRs (Nielsen et al. 2011; Mohammed et al. 2016) and the known decrease in solubility of Cr(III) as solution pH is raised (Bartlett and Kimble 1976). It is known that Cr is nonessential for plants (Hayat et al. 2012), so the decrease in the soil solution Cr concentration observed when seeps 2 and 3 were treated with the amendments is a good result in terms of remediation.

In very acid soils, the Fe concentration in soil solution can exceed 2 mg/L (Kabata-Pendias 2010), and it is the soil pH that typically controls Fe content in soil solutions (Willard 1979). Therefore, the observed decrease in Fe in the solutions of all amended seep soils is most likely related to enhancing the soil pH through addition of the amendments. The decrease in Fe in the soil solutions had a corresponding decrease in element Fe

content in the plants of some treated seeps, which is consistent with the well-understood process of Fe being obtained by plants via the soil solution. However, because no evidence of induced chlorosis was visible (i.e., no yellowing of tissues), the decreases in soil solution Fe were not linked to any negative effects.

The complicated chemistry of Mn, which has common valence states of +2, +3, +4, +6, and +7, means that mobility of the element is heavily influenced by Eh–pH conditions as well as sorption processes which therefore affect the Mn content of the soil solution (Willard 1979). Therefore, the observed decrease in Mn in all amended soil solutions in seeps 2 and 3 is most likely related to enhancing the soil pH as a result of the addition of the amendments despite the possibility that the WTRs might be a source of available Mn (i.e., they have considerable Mn content). The decrease in Mn in some of the soil solutions did not have any consistent relationship with either increases or decreases in Mn in the plants, reflecting the many complex processes that control Mn availability that include reduction of MnO_2 forms and complexing by root exudates (Hodgson et al. 1965) coupled with Fe oxide interactions and microbiological soil activity that also have impacts on the redox of Mn compounds (Zajic 1969). Because of this, it is difficult to draw any firm conclusion on how the amendments will affect Mn in soil solutions.

The concentrations of Ni in solutions of untreated seep soils were within the range of those reported for Ni-contaminated soils from an Ni ore smelting region in Canada, that is, mostly 120 to 28 700 $\mu\text{g/L}$ (Nolan et al. 2009), and those for a set of European soils that had been deliberately dosed to a total Ni concentration expected to cause 10% reduction in plant growth (Ma et al. 2013). This would suggest that the levels of Ni in the solutions of the untreated seep soils would have probable negative effects on soil biota if not addressed. All treatments reduced the soil solution Ni, with lime achieving the greatest level of decrease, which would indicate that the soil pH enhancement was the primary reason for the changes. Of the 2 WTR types, Al-WTRs achieved a greater reduction in Ni concentrations. Previous work had shown the capacity of Fe-WTRs to sorb Ni from solution, with an addition rate in sediment of 250 mg/g of Fe-WTR achieving a sediment pore-water Ni decrease of $>80\%$ (Chiang et al. 2012). The decrease in soil solution Ni did have a corresponding decrease in plant Ni for all amendments in all seeps in both trials, indicating that the amendments were able to control the excess Ni in solution and render it less bioavailable. This is an important and a positive outcome in these seep soils which, in the untreated state, had soil solution Ni in the potentially toxic range.

Lead is not known to be an essential or beneficial element for any living organisms, and therefore, Pb deficiency is not a concern. The average natural abundance of Pb in soil solution has been estimated at 1.04 $\mu\text{g/L}$ (Wolt 1994), and a number of parameters such as soil pH, CEC, clay content, CaCO_3 , organic matter content, and Pb concentration govern Pb sorption–desorption processes in agricultural soils (Hooda and Alloway 1998). The untreated seep soils had soil solution Pb concentrations (all $<6 \mu\text{g/L}$) that were below or marginally above the

estimated typical background levels. One study (Zhang et al. 2019) showed that even in a very sensitive soil from Germany the concentration causing just a 10% reduction in the reproduction (i.e., the reproduction EC10) of the *Enchytraeus crypticus* worm was 6 µg/L, whereas the EC10 values in the other soils tested ranged from 21 to 90 µg/L. This would suggest that the Pb soil solution concentrations in the seep soils would not pose any substantial risk to invertebrates. All amended seep 2 and 3 soils had lower Pb concentrations in soil solution than that of non-amended soil, which suggests that the amendments immobilized the Pb either directly by sorption or indirectly by their effect on pH. An exception to the decreased solution Pb was observed in seep 1 soil amended with lime, in which a large increase was observed. However, there was great variability among the replicates for that soil–treatment combination, so the result for it is questionable. It is possible that a contaminant was introduced during the analysis or that a particle of Pb had been incorporated into the portion of lime added.

The average natural abundance of Zn in soil solution has been estimated at 7.3 µg/L (Wolt 1994); but it varies greatly, and generally, soil solution Zn concentrations rise with pH decrease. For example, a heathland soil from Belgium with a pH of 3.5 had a Zn soil solution concentration of 330 µg/L (Degryse et al. 2003), whereas a grassland soil from Rhydtalog in the United Kingdom with pH 4.8 had 1200 µg/L (Smolders et al. 2004). Adsorption of Zn onto pH-dependent binding sites of oxyhydroxide minerals and organic matter as well as ion-exchange reactions on clay minerals at high Zn concentrations are the main processes governing the Zn content in soil solution (Alloway 2012). The effects of Zn in solution on soil biota can vary widely, with the EC10 values determined for microbial processes having been found to span 100 to 296 000 µg/L in a broad set of European soils (data from Smolders et al. 2004). The Zn concentrations in the solutions of the untreated seep soils (1182–2420 µg/L) were within this very wide range. There was a clear decrease in Zn in the soil solution of amended soils with the exception of seep 1 amended with Fe-WTRs, for which there was no significant change. Too much of a decrease in the soil solution Zn concentration would be undesirable because Zn is an important plant nutrient; however, as discussed, in the plant trial the amounts of Zn assimilated by plants were in the healthy range (i.e., no deficiency).

CONCLUSIONS

The investigation has shown that application of WTRs to acidic soils impacted by former mining activities led to significant improvements in pH, plant yield, and earthworm survival that were comparable to, or in some cases better than, those achieved by liming. This indicates that the WTRs could be used successfully as soil amendments to immobilize contaminants and raise pH and could therefore be used as a cheap alternative to lime in soil remediation. The liming aspect may be of particular benefit to acidic soils but only if commonly employed regulations, which typically limit WTR application to soils with pH >6, were adapted. In general, the addition of WTRs also resulted in soil solution element concentrations

being adjusted to and/or maintained at desirable or tolerable levels and therefore would enhance, or at least not negatively impact, plant growth and microbial function.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at <https://doi.org/10.1002/etc.4706>.

Acknowledgment—The authors gratefully acknowledge the Ministry of Higher Education and Scientific Research (Iraq) for funding support.

Data Availability Statement—Data, associated metadata, and calculation tools are available from the corresponding author (i.oliver@keele.ac.uk).

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