

K.A.H. Arab et al.

Remediating mining soils with water treatment residuals

## 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<sup>a, c</sup>, David F. Thompson<sup>b</sup> and Ian W. Oliver<sup>a\*</sup>

<sup>a</sup> School of Geography, Geology and the Environment, Keele University, Keele, UK, ST5 5BG

<sup>b</sup> School of Chemical and Physical Sciences, Keele University, Keele, UK, ST5 5BG2

<sup>c</sup> Department of Ecology, College of Science, University of Kufa, Najaf, Iraq.

*(Submitted 28 October 2019; Returned for Revision 17 February 2020; Accepted 3 March 2020)*

**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. Aluminium-based (Al-WTR) and iron-based (Fe-WTR) materials were applied at 10% w/w to degraded, bare (un-vegetated) 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 in 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

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/etc.4706.

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 biomass of plants and, in some treatments, survival of earthworms was also enhanced compared to non-amended 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.

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

This article includes online-only Supplemental Data.

\*Address correspondence to I.Oliver@keele.ac.uk

Published online XXXX 2020 in Wiley Online Library (www.wileyonlinelibrary.com).

DOI: 10.1002/etc.xxxx

---

## 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 UK (ca. 1913), a million people were directly employed across 1600 active mines producing ~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 pre-date 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 communities, habitat and ecosystems (e.g. Anawar, 2015, Kostarelos et al., 2015).

Remediation and restoration of mining impacted areas has become a major undertaking, 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 public general 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 this study we test 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 aluminium or iron based) to coagulate and flocculate impurities and remove them via settling and sedimentation. This process generates a sludge or residue material (water treatment residuals, WTRs) that comprise the removed impurities and the reaction/precipitation products of the added metal salts (Howe et al., 2012).

When aluminium or iron coagulant adds to the water, they react with natural or supplemented alkalinity of the water producing aluminium or iron hydroxides respectively. Typical constituents and properties of partially dried water treatment residuals (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 aluminium-based salts (generating what can be referred to as Al-WTR) and 181,000 tonnes from ferric-based salts (Fe-WTR) annually, while the USA generates more than 2 million tons of WTRs every day (Prakash and SenGupta, 2003). WTRs are considered as an inert waste under the European Union Council Directive 99/31/EC (1999), as cited in Keeley et al. (2014), and can be used as construction materials such as for ceramics and bricks (Goldbold et al., 2003) and for geotechnical works materials (Carvalho and Antas, 2005). Another use that has been proven successful is as the main substrate in constructed reedbeds for waste water 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 (Ociński et al., 2016, Makris et al., 2006, Hovsepyan and Bonzongo, 2009, 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 performed significantly better than 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 over-fertilised or otherwise over-enriched 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 materials recycling. The use of WTRs in the remediation of mining and metal contaminated soils has yet to be comprehensively investigated. Moreover, while 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 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 study, therefore, were to assess the remediation of mining contaminated soils using two types of WTRs from central England, UK, 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 (WTRs) from two 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  $7.34 \pm 0.06$ , Al content  $11.64 \pm 1.08\%$  w/w, organic matter (OM) content  $28.0 \pm 0.1\%$  w/w, Fe  $0.91 \pm 0.08\%$  w/w and those of Fe-WTRs were pH  $7.37 \pm 0.01$ , Fe  $17.69 \pm 0.19\%$  w/w, OM  $25.9 \pm 0.2\%$  w/w, and Al  $0.71 \pm 0.12\%$  w/w. The WTRs were dried at  $30^\circ\text{C}$  until stable mass and were 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,

vegetation grows (Figure 1), suggesting that the mining legacy at the site still impacts the soil either through remaining contamination hotspots 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 ~200 m 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 homogenised for use in the experiments.

Loss on ignition ( $\geq 4$ h at 450°C) was used to determine organic matter content (Nelson and Sommers, 1996), and pH was determined in 0.001M CaCl<sub>2</sub> 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 sup. information Table S1 for procedures, quality control measures and determined values).

## REMEDICATION of contaminated soils using water treatment residuals

*Plant growth trial.* Soil from each of the three seep collection points were 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 per 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 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 as it was thought to represent the upper limit of what might realistically be used in a remediation scenario but still avoid the worst of the reductions in available soil phosphorus reported at rates of WTR application above this level by (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 and allowing to drain and calculating water retained) to all samples and moisture was maintained every day by watering to mass using ultrapure water. 1.5 g of Perennial ryegrass (*Lolium perenne*) seeds that had been moistened were added to the top of the soil followed by adding vermiculite (1 g) in order to decrease loss from evaporation. To allow full access to natural light, the pots were placed in an un-heated incubator next to a large window. The two growth periods were 4 weeks (28 days) in each of November and January in the UK. The humidity inside the incubator was maintained by placing 100 ml of ultrapure water in a glass beaker inside the incubator. At 28 days after sowing, shoots were removed by cutting at the surface with scissors and were dried at 65-70 °C in an oven for 48 hours followed by recording mass of dry weights.

Once dry mass was recorded, samples were cut into small pieces with scissors and digested in nitric acid (Yilmaz, 2007). In this method about 0.4 g of dry plant material is placed in the digestion vessel then 10 mL of high purity concentrated (16 M) HNO<sub>3</sub> is added and the digestion is carried out using a CEM-MARS 6 microwave (CEM Corporation Mathews, NC, USA). 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<sub>3</sub>, and filtered through a 0.45 µm syringe filter into plastic vials. Nutrients and heavy metals concentrations were analysed using 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 OECD protocol 222. Treatments and controls (i.e. 0 %, 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 above for the plant test. Once prepared, control or treatment soils were placed in plastic containers (approximately 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), in order to verify that the earthworm assay design and conditions met the validity criteria of the OECD 222 protocol (viz. adult mortality ≤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, about 2 g, was added as a food source. Cling film was used to cover the containers to prevent escape and was pierced to facilitate air flow. Oatmeal was added every week. After 4 weeks survival was determined and living worms were allowed to depurate for a day then rinsed with ultrapure water, then patted dry, weighed and frozen. To determine element contents, the worms were dried at 70-100 °C for 48 hours in borosilicate glass beakers, weighed and then digested in 10 ml of HNO<sub>3</sub> (Primar Plus trace analysis) on a hotplate. The digest solutions then were transferred to a centrifuge tube and made up to 20 ml with 0.1% HNO<sub>3</sub>. The solutions were filtered through a 0.45 µm syringe filter into a plastic vial. Nutrients and heavy metals concentrations were analysed 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 ~ 3 days in order to generate simulated soil porewater (Ardestani and van Gestel, 2013, Ma et al., 2006). Soil solution was then extracted from each pot by centrifugation for 20 minutes at 3500 rpm. The resulting extracted solutions were filtered using 0.45 µm

syringe filters then acidified with 0.1 mL concentrated HNO<sub>3</sub> and kept cold at 4°C until the solutions were analysed using ICP-MS/OES.

Examinations of the effects of a wetting-drying cycle on plant yield, earthworm survival, and element uptake in amended and non-amended 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 one week followed by re-grinding and homogenisation and determination of remaining water content (a small subsample was also removed for determination of soil pH following treatments). Ultrapure water was added to re-establish 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 described above.

#### STATISTICAL analyses

Statistical assessment of differences amongst treatments and controls were conducted via T-tests and 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 (OM) effects

Despite the high organic matter content of the WTRs (typically 28% in the Al-WTR and 26% in the Fe-WTR) their addition at 10% w/w had 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 as 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), while the two WTRs were each found to have 45% - 50% lime effect equivalent value on average in terms of capacity to raise pH in the soils (Supp. Information 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 non-amended 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, while those from the trial following the wet-dry cycle are presented in Supplementary Information 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 micro-nutrients Ca, Cu, Mg and K in almost every case across the two 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.

## 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 non-amended 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 Supplementary Information 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 amongst replicates within treatments, with analysis of variance 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 is 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 (Supp. Inf. Table S4). Unsurprisingly, in both trials, the addition of lime increased the Ca concentrations in earthworms. The mean water contents (% 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-WTRs and Fe-WTRs amendment, but were 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  $\sim 11 \mu\text{g/L}$  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  $\sim 100$  to  $330 \mu\text{g/L}$ . Fe, Ni and Zn concentrations were all generally reduced by each of the treatments whereas K was increased in every case, with the degree of change rather variable amongst the treatments and amongst 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.  $\sim 161 \mu\text{g/L}$  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 (OM) content of the tested soils as determined by loss on ignition (LOI). However, the LOI method does not indicate the relative ecological importance of the OM determined and does not distinguish ecologically active OM from combustible materials left behind from a coal mining history. Therefore, total OM is not the only consideration, for example, humic acids can immobilise Cr, Pb, Cd, and Cu by binding them (Alvarenga et al., 2009, O'Dell et al., 2007, Song and Greenway, 2004, Walker et al., 2004) while other organic forms may mobilise 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 on amendment properties e.g pH, CEC, EC, and moisture content (Walker et al., 2004, Bernal et al., 2007, Shuman, 1999).

Addition of WTRs raised soil pH by 0.5 to >2 units, indicating the materials have substantial but variable liming capacities perhaps arising from varying carbonate concentration, hydroxide content, surface reactivity and cation exchange capacity. Differences in buffering capacity/ liming effect of different WTRs have also been noted elsewhere (Howells et al., 2018, Heil and Barbarick, 1989), and the liming potential of WTRs has also been effectively utilised 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 so 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 non-treated 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 are 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 3.7-4.1, sandy loam soil (Alvarenga et al., 2009) indicates that the WTRs used here achieved better plant yield increases than that by sewage sludge and garden waste compost in all sites except at 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 is 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 non-amended 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 occasions elsewhere (and what has sometimes been the main aim in some field application situations) following application of WTRs, i.e. immobilisation of excess P in over-fertilized soils (Makris et al., 2004). Such immobilisation 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 ~6.3-7.5 (Weil, 2016). Added to this, the chemistry of mining-affected soil might be different from that which have been studied previously (i.e. mostly agricultural soils) and therefore the increase in the P assimilation noticed at seep 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 less than 1.7% w/w

(Reuter and Robinson, 1997) indicating that further supplements may be required to reach optimum plant growth here. For seep 3, all amendments resulted in plants moving from within the K deficiency range into the K sufficient range, while 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  $\text{Cu}^{2+}$  ions are more mobile at lower pH (Cavallaro and McBride, 1980, Sauvé et al., 1997), it is known that organic matter induced mobilisation of Cu is maximised 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 and 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 and so Mn toxicity is not expected in these soils following WTRs 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 WTRs 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, confirms 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 in immobilizing As in As-contaminated soils. Here, 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 re-grinding might have exposed fresh surfaces on the WTRs or the lime that could better sorb As. It should be borne in mind, however, that the plant As concentrations were very low in this study.

Although Ni immobilisation 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 this study in both plant trials.

#### EARTHWORM survival and element uptake

Survival of earthworms in non-amended 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 an important factor. Other studies have shown that *Eisenia fetida* can survive at pH 4 and are content at pH 5 if other soil factors are favourable (Spurgeon and Hopkin, 1996, Dominguez and Edwards, 2011), but here the soil was too acidic without amendment. It may also be that the soil had toxic components that needed neutralisation 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 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 non-amended 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 whitish 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 artefacts or errors aside, the wet/dry cycle (and possibly the re-

grinding 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, trials and, in some instances, amongst replicates. This makes interpretation challenging, as does the 100% mortality in the non-treated seep soils which prevents evaluation of whether the treatments reduced the assimilation of potentially toxic elements (i.e. with no values for non-treated seep soils there is no baseline to compare with). However, 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; Table 9), suggesting that the wet/dry and re-grinding 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 ~1600 mg/kg value 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 here 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 - 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 (viz. ~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  $\mu\text{g}/\text{kg}$  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 *Eisenia 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 10000 mg/kg and 8600 mg/kg, respectively), but differed in the second experiment where the highest concentrations were noted in the Fe-WTR treatment (19534 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; Gunya et al., 2016; Hartenstein et al., 1980), but it is difficult to determine whether the measured body burdens would have any negative effects and 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 e.g. typical Pb concentrations reported at up to 16.4 mg/kg for a related *Eseinia* 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 do 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 elements 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 soils 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), while slight injuries on roots of coffee plants have been observed at Al concentrations of 1 mg/l and medium or severe injuries at a 4 mg/l (Pavan and Bingham, 1982). Comparing the Al concentrations in the soil solutions of the untreated seep soils here (i.e. ~3.4 mg/l to 154 mg/l) with those levels 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 discussed above) whereas seep 2 and 3 soils, once treated, would have Al concentrations in their soil solutions that were below the levels causing injury. While 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 to 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), while concentrations reported to cause a 10% inhibition (EC10) in growth of cucumber (*Cucumis sativa*) ranged 2.2 µg/l to 697 µg/l across a selection of soils from Australia (Lamb et al., 2016). An example of increased arsenic in pore water of arsenic-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 µg/l to 12.2 µg/l). A similar increase in porewater As was reported for soils amended with biochar, with the effect attributed to mobilisation 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 (mobilisation) of arsenic can also occur in the presence of nutrient anions such as  $\text{PO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  (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 suggests 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 seep 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 mg/l and 204 mg/l even in non-contaminated soils (Barber, 1995), so the Mg contents observed in this study do not appear to present an environmental problem.

Large increases in K in the soil solutions following all treatments in all seeps suggests 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 mobilised and low concentrations are expected in soil solution with the concentration ranges typically between 0.3 and 87 µg/l (Kabata-Pendias, 2010). In the present study, soil solution Co in non-treated seep 2 and 3 was much elevated above this typical range, with both having >500 µg/l. All treatments reduced the solution Co concentrations in seep 2 and 3 soils to <50 µg/l. Seep 1 soil had ~100 µg/l in the untreated state and this decreased to <50 µg/l following Al-WTR and lime treatments, but increased to 331 µg/l following Fe-WTR treatment. The results of the two plant growth trials discussed above 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, as organic matter differences have been reported to have the potential to mobilise 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 immobilise Co in the soil solution since 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 (NOEC, 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 stated as 62200 µg/l and 9440 µg/l respectively in the two 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 µg/l (Wolt, 1994) and all 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 (Mohammed et al., 2016, Nielsen et al., 2011) and the known decrease in solubility of Cr(III) as solution pH is

raised (Bartlett and Kimble, 1976). It is known that Cr is non-essential 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, 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 effects 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 due to 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<sub>2</sub> forms and complexing by root exudates (Hodgson et al., 1965) coupled with Fe oxides interactions and microbiological soil activity that also have impacts on 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 a Ni ore smelting region in Canada, i.e. mostly 120 – 28700 µg/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 two WTR types, Al-WTRs achieved a greater reduction in the 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 porewater Ni decrease of more than 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.

Pb is not known as an essential or as a 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,  $\text{CaCO}_3$ , 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  $\mu\text{g/l}$ , while the EC10 values in the other soils tested range 21 to 90  $\mu\text{g/l}$ . 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 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 amongst the replicates for that soil-treatment combination and 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  $\mu\text{g/l}$  (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  $\mu\text{g/l}$  (Degryse et al., 2003) while a grassland soil from Rhydtalog in the UK with pH 4.8 had 1200  $\mu\text{g/l}$  (Smolders et al., 2004). Adsorption of Zn onto pH-dependent binding sites of oxyhydroxides 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 296000  $\mu\text{g/l}$  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  $\mu\text{g/l}$ ) 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 previous sections, in the plant trial the amounts of Zn assimilated by plants was 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 immobilise 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 WTRs 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 DOI: 10.1002/etc.xxxx.

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

---

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

## REFERENCES

- Abdullahi M (2015) Soil contamination, remediation and plants: prospects and challenges (Chapt. 18, 525-546). Soil Remediation and Plants, Elsevier
- Alloway BJ (2012) Heavy metals in soils: trace metals and metalloids in soils and their bioavailability vol 22. Springer Science
- Alvarenga P, Gonçalves A, Fernandes R, De Varennes A, Vallini G, Duarte E, Cunha-Queda A (2009) Organic residues as immobilizing agents in aided

phytostabilization:(I) Effects on soil chemical characteristics. *Chemosphere*  
74:1292-1300

Alvarez-Tinaut M, Leal A, Martínez LR (1980) Iron-manganese interaction and its  
relation to boron levels in tomato plants. *Plant and Soil* 55:377-388

Anawar HM (2015) Sustainable rehabilitation of mining waste and acid mine drainage  
using geochemistry, mine type, mineralogy, texture, ore extraction and climate  
knowledge. *Journal of Environmental Management* 158:111-121

Ardestani MM, van Gestel CA (2013) Using a toxicokinetics approach to explain the  
effect of soil pH on cadmium bioavailability to *Folsomia candida*. *Environmental  
Pollution* 180:122-130

Babatunde A, Zhao Y (2007) Constructive approaches toward water treatment works  
sludge management: an international review of beneficial reuses. *Critical Reviews  
in Environmental Science and Technology* 37:129-164

Barber SA (1995) *Soil nutrient bioavailability: a mechanistic approach*. John Wiley &  
Sons

Bartlett R, Kimble J (1976) Behavior of Chromium in Soils: I. Trivalent Forms. *Journal  
of Environmental Quality* 5:379-383

Basibuyuk M, Kalat D (2004) The use of waterworks sludge for the treatment of  
vegetable oil refinery industry wastewater. *Environmental Technology* 25:373-  
380

Beesley L et al. (2013) Biochar addition to an arsenic contaminated soil increases arsenic concentrations in the pore water but reduces uptake to tomato plants (*Solanum lycopersicum* L.). *Science of the Total Environment* 454:598-603

Beesley L, Moreno-Jiménez E, Gomez-Eyles JL (2010) Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. *Environmental Pollution* 158:2282-2287

Bernal M, Clemente R, Walker D (2007) The role of organic amendments in the bioremediation of heavy metal-polluted soils. *Environmental Research at the Leading Edge*:1-57

Bustos V, Mondaca P, Verdejo J, Sauvé S, Gaete H, Celis-Diez JL, Neaman A (2015) Thresholds of arsenic toxicity to *Eisenia fetida* in field-collected agricultural soils exposed to copper mining activities in Chile. *Ecotoxicology and Environmental Safety* 122:448-454

Carvalho M, Antas A Drinking water sludge as a resource. In: *Proceedings of IWA Specialized Conference on Management of Residues Emanating from Water and Wastewater Treatment*, Johannesburg, South Africa, 2005.

Castaldi P, Mele E, Silvetti M, Garau G, Deiana S (2014) Water treatment residues as accumulators of oxoanions in soil. Sorption of arsenate and phosphate anions from an aqueous solution. *Journal of Hazardous Materials* 264:144-152

Cavallaro N, McBride M (1980) Activities of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  in Soil Solutions as Affected by pH. *Soil Science Society of America Journal* 44:729-732

Chiang YW, Ghyselbrecht K, Santos RM, Martens JA, Swennen R, Cappuyns V, Meesschaert B (2012) Adsorption of multi-heavy metals onto water treatment residuals: Sorption capacities and applications. *Chemical Engineering Journal* 200-202:405-415

Conder JM, Lanno RP, Basta NT (2001) Assessment of metal availability in smelter soil using earthworms and chemical extractions. *Journal of Environmental Quality* 30:1231-1237

Dayton E, Basta N (2001) Characterization of drinking water treatment residuals for use as a soil substitute. *Water Environment Research* 73:52-57

Degryse F, Smolders E, Oliver I, Zhang H (2003) Relating soil solution Zn concentration to diffusive gradients in thin films measurements in contaminated soils. *Environmental Science & Technology* 37:3958-3965

Dermont G, Bergeron M, Mercier G, Richer-Lafèche M (2008) Soil washing for metal removal: a review of physical/chemical technologies and field applications. *Journal of Hazardous Materials* 152:1-31

Dominguez J, Edwards CA (2011) Biology and ecology of earthworm species used for vermicomposting *Vermiculture technology: earthworms, organic wastes, and environmental management*. CRC Press USA Elvira, C, Sampedro

- Elliott HA, Dempsey BA (1991) Agronomic effects of land application of water treatment sludges. *Journal-American Water Works Association* 83:126-131
- Garau G, Silvetti M, Castaldi P, Mele E, Deiana P, Deiana S (2014) Stabilising metal (loid) s in soil with iron and aluminium-based products: microbial, biochemical and plant growth impact. *Journal of Environmental Management* 139:146-153
- Goldbold P, Lewin K, Graham A, Barker P (2003) The potential reuse of water utility products as secondary commercial materials. WRC Report No UC 6081
- Gomez-Eyles JL, Sizmur T, Collins CD, Hodson ME (2011) Effects of biochar and the earthworm *Eisenia fetida* on the bioavailability of polycyclic aromatic hydrocarbons and potentially toxic elements. *Environmental Pollution* 159:616-622
- Gunya B, Masika PJ, Hugo A, Muchenje V (2016) Nutrient composition and fatty acid profiles of oven-dried and freeze-dried earthworm *Eisenia foetida*. *Journal of Food and Nutrition Research* 4:343-348
- Hackett C (1965) Ecological Aspects of the Nutrition of *Deschampsia Flexuosa* (L.) Trin.: II. The effects of Al, Ca, Fe, K, Mn, N, P and pH on the growth of seedlings and established plants. *The Journal of Ecology* 53:315-333
- Hartenstein R, Leaf AL, Neuhauser EF, Bickelhaupt DH (1980) Composition of the earthworm *Eisenia foetida* (savigny) and assimilation of 15 elements from sludge during growth. *Comparative Biochemistry and Physiology Part C: Comparative Pharmacology* 66:187-192

- Hayat S, Khalique G, Irfan M, Wani AS, Tripathi BN, Ahmad A (2012) Physiological changes induced by chromium stress in plants: an overview. *Protoplasma* 249:599-611
- Heil D, Barbarick K (1989) Water treatment sludge influence on the growth of sorghum-sudangrass. *Journal of Environmental Quality* 18:292-298
- Henderson J, Raucher R, Weicksel S, Oxenford J, Mangravite F (2009) Supply of Critical Drinking Water and Wastewater Treatment Chemicals—A White Paper for Understanding Recent Chemical Price Increases and Shortages, 4225 Water Research Foundation, Denver, CO
- Hodgson J, Geering H, Norvell W (1965) Micronutrient Cation Complexes in Soil Solution: Partition Between Complexed and Uncomplexed Forms by Solvent Extraction. *Soil Science Society of America Journal* 29:665-669
- Homan C, Beier C, McCay T, Lawrence G (2016) Application of lime ( $\text{CaCO}_3$ ) to promote forest recovery from severe acidification increases potential for earthworm invasion. *Forest Ecology and Management* 368:39-44
- Hooda P, Alloway B (1998) Cadmium and lead sorption behaviour of selected English and Indian soils. *Geoderma* 84:121-134
- Hovsepyan A, Bonzongo J-CJ (2009) Aluminum drinking water treatment residuals (Al-WTRs) as sorbent for mercury: Implications for soil remediation. *Journal of Hazardous Materials* 164:73-80

- Howe KJ, Crittenden JC, Hand DW, Trussell RR, Tchobanoglous G (2012) Principles of water treatment. John Wiley & Sons,
- Howells AP, Lewis SJ, Beard DB, Oliver IW (2018) Water treatment residuals as soil amendments: Examining element extractability, soil porewater concentrations and effects on earthworm behaviour and survival. *Ecotoxicology and Environmental Safety* 162:334-340
- Jiao J, Zhao J, Pei Y (2017) Adsorption of Co(II) from aqueous solutions by water treatment residuals. *Journal of Environmental Sciences* 52:232-239
- Johnston D, Potter H, Jones C, Rolley S, Watson I, Pritchard J (2008) Abandoned mines and the water environment Environment Agency: Bristol, UK
- Kabata-Pendias A (2010) Trace elements in soils and plants. CRC press
- Kamprath E (1978) Lime in relation to Al toxicity in tropical soils Mineral nutrition of legumes in tropical and subtropical soils. CSIRO Aust
- Keeley J, Jarvis P, Judd SJ (2014) Coagulant recovery from water treatment residuals: a review of applicable technologies. *Critical Reviews in Environmental Science and Technology* 44:2675-2719
- Kostarelos K, Gavriel I, Stylianou M, Zissimos AM, Morisseau E, Dermatas D (2015) Legacy soil contamination at abandoned mine sites: Making a case for guidance on soil protection. *Bulletin of Environmental Contamination and Toxicology* 94:269-274

- Lamb DT, Kader M, Wang L, Choppala G, Rahman MM, Megharaj M, Naidu R (2016) Pore-water carbonate and phosphate as predictors of arsenate toxicity in soil. *Environmental Science & Technology* 50:13062-13069
- Langdon CJ, Hodson ME, Arnold RE, Black S (2005) Survival, Pb-uptake and behaviour of three species of earthworm in Pb treated soils determined using an OECD-style toxicity test and a soil avoidance test. *Environmental Pollution* 138:368-375
- Lange B, Pourret O, Meerts P, Jitaru P, Cancès B, Grison C, Faucon M-P (2016) Copper and cobalt mobility in soil and accumulation in a metallophyte as influenced by experimental manipulation of soil chemical factors. *Chemosphere* 146:75-84
- Lock K, Becaus S, Criel P, Van Eeckhout H, Janssen C (2004) Ecotoxicity of cobalt to the springtail *Folsomia candida*. *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology* 139:195-199
- Lombi E, Stevens D, McLaughlin M (2010) Effect of water treatment residuals on soil phosphorus, copper and aluminium availability and toxicity. *Environmental Pollution* 158:2110-2116
- Lucas JB, Dillaha TA, Reneau RB, Novak JT, Knocke WR (1994) Alum sludge land application and its effect on plant growth. *Journal-American Water Works Association* 86:75-83
- Ma Y, Lombi E, McLaughlin MJ, Oliver IW, Nolan AL, Oorts K, Smolders E (2013) Aging of nickel added to soils as predicted by soil pH and time. *Chemosphere* 92:962-968

- Ma Y, Lombi E, Oliver IW, Nolan AL, McLaughlin MJ (2006) Long-term aging of copper added to soils. *Environmental Science & Technology* 40:6310-6317
- Makris KC, Harris WG, O'Conno GA, Obreza TA (2004) Phosphorus immobilization in micropores of drinking-water treatment residuals: implications for long-term stability. *Environmental Science & Technology* 38:6590-6596
- Makris KC, Sarkar D, Datta R (2006) Aluminum-based drinking-water treatment residuals: A novel sorbent for perchlorate removal. *Environmental Pollution* 140:9-12
- Marschner H (1988) Mechanisms of manganese acquisition by roots from soils. In: *Manganese in soils and plants*. Springer, pp 191-204
- Marschner P, Rengel Z Interactions between rhizosphere microorganisms and higher plants for iron and manganese—an overview. In: *ICOBTE, 8 Int. Conf, 2005*. pp 488-489
- Mohammed A, Al-Tahmazi T, Babatunde AO (2016) Attenuation of metal contamination in landfill leachate by dewatered waterworks sludges. *Ecological Engineering* 94:656-667
- Nelson DW, Sommers LE (1996) Total carbon, organic carbon, and organic matter. *Methods of soil analysis part 3—chemical methods*:961-1010

- Nielsen SS, Petersen L, Kjeldsen P, Jakobsen R (2011) Amendment of arsenic and chromium polluted soil from wood preservation by iron residues from water treatment. *Chemosphere* 84:383-389
- Nolan AL, Ma Y, Lombi E, McLaughlin MJ (2009) Speciation and isotopic exchangeability of nickel in soil solution. *Journal of Environmental Quality* 38:485-492
- O'Dell R, Silk W, Green P, Claassen V (2007) Compost amendment of Cu–Zn minespoil reduces toxic bioavailable heavy metal concentrations and promotes establishment and biomass production of *Bromus carinatus* (Hook and Arn.). *Environmental Pollution* 148:115-124
- Ociński D, Jacukowicz-Sobala I, Mazur P, Raczyk J, Kociołek-Balawejder E (2016) Water treatment residuals containing iron and manganese oxides for arsenic removal from water – Characterization of physicochemical properties and adsorption studies. *Chemical Engineering Journal* 294:210-221
- Oliver IW, Grant CD, Murray RS (2011) Assessing effects of aerobic and anaerobic conditions on phosphorus sorption and retention capacity of water treatment residuals. *Journal of Environmental Management* 92:960-966
- Pavan MA, Bingham F (1982) Toxicity of Aluminum to Coffee Seedlings Grown in Nutrient Solution. *Soil Science Society of America Journal* 46:993-997

- Prakash P, SenGupta AK (2003) Selective Coagulant Recovery from Water Treatment Plant Residuals Using Donnan Membrane Process. *Environ Sci Technol* 37:4468-4474
- Reed D (2002) Resource extraction industries in developing countries. *Journal of Business Ethics* 39:199-226
- Reuter D, Robinson JB (1997) Plant analysis: an interpretation manual. CSIRO publishing,
- Sarkar D, Makris KC, Vandanapu V, Datta R (2007) Arsenic immobilization in soils amended with drinking-water treatment residuals. *Environmental pollution* 146:414-419
- Sauvé S, McBride MB, Norvell WA, Hendershot WH (1997) Copper solubility and speciation of in situ contaminated soils: effects of copper level, pH and organic matter. *Water, Air, and Soil Pollution* 100:133-149
- Shahin SA, Mossad M, Fouad M (2019) Evaluation of copper removal efficiency using water treatment sludge. *Water Science and Engineering* 12:37-44
- Shuman LM (1999) Effect of organic waste amendments on zinc adsorption by two soils. *Soil Science* 164:197-205
- Smolders E, Buekers J, Oliver I, McLaughlin MJ (2004) Soil properties affecting toxicity of zinc to soil microbial properties in laboratory-spiked and field-contaminated soils. *Environmental Toxicology and Chemistry* 23:2633-2640

- Song QJ, Greenway GM (2004) A study of the elemental leachability and retention capability of compost. *Journal of Environmental Monitoring* 6:31-37
- Spurgeon D, Hopkin S (1996) Effects of variations of the organic matter content and pH of soils on the availability and toxicity of zinc to the earthworm *Eisenia fetida*. *Pedobiologia* 40:80-96
- Turner T, Wheeler R, Stone A, Oliver I (2019) Potential Alternative Reuse Pathways for Water Treatment Residuals: Remaining Barriers and Questions—a Review. *Water, Air, & Soil Pollution* 230:227
- Üçer A, Uyanik A, Aygün Ş (2006) Adsorption of Cu (II), Cd (II), Zn (II), Mn (II) and Fe (III) ions by tannic acid immobilised activated carbon. *Separation and purification technology* 47:113-118
- Ulén B, Etana A, Lindström B (2012) Effects of aluminium water treatment residuals, used as a soil amendment to control phosphorus mobility in agricultural soils. *Water Science and Technology* 65:1903-1911
- Van Rensburg L, Morgenthal T (2003) Evaluation of water treatment sludge for ameliorating acid mine waste. *Journal of Environmental Quality* 32:1658-1668
- Violante A, Del Gaudio S, Pigna M, Pucci M, Amalfitano C (2008) Sorption and desorption of arsenic by soil minerals and soils in the presence of nutrients and organics. In: *Soil Mineral Microbe-Organic Interactions*. Springer, pp 39-69

- Virtanen S, Simojoki A, Hartikainen H, Yli-Halla M (2014) Response of pore water Al, Fe and S concentrations to waterlogging in a boreal acid sulphate soil. *Science of the Total Environment* 485:130-142
- Walker DJ, Clemente R, Bernal MP (2004) Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. *Chemosphere* 57:215-224
- Wang C, Wang Z, Lin L, Tian B, Pei Y (2012) Effect of low molecular weight organic acids on phosphorus adsorption by ferric-alum water treatment residuals. *Journal of Hazardous Materials* 203:145-150
- Weil RR, Nyle C. (2016) *The nature and properties of soils vol 13*. Prentice Hall, USA.
- Willard LL (1979) *Chemical equilibria in soils*. Chichester, UK: John Wiley & Sons,
- Wolt JD (1994) *Soil solution chemistry: applications to environmental science and agriculture*. J Wiley
- Yilmaz DD (2007) Effects of salinity on growth and nickel accumulation capacity of *Lemna gibba* (Lemnaceae). *Journal of Hazardous Materials* 147:74-77
- Zajic JE (1969) *Microbial biogeochemistry*
- Zhang L, Verweij RA, Van Gestel CA (2019) Effect of soil properties on Pb bioavailability and toxicity to the soil invertebrate *Enchytraeus crypticus*. *Chemosphere* 217:9-17

Zhang Q, Zhu L, Wang J, Xie H, Wang J, Han Y, Yang J (2013) Oxidative stress and lipid peroxidation in the earthworm *Eisenia fetida* induced by low doses of fomesafen. *Environ Sci Pollut Research* 20:201-208

Zhao Y, Wendling LA, Wang C, Pei Y (2015) Use of Fe/Al drinking water treatment residuals as amendments for enhancing the retention capacity of glyphosate in agricultural soils. *Journal of Environmental Sciences* 34:133-142

---

Zhao YQ, Babatunde AO, Hu YS, Kumar JLG, Zhao XH (2011) Pilot field-scale demonstration of a novel alum sludge-based constructed wetland system for enhanced wastewater treatment. *Process Biochemistry* 46:278-283

**Figure 1 Soil sample collection general location in Staffordshire, England (inset maps) and example of the bare soil ‘seep’ points (main image).**



**Table 1. Typical constituents and properties of partially dried water treatment residuals (WTRs) (Babatunde and Zhao, 2007, Castaldi et al., 2014, Lombi et al., 2010, Ulén et al., 2012, Wang et al., 2012)**

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

**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	Non-amended (control)	Al-WTR amended	Fe-WTR amended	Lime amended	Buffering capacity#
----- 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*	21400 $\pm$ 0.00
Seep 2	3.83 $\pm$ 0.06*	5.67 $\pm$ 0.10*	6.01 $\pm$ 0.05*	6.88 $\pm$ 0.03*	32700 $\pm$ 0.00
Seep 3	3.40 $\pm$ 0.01*	5.23 $\pm$ 0.06*	5.42 $\pm$ 0.02*	7.15 $\pm$ 0.06*	26600 $\pm$ 0.00

\*Significantly different from non-amended ( $P < 0.05$ ); #based on lime addition and measured pH, with units: mg CaCO<sub>3</sub>/kg soil/pH unit; n/a = not applicable.

**Table 3. Mean above ground dry plant mass per pot (g,  $\pm$  standard deviation) in the original plant trial and following a wet-dry cycle**

Site	Non-amended	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 non-amended ( $P < 0.05$ )

**Table 4. Mean element content in above ground plant tissue (mg/kg  $\pm$  standard deviation, or % w/w where indicated) from the initial plant growth trial**

Element	Soil	Non-amended 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 <sup>#</sup>	33.23 $\pm$ 0.58 <sup>#</sup>	35.42 $\pm$ 1.39 <sup>#</sup>

	Seep 3	602.69±24.15	30.05±0.07*	32.49±0.06*	37.03±4.13*
As	Seep 1	0.14±0	1.31±1.12	0.98±0.65	0.28±0.05
	Seep 2	0.34±0.05	0.32±0.04	0.29±0.03	0.28±0.07
	Seep 3	0.27±0.09	0.10±0.01*	0.08±0.00*	0.09±0.01*
Ca%	Seep 1	0.15±0.00	0.78±0.02*	1.17±0.01*	0.89±0.00*
	Seep 2	0.3±0.00	0.55±0.00*	0.67±0.01*	0.64±0.05*
	Seep 3	0.27±0.00	0.85±0.00*	1.31±0.06*	1.26±0.09*
Cd	Seep 1	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
	Seep 2	0.06±0.05	0.00±0.00	0.00±0.00	0.00±0.00
	Seep 3	0.07±0.05	0.00±0.00	0.00±0.00	0.01±0.01
Co	Seep 1	0.55±0.01	0.20±0.00*	0.51±0.02	0.1±0.00*
	Seep 2	9.2±0.33	1.02±0.00*	1.3±0.09*	1.19±0.08*
	Seep 3	9.54±0.43	0.45±0.00*	0.63±0.01*	0.74±0.00*
Cr	Seep 1	1.37±0.24	1.4±0.13	1.32±0.15	3.87±2.7
	Seep 2	1.03±0.14	1.2±0.10	1.2±0.00	1.03±0.17
	Seep 3	2.47±0.30	1.31±0.12*	1.03±0.15*	0.75±0.06*

Cu	Seep 1	11.61±0.67	15.62±0.11*	13.5±0.42*	14.15±0.11*
	Seep 2	11.85±0.2	15.85±0.32*	14.54±0.09*	13.57±0.53*
	Seep 3	10.81±0.41	13.05±0.36*	12.41±0.61*	13.11±0.16*
Fe	Seep 1	522.19±37.11	179.24±22.02*	402.85±62.03	230.48±12.76*
	Seep 2	205.91±29.87	135.75±2.97	132.07±3.75	102.17±3.29
	Seep 3	1446.76±59.51	112.64±1.82*	112.82±1.39*	104.5±4.34*
K%	Seep 1	0.56±0.03	0.79±0.02*	0.94±0.02*	1.57±0.35*
	Seep 2	2.39±0.03	3.52±0.01*	3.13±0.01*	3.68±0.01*
	Seep 3	1.44±0.00	2.04±0.05*	2.31±0.14*	2.95±0.15*
Mg%	Seep 1	0.16±0.00	0.3±0.01*	0.32±0.00*	0.2±0.00*
	Seep 2	0.34±0.00	0.38±0.00*	0.36±0.00*	0.24±0.00*
	Seep 3	0.32±0.01	0.36±0.00	0.42±0.00#	0.24±0.01
Mn	Seep 1	45.3±0.43	339.45±8.32*	286.02±11.36*	60.17±3.26*
	Seep 2	372.05±0.51	283.03±3.45*	190.21±5.69*	101.89±2.05*
	Seep 3	298.41±4.85	342.4±4.48*	247.23±1.92*	125.34±7.93*
Ni	Seep 1	9.59±0.82	7.1±0.31	7.24±0.16	5.33±0.1

	Seep 2	37.33±2.17	28.24±1.66*	13.71±1.13*	6.59±0.17*
	Seep 3	28.98±5.54	14.92±2.5	7.55±0.35*	7.09±0.34*
P%	Seep 1	0.80±0.05	1.14±0.01*	0.95±0.01 <sup>#</sup>	0.99±0.03
	Seep 2	0.97±0.01	0.79±0.01*	0.72±0.01*	0.74±0.01*
	Seep 3	0.61±0.03	0.88±0.02*	0.77±0.04*	0.82±0.00*
Pb	Seep 1	0.71±0.08	0.65±0.20*	0.58±0.03*	1.33±0.48
	Seep 2	0.65±0.17	0.26±0.02*	0.27±0.03*	0.32±0.05
	Seep 3	0.39±0.06	0.09±0.02*	0.09±0.01*	0.35±0.23
S%	Seep 1	2.61±0.03	3.65±0.06*	2.39±0.03*	4.12±0.13*
	Seep 2	4.82±0.13	5.89±0.05*	2.73±0.15*	5.17±0.09*
	Seep 3	4.44±0.09	4.57±0.23	2.71±0.05*	4.97±0.07 <sup>#</sup>
Zn	Seep 1	74.22±4.89	65.05±4.79	53.6±1.28	45.91±0.24 <sup>#</sup>
	Seep 2	72±1.09	59.99±0.31*	53.9±1.24*	61.88±0.58*
	Seep 3	79.54±1.67	52.66±0.40*	48.12±1.55*	49.42±0.31*

\*Significantly different from non-amended (P < 0.05); <sup>#</sup> almost significantly different from non-amended (P ~ 0.06).

**Table 5. Earthworm survival percentage in treated and control soils (mean±SE).**

Site	Non-amended	Al-WTR	Fe-WTR	Lime
-----Survival percentages of earthworms in original trial----- --				
Seep 1	0.00±0.00	80±8.16*	40±8.16*	100±0.00
Seep 2	0.00±0.00	53.33±29.05	20±11.54	100±0.00
Seep 3	0.00±0.00	0.00±0.00	85±9.57*	100±0.00
-----Survival percentages of earthworms in the trial after wet-dry cycle----- -				
Seep 1	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Seep 2	13.33±13.33	80±20.00 <sup>#</sup>	100±0.00*	93.33±6.66*
Seep 3	0.00±0.00	60±20.00	100±0.00*	100±0.00*

\*Significantly different from non-amended ( $P < 0.05$ ); <sup>#</sup> almost significantly different from non-amended ( $P \sim 0.06$ ).

**Table 6. Mean element concentrations in earthworm tissue (mg/kg or µg/kg, as indicated, ± SE) following the initial trial**

Element	Site	Al-WTR	Fe-WTR	Lime
Al mg/kg	Seep 1	290.20±181.381	33.55±8.5	121.18±27.44
	Seep 2	603.78±178.56	380.14±350.26	207.64±34.56
	Seep 3	N.R	431.02±60.62*	227.96±75.37

As μg/kg	Seep 1	B.D	3.69±3.69	4.16±2.2
	Seep 2	11.14±3.84	B.D	B.D
	Seep 3	N.R	B.D	4.24±3.03
Ca mg/kg	Seep 1	1693.03±144.99	1890.22±258.86	6166.19±698.69
	Seep 2	1989.83±231.28	10148.77±9234.85	8106.78±1048.33
	Seep 3	N.R	2796.43±386.15	6776.81±2625.36
Co μg/kg	Seep 1	6.19±1.49	18.63±7.85	1.92
	Seep 2	1.24	2.01±0.42	2.86±1.75
	Seep 3	N.R	4.16±1.41	1.11±0.49
Cr μg/kg	Seep 1	4.79±2.88	27.19±8.36	B.D
	Seep 2	B.D	B.D	4.29
	Seep 3	N.R	2.77±1.18	B/D
Cu μg/kg	Seep 1	19.9±1.87	40.22±12.45	15.23±2.96
	Seep 2	12.15±2.29	6.12±2.62	10.27±0.27
	Seep 3	N.R	9.59±1.64	4.53±1.14
Fe	Seep 1	6585.79±4833.78	1252.11±274.93	10250.5±2544.85

mg/kg	Seep 2	3722.8±722.61	7767.2±N.R	6317.71±714.82
	Seep 3	N.R	8657.76±779*	3387.83±461.58
K mg/kg	Seep 1	7045.24±111.77	7283.72±651.26	6417.23±389.89
	Seep 2	6613.93±583.44	9074.32±4198.43	6364.92±449.61
	Seep 3	N.R	6087.23±614.85	4995.38±1066.11
Mg mg/kg	Seep 1	462.09±55.9	319.04±83.49	402.33±7.96
	Seep 2	427.44±18.73	797.64±651.12	613.38±48.3
	Seep 3	N.R	663.44±56.87	499±125.48
Mn mg/kg	Seep 1	28.78±10.11	31.59±7.48	5.55±1.68
	Seep 2	17.56±3.5	19.16±9.05	21.13±1.98
	Seep 3	N.R	40.69±4.46*	13.94±0.46
Ni µg/kg	Seep 1	1.91±0.88	8.3±4.18	1.55±0.92
	Seep 2	0.93±0.93	B.D	2.99±0.97
	Seep 3	N.R	3.22±1.37	0.64±0.34
Pb µg/kg	Seep 1	4.26±1.6	2.86±1.95	4.16±0.5
	Seep 2	1.21±0.33	9.4±3.45	10.64±2.88

	Seep 3	N.R	4.71±1.33	3.68±1.88
Zn µg/kg	Seep 1	75.63±6.54	105.7±29.35	55.77±5.33
	Seep 2	56.79±9.2	133.67±9.3	66.95±6.22
	Seep 3	N.R	72.51±10.84	49.04±7.46

\*significantly different ( $p < 0.05$ ) from Al-WTR. B.D refers to below detection, N.R = not reported because no earthworms survived hence element analysis was not possible.

**Table 7. Mean element concentrations (µg/l or mg/l, ± SE) in simulated soil solutions**

Element	Site	Non-amended	Al-WTR	Fe-WTR	Lime
Al mg/l	Seep 1	154.39±44.36	54.07±8.32	6.96±2.93*	1.05±0.21*
	Seep 2	3.38±1.6	0.3±0.20 <sup>#</sup>	0.07±0.00 <sup>#</sup>	0.06±0.00 <sup>#</sup>
	Seep 3	34.85±11.27	0.22±0.05 <sup>#</sup>	0.07±0.00 <sup>#</sup>	N.R
As µg/l	Seep 1	2.86±0.21	3.54±0.38*	4.09±0.2*	12.2±0.44*
	Seep 2	19.68±5.82	12.61±1.95	7.5±2.61	6.52±0.87
	Seep 3	12.24±1.56	23.63±6.94	9.98±2.1	N.R
Ca mg/l	Seep 1	201.21±12.5	240.54±3.86	236.57±1.16	231.88±0.25
	Seep 2	247.4±0.44	253.53±1.78*	252.09±1.78*	268.72±0.94*
	Seep 3	251.37±1.27	249.96±8.46	269.41±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 <sup>#</sup>
	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±18.65	446.62±41.31*	408.81±21.69*	327.97±14.73*
	Seep 3	51.57±2.42	151.84±21.42*	142.12±9.94*	N.R
Mg mg/l	Seep 1	93.96±5.07	135.79±2.51*	159.31±6.54*	98.81±8.98
	Seep 2	261.17±1.73	198.12±12.67*	209.06±13.46*	124.05±5.09*
	Seep 3	231.68±0.92	140.76±14.93*	158.72±1.56*	N.R
Mn mg/l	Seep 1	9.99±0.76	60.7±2.85	114.25±16.69	0.23±0.04
	Seep 2	68.9±2.61	17.97±2.98*	27.66±4.21*	0.17±0.01*
	Seep 3	45.49±1.75	18.18±7*	32.43±0.62*	N.R
Ni µg/l	Seep 1	962.35±73.95	124.46±13.33*	501.59±176.86*	6.06±1.65*
	Seep 2	2425.22±248.02	22.03±2.79*	53.76±10*	11.06±0.29*
	Seep 3	2289.93±261.57	36.55±6.7*	76.06±6.44*	N.R
Pb µg/l	Seep 1	0.54±0.2	0.83±0.57	0.79±0.35	161.05±89.51
	Seep 2	4.86±1.01	2.67±1.59	0.47±0.14*	0.8±0.32*
	Seep 3	5.69±1.03	1.09±0.34*	0.31±0.13*	N.R
Zn µg/l	Seep 1	1182.15±133.4	415.46±43.32*	1128.03±342.36	26.76±1.57*
	Seep 2	1453.84±341.3	25.2±2.19*	50.12±12.78*	6.19±0.9*

	Seep 3	2420.86±471.37	27.39±2.48*	46.97±3.62*	N.R
--	--------	----------------	-------------	-------------	-----

\* P value < 0.05 (indicating significant difference from non-amended control); # P value ~ 0.06; N.R. = not reported due to sample loss.