THE USE OF COAL ASH FROM POWER PLANTS AS A SOIL CONDITIONER

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ABSTRACT

The disposal of coal ash, produced in large quantities by power plants as a by-product of coal combustion, is a significant environmental concern. Coal ash can be used as an agricultural soil conditioner because of its liming potential and the presence of many essential plant nutrients. However, recommendations for the agricultural use of coal ash should be based on sound knowledge of the coal ash characteristics, particularly the concentrations of potentially toxic elements (PTEs) in the ash. Due to the uptake of PTEs by crop plants it may pose risks to human health following the consumption of food crops.

The aim of this study was to evaluate the potential for the safe application of power station derived coal ash to soil as a beneficial disposal route. The specific objectives included; (i) testing the variability of fly ash obtained from different sources in the UK, Czech Republic and Tanzania, (ii) quantifying the short- and long-term changes in soil characteristics induced by applications of ash, (iii) determining the effects of coal ash on soil enzyme activities, (iv) quantifying the utility of coal ash as a fertilizer by evaluating its effect on growth and yield of wheat and (v) assessing risks of long-term use/multiple applications of coal ash to arable soils.

Coal ash from the Czech Republic, the UK and Tanzania was characterized; the latter two were used in pot experiments to determine their effects on soil enzyme activities, wheat growth and PTE uptake when added to two contrasting soil types (woodland and arable sandy loams). Two incubation experiments were undertaken to quantify short- and long-term effects of the coal ashes on soil characteristics. Calculations were also performed to evaluate the probable risks of increased contamination of soil and plant material as well as human ingestion of PTEs following repeated applications of fly ash to arable soils.

Coal ashes from each source contain varying quantities of essential nutrients and PTEs due to differences in coal ranks and the combustion conditions of the power plants producing each ash. Different batches of ash from the UK and from Tanzania had different characteristics, despite coming from the same industrial source within the respective countries. Application of the first batch of ash collected in the UK (UK1) to woodland soil increased the soil pH, soil

respiration and nutritional status during a two-year incubation experiment. Soil amendment with high UK1 ash concentrations (8-16%) contaminated the soil with PTEs through the experiment. In a four-month incubation experiment, the effects of different coal ashes applied to acidic woodland soil varied depending on the characteristics of each individual ash and the amount of ash applied.

In a pot experiment designed to evaluate the effect of coal ash on microbial activities, soil amendment with the UK1 ash increased the pH of woodland and arable soils, while application of the TZ1 ash reduced the pH of both soils. Application of low concentrations (0-4%) of UK1 ash to both soils increased dehydrogenase and urease activities and wheat growth while application of TZ1 ash at high concentrations (8-16%) inhibited the enzyme activities. In pot experiments to evaluate the effects of ash on wheat growth, application of 0-32% of the UK1 ash to woodland and arable soils increased soil pH while application of the TZ1 ash at 0-32% decreased the pH of both soils. Soil amendment with 0-4% of either UK1 or TZ1 ash increased the concentrations and extractability of nutrients and wheat growth and yield, but application of 16-32% of both ashes to both soils contaminated the soils and wheat plants with PTEs. Despite PTE uptake by plants, grain PTE concentrations were within the FAO/WHO 'safe' limits for ingestion, except for As and Cd in grains from plants grown in woodland soil amended with the highest concentrations of UK1 and TZ1 ash respectively, which were both present in higher than acceptable concentrations.

Soil and plant concentrations and human consumption of selected PTEs (As, Cd, Cr, Pb and Zn) were calculated following simulated annual applications of TZ1 ash to an arable soil for five consecutive years. This showed that, even when residual contamination over a 25-year period was considered, applications of 2% ash to the soil are unlikely to breach 'permissible' standards for soil, wheat grain contamination and human dietary intake of PTEs, which were far below 'permissible' limits. It would be possible to apply ash with similar characteristics to TZ1 more frequently or over more than five cropping cycles.

In conclusion, coal ash can be used as an agricultural soil conditioner; however, low concentrations (0-4%) and the strategic agronomical use of ash, specifically targeting problematic soils, are highly recommended for future studies.

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DEDICATION

I would like to dedicate this work to;

My parents, Mr and Mrs Gerald Mwasanga for their love and encouragement.

My husband Demas for his love, support and continuous encouragement.

My lovely daughter Christabella and my son Miguel for always making me smile.

LIST OF ACRONYMS

UK1	UK ash sample batch 1
UK2	UK ash sample batch 2
TZ1	Tanzania ash sample batch 1
TZ2	Tanzania ash sample batch 2
CR	Czech Republic ash sample
HCV	Health criteria value(s)
LLTC	Low Levels of Toxicological Concern
C4CSL	Category 4 Screening Level
GAC	Generic Assessment Criteria
DEFRA	Department of Environment, Food and Rural Affairs
OC	Organic carbon
CEC	Cation exchange capacity
EC	Electric conductivity
GDP	Gross domestic product
C	Carbon
N	Nitrogen
PTEs	Potentially Toxic Elements
DM	Dry matter
TTC	Triphenyl tetrazolium chloride
TPF	Triphenyl formazan
STAMICO	State Mining Company
CCPs	Coal combustion by-products
MT	Metric tonnes
RPM	Revolution per minute
LSD	Least Significant Difference

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1 GENERAL INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

Coal is the carbonaceous fossil fuel most extensively used as a source of electricity in many countries of the world. Following sustained increases in prices of oil and natural gas, the use of coal as a fuel in electricity generation is economically attractive, especially in those countries rich in coal resources such as China, India and the USA (Lior, 2010). Based on data from 2012, the top 10 national consumers of coal for electricity production are China (50.2%), USA (11.7), India (8%), Japan (3.3%), the Russian Federation (2.5%), South Africa (2.4%), South Korea (2.2), Germany (2.1%) and Poland and Indonesia combined (1.4%) (Figure 1.1, Yao et al., 2015). Commercial burning of coal for electricity production has increased in recent years. In 2011, the global annual electricity production from coal was estimated to be 29.9% (Yao et al., 2015); in 2014 it was 40% (Bhangare et al., 2014) and it is expected to increase to 46% in 2030 (Yao et al., 2015).

Coal ashes are industrial by-products of coal combustion produced from power plants; they include fly ash, bottom ash and boiler slag (Jala and Goyal, 2006). Together with the products of flue gas desulphurization, they are collectively termed coal combustion by-products (CCPs) or coal solid wastes. The average global ash content in coal ranges from 10% to 15% by weight of the feed coal (Ferraiolo et al., 1990), but depending on the type of coal being burnt and the combustion efficiency, the proportion of ash in coal may reach 20% or more. Coal fly ash in particular is an amorphous ferroalumino silicate with a matrix similar to soil. Its major constituents are silica, alumina and iron oxides, together with a range of elements which always vary in their concentrations, including carbon, calcium, magnesium and sulphur (Shaheen et al., 2014).

Commercial burning of coal for electricity production always produces large quantities of fly ash. In 2012, global annual fly ash generation accounted for about 750 MT (Blissett and Rowson, 2012). The current worldwide annual utilization of this fly ash was estimated to be 25% (i.e. 188 MT) (Yao et al., 2015). Fly ash is mainly used in the building industry, especially in brick and tile making, in concrete to replace cement, as a raw material for cement

making, filling up road base embankments and as an absorbent to reclaim heavy metal contaminated water (Ali et al., 2012).

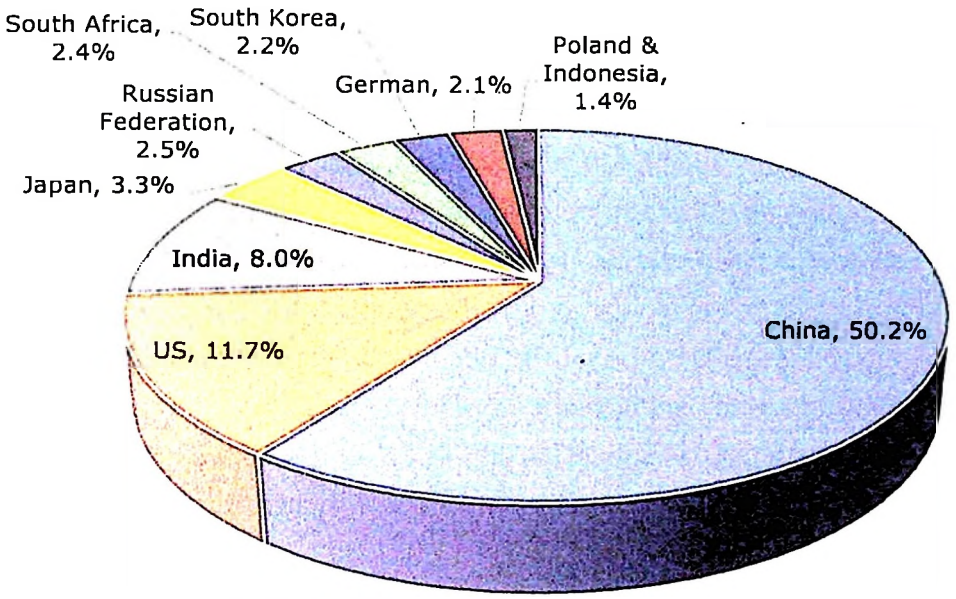

Figure 1-1: *The major 10 countries consuming coal for electricity production in 2012 (source Yao et al., 2015).*

Even though some countries like Germany, the UK, the Netherlands, Denmark, France and the USA have managed to utilize up to 70% of fly ash in building industries (Aggarwal et al., 2009), use of fly ash in other countries is limited. Most fly ash materials are disposed of in landfills, lagoons, ponds, or are stock-piled near power plants, which create environmental concerns. In Tanzania, coal is used as a source of energy in many industries such as the 21st Century Textile Industry (Morogoro region), Mbeya cement industry and Mbeya plastic industry (Mbeya region), STAMICO (Mbeya region), Dangote cement company (Mtwara region) and Tanga cement industry (Tanga region); however, no information is available regarding the potential use or disposal of ash from these industries. Globally, ash disposal is a great concern due to the significant increase in coal consumption for electricity production worldwide (Yao et al., 2015). Based on the data cited by Ram and Masto (2014), coal fly ash generation and utilization from 10 selected countries in the world are presented in Table 1-1.

The use of fly ash in agriculture as a soil conditioner has been reported (Yeledhalli et al., 2007; Gupta et al., 2012; Saraswat and Chaudhary, 2014), and its positive effects on soil properties and crop yields have been demonstrated in several studies (Skousen et al., 2013). This can be an acceptable and viable use for large scale disposal of fly ash because fly ash contains almost all the essential plant nutrients (Singh et al., 2014), thus it can be used to fertilize plants grown in nutrient deficient soils. In addition, most fly ashes are alkaline in nature, although the pH can range from 4.5 - 13.5 (Shaheen et al., 2014). Alkaline fly ash can be used to raise the pH of acidic soils (Skousen et al., 2013) in agricultural, horticultural, forest and coal mine sites, hence improving nutrient availability. However, apart from the presence of essential plant nutrients, fly ash also contains several potentially toxic substances such as heavy metals, metalloids and naturally occurring radionuclides (Papastefanou et al., 2010; Nalbandian, 2012; Skousen et al., 2013) which may affect the soil environment, crop productivity, crop quality and human health.

Table 1-1: *Coal ash production and utilization in 10 selected countries (taken from Ram and Masto, 2014)*

	Country	Year	Fly ash generation (MT)	Fly ash utilization (MT)	Fly ash utilization (%)
1	China	2010	480.00	321.6	67.0
2	India	2010-11	131.09	73.1	55.8
3	USA	2011	59.90	23.0	38.4
4	Australia	2008	14.50	4.6	32.0
5	EU 15	2010	48.00	43.9	91.4
6	Japan	2006	10.96	10.7	97.2
7	Canada	2007-2008	6.09	1.9	31.0
8	Israel	2012	1.45	1.4	94.1
9	Germany	2010	15.26	15.3	100.0
10	Turkey	2012	24.00	-	10[b]

b=data from 2003-2006

1.2 EFFECTS OF COAL ASH ON SOIL CHARACTERISTICS

The geology and characteristics of coal are described in Chapter 3, Section 3.1.3. The detailed chemical and physical composition of coal ash including naturally occurring radionuclides in coal ash are described in Section 3.1.2. Here, the effects of applying coal ash on the properties of soils are considered.

1.2.1 Effect of ash on soil physical properties

Application of fly ash onto poor soils tends to improve physical properties such as bulk density, water retention, soil porosity and texture. However, the extent of improvement varies depending on the amount, type and physical characteristics of the ash added and the physical characteristics of a given soil (Shaheen et al., 2014). Adriano and Weber (2001) reported enhancement of physical characteristics of sandy and clayey top soils after mixing them with a fly ash. From this observation, it was suggested that mixing the top soil of sandy or clayey soils with fly ash can be an appropriate method to safeguard highly eroded areas where substantial amounts of topsoil are lost during harvesting of grasses. Pathan et al. (2003) found a significant reduction in soil hydraulic conductivity and enhanced water retention and availability to plants after application of fly ash to sandy soil. Similarly, Muir et al. (2007) and Yunusa et al. (2011) showed that application of fly ash reduced the hydraulic conductivity and improved the soil water holding capacity of sandy soil. Kalra et al. (2000) reported a significant increase in soil moisture retention at field capacity with a corresponding increase in ash content from 10% to 40% w/w when the ash was added to medium- and course-textured soils (sandy, sandy loam and sandy clay loam). During this study, application of similar rates of fly ash reduced the moisture content retained at field capacity for a clayey soil. This was translated to an increase and a decrease in plant available water in the coarser soils and the clayey soils respectively. The reduction in plant available water in soils amended with fly ash could be attributed to the retention of more water by capillary action of the ash. Application of high rates of unweathered fly ash (280, 560 and 1120 tonnes ha^{-1}) to silt loam soil improved soil porosity (microporosity) and water retention characteristics (plant available water, water holding capacity and hydraulic conductivity), but improvement of water retention characteristics was only significant at the highest additions of fly ash at 560 and 1120 tonnes ha^{-1} (Adriano and Weber, 2001). Regardless of

the differences in rooting depth of maize, wheat, rice and mustard crops, application of different rates of fly ash (10, 20, 30, 40 and 50 tonnes ha^{-1}) to farmers' fields gave improvements in plant available water in all the above crops. Changes in soil hydrological functions after fly ash application could be attributed to modifications of particle size distribution, total porosity and pore size distribution in soils since fly ash is dominated by silt sized particles. In the study by Adriano and Weber (2001), a substantial improvement in plant available water in fly ash amended sandy soils compared to unamended soil was associated with the enhanced soil porosity and a shift in pore size distribution from macropores to micropores.

Contrasting results regarding the effect of fly ash addition on bulk density have been reported. Reduction in bulk density in soil amended with fly ash was reported by several authors (Kalra et al., 1997, 2000 and Yunusa et al., 2011). Yunusa et al. (2011) found an increase in top soil (0-10 cm) bulk density of sandy and sandy loam soils after application of acidic fly ash from Western Australia at rates of 12 and 36 tonnes ha^{-1}, but after increasing the ash concentration to 108 tonnes ha^{-1}, the bulk density decreased. Application of 108 tonnes ha^{-1} of fly ash from New South Wales also decreased the bulk density of the top soil (0-10 cm). No changes in bulk density or soil temperature were noted after application of high rates of fly ash (280, 560 and 1120 tonnes ha^{-1}) to a silt loam soil (Adriano and Weber, 2001).

Improved soil aggregation as a result of fly ash application was reported by Yunusa et al. (2011) where addition of fly ash to top soil (0-10 cm) significantly increased macro-aggregation in the subsurface soil layer (10-20 cm). Kalra et al. (2000) found an increase in soil strength with a corresponding increase of fly ash content after incorporation into soil belonging to different textural classes. From this study, an increase in soil strength for application rates of 10%, 20%, 30% and 40% w/w (fly ash-soil mixtures) followed the trend: sandy clay loam < sandy clay < clay < sandy soil. Yunusa et al. (2011) suggested a fly ash application rate of $\leq$36 tonnes ha^{-1} to be optimum for improving several key physical properties of coarse- to medium-textured soils.

1.2.2 Effects of coal ash on soil chemical properties

The effects of fly ash on the chemical characteristics of soils depend mainly on the original characteristics of both soils and fly ash, especially pH. The pH of fly ash varies from 4.5-13.5 (Adriano and Weber, 2001; Shaheen et al., 2014) depending on the sulphur and CaO contents of the parent coal which, in turn, affect the composition of the fly ash. Incorporation of an alkaline fly ash into acidic soils in most cases will increase the soil pH, thus ameliorating acidity and improving nutrient availability; conversely, addition of acidic fly ash to an alkaline soil in most cases will lower the soil pH. Varying results regarding the effects of fly ash on soil pH have been reported. On application of fly ash with a pH of 7, Kalra et al. (2000) reported decreased pH of alkaline soils (pH 8.3-8.8) and increased pH of an acidic soil (pH 5.6). Decreasing pH of alkaline sandy, sandy clay loam and sandy loam soils upon fly ash incorporation was noted by Kalra et al. (1997). An increase in pH of calcareous soil upon fly ash application was also reported (Riehl et al., 2010 and Elseewi at al., 1980).

Increased electrical conductivity (EC) of soils amended with fly ash has been found by many researchers (Adriano and Weber, 2001; Kalra et al., 1997, 2000); however, these increases were short term and EC tended to decrease with time. This was attributed to leaching of soluble salts within the fly ash with time. Application of fly ash is likely to induce soil salinity, especially at the beginning of the application time and when repeatedly high rates of unweathered fly ash are used. Kalra et al. (2000) reported an increase in soil EC by 40%, 60%, 88% and 122% in sandy, sandy loam, sandy clay loam and clayey soils, respectively following addition of 40% ash in each soil. This implies a stronger influence of fly ash on EC for finer textured soils than coarser textured soils. Similar observations have been reported for boron which tends to increase and decrease with time when soil is amended with fly ash (Adriano and Weber, 2001); from this study, it was noted that boron in soil occurs as an anion or neutral form, so it is not easily adsorbed onto colloidal surfaces and thus tends to leach easily as soluble salts. El-Mogazi et al. (1988) noted reduced plant uptake and phytotoxic effect of boron with time after conducting sequential cropping experiments. Therefore, salinity and boron toxicity are expected to be short term problems, particularly when weathered fly ash is used and when the longer-term impacts of fly ash are considered.

Soil organic carbon (OC) has been reported to increase with increasing fly ash concentration in coarser textured soils (sand and sandy loams) and the opposite trend was reported in finer textured sandy clay loam and clayey soils. Kalra et al. (2000) and Yeledhalli et al. (2007) found an increase in soil OC when different rates of fly ash (25, 50, 75 and 100 tonnes ha^{-1}) were applied with or without a recommended dose of NPK.

Fly ash contains higher concentrations of all elements (except N) than soils (Kalra, 2006), so application of fly ash to agricultural soils will improve soil fertility and thus, crop yields. Improvements in the soil status of plant nutrients (macro- and micro-nutrients) such as Ca, Mg, K, Zn, Fe, Mn and Cu after fly ash applications have been reported in several studies (Adriano and Weber, 2001; Kalra at al., 2000, 2006; Yeledhalli et al., 2007) due to the presence of these nutrients in fly ash. Application of different concentrations of fly ash, with or without recommended doses of NPK fertilizers, improved almost all the essential nutrients such as N, P, K, Ca, Mg, Zn, Fe, Mn and Cu in silt clay loamy soils (Yeledhalli et al., 2007). From this study, a significant increase in alkaline exchangeable cations, cation exchange capacity (CEC) and percentage base saturation with increasing fly ash concentrations was also noted regardless of the presence or absence of the recommended doses of NPK fertilizers. However, contradictory results regarding the effect of ash addition on soil nutrients were reported by Kalra et al. (1997), who found that levels of P, Ca and K decreased following soil amendment with fly ash. Sometimes, fly ash addition may also induce P deficiency and low uptake by plants, attributable to the presence of Fe and Al in fly ash which tend to fix P through the formation of insoluble complexes (Weeldreyer and Fine, 1981). Gupta et al. (2012) found high phosphorus (P) concentrations (400-8000 mg kg^{-1}) in fly ash which were not readily available to the plant.

1.2.3 Effects of coal ash on soil biological properties

The microbiological properties of soils are among the most important indicators of biological soil quality. In the soil, microbes are very sensitive to any changes in soil conditions (physical and chemical), thus they respond quickly to any changes in physico-chemical properties of the soil, e.g. pH, bulk density or heavy metal content. Application of fly ash to soils has been noted to induce both positive and negative effects on soil microbial activities. Surridge et al.

(2009) noted a significant increase in bacterial counts following application of 50 tonnes ha^{-1} of fly ash from South Africa which was linked to the liming effect of the fly ash and increased mobility of Ca and hydroxides after ash application. However, in the same study, soil amendment with 100 tonnes ha^{-1} of fly ash significantly decreased bacterial counts. An increase of microbial abundance (phosphorus solubilizing bacteria, actinomycetes and arbuscular mycorrhizal fungi) and the stimulation of microbial activity (measured by CO_2 evolution) was reported by Parab et al. (2015) following soil amendment with 50 tonnes ha^{-1} of fly ash from India. In this study, application of 100 tonnes ha^{-1} of fly ash reduced microbial abundance and this decrease was attributed to the reduction of availability of substrates including organic carbon and other nutrients apart from N, P, Ca and Mg in the fly ash amended soil. Using Korean ash, Lim and Choi (2014) noted a negative effect on soil microbial dynamics and activities which was linked to an increase in As and B availability in the soil following amendment with 10% fly ash. Contrary to the study by Lim and Choi (2014), Rippon and Wood (1975) reported a significant increase in the soil microbial population following soil amendment with 10% fly ash. In this study, an increase in soil microbial carbon and dehydrogenase activity was linked to an increase in nutrient release in soils amended with fly ash. Schutter and Fuhrmann (2001) also reported an increase in the density of the soil microbial community following soil amendment with 505 tonnes ha^{-1} of fly ash.

1.3 EFFECTS OF FLY ASH ON PLANT GROWTH AND YIELD

The applicability of fly ash as a soil amendment depends on the chemical composition and the rate of application, although no optimal rate has been recommended internationally. Fly ash application can result in a positive or negative effect on soil properties, plant growth and yields depending on the rate of application used. Kalra et al. (2003) reported improvement of physico-chemical characteristics of the soil and enhanced wheat yields after applications of 5-12 tonnes ha^{-1} $year^{-1}$ of fly ash. Contrasting results were reported by Sing et al. (2008) where application of fly ash at rates up to 20 tonnes ha^{-1} in combination with nitrogen fertilizer at a rate of 0-40 kg ha^{-1} adversely affected germination, early growth and yield of wheat. A slight increase in the yields of wheat and sorghum following application of fly ash at rates up to 20 tonnes ha^{-1} in combination with nitrogen at rates 0-100 kg ha^{-1} for wheat and 0-40 kg ha^{-1} for sorghum was reported by Aggarwal et al. (2009). In their study, an

adverse effect of fly ash on germination and early plant growth was only noted in the wheat crop. Sarangi et al. (2001) reported a significant increase in the total biomass and grain yields of crops with a corresponding increase in fly ash application rates up to 20 tonnes ha^{-1}. A positive effect on tomato plant growth with a corresponding increase in fly ash concentration from 10-100% by volume was reported by Khan and Khan (1996). Nayak et al. (2015) noted a delay in rice flowering by six and ten days and a significant decrease in grain and straw yield of rice when the soil was amended by fly ash at 40% and 100% concentration (by soil volume), respectively. In this study, application of fly ash at rates up to 20% (on a soil volume basis) improved growth of rice plants and significantly increased grain and straw yields of rice when compared with control treatments. Singh et al. (2008) noted a significant reduction in growth, biomass and yields of *Beta vulgaris* when soil was amended with up to 20% w/w fly ash, attributed to the accumulation of heavy metals from the applied fly ash. Wong and Wong (1990) noted the highest yield of two vegetables, *Brassica parachinensis* and *Brassica chinensis,* in sandy soil after fly ash application at a rate of 3% w/w but an increase in fly ash amendment up to 12% w/w decreased the yields of both crops significantly. However, in sandy loam soil these vegetables attained their highest yields at different fly ash rates, 3% and 12% for *Brassica chinensis* and *Brassica parachinensis,* respectively. This implies that the concentration/application rate of fly ash required to improve crop yield varies with the crop type, soil type and the characteristics of the applied ash.

Application of the highest rates of fly ash seems to induce some undesirable changes to soil characteristics which may in turn affect plant growth and yields. Generally, improper use of fly ash may result in deterioration of soil texture and structure of top soils. Negative effects include surface crust formation which inhibits water infiltration, addition of some potentially toxic elements and alteration of soil physico-chemical characteristics such as CEC, EC and pH (Kalra et al., 2003). Applications of higher rates of fly ash may result in a strong reduction in crop yields due to compaction and poor soil aeration induced by the pozzolanic effects of fly ash (Yeledhalli et al., 2007). Sarangi et al. (2001) noted decreased root biomass and horizontal growth of most roots in soil amended with fly ash at rates of 10-17.5 tonnes ha^{-1}. These observations were associated with the occurrence of soil compaction induced by fly ash

incorporation. Delayed germination and reduced biomass of plants at early growth stages were reported by Kalra et al. (1997) and this was associated with the mechanical impedance of germinating seeds induced by fly ash incorporation in soils. Adriano and Weber (2001) reported inducement of the bioavailability of trace elements like arsenic, molybdenum and selenium following application of the higher rates of fly ash from 0, 280, 560, 1120 tonnes ha^{-1} in silt clay loam soil. To avoid the long-term bioavailability of As, Se and Mo in the food chain, Adriano and Weber (2001) suggested that high rates of fly ash could be applied to non-food/fodder crops such as centipede grass. In addition, high rates of application affected the bioavailable forms of secondary nutrients such as Ca and Mg, where fly ash induced more extractable Ca than extractable Mg. Increased B and salinity in soils were found when unweathered fly ash was used, and this may inhibit seed germination and early establishment of plants.

1.4 EFFECTS OF COAL ASH ON SOIL AND PLANT CONTAMINATION

Apart from the presence of almost all the essential plant nutrients, fly ash contains some potentially toxic substances such as heavy metals and metalloids and naturally occurring radionuclides. Therefore, application of fly ash may result in contamination of soil and increased plant concentrations of potentially toxic substances.

Singh et al. (2008) found an increase in concentrations of heavy metals (Cd, Pb, Ni, Cr, Cu) in soil amended with up to 20% w/w fly ash. In this study, application of fly ash, even at a low rate of 5%, affected the growth and yield of *Beta vulgaris* (beet). This was attributed to the negative effect of heavy metals within the fly ash amended soil. Similar effects are probable in other leafy vegetables depending on the relative sensitivity of individual crop species to metal toxicity; thus, more investigations are required.

Wong and Wong (1990) found a significant increase in molybdenum and manganese contents in the soil with increasing fly ash concentrations up to 12% w/w, while no significant effect on Ni and Cu content was observed. In this study, significant decreases in Fe and Zn were noted in response to increasing fly ash applications which implies lower availability of these micronutrients in soil amended with fly ash. Sharma et al. (2002) found less

uptake of the trace metals Zn, Cu, Fe, Mn and Cd in wheat grain harvested from fly ash amended soil, and this was associated with the occurrence of these metals in oxide forms in fly ash; these forms are less soluble in water and less readily available to the plant.

Application of highly alkaline fly ash to acidic soils tends to reduce the solubility of most metals like Fe, Mn, Ni, Co and Pb due to its influence on soil pH. However, the release of these metals when the fly ash is applied to alkaline soils tends to remain unchanged (el-Mogazi et al., 1988). Therefore, application of fly ash may decrease plant uptake of some elements like Cd, Cu, Cr, Fe, Mn and Zn due to decreased solubility when the pH increases after fly ash addition.

1.5 GENERAL SOIL CHARACTERISTICS AND INORGANIC FERTILIZERS IN USE IN TANZANIA

Agriculture is the dominant sector in the Tanzanian economy providing livelihood, income and employment to over 80% of the population. It accounts for 27% of GDP, 30% of export earnings and 65% of raw materials for domestic industries (Tumbo et al., 2011). Food crop production accounts for 65% of the agricultural GDP and within these crops, maize is the most important, followed by rice, beans, cassava, sorghum and wheat (ASDP, 2006). The agriculture sector in Tanzania, which is predominantly crop based, is typically rain fed and is dominated by small holder or subsistence farmers. Besides the importance of the agriculture sector in the country, it is constrained by low productivity which is mainly due to poor soil fertility, climate change and variability, as well as poor production technologies (Tumbo et al., 2011).

Based on the review of the history of soil survey in Tanzania by Msanya et al. (2002), there are 9 types of soils in the country, namely; Cambisols, Ferralsols, Acrisols, Andosols, Arenosols, Gleysols, Luvisols, Nitosols and Vertisols. Cambisols, Ferralsols and Acrisols are the major soil groups dominating large parts of the country with proportions of 39.7%, 13.4% and 9.6%, respectively. These soils are highly weathered (based on their age), acidic and with low inherent fertility status (MAFSC, 2006). Following intensive farming by small holder farmers, the fertility status of these soils has been declining due to inadequate replenishment of nutrients (Kalvig et al., 2012) through important

soil management practices such as manuring, liming and fertilization. Therefore, most agricultural soils in the country are highly degraded, with low reserves of important nutrients like N, K, S, Ca and Mg particularly in regions such as Kigoma, Mbeya, Morogoro, Tanga, Kilimanjaro, Tabora, and Mtwara (MAFSC, 2006). Generally, poor soils are major causes of poverty in Sub-Saharan Africa, so restoration of soil fertility is a significant challenge for sustainable agriculture (Kalvig et al., 2012).

The common fertilizers used in Tanzania to improve soil fertility and increase crop yield (including their proportional use status) are illustrated in Figure 1-2. All these fertilizers are imported except Minjingu rock phosphate which is mined from major phosphate deposits located in the northern part of Tanzania. Routine application of these fertilizers is needed to supply nutrients such as N, P and K to agricultural soils. However, due the high cost of these fertilizers (approximately £20-25 per 50 kg bag) (MAFSC, 2018) and low income of the small-scale farmers who dominate the agricultural sector in the country, the use of these fertilizers is still low. The fertilizer application rate in Tanzania is 19.3 kg ha^{-1} which is lower in comparison with other African countries such as Kenya (100 kg ha^{-1}) (World Bank, 2012). Moreover, the long-term use of inorganic fertilizers particularly ammonium-based fertilizers such as urea and sulphate of ammonia, has been noted to acidify soils in Tanzania and neighbouring countries (Lungu et al., 2008), thus accelerating the problem of soil acidity in most agricultural soils.

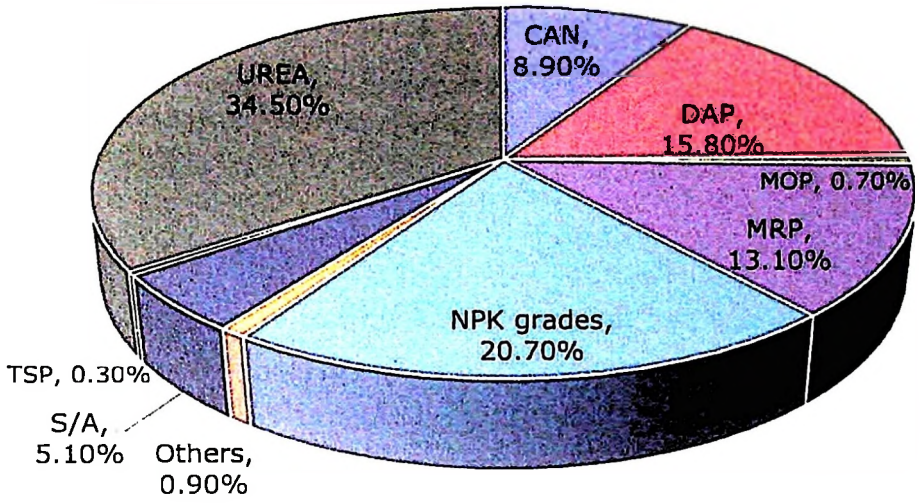

Figure 1-2: Type and quantity of fertilizer used in Tanzania. Source: Ministry of Agriculture and Food Security Cooperatives (MAFSC-2011) as cited by Lema et al., 2014. ***Key:*** *NPK - various nitrogen (apart from urea), phosphorus and potassium grades; DAP - di-ammonium phosphate; MOP - muriate of potash; MRP - Minjingu rock phosphate; CAN - calcium ammonium nitrate; S/A - sulphate of ammonia; TSP - triple super phosphate.*

1.6 COAL MINING AND ITS USE IN TANZANIA

Tanzania has been endowed with coal reserves of about 1,200 M tonnes, of which 304 M tonnes (30%) can be mined (ECS, 2015). Most coal deposits are in the southern part of the country in areas like Ngaka (Ruvuma region), Mchuchuma/Katewaka (Njombe region) and Kiwira (Mbeya region) and in the northern part of the country around the Lake Victoria regions (ECS, 2015).

Coal is one among several energy sources in the country, contributing 1% of total energy (together with wind and solar) and other sources of energy are biomass (88%), electricity (3%) and oil and gas (8%) (Mwakaje, 2017). Currently, coal is mined in several places to generate electricity, but it is mainly used as a source of energy in several cement and paper mill industries (Kusekwa et al., 2011) within the country. Following significant problems with hydropower energy (the main source of electricity in Tanzania, contributing 65%) due to prolonged drought and erratic rains (Mwakaje, 2017), the country is planning to expand electricity production by producing two thirds of the electricity from coal and natural gas (Makoye, 2014) to reduce problems of power shortages and rationing. Therefore, large quantities of coal waste, particularly coal ash, are expected. Even though coal ashes have been used for

several purposes such as in brick making, filling up road embankments and in fire briquette production, generally, their disposal is still a problem since these uses account for a small proportion of the total waste produced. This leads to an accumulation of coal ashes in mining areas and in industries which use coal as a source of energy, thus polluting the environment.

Therefore, the use of coal ashes which are locally available in the country as an agricultural soil conditioner to supplement inorganic fertilizer or liming material (due to the alkalinity of most ashes) will help to improve the soil fertility status, crop productivity and food security in the country. This will be in tandem with the country policy of *Kilimo Kwanza (Agriculture first)* which is meant to transform agriculture into a modern and commercial sector. The use of coal ash as a soil conditioner will also help the coal industry to dispose of coal wastes, thus reducing environmental pollution.

Figure 1-3: *Pile of coal ash around the compound of the 21st Century Textile Industry in Morogoro-Tanzania (photograph taken during coal ash sample collection - 2017).*

1.7 RESEARCH RATIONALE

Based on the chemical characteristics (nutrient content) and the alkalinity of most coal ashes, coal ash may be used to supplement or replace fertilizers and agricultural limes (Skounsen et al., 2013). However, the presence of potentially toxic elements and naturally occurring radionuclides may limit the use of coal ash as a soil conditioner. Contradictory results regarding the effect of coal ash on soil characteristics (physical, chemical and biological) and plant growth have been demonstrated by several studies (Adriano and Weber, 2001; Singh et al., 2008; Aggarwal et al., 2009; Nayak et al., 2015). Differing observations have been attributed to variations in ash characteristics, concentrations of the applied ash, characteristics of the recipient soils and the types of crop grown in coal ash amended soils. Soil and plant contamination have also been demonstrated in several studies of fly ash amended soils which may pose health risks to humans following the consumption of contaminated agricultural produce.

Given the infertility and acidity of most Tanzanian soils, the low use of fertilizers by small scale farmers and the availability of coal ash within the country, the use of coal ash as a soil conditioner could be a feasible technology to improve the soil fertility and crop productivity in Tanzania. However, recommendations for the agricultural use of coal ash should be based on sound knowledge of the coal ash characteristics, the concentrations of potentially toxic elements (PTEs) present in the coal ash, the effects of short and long-term use of coal ash on soil characteristics and plant growth, the uptake of PTEs by crop plants, and risks to human health following consumption of food crops grown in coal ash amended soils. This calls for more research to evaluate the agro-ecological value of the coal ash materials.

1.8 RESEARCH AIM AND OBJECTIVES

Aim: The overall aim of this project was to evaluate the potential for the safe application of power station derived coal ash to the soil as a beneficial disposal route. This key aim was addressed by the following objectives:

- Testing the variability of fly ash obtained from different sources (UK, Czech Republic and Tanzania) at different production times (between 2 batches of the UK ash and between 2 batches of the Tanzania ash).
- Quantifying the short- and long-term changes in soil characteristics induced by applications of ash.
- Determining the effects of coal ash on microbial activities in soil, particularly enzyme production.
- Quantifying the potential use of coal ash as a fertilizer, particularly evaluating its effect on growth and yield of wheat.
- Risk assessment following the long-term use/multiple application of coal ash to arable soils.

Hypotheses addressed in this project were:

- Fly ash collected from different countries are variable in terms of their chemical characteristics.
- Application of fly ash to the soil will positively influence the chemistry and biological characteristics of the soil and these changes may either be over the short-term or persist over the long-term.
- Application of fly ash to the soil will positively influence the growth and yield of wheat.
- Application of fly ash to the soil will not contaminate soil/plants with PTEs.
- Long-term use/multiple application of fly ash will pose minimum risks to soil, plants and human health with respect to accumulation of PTEs in the soils, absorbed by plants and ingested by human consumers.

2 GENERAL MATERIALS AND METHODS

2.1 SOIL SAMPLE COLLECTION, PREPARATION AND STORAGE

Two experimental soils (arable and woodland soil) were collected from the University of Nottingham farm at the Sutton Bonington campus (52.830°N, 1.239°W). The soils were both sandy loam (Wick/Arrow series). Top soils (0-20 cm depth) were collected from different points within a woodland (Domleo's Spinney) and an adjacent arable field. Samples from different points within each site were mixed together to make one composite sample, representative of either the woodland or the arable field. The aim of selecting soils from two adjacent sampling areas was to obtain soils with a common origin but with contrasting characteristics, due to the different vegetation types present and land management. In addition, the woodland soil was included to encompass the potential future application of fly ash in forestry. Soils were collected on two occasions, the first in January 2015 and the second in March 2017. Soils were air dried and sieved using a 4 mm sieve to remove plant debris and gravel and to maintain the natural crumb structure. Sieved soils were stored in plastic bags and kept in a cold room (4°C) for further use in experiments.

2.2 FLY ASH SAMPLE COLLECTION AND STORAGE

Fly ash samples used in this research were collected from the UK, the Czech Republic and Tanzania. In the UK, ash samples were collected from Ratcliffe-on-Soar power plant in Nottingham. Two sample batches of fly ash were collected: the first batch was collected in January 2015 and the second batch in July 2015. This power plant burns pulverized coals sourced from various parts of the world so the exact origins of the two batches are unknown. In Tanzania, two batches of coal ash were collected from 21st Century Textile Industry in the Morogoro region. The coal combusted in this industry is bought from TANCOAL Company, a company which mines bituminous coal from the Ngaka coal field in the Ruhuhu Basin, Ruvuma region, Tanzania. The first batch was collected in April 2015 and the second batch in January 2017. In the Czech Republic, the ash was collected from Počerady power station situated between the towns of Louny, Zatec and Most. Coal in this plant is obtained from the Vršany coal mine, an open cast lignite mine 8 km to the NW of Počerady, adjacent to the town of Most. One ash sample was collected from this plant in September 2015. Before analysis, all collected ash samples were stored in a cold room at 4°C.

2.3 ANALYSES

2.3.1 Moisture content

The percentage moisture content of the soil and fly ash samples was determined gravimetrically following the method reported by Black (1965). Samples were weighed into aluminium cups and the weight in each cup was recorded as weight of the fresh samples. Soil and fly ash samples were dried in an oven at 105°C for 24 hrs and then cooled and reweighed; once constant weight was attained this weight was recorded as the weight of the dried samples. The percentage moisture content in each soil and fly ash sample was then calculated using the formula below (equation 2-1);

$$\%\, Moisture = \left(\frac{M\ of\ fresh\ S\ or\ A - M\ of\ dry\ S\ or\ A}{M\ of\ dry\ S\ or\ A}\right) * 100 \qquad Equation\ 2-1$$

Where: M = Mass (g)
S = Soil
A = Fly ash

2.3.2 pH

The pH of each soil and fly ash sample was determined by the method reported by Rowell (1994). The air dried soil and fly ash samples (sieved to < 2 mm) were weighed and mixed with ultra-pure water in Falcon tubes at a ratio of 1:2.5. Tubes were then stoppered and shaken for 30 minutes on an end-over-end rotary shaker (30 rpm) to attain equilibrium. pH measurements were taken using a pH meter (model Hanna pH-209 with a combined glass electrode (Ag/AgCl; PHE 1400) calibrated against pH 4.01 and 7.0 buffer solutions. The pH electrode was allowed to stabilize for 2 minutes in the soil or fly ash suspensions before the reading was recorded.

2.3.3 Total carbon and nitrogen

The total carbon and nitrogen (in solid samples) of soil and fly ash samples were determined using a CN analyser (Thermo Scientific FlashEA 1112 Nitrogen and Carbon Analyser).

Each sample of soil and fly ash was placed in an empty tin (Sn) capsule. Approximately, 0.02 g of air dried and ball-milled (Model PM400; Retch GmbH and Co., Germany) soil or fly ash sample was weighed on an analytical balance

and placed in each tin capsule. The capsules were then sealed, folded and placed in a plastic box with numbered wells. The samples in the folded capsules were arranged in the wells following the embossed box well numbering system and the template for sample arrangement. Aspartic acid was used as a bypass (occupying the first well), followed by a blank (an empty, folded tin capsule) in the next well, then two quality controls (QCs) and two standards (peaty soil in both quality controls and standards) in the next four wells. The samples occupied the following wells. The last two wells following the samples, were occupied by the QCs (peaty soil). The capsules were transferred to the autosampler for analysis of total C and N through combustion, producing CO_2, N_2 and H_2O in high temperature reactor chambers.

2.3.4 Extractable carbon and nitrogen

The total extractable carbon (TC) and nitrogen (TN) were determined using a CN analyser (Model Shimadzu TOC-VCPH, PC-controlled high-sensitivity model) after extracting the fly ash or soil samples with 0.5 M K_2SO_4 solution in the ratio of 1:5. The soil or fly ash samples were shaken overnight (12 hours) using an end-over-end vertical rotary shaker at 30 rpm and then filtered using qualitative filter papers (Fisher brand). All soil or fly ash sample filtrates were then diluted with ultra-pure water in the ratio of 1:10.

2.3.4.1 TC measurement in sample filtrates

Carrier gas (purified air) is passed at a controlled flow rate of 150 mL min^{-1} through an oxidation catalyst-filled TC combustion tube, heated to 680°C. When the sample pre-treatment/injection system injects the sample into the combustion tube, the TC in the sample is oxidized or decomposes to create carbon dioxide. The carrier gas carrying the combustion products from the combustion tube is cooled and dehumidified in a dehumidifier before passing via a halogen scrubber into the sample cell of a non-dispersive infrared detector (NDIR), where carbon dioxide is detected. The NDIR analogue signal forms a peak and the data processor calculates the peak area. To measure the TC concentration of each sample, the relationship between the TC concentration and peak area (calibration curve) is predetermined using a TC standard solution, to express the peak area as a ratio of the TC concentration. TC comprises TOC (total organic carbon) and IC (inorganic carbon).

2.3.4.2 IC (inorganic carbon) measurement

The acidified sample is sparged with the carrier gas (purified air) to convert only the IC in the sample to carbon dioxide. This carbon dioxide is detected by the NDIR and the sample IC concentration is measured in the same way as TC. The IC is a combination of carbonate and bicarbonate.

2.3.4.3 TOC (total organic carbon) measurement

The total organic carbon was determined by subtracting the IC concentration from the TC concentration i.e. TOC = (TC-IC)

2.3.4.4 TN (total nitrogen) measurement in sample filtrates

Carrier gas (purified air) is passed at a controlled flow rate of 150 mL min^{-1} through a combustion tube that is filled with thermal decomposition catalyst and heated to 720°C. When the sample pre-treatment/injection system injects the sample into the combustion tube, the TN in the sample thermally decomposes to create nitrogen monoxide. The carrier gas carrying the nitrogen monoxide from the combustion tube is cooled and dehumidified in the dehumidifier before passing into a chemiluminescence detector, where the nitrogen monoxide is detected. The chemiluminescence detector utilizes the gas-phase chemiluminescence of ozone and nitrogen monoxide, such that the detected nitrogen monoxide analogue signal forms a peak. To measure the TN concentration of the sample, the relationship between the TN concentration and peak area (calibration curve) is predetermined using a TN standard solution, to express the peak area as a ratio of the TN concentration. The measured values from the CN analyser (mg L^{-1}) were then converted into mg kg^{-1} following the formula below (equation 2-2);

$$\textbf{\textit{Extractable C or N}} = \frac{[(C \text{ or } N - AB) \cdot D \cdot V]}{W} \qquad \textbf{\textit{Equation}}\ 2-2$$

Where: C or N = measured C or N (mg L^{-1})

AB = average of blanks (mg L^{-1})

D = dilution factor

V = volume of extractant (mL)

M = mass of soil (g)

2.3.5 Water extraction (for analysis of extractable nutrients and PTEs in soil and fly ash)

The water extractable nutrients and potentially toxic elements (PTEs) were determined by extracting the equivalent weight of 2 g fresh soil or fly ash samples, with ultra-pure water in the ratio of 1:10. Soil or fly ash sample mixtures were shaken for 4 hours using an end-over-end vertical rotary shaker at 30 rpm and then filtered using qualitative filter papers (Fisher brand) and syringe filters (0.22 µm) to remove any precipitates. The extracts were then diluted with 50% nitric acid in the ratio of 9.6 mL of sample + 0.4 mL acid. This ratio and acid concentration were used instead of the more usual 2% concentration of nitric acid and ×10 dilution factor for ICP-MS analysis, to maximize the amount of sulphur in the extracted soil and fly ash samples because the S concentration in fly ash was below the lowest standard concentration during the ICP-MS analysis. The sample dilution was performed soon after sample extraction to reduce the effect of evaporation. A multi-elemental analysis of the diluted samples was then performed using ICP-MS (Section 2.3.8).

2.3.6 Ammonium nitrate extraction (for analysis of exchangeable nutrients and PTEs in soil and fly ash)

The exchangeable nutrients and the potentially toxic elements (PTEs) were determined by extracting the equivalent weight of 2 g fresh soil or fly ash samples with 1M NH_4NO_3 in the ratio of 1:10. Soil or fly ash sample mixtures were shaken for four hours on an end over end vertical rotary shaker at 30 rpm and then filtered using qualitative filter papers (Fisher brand) and syringe filters (0.22 µm) to remove any precipitates. The extracts were then diluted with 50% nitric acid in the ratio of 9.6 ml of sample + 0.4 ml acid. This procedure was followed for the same reason described in Section 2.3.5. The sample dilution was performed soon after sample extraction to reduce the effect of evaporation. Multi-elemental analysis of the diluted samples was then performed using ICP-MS.

2.3.7 Aqua regia digestion (for analysis of total nutrients and PTEs in soil and fly ash)

The total concentrations of nutrients and PTEs in soil and fly ash samples were determined by digesting the samples using aqua regia. The air-dried soil samples were ground in an agate planetary ball mill (Model PM400; Retch GmbH and Co., Germany). The soil samples were weighed in 50 mL 'DigiTUBEs'

then digested using aqua regia. Four replicates consisting of 0.4 g of soil or fly ash samples were digested in 1.0 mL HNO_3 and 3.0 mL hydrochloric acid in a 48-place Teflon-coated graphite block digester (Model A3, Analysco Ltd., UK) situated in a fume cupboard. The samples were heated at 95°C for 2 hours and 30 minutes then allowed to cool down for 10 minutes before making up to 10 mL with 6 mL ultra-pure water. During the digestion, DigiTUBEs were covered with transparent tops to reduce evaporation. Samples were then filtered through qualitative filter papers (Fisher brand) to remove any precipitate and stored un-refrigerated in 20 mL Universal sample tubes pending elemental analysis. The multi-elemental analysis was then performed by ICP-MS after diluting the digest with ultra-pure water in the ratio of 0.625ml + 9.375ml (×16 dilution factor). A dilution factor of 16 was used to ensure that sulphur was above the detection limit of the ICP-MS.

2.3.8 Multi-element analyses by ICP-MS

Multi-element analyses of diluted solutions (water and NH_4NO_3 extracts and aqua regia digests) were undertaken by ICP-MS (Thermo-Fisher Scientific iCAP-Q; Thermo Fisher Scientific, Bremen, Germany). The instrument was run in three operational modes, including (i) a collision-cell (Q cell) using He with kinetic energy discrimination (He-cell) to remove polyatomic interferences, (ii) standard mode (STD) in which the collision cell is evacuated and (iii) hydrogen mode (H_2-cell) in which H_2 gas is used as the cell gas. Samples were introduced from an autosampler (Cetac ASX-520) incorporating an ASXpress™ rapid uptake module through a PEEK nebulizer (Burgener Mira Mist). Internal standards were introduced to the sample stream on a separate line via the ASXpress unit and included Ge (10 µg L^{-1}), Rh (10 µg L^{-1}) and Ir (5 µg L^{-1}) in 2 % trace analysis grade (Fisher Scientific, UK) HNO_3. External multi-element calibration standards (Claritas-PPT grade CLMS-2 from SPEX Certiprep Inc., Metuchen, NJ, USA) included Ag, Al, As, Ba, Be, Cd, Ca, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Se, Sr, Tl, U, V and Zn, in the range 0 – 100 µg L^{-1} (0, 20, 40, 100 µg L^{-1}). A bespoke external multi-element calibration solution (PlasmaCAL, SCP Science, France) was used to create Ca, Mg, Na and K standards in the range 0-30 mg L^{-1}. Phosphorus, boron and sulphur calibration utilized in-house standard solutions (KH_2PO_4, K_2SO_4 and H_3BO_3). In-sample switching was used to measure B and P in STD mode, Se in H_2-cell mode and all other elements in He-cell mode. Sample processing was undertaken

using Qtegra™ software (Thermo-Fisher Scientific) utilizing external cross-calibration between pulse-counting and analogue detector modes when required.

All elemental concentrations (µg L^{-1}) were converted to mg kg^{-1} following the equation below (Equation 2-3);

$$Csoil = \frac{Csol - Cblank}{M\ soil} X\ Vol \qquad Equation\ 2-3$$

Where: C_{soil} = the elemental concentration (mg kg^{-1}) in the soil (or ash)

C_{sol} and C_{blank} = the concentrations (µg L^{-1}) in the soil (or ash) and blank extract/digests respectively

Vol = the volume of the digest/extractant (10 for aqua regia digested samples and 20 for water and ammonium nitrate extracted samples)

M_{soil} = the mass of soil digested (0.4 g for aqua regia and 2 g for water and ammonium nitrate extractions).

2.3.9 Quality control

All analyses were performed following previously published methods and local standard operating procedures, and some methods (e.g. enzyme assays, Chapter 5) were tested prior to application. All the experiments were carried out in controlled environment (growth rooms, constant temperature rooms or an incubator) and a randomized block design for each experiment was used to control any source of variation in these rooms/incubator. In each experiment, controls were included and treatments were replicated 4 times to minimize variations between samples and this was verified by the relatively small calculated standard errors for data sets.

In pot experiments, plants were watered with deionised water to avoid soil contamination with minerals from tap water, and in all chemical analyses, utra pure-water was used. For ICP-MS analyses, in-house calibration standards (KH_2PO_4, K_2SO_4 and H_3BO_3), internally introduced standards, external multi-elemental calibration standards (Claritas-PPT grade CLMS-2 from SPEX Certiprep Inc., Metuchen, NJ, USA) and a bespoke external multi-element

calibration solution (PlasmaCAL, SCP Science, France), plus incorporation of blanks were used for quality control.

For carbon and nitrogen analysis, certified reference materials such as aspartic acid, peat soil and tomato leaves were used depending on the material being analysed and were incorporated at regular intervals throughout each sample batch in addition to standards. For gas measurements in the GC, the gas standards with concentrations of 500 ppm for CO_2, 50 ppm for CH_4 and 500 ppb for N_2O (BOC limited, Surrey, UK) were used. Three standards were injected to flood the system prior to sample gas analysis and standards were injected after every 16 samples.

Other methods are chapter-specific and are described in the relevant chapters.

3 CHEMICAL CHARACTERIZATION OF COAL ASH FROM UK, CZECH REPUBLIC AND TANZANIA WITH RESPECT TO AGRICULTURAL USE

3.1 INTRODUCTION

Coal is the carbonaceous fossil fuel most extensively used around the world as a source of energy by industrialized and developing countries. Following the sustained increase in prices of oil and natural gas, the use of coal as a fuel in electricity generation seems to be economically attractive, especially in those countries rich in coal resources such as China, India and USA (Lior, 2010). Commercial burning of coal for energy production usually produces large quantities of ash; globally, ash accounts for 5–20% by weight of feed coal (Yao et al., 2015). The industrial by-products of coal combustion in power plants include fly ash, bottom ash, boiler slag and gypsum from flue gas desulphurization (Jala and Goyal, 2006): they are collectively known as coal combustion by-products (CCPs) or coal solid wastes. Fly ash and bottom ash are the common ash by-products from power plants, with the proportions of 85–95% and 5–15% by weight of the total ash generated respectively (Yao et al., 2015).

3.1.1 Differences between fly ash and bottom ash

Fly ash refers to the fine particles which are captured from flue gas and collected by electrostatic or mechanical precipitation while, in contrast, bottom ash refers to the ash that is collected at the bottom of the boiler during coal combustion and which is mechanically removed (Jala and Goyal, 2006). Physically, fly ash is fine-textured while bottom ash is coarse-textured. Generally, the chemical properties of both types of ash are similar (Tharaniyil, 2013), except bottom ash has a higher carbon content than fly ash.

3.1.2 General fly ash characteristics

Regarding the chemical composition, fly ash is an amorphous ferroalumino-silicate with a matrix similar to soil. The major part of fly ash is composed of silica, aluminium and iron oxides together with other constituents which always vary in their amount, including carbon, calcium, magnesium and sulphur (Shaheen et al., 2014). Singh et al. (2014) reported the proportion of fly ash by composition where 95-99%, is Si, Al, Fe and Ca oxides and 0.5-3.5% is Na, P, K and S with the remaining proportion consisting of trace elements. Based

on the American Society for Testing Materials (ASTM 2000), fly ash can be divided into two classes; class F and C. Class F fly ash is normally produced from burning anthracite or bituminous coal while Class C fly ash is normally produced from lignite or sub-bituminous coal. Class F fly ash is characterized by lower lime content (1-12% Ca), lower alkaline content (combined Na and K) (Seshadri, 2010), high sulphur content, and >70% silica, aluminium and iron oxides (Adriano et al., 2002). In contrast, Class C fly ash is characterized by a higher lime content (30-40% Ca), higher alkaline (combined Na and K) (Seshadri et al., 2010), low sulphur content and 50-70% silica, aluminium and iron oxides (Adriano et al., 2002).

Physically, fly ash consists of fine, powdery particles that are predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature (Singh et al., 2014). The particle size distribution of fly ash ranges from 0.01-100 μm (Pandey and Singh, 2010). From the perspective of plant nutrition, fly ash comprises almost all the essential macro- and micro-nutrients required by plants (i.e. Ca, P, Mg, Na, K, Cu, Fe, Mn, Mo, Zn and B) except nitrogen, which tends to oxidize during the coal combustion process (Singh et al., 2014). The pH values of fly ash vary from 1.2 to 12.5, with most ashes tending toward alkalinity (Page et al., 1979; Kolbe et al., 2011; Yao et al., 2015). Since all the naturally existing elements tend to occur in coal, fly ash also contains many potentially toxic elements such as As, Cr, Cd, Pb, Ni, Ba, Cu, V and Zn (Sikka and Kansal, 1994; Goodarzi, 2006) which may be of great environmental concern. Coal also contains naturally occurring radionuclides such as ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K (Sahu et al., 2014; Ozden et al., 2017) and during coal combustion, these radionuclides tend to concentrate in coal ash at significantly higher concentrations than in feed coal. Sahu et al. (2014) noted the highest concentration of radionuclides in bottom ash and fly ash compared with the original feed coal which was attributed to the association of radionuclides with the remaining mass when the carbonaceous components are oxidised. From this study, comparisons of radionuclide concentrations between these ashes revealed higher concentrations of radionuclides in fly ash than in bottom ash due to an inverse relationship between radionuclide enrichment behaviour and ash particle size.

3.1.3 Geology and characteristics of coal

Based on the stages of transformation of coal from peat, which also correspond to coal maturity, there are four types or ranks of coal (Seshadri, 2010);

- lignite being the lowest rank,
- sub-bituminous,
- bituminous and
- anthracite.

Each of these coals varies in terms of calorific value, chemical composition, ash content and geological origin. Haering, (1991) reported a higher content of Fe, K, S and lower content of Mg and Ca in bituminous coals from the eastern US than that from sub-bituminous and lignite coals from western US. Also, the low pH and higher concentrations of trace elements such as As, Cd, Cr, Pb, V and Zn were observed in bituminous coals of the eastern US. High sulphur and low sulphur bituminous coals have also been reported from Canada (Goodarzi, 2006). The pH of the coal fly ash depends mostly on the sulphur and CaO content of the parent coal being burnt (Shaheen et al., 2014; Adriano et al., 2002). The fly ash produced from coals with high sulphur content is likely to be acidic, whilst ash from low sulphur coals is likely to be alkaline.

The geology of Tanzanian coal is Lower Permian and it is ranked as bituminous (Semkiwa et al., 2003). These are black coals characterized by highly volatile C, high ash content (22-49 wt.%), highly variable sulphur contents (0.17-9.2 wt.%) (Semkiwa et al., 2003) and a high calorific value ranging from 20,093 KJ kg^{-1} to 29,501 KJ kg^{-1} (Mashingo et al., 2011).

In the Czech Republic, a fly ash sample was collected from Počerady power plant which burns coal from Vršany coal mine, adjacent to the town of Most. The sedimentary basin in which the Vršany coal mine lies is of Tertiary age, formed mainly during the Miocene era, and the coal is ranked as lignite (lowest/younger coal rank). These coals are characterized by lower C content than black coal and lower calorific value of 10-18 MJ t^{-1} (Rečková et al., 2017). The chemical composition of the coal combustion products (CCP) depends on the type of feed coal, percentage incombustible matter in the coal, sulphur content, the pulverization process, furnace types, the efficiency of the combustion process, storage and handling (Jala and Goyal, 2006; Tharaniyil, 2013). Therefore, the characteristics of ash derived from anthracite,

bituminous, sub-bituminous and lignite coals are likely to differ depending on the chemical composition of these individual grades of coal.

In Tanzania, the main source of energy in many industries is bituminous coal but no information is available regarding the potential use or disposal of ash from these industries. Globally, ash disposal is a great concern due to a significant increase in coal consumption for electricity production worldwide (Yao et al., 2015). Since coal ash contains plant nutrients, has a generally alkaline pH (Adriano et al., 1980; Singh et al., 2014; Shaheen et al., 2014) and is reported to improve plant growth and yields (El-Mogazi et al., 1988; Pathan et al., 2001; Kalra et al., 2003; Nayak et al., 2015) when used to amend soils, there is much interest in using these materials as a soil conditioner. Having a higher concentration of all elements (except N) than soils (Sharma, 2006), fly ash can be used as a potential soil amendment of agricultural soils to improve the fertility status of nutrient-deficient soils and thus, to increase crop yields. Increases in plant nutrients such as Ca, Mg, K, Zn, Fe, Mn and Cu after fly ash applications to soils have been reported in many studies (Adriano et al., 2002; Kalra et al., 2000, 2006; Yeledhalli et al., 2007) due to the presence of these nutrients in fly ash. In addition, incorporation of an alkaline fly ash to acidic soils in most cases will increase the soil pH, thus ameliorating acidity and improving nutrient availability. However, the presence of potentially toxic elements and low-level radionuclides could be a limiting factor in determining the suitability of some sources of fly ash as soil amendments (Page et al., 1979; Adriano et al., 1980).

Knowledge of chemical characteristics of fly ash is important in determining potential utilization in agriculture, horticulture and forestry and in predicting the environmental hazards such use poses (Sikka et al., 1994). The analyses reported in this Chapter were undertaken with the aim of evaluating the spatial and temporal variation of fly ash from coal-fired power plants in the UK, the Czech Republic and Tanzania, with respect to chemical characteristics which may be beneficial or potentially toxic if the ash were to be used as an agricultural amendment. Results are compared to published data and are discussed in this Chapter. The specific objectives were;

i) To evaluate and compare the chemical and elemental composition of ash collected from coal-fired power plants in the UK, the Czech Republic and Tanzania.

ii) To compare the results of chemical and elemental composition of ash collected from the UK, the Czech Republic and Tanzania to previously published data.

iii) To compare the chemical and elemental composition of ash between two batches of ash from the UK and two batches of ash from Tanzania collected at different time points.

iv) To evaluate and compare the extractability of nutrients and PTEs from coal ashes in order to account for their bioavailability when applied to soil.

3.2 MATERIALS AND METHODS

3.2.1 Ash sample collection in the UK, the Czech Republic and Tanzania

In the UK, two batches of ash samples were collected from Ratcliffe-on-Soar Power plant in Nottingham. In Tanzania, two batches of coal ash were collected from 21st Century Textile Industry in the Morogoro region. In the Czech Republic, ash was collected from Počerady power station situated between the towns of Louny, Zatec and Most. For more details refer to Chapter 2 (Section 2.2). For clarification, the UK and Czech Republic ashes were fly ashes and the Tanzania ashes were bottom ashes.

3.2.2 Analysis of pH, total and extractable C, N, macro- and micro-elements

Please refer to Chaper 2 (Section 2.3) for full methodology.

3.2.3 Determination of radionuclide activities in coal ash samples

A high-resolution gamma-ray spectrometry system consisting of two high-purity germanium (HPGe) detectors was used to determine the activity concentrations of radionuclides in ash samples collected from the UK, the Czech Republic and Tanzania. The analytical procedure was as follows:

3.2.3.1 Preparation of samples

Before counting ash samples by gamma-ray spectrometry, dried and homogenised ash samples were packed into plastic Petri dishes of 5.4 cm diameter. The internal volume of the Petri dish was completely filled with sample and the dish plus loose-fitting lid were sealed using Parafilm. Counting time per sample was 24 hours.

3.2.3.2 Calculation of activity concentrations of ^{210}Pb, ^{228}Ac, ^{226}Ra and ^{40}K

Activity concentrations of ^{210}Pb, ^{228}Ac, ^{226}Ra and ^{40}K were directly calculated using the equation;

$$Bq(\gamma) = \frac{cps}{\varepsilon I W} \qquad \textbf{Equation 3-1}$$

Where Bq = calculated activity concentration of ash sample (Bq kg^{-1})

cps = counts per second obtained from the area of the gamma-ray peak of interest

I = gamma ray intensity of the peak of interest (0.04 for ^{210}Pb; 0.36 ^{228}Ac; 0.04 ^{226}Ra and 0.11 for ^{40}K)

W = weight of sample (kg)

ε = efficiency of detection of the peak of interest

The efficiency of detection for each gamma-ray peak of interest was determined using a calibrated mixed gamma-ray standard obtained from the National Physical Laboratory, Teddington (UK), prepared in a standard matrix of identical geometry to the coal ash samples.

3.2.4 Statistical analysis

Statistical analyses were performed using Genstat 17th Edition (VSN International, Hemel Hempsted, UK). A generalized one way analysis of variance was conducted on all parameters (pH, %C, %N, extractable C, extractable N, total nutrients, total PTEs, extractable nutrients and extractable PTEs) using fly ash type (based on country) as the main factor. Normality was tested by plotting residuals against expected normal quantiles and post-hoc

comparisons between means were based on Tukey's test at 0.05 probability level.

3.3 RESULTS

3.3.1 pH, total C and N concentrations of the ash

The chemical properties of five coal ash samples collected from the United Kingdom (two sample batches, UK1 and UK2, coded according to collection date), the Czech Republic (CR) and Tanzania (two sample batches, TZ1 and TZ2, also coded according to collection date) are presented here. There was a significant difference in pH between ash from different sources (Figure 3-1; $p<0.001$) with values ranging from pH 4.2 to pH 12.3. The highest pH was recorded in UK1 ash and the lowest pH in TZ1 ash; the general trend was UK1>UK2>TZ2>CR>TZ1.

The total C and N in all ash samples ranged from 5.24-31.94% and 0.003-0.47%, respectively. The highest concentrations of both C and N were recorded in Tanzanian ash. Concentrations of both elements were similar in the UK and CR ashes and lower than in the Tanzanian ashes (Figure 3-1; $p<0.001$).

Despite the higher concentration of total C in the Tanzanian ashes, these yielded the lowest concentration of extractable C, with the highest concentration extracted from the UK ashes (Figure 3-1; $p<0.001$). There were no significant differences between the Tanzanian and Czech Republic ashes.

Total extractable N was highest from the TZ1 ash compared to all other ash sources, whilst no significant differences in total extractable N were noted for CR, TZ2 and UK2 ashes (Figure 3-1; $p<0.001$). UK1 ash had a significantly lower total extractable N compared to the CZ and TZ1 ashes.

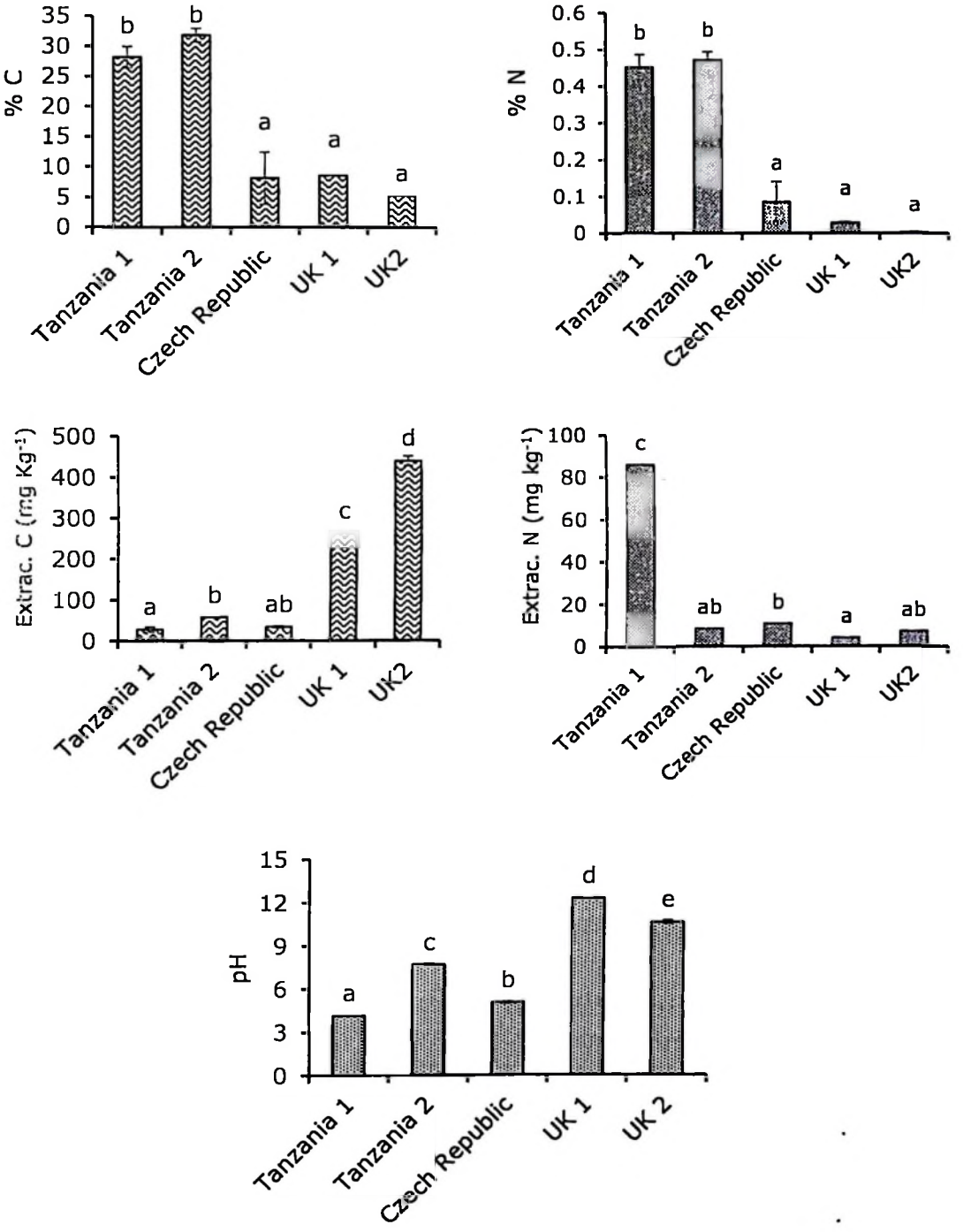

Figure 3-1: *Chemical properties of coal ash samples collected from UK, the Czech Republic and Tanzania. Values given are means of four replicates ± standard errors. Total extractable C and N were extracted by 0.5M K_2SO_4 1:5 ratio. Columns similarly superscripted are not significantly different (Tukey's Test). Total extractable C = sum of total extractable organic carbon (TOC) and inorganic carbon (IC).*

3.3.2 Total nutrient concentrations within the ashes

The UK ash contained the highest concentration of total phosphorus (following acid digestion), followed by the Tanzanian ash; the CR ash had the lowest P concentration (Figure 3-2; $p<0.001$). The highest concentration of total potassium was present in the TZ2 ash followed by the UK2 ash, but the total K concentration in TZ1 and UK1 ash was almost the same (Figure 3-2; $p<0.001$). The general trend for K in all ash samples followed the order TZ2>UK2>UK1>TZ1>CR.

The total concentrations of Ca, Mg and B showed similar trends with each ash type being significantly different from each other (Figure 3-2; $p<0.001$), with the lowest concentrations in the Tanzanian ashes. The general trend was UK2>UK1>CR>TZ2>TZ1. Boron concentration in the TZ1 ash was below detection limit and is therefore not shown in Figure 3-2. The highest total sulphur concentration was measured in the TZ1 ash followed by UK2 ash, but the S was similar in the UK1 and TZ2 ashes (Figure 3-2; $p<0.001$). The concentration of sulphur in the CR ash was below the detection limit.

The total concentrations of P, K, Ca, Mg, B and Mn in the ash samples analysed in this study were within published ranges except for K, which was lower than published K concentrations for USA, Indian and other European fly ash (Table 3-1).

3.3.3 Extractable nutrient concentrations within the ashes

The water-extractable nutrients in all ash samples are shown in Figure 3-3. Generally the water-extractable P in all ash samples studied was very low or negligible except in Tanzania2 ash which had significantly higher extractable P than all other ashes (Figure 3-3; $p<0.001$). The highest concentration of water-extractable K was measured from the UK2 ash followed by the Tanzania2 ash, but the water-extractable K concentrations in CR and UK1 ash were almost the same (Figure 3-3; $p<0.001$). The general trend of K in all ash was UK2>TZ2>CR=UK1>TZ1.

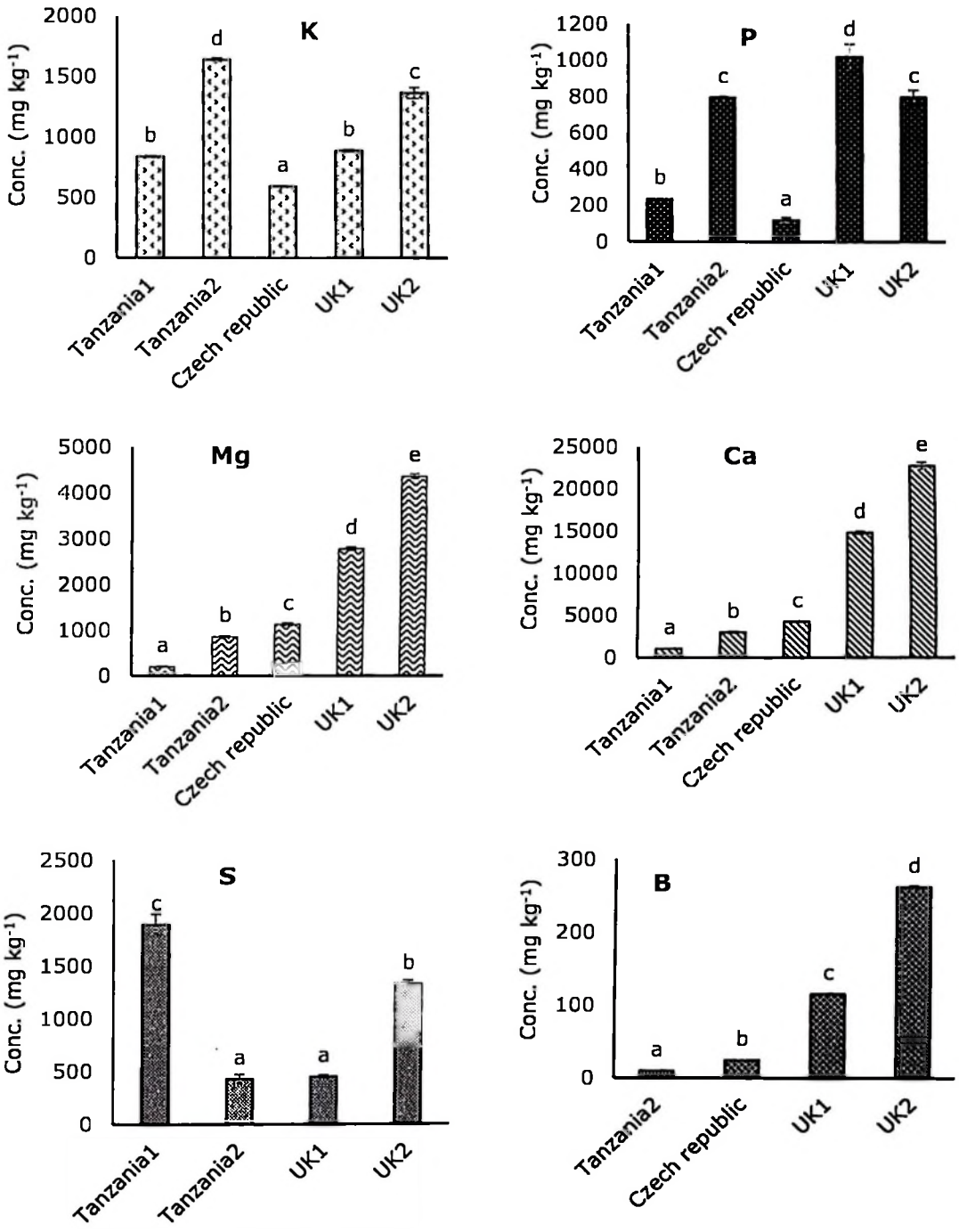

Figure 3-2: *Total concentrations (mg kg^{-1}) of nutrients in ash from the UK, Czech Republic and Tanzania. Values given are means of four replicates ± standard errors. Columns similarly superscripted are not significantly different (Tukey's Test). S content in Czech Republic ash and B content in Tanzania1 ash are not presented because they were below the detection limit.*

The highest concentrations of water-extractable Ca, Mg, and S were recorded in UK1 ash followed by TZ1 ash; the trends were UK1>TZ1>UK2=TZ2>CR for Ca; UK1>TZ1>UK2>TZ2=CR for S and UK1>TZ1>TZ2=CR>UK2 for Mg. Water-extractable B was higher in the UK ash than in other ash samples and the general trend was UK1>UK2>CR>TZ1=TZ2. The differences between the water-available concentrations of Ca, Mg, S, and B across the ash types were significant (Figure 3-3; $p<0.001$ for each extractable element).

The NH_4NO_3 extractable nutrient concentrations (also referred to as 'exchangeable' nutrients here) are shown in Figure 3-4. Only the Tanzania2 ash yielded a significant concentration of exchangeable P. Apart from the TZ2 and UK1 ash, exchangeable P in other ash samples was below the detection limit. The highest concentration of exchangeable K was measured in from the UK2 ash, followed by TZ2 ash, but the general trend was UK2>TZ2>CR>UK1>TZ1. Ash was a significant factor in ANOVA for exchangeable P and K concentrations (Figure 3-4; $p<0.001$ for both elements).

The concentrations of exchangeable Ca and Mg were different across all ashes (Figure 3-4; $p<0.001$ for each element), with the UK ashes having higher concentrations than the Tanzania ashes. The general trend was UK ash>TZ ash>Czech Republic ash. Higher concentrations of exchangeable S and B were recorded in UK2 ash than in other ash sources. Exchangeable B from Tanzania ashes was undetectable. The trends followed the order of UK2>TZ1>UK1>TZ2=CR and UK2>UK1>CR>T1=TZ2 for S and B respectively.

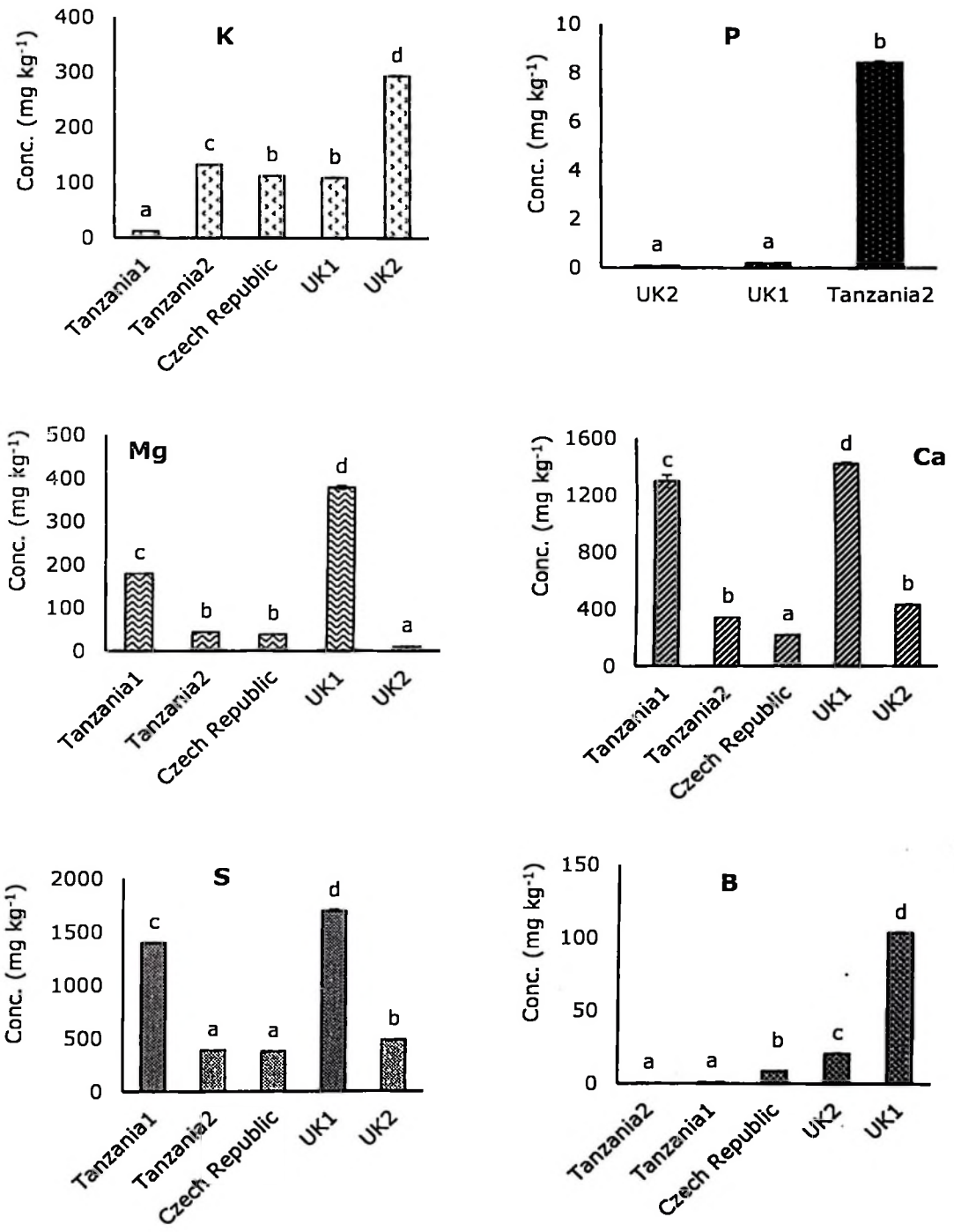

Figure 3-3: *Water-extractable concentrations (mg kg^{-1}) of nutrients in ash from the UK, Czech Republic and Tanzania. Values given are means of four replicates ± standard errors. Columns similarly superscripted are not significantly different (Tukey's Test). P content in Tanzania1 and Czech Republic ashes is not presented because it was below detection limit.*

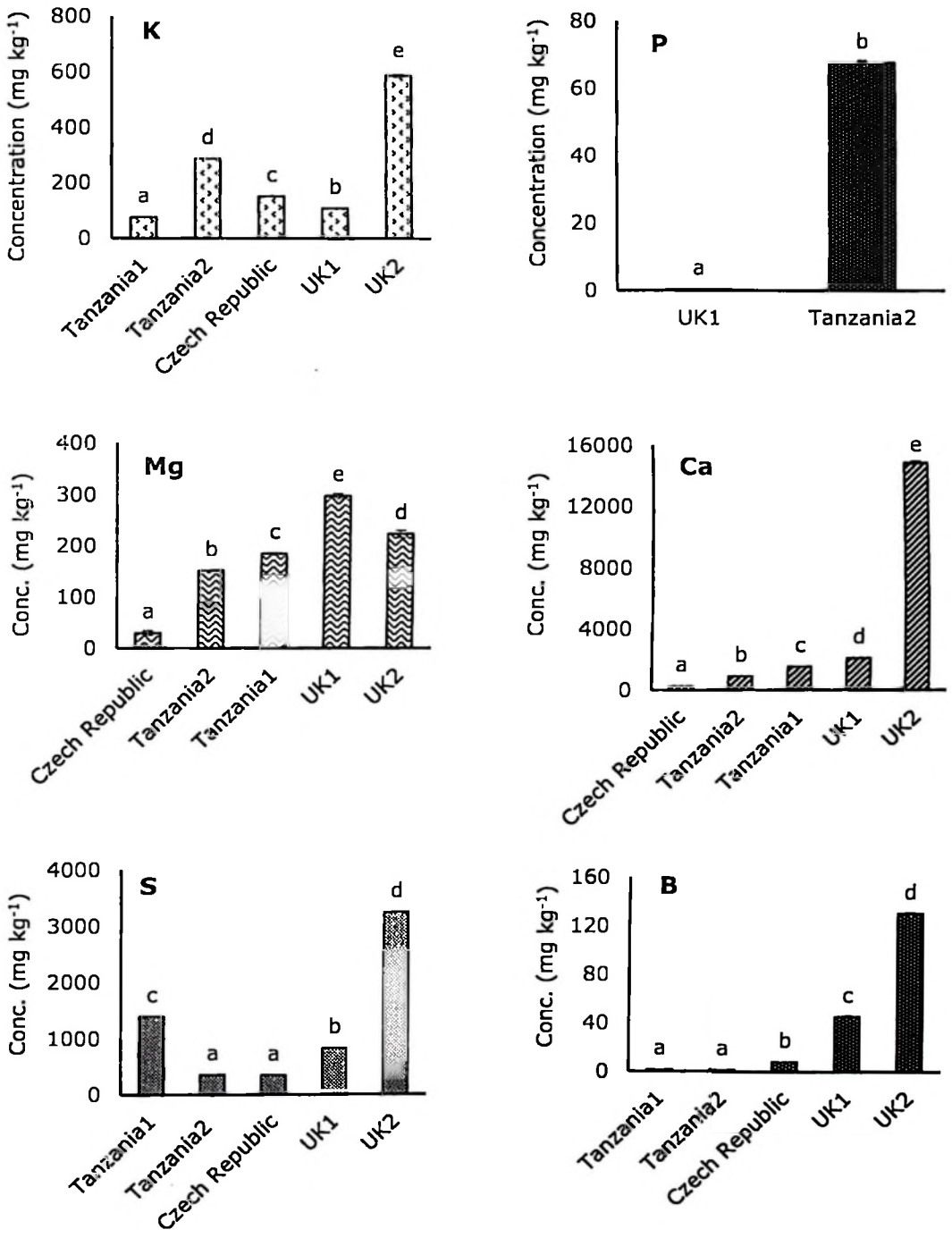

Figure 3-4: *Exchangeable concentrations (mg kg^{-1}) of nutrients in ash from UK, Czech Republic and Tanzania. Values given are means of four replicates ± standard errors. Columns similarly superscripted are not significantly different (Tukey's Test). P content in Tanzania1, UK2 and Czech Republic ashes is not presented because it was below detection limit according to the standards during ICP analysis.*

Table 3-1: *Comparison between the total concentrations of nutrients (mg kg^{-1}) in fly ash from published sources and the experimental data*

	Selected total elements in fly ash (mg kg^{-1})				
	Punshon et al., 2002 (USA fly ash)	Adriano et al., 2002 (USA fly ash)	Sharma and Kalra, 2006 (Indian ashes)	Mureno et al., 2005 (European fly ashes)	**Experimental data**
P	956–1002	1388–1432	400-8000	436.3-7417.4	122-1023
K	21000-23000	20800-21900	1500-3.5 $X10^4$	3320.4-33204	594-1643
Ca	5300-5700	13000-14000	1100-221000	3572-136500	1054-22850
Mg	4977–5494	5179–5426	400-76000	3618-22914	201-4353
S	3.0–3.6	19.9–21.1	10-618	NR	10-261
Mn	392–423	282–305	58-3000	232.4-775	39-450

For European ash (Mureno et al., 2005), data were converted from oxides to elemental concentrations by dividing the values of K_2O, CaO, MgO and MnO by the factors 0.8301, 0.7143, 0.603 and 0.7745 respectively and multiplying by a factor of 2.2919 for P_2O_5
NR = Not reported

3.3.4 Total potentially toxic elements within the ashes

Concentrations of total potentially toxic elements (PTEs) in all ash samples are shown in Table 3-2. The total concentrations of the PTEs Zn, Cr, Ni, As, Cd, and Pb were significantly higher in UK ash than in other ash samples studied, but the concentrations of Cu in UK and Tanzanian ashes were similar (Table 3-2; $p<0.001$ for each PTE). The general trend for Zn, Ni and Pb followed the order UK ash>TZ ash>CR ash while for Cr, As and Cd the trend was UK ash>CR ash>TZ ash. ANOVA showed a significant difference in total concentrations of Zn, Ni, Pb, Cr, As, Cd and Cu between all ash samples collected (Table 3-2; $p<0.001$ for each PTE). The total concentration of Co was significantly higher in Tanzanian ashes than in other ashes collected and the general trend was Tanzanian ash>UK ash>CR ash (Table 3-2; $p<0.001$).

Comparing the total concentrations of all PTEs in the studied ash with the data published from US, South Africa, India and Europe for fly ash (Table 3-3), all PTEs were either slightly lower, or within, the ranges published.

Table 3-2: *Total concentrations of PTEs (mg kg^{-1}) in ash collected from the UK, the Czech Republic and Tanzania*

Ash type based on country	Cu	Zn	Cr	Co	Ni	As	Cd	Pb
UK1	27 ±0.7^{b}	331.4±2.7^{c}	23.17±0.3^{c}	8.3 ±0.1^{b}	24.2 ±0.2^{b}	66 ±1^{d}	17 ±0.5^{c}	546 ±15.2^{c}
UK2	39 ± 0.6^{c}	440± 3.5^{d}	39 ±0.5^{d}	13.5 ±0.5^{c}	41 ±0.3^{d}	97.4 ±1.4^{e}	15±0.4^{b}	364.1±7.4^{b}
Czech Republic	16 ±0.3^{a}	18 ±0.4^{a}	11.2 ±0.4^{b}	6.4 ±0.1^{a}	20 ±0.4^{a}	11 ±0.3^{c}	0.15 ±0^{a}	2.1 ±0.1^{a}
Tanzania 1	36 ±1.4^{c}	74.3 ±2.3^{b}	11.1 ±0.2^{b}	21 ±0.3^{e}	31.1 ±0.6^{c}	6 ±0.1^{b}	0.5 ±0.02^{a}	18 ±0.6^{a}
Tanzania 2	24.15±0.3^{b}	25 ±1.7^{a}	8 ±0.3^{a}	18 ±0.8^{d}	25 ±1.1^{b}	2 ±0.04^{a}	0.1 ±0.01^{a}	5.2 ±0.2^{a}

- *Values given are means of four replicates ± standard* errors.
- *Values followed by the same letter within a column are not significantly different (Tukey's Test, $p<0.05$).*

Table 3-3: *Total concentrations of potentially toxic elements (mg kg^{-1}) in coal combustion products as reported in the literature*

Coal type	Ash type	Cu	Zn	Cr	Co	Ni	As	Cd	Pb	Source
Bituminous **(USA)**	Fly ash	45-1452	25-2880	11-651	7.3-124	23-353	8.1-1385	<0.11-17	13-2120	EPRI report, 2014
	Bottom ash	20-146	3.8-717	<24-4710	NA	<12-1267	<1.3-56	<5.5	<2.1-843	
Bituminous **(South Africa)**	Fly ash	18.76	20.03	72.97	5.45	13.94	16.61	0.16	24.38	Ayanda et al., 2012
Lignite **(India)**	Fly ash	119.8	19.85	44.15	19.81	28.31	0.19	1.28	55.07	Ram et al., 2015
	Bottom ash	70.02	11.35	61.16	18.87	12.4	0.12	1.19	110.6	
Europe	Fly ash	ND	70-924	47-281	ND	49-377	22-162	1-6	40-1075	Moreno et al., 2005

For the report by Electric Power Research Institute (EPRI 2014), data were collected from different power plants for 30 years of EPRI research, analyzed and compiled together in this report. ND=not determined.

Table 3-4: *Water-extractable and exchangeable PTE concentrations in ash samples collected in the UK, the Czech Republic and Tanzania*

Water-extractable PTEs (mg kg^{-1})								
Ash type based on country	**Cu**	**Zn**	**Cr**	**Co**	**Ni**	**As**	**Cd**	**Pb**
UK1	0.001 ±0^{a}	BDL	0.3±0.001^{c}	0.0002 ±0^{a}	BDL	0.23 ±0^{c}	0.01 ±0^{b}	0.002±0^{a}
UK2	0.1 ± 0.01^{b}	0.01± 0^{a}	0.5±0.001^{d}	0.0004 ±0^{a}	BDL	0.13 ±0^{b}	0.01±0^{b}	0.003±0^{b}
Czech Republic	0.3 ±0.02^{d}	0.8 ±0.02^{b}	BDL	0.1 ±0^{b}	0.4±0.01^{b}	0.001±0^{a}	0.02 ±0^{b}	0.001 ±0^{a}
Tanzania 1	0.15±0.003^{c}	14 ±0.13^{c}	0.003 ±0^{a}	4.3±0.04^{c}	4.5±0.04^{c}	BDL	0.1 ±0.001^{d}	0.003±0^{b}
Tanzania 2	0.05±0.01^{b}	0.03±0.04^{a}	0.005 ±0^{ab}	0.01 ±0^{a}	0.01±0.01^{a}	2.14±0^{b}	0.04±0^{a}	0.001±0^{a}
Exchangeable PTEs (mg kg^{-1})								
Ash type based on country	**Cu**	**Zn**	**Cr**	**Co**	**Ni**	**As**	**Cd**	**Pb**
UK1	0.3 ±0.01^{b}	1.1±0.04^{c}	0.3 ±0.01^{b}	BDL	BDL	0.6±0.01^{d}	0.2 ±0.001^{d}	BDL
UK2	3.4 ± 0.03^{c}	9.1± 0.1^{d}	1.4 ±0.01^{c}	BDL	0.2 ±0^{a}	0.4 ±0^{c}	0.3±0.001^{e}	BDL
Czech Republic	0.3 ±0.01^{b}	1 ±0.1^{b}	0.003 ±0^{a}	0.14 ±0^{a}	0.5 ±0^{c}	0.01 ±0^{a}	0.02 ±0^{b}	0.01 ±0^{a}
Tanzania 1	BDL	13 ±0.04^{e}	0.001 ±0^{a}	4.1 ±0.2^{b}	4.4 ±0.01^{d}	0.01 ±0^{a}	0.1 ±0^{c}	0.01±0.01^{b}
Tanzania 2	0.1±0.1^{a}	0.2±0.01^{a}	0.001 ±0^{a}	0.03 ±0^{a}	0.2±0.003^{b}	0.23 ±0^{b}	0.002 ±0^{a}	BDL

Values given are means of four replicates ± standard errors. BLD= below detectable limit based on standards during ICP analysis. Values followed by the same letter in a column are not significantly different (Tukey's Test, P<0.05).

Generally, the extractability of PTEs in both ammonium nitrate (exchangeable) and in water (Table 4-4) was very low or negligible. Zn, Co and Ni were only extractable in Tanzania1 ash (for both ammonium nitrate and water extractions) while Cu, Zn and Cr were only extractable in UK2 ash (ammonium nitrate extraction). Besides the low extractability of these PTEs in water and ammonium nitrate, concentrations were significantly different between the ash types (Table 4-4; $p<0.001$ for each extracted PTE).

3.3.5 Radionuclide activity concentrations in coal ash

Results for the radionuclide activity concentrations determined in coal ash samples from the UK, the Czech Republic and Tanzania are presented in Table 3-5. Four radionuclides, ^{210}Pb, ^{228}Ac, ^{226}Ra and ^{40}K, were measured in the ash samples. The general ranges of radionuclide concentrations (Bq kg^{-1}) in all 5 ashes were 29.0 ±5 - 137.6 ±6.4 for ^{210}Pb, 46.2 ±0.4 - 86.0 ±0.4 for ^{228}Ac, 131.7 ±10 - 278.5 ±11.3 for ^{226}Ra and 176.6 ±15 - 524.4 ±16.1 for ^{40}K.

Table 3-5: *Activity concentrations of radionuclides in coal ash samples collected from the UK, the Czech Republic and Tanzania (Bq kg^{-1})*

Ash type	Density (g cm^{-1})	^{210}Pb	^{228}Ac	^{226}Ra	^{40}K
Tanzania 1	0.72	126.7±6	73.1 ±3.1	152.3 ±9.4	176.6 ±15
Tanzania 2	0.68	29.0 ±5	75.9 ±3.1	131.7 ±10	248.6 ±14.3
UK 1	0.78	83.4 ±4.7	86.0 ±0.4	278.5 ±11.3	500.8 ±18
UK2	0.75	137.6 ±6.4	46.2 ±0.4	261.3 ±11	497.3 ±18
Czech Republic	0.93	81.2 ±4.7	62.5 ±0.4	149.5 ±8.3	524.4 ±16.1

The errors presented for each radionuclide are the analytical standard deviation and not from replications.

3.3.6 Temporal comparison of ashes collected from Tanzania and the UK

Comparing the nutrient composition of the two batches of ash collected in the UK, it was found that for all nutrients studied (P, K, Ca, Mg, S, and B), the total concentrations of these elements were higher in the UK2 than the UK1 batch of ash except for P (Figure 2-2; $p<0.001$ for each nutrient). The total %C and %N was the same in both UK ashes, but extractable N was also higher in the UK2 than in the UK1 sample (Figure 1-1). The ash pH and extractable C were significantly higher in the UK1 than in the UK2 ash (Figure 1-1; $p<0.001$).

Regarding PTE concentrations in these ashes, the total concentrations of all the PTEs studied (As, Co, Cr, Cu, Ni, Se, Zn, Cd and Pb) were also higher in the UK2 ash than in the UK1 sample, except for Cd and Pb (Table 2-1; $p<0.001$ for each PTE). Besides the highest PTE concentrations in UK2, only Cu, Zn and Cr were extractable in ammonium nitrate and the PTE extractabilities from UK1 ash were very low, or below the detection limit.

For Tanzanian ash, the total concentrations of all nutrients studied (P, K, Ca, Mg, S, and B) were significantly higher in the TZ2 batch than in the TZ1 ash, except for S (Figure 2-2; $p<0.001$ for each nutrient). However, the total concentrations of all the PTEs studied (As, Co, Cr, Cu, Ni, Se, Zn, Cd and Pb) were significantly higher in the TZ1 ash than in the TZ2 batch, except Cd and Pb which were the same in both ashes (Table 2-2; $p <0.001$). Also, the total %C and %N were the same in both ash batches. The pH and extractable C were higher in the TZ2 ash than TZ1 sample, while the extractable N was higher in TZ1 than TZ2 ash.

3.4 DISCUSSION

3.4.1 Variation between properties of coal ash from the UK, the Czech Republic and Tanzania

Generally, the results from this experiment have shown a high variation in coal ash properties between the countries where the ash samples were collected (UK, Czech Republic and Tanzania) and between sampling times for the ash collected from the same country (two batches of UK and two batches of Tanzania ash). This may be associated with the variability of parent coal characteristics depending on calorific value, chemical composition, ash content, and geological origin (Seshadri et al., 2010) for the coals combusted in these countries. French and Smitham (2007) noted variability of coal characteristics from Europe and East Asian countries which arose from different countries, different coal sources within the country and different coal properties within the same source. Coal from Tanzania and the Czech Republic were bituminous and lignite respectively, thus variation in properties of these coals together with the properties of the ash derived from these coals is to be expected.

3.4.1.1 Chemical properties of coal ash

The lower ash pH (4.2 and 5.1) noted in Tanzania1 and the Czech Republic ash may be linked to the low content of basic cations (Ca and Mg) noted in both ashes and the high content in Tanzania1 ash. Izquierdo and Querol (2012) noted a strong dependence of pH in ash-water mixtures on the amount of Ca and S in fly ash. Since S was below detectable limit in the Czech Republic ash, most likely due to its removal by the desulfurization process during coal combustion, the lower pH of this ash implies the presence of high S concentrations in the original lignite coal combusted. Matsi and Keramidas (1998) reported the existence of extremely acidic (pH 3-4) fly ash, though it was usually extremely alkaline (pH 10-12) due to the presence of hydroxides and carbonate salts of Ca and Mg in fly ash.

The higher pH value (7.7) of Tanzania2 ash in comparison to Tanzania1 (4.2) ash may be associated with a significantly higher content of basic cations (Ca and Mg) and a significantly lower S content in Tanzania 2 ash. In this study, the highest pH values (10.6 and 12.3) were noted in the UK ash. The alkalinity of these ashes may also be attributed to the low S content and high

concentrations of Ca and Mg, as previously noted. Sing et al. (2011) and Nayak et al. (2015) associated the alkalinity of Indian ashes to the low content of S in the parent coal and to the presence of high concentrations of hydroxides and carbonates of Ca and Mg.

Even though the %C and %N have been reported to be negligible in ash (Carlson and Adriano, 1993; Matsi and Keramidas, 1998), the %C of the ashes used in this study ranged from 5.2-32%. Variation in total %C between the ash samples studied here can be linked to the specific differences between the ash types: UK and CR ashes were fly ash (%C, 5.2-8.6) while Tanzanian ashes were bottom ash (%C, 28-32). Moreno et al. (2005) classified the %C of 23 European fly ashes as high (6.2-7.6%), intermediate (2.3-4.6%) and low (0.6-1.9%). Based on this classification, the %C in both the UK ash and the Czech Republic ash ranged from intermediate to high. Tharaniyil (2013) reported the similarity in chemical composition between these two ash types, though the C content is typically higher in bottom ash than in fly ash. This variation may also be associated with the differences in the parent coal of these ashes: Tanzanian coal is bituminous with a high percentage of fixed C (based on its rank), while Czech Republic coal is lignite with a low percent of fixed C (based on its rank). Coal in the UK is derived from various parts of the world thus its origin needs to be traced to know the coal type. Variations in total %N in the ash samples studied can be linked to variations in combustion conditions in power plants because N tends to be oxidized during combustion (Shaheen et al., 2014). Moreno et al. (2005) noted very low values of %N (0.02-0.14%) in fly ash collected from 23 European power plants. The slightly higher values of N noted in Tanzanian ash (0.45%) may also be linked to the quality of combustion conditions within the industry where the ash was collected.

The total extractable C was calculated by taking the sum of TOC and IC. In UK ash, the IC was higher than TOC while in Tanzanian and Czech Republic ashes, the TOC was higher than IC. The higher total extractable C in UK ash compared with other ashes in this study may be associated with the highest concentration of IC in these ashes.

3.4.1.2 Nutrient composition of coal ash

Total concentrations of some nutrients (P, Ca, Mg, and B) were higher in the UK ash than in the other ashes studied, though the highest K concentration was measured in Tanzania2 ash. Comparison of UK ash (fly ash) with Tanzanian ash (bottom ash) seems to contradict the similarities in chemical composition of fly ash and bottom ash reported by Tharaniyil (2013). However, similar findings regarding the higher elemental composition in fly ash than bottom ash was noted by Meij (1994). Cope and Dacey (1984) studied the relationship between coal ranks and fly ash major element chemistry specifically looking at basic oxides from nine power plants burning bituminous, sub-bituminous and lignite coals. They found the highest basic oxide content (CaO, MgO, K_2O, Na_2O and Fe_2O_3) in lignite coal (50-90%) followed by sub-bituminous coal (25-60) and, lastly, bituminous coal (5-35%). Since Na content (results not presented) and pH values were also high in UK ash, these ashes were probably from lignite or sub-bituminous coal. The lower Ca content in Tanzanian ashes compared with the other ashes in this study may be associated with low Ca content in the parent coal (bituminous). Tharaniyil (2013) reported the presence of lower Ca content in ash derived from bituminous coal than in ash derived from sub-bituminous coal and lignite.

Comparing the total concentrations of nutrients (P, K, Ca, Mg, B and Mn) in the ash samples studied and data from publications for USA, Indian and European fly ashes, all the nutrients were within the published range except for K.

3.4.1.3 Nutrient extractability from coal ash

The extractabilities of the nutrients P, K, Ca, Mg and B in water and ammonium nitrate from all collected ashes were low and highly variable. The mode of occurrence of an element in the parent coal, pH of the ash-water system (as a function of Ca content) and the concentrations of elements in fly ash are the major factors determining the solubility of elements from fly ash (Izquierdo and Querol, 2012). Limited solubility of P in all collected ash samples may be linked to its occurrence within the silicate matrix of fly ash, or as insoluble calcium phosphate (Izquierdo and Querol, 2012). Besides the highest total concentration of P noted in UK ash, limited extractability of P could be linked to pH (10 and 12.3) and higher concentration of Ca in these ashes. Gupta et al. (2012) reported the presence of higher P concentration in fly ash (400-8000

mg kg^{-1}), which was not readily available to the plant. The concentration of water-extractable P (8.5 mg kg^{-1}) from Tanzania2 was almost the same as the range (<1- 6 mg kg^{-1}) noted from European fly ashes (Moreno et al., 2005).

K and Mg tend to occur within the glassy matrix of the fly ash which may limit solubility (Izquierdo and Querol, 2012). The higher extractability of K noted in UK2 and TZ2 ashes than in UK1 and TZ1 in both ammonium nitrate and water extractions perhaps can be explained by the higher total concentration of K in these ashes. The higher extractability of Ca and Mg in UK ash than in other ashes studied may be linked to the prime mode of occurrence of Ca as lime, thus becoming highly soluble (Izquierdo and Querol, 2012), and to the dominance of Ca and Mg on fly ash exchange sites (Sikka et al., 1994). However, limited extractability from Czech Republic and Tanzanian ash could be associated with the Ca speciation (e.g. as unhydrite or calcite, which are relatively insoluble) and with limited solubility of Mg in water and in acidic fly ashes (for pH values above 4) (Kim et al., 2003). Alternatively, limited Ca extractability from the acidic ashes may be a reflection of its lower concentration within these ashes. The extractability of S from Tanzania1 ash may be linked to its association with the surface of fly ashes and thus easily solublized (even though the Tanzania1 ash is a bottom ash), and to the positive correlation with its total concentration (Izquierdo and Querol, 2012).

3.4.1.4 Potentially toxic elements in coal ash

The potential toxic elements (PTEs) Zn, Cu, Cr, Ni, As, Cd, and Pb were found in all ashes studied, but their total concentrations were higher in the UK ash than in the other ashes. Nalbandian (2012) showed that Ni, Co, Mn, Cu and Zn are among the trace elements that are usually retained in coal combustion by-products while As, B, Cd, Cr, Mo and Pb are among the trace elements that are partially retained in coal combustion by-products. Nalbandian (2012) categorized trace elements into two groups based on their enrichment in coal combustion products: i) As, Cd and PB were enriched in fly ash rather than bottom ash and ii) Mn, Co and Cr were present in equal concentrations in fly ash and bottom ash. When comparing the UK and Czech Republic ashes, PTE concentrations seem to vary depending on the ash type. Considering the UK and Czech Republic ashes as fly ash and Tanzania ashes as bottom ash, the results show that almost all PTEs were more prevalent in the fly ash than in the

bottom ash. Whether this is the result of enrichment is unknown because the original coal and corresponding fly/bottom ash are unavailable for analysis.

Goodarzi, (2006) noted the association of the PTEs As, Cd, Hg, Mo and Pb with sulphide minerals and these PTEs were high in fly ash derived from high S-containing coal.

Comparing the total concentrations of all PTEs in the ash studied here with the data published from the USA, South Africa, India and European fly ashes (Table 3-4), all PTEs were either slightly lower or within the range of published data. This slight variation could be related to variations in sample sizes. For example, for European ashes (Moreno et al., 2005), a total of 23 fly ash samples from different power plants were analyzed while in this experiment only 5 samples from 3 countries were analyzed.

3.4.1.5 Extractability of PTEs from coal ash

Besides the highest concentrations of PTEs noted in UK ashes compared with other ashes studied, the solubility of these PTEs (in both water and ammonium nitrate) was very low and negligible. In the UK2 ash, the PTEs Cu, Zn and Cr were only extractable by ammonium nitrate solution and not water. In contrast, the PTEs Zn, Co and Ni were extracted by both ammonium nitrate and water from Tanzania1 ash. Variations in the solubilities of PTEs in these ash samples may be linked to their pH as it was reported by Jegadeesan et al. (2008) that pH and geochemical distribution of metals are the principal factors determining metal solubility in coal fly ash. The lowest extractability of PTEs in UK ash contradicts the findings reported by Wang et al. (2006) and Jankowsk et al. (2006) regarding the higher solubility of metal from coal fly ash at lower and high pH and the lower solubility at neutral pH. However, this result may be related to the limited solubility of most cationic metals such as Pb, Cu and Ni due to the alkaline nature of fly ash reported by Kim (2006).

3.4.1.6 Radionuclide activity concentrations in coal ash

Activity concentrations of ^{226}Ra (149.5-278.5 Bq kg^{-1}) in fly ash collected from the UK and Czech Republic were within the range of fly ash produced in Greece (142-605 Bq kg^{-1}) (Papastefanou et al., 2010), but above the range of fly ash produced in India (60-105.7 Bq kg^{-1}) (Sahu et al., 2014). The activity

concentration of ^{210}Pb (81.1-136.7 Bq kg^{-1}) and ^{40}K (497.3-524.4 Bq kg^{-1}) of fly ashes collected from the UK and the Czech Republic were within the range for fly ash produced in Poland (43.5-264.3 and 448.5-615 Bq kg^{-1}) for ^{210}Pb and ^{40}K (Bem et al., 2002), respectively. Lower activity concentrations of ^{226}Ra and ^{40}K in Tanzanian ashes (bottom ash) than in UK and Czech Republic ashes (fly ash) are consistent with enrichment of radionuclides in fly and bottom ashes reported in earlier studies (Zielinski et al., 1998; Sahu et al., 2014 and Lauer et al., 2015). However, activity concentrations of ^{210}Pb in Tanzania1 ash were approximately the same as ^{210}Pb in fly ash from the UK and Czech Republic which perhaps implies that it was less volatile during the combustion process. Karangelos et al. (2004) related the variations in radionuclide enrichment processes in different types of coal ashes (fly ash and bottom ash) to the compositions and origins of coal, firing systems, furnace designs and furnace temperatures. ^{228}Ac is a daughter in the thorium series and information regarding its occurrence in coal combustion residuals is limited. Activity concentration of ^{228}Ac noted in this study (in both fly ashes and bottom ashes) may be linked to the association of thorium and its decay series radionuclides with inorganic materials such as ash matrix reported by Papastefanou (2010).

3.4.2 Temporal comparison of ashes from UK and Tanzania

The characteristics of two UK fly ash samples collected from the same power plant (Ratcliffe-on-Soar power plant in Nottingham) on two different occasions (January and July 2015) were highly variable. Nutrients, PTE composition and radionuclide activity concentrations of ^{210}Pb were higher in UK2 than in UK1 ash, while radionuclide activity concentrations of ^{228}Ac, ^{226}Ra and ^{40}K were higher in UK1 than UK2 ash. Even though the total %C and %N were similar in both ashes (UK1 and UK2), variability in characteristics like pH, nutrient composition (P, K, Ca, Mg, S and B), PTE composition (As, Co, Cr, Cu, Ni, Se, Zn, Cd and Pb) and radionuclide activity concentrations of ^{210}Pb, ^{228}Ac, ^{226}Ra and ^{40}K shows that the sampling period influenced the ash characteristics. Since coal combusted at this power plant comes from various parts of the world, the variation in fly ash characteristics was probably attributable to variations in the parent coal combusted (Jala and Goyal, 2006; Tharaniyil 2013; Karangelos et al., 2004).

The two Tanzanian ash samples (TZ1 and TZ2) were collected from the same industry (21st Century Textile Industry in Morogoro) in April 2015 and January 2017, respectively. Even though this industry burns bituminous coal from the same coal mine (Ngaka coal mine in Ruvuma region Tanzania), the characteristics of the ash collected at different times were highly variable. The %C and %N were similar in ash collected on both occasions, but the nutrient composition and pH was higher in TZ2 ash than in TZ1 ash and the PTE composition was higher in TZ1 than in TZ2 ash. In addition, the activity concentrations of ^{210}Pb and ^{226}Ra were higher in TZ1 than TZ2 ash while ^{228}Ac and ^{40}K were higher in TZ2 than in TZ1 ash. Even though Popovic et al. (2008) suggested characteristics of ashes collected from the same power plant receiving the same feed coal should be consistent, results from the Tanzanian ash seem to contradict this observation. Since the parent coal of these ashes was the same bituminous coal, the observed variations can be ascribed to the variation of coal characteristics within the coal field itself.

3.5 CONCLUSION

The general observations from this study show that the chemistry of coal ashes collected from different countries (UK, Czech Republic and Tanzania) are highly variable. This variation can be attributed to the differences in coal ranks and the combustion conditions of the power plants/industries in these countries. Moreover, sampling time also had a great influence on the characteristics of ash collected besides the similarity of the feed coal in the same power plant. Therefore, studies on the specific relationships between the chemistry of coal rank and its combustion residues and the influence of other factors on ash characteristics are recommended.

4 LONG- AND SHORT-TERM EFFECTS OF THE UK, CZECH REPUBLIC AND TANZANIAN COAL ASHES ON SELECTED SOIL PROPERTIES

4.1 INTRODUCTION

Fly ash is one of several coal combustion by-products constituting 70% of the total residues produced in coal fired power plants (Elseewi et al., 1980). It is mainly composed of silica, alumina and iron oxides and other constituents which always vary in their proportions like carbon, calcium, magnesium and sulphur (Shaheen et al., 2014). Practically, fly ash comprises almost all the known elements including potentially toxic elements and radioactive elements in trace quantities (Singh et al., 2014). Since it has a similar physical composition to soil and contains both essential plant nutrients and trace elements (Singh et al., 2014), application of fly ash to the soil has been found to induce some changes in soil properties and thus affects soil productivity. Improvement of soil nutritional status following soil amendment with fly ash has been well documented (Adriano and Weber, 2001; Kalra et al., 2003; Yeledhalli et al., 2007). However, reduction of some soil nutrients following amendment with fly ash has also been reported (Kalra et al., 1997; Gupta et al., 2012). Positive and negative effects of fly ash on soil pH following amendment with fly ash has also been reported (Elseewi et al., 1980; Kalra et al., 2000; Riehl et al., 2010).

Little effect on, or no inhibition of, microbial activities in soils amended with low doses of ash has been reported. Conversely, inhibition of microbial activities in soils amended with high concentrations of fly ash does occur (Wong and Wong, 1986; Pati et al., 2004; Nayak et al., 2014). Soil amendment with fly ash has also been found to either increase concentrations of potentially toxic elements (PTE) (Wong and Wong, 1990; Singh et al., 2008) due to the presence of these PTEs in the ash, or to reduce the solubilities of PTEs in the soil (Sharma et al., 2002) due to the effect of fly ash on soil pH. The effect of fly ash on soil characteristics varies depending on the characteristics of the recipient soil and the characteristics of the applied fly ash which, in turn, depends on the inherent characteristics of the parent coal, the efficiency of the combustion process, storage and handling (Jala and Goyal, 2006). Therefore, direct effects of fly ash on soil characteristics have been studied, but due to the high variation in the properties of individual fly ashes, results regarding the effect of fly ash on soil properties can be contradictory. Besides many studies on the direct effect of

ash on soil characteristics, work pertaining to long-term effects is scarce. Several studies have reported the effect of ash on soil characteristics after conducting short-term incubation experiments (e.g. Wong and Wong (1986) - 42 days; Lai et al. (1998) - 63 days; Masto et al. (2012) - 60 days); however, there are few data regarding long-term persistent changes in soil characteristics caused by application of ash to soil.

The present study was therefore undertaken with the aim of evaluating the long- and short-term changes in soil characteristics following application of a range of concentrations of different coal ashes from the UK, Czech Republic and Tanzania (UK1, UK2, TZ1, TZ2 and CR) to woodland soil.
The specific objectives were;

i) To evaluate the effects of different fly ash concentrations (UK1; 0-16%) on changes in soil characteristics over a two year period.
ii) To evaluate and compare the effects of increasing concentrations of different coal ashes (UK2, TZ1, TZ2 and CR) on changes in soil respiration over four months.
iii) To evaluate and compare the effects of increasing concentrations of different coal ashes (UK2, TZ1, TZ2 and CR) on changes in soil characteristics after four months.

In order to fulfill these objectives the study included two incubation experiments. In the first experiment, one fly ash collected from the UK (UK1) was used and the soil was incubated for 2 years. In the second experiment, four fly ashes collected from the UK (second batch-UK2), Tanzania (two batches, TZ1 and TZ2) and the Czech Republic (CR) were used and the soil was incubated for 16 weeks.

4.2 MATERIAL AND METHODS

4.2.1 Experimental approach

Two incubation experiments were conducted. In each experiment a woodland soil collected from Domleo's Spinney (Chapter 2, Section 2.1) was incubated for two years (Experiment 1) and for 16 weeks (Experiment 2). In Experiment

1, soils were amended with the fly ash collected from the UK (UK1) at concentrations of 0, 4 and 16%. In Experiment 2, soils were amended with a range of fly ashes collected from the UK (UK2), the Czech Republic (CR) and Tanzania (TZ1 and TZ2) at the same concentrations as in Experiment 1. In both experiments, the equivalent fresh weight of 100 g dry weight of soil was adjusted to 30% moisture content and mixed thoroughly with each of the above three concentrations of fly ash; these mixtures were then incubated in Duran® bottles (250 mL volume) as described below. Both experiments were designed to evaluate the effect of fly ash application on soil respiration, soil pH, total nutrients, PTE concentration and the extractability of nutrients and PTEs from the soil.

4.2.2 Experimental set up

4.2.2.1 Experiment 1 - UK1 fly ash

The calculated masses of the UK1 fly ash at 0, 4 and 16% (on a soil dry weight basis), which correspond to 0, 100 and 400 t ha^{-1}, were added to the equivalent fresh weight of 100 g dry weight (129 g) of soils in each Duran® bottle (250 mL volume) prior to incubation. Seven sets of each fly ash treated soil, including the control were prepared. This design allowed sacrificial analyses of individual bottles at 7 sampling points at 0, 1, 2, 3, 6, 11 and 24 months. Each treatment was replicated 4 times giving a total of 84 experimental units. The soil moisture content for each soil/fly ash mixture was calculated, then the moisture contents in all 84 Duran® bottles were adjusted to 30% taking into consideration the initial moisture content of the soil. All bottles were covered with Parafilm® to control water loss by evaporation, but allow gas exchange. All Duran® bottles were arranged in a randomized block design in a constant temperature room (20°C) for the duration of the experiment. The soil moisture content in the bottles was monitored every week by weighing the bottles and adding any water lost to maintain the moisture at 30% throughout the incubation period (2 years). Soils were left to stabilize (equilibrate) for 10 days before the first analyses were performed. At each sampling period, the measurement of CO_2 evolution (soil respiration) was conducted in undisturbed samples before sacrificing soils in bottles for other analyses.

4.2.2.2 Experiment 2 - UK2, CR, TZ1 and TZ2 ashes

The calculated masses of the UK2, CR, TZ1 and TZ2 fly ashes at 0, 4 and 16 % (on soil dry weight basis) which correspond to 0, 100 and 400 t ha^{-1}, were added to the equivalent fresh weight of 100 g dry weight of soils in each Duran® bottle (250 mL volume) prior to incubation. The experimental set-up was as described above (Section 4.2.2.1) except that the duration of the experiment was 16 weeks, the bottles were maintained in a 20°C incubator and the sacrificial soil sampling occurred after 16 weeks. Measurement of CO_2 evolution (soil respiration) was conducted at 0, 8 and 16 weeks after the start of incubation (repeated measurements on the same bottles) but all other analyses were performed at the end of the incubation experiment (i.e. after 16 weeks).

4.2.3 Gas sampling

At each sampling interval, before disturbing the soil, gas samples were collected to determine changes in soil respiration with time. Microbial respiration was determined by measuring the gas flux (evolving CO_2 gas) from the incubated samples. This was performed at 0, 1, 2, 3, 6, 11 and 24 months.

The gas vials (Exetainer® vial - Labco Ltd, UK) were pre-evacuated twice using a 20 mL syringe and needle (0.6×30 mm) to remove 20 mL of gas from the vial, thus creating a partial vacuum. The Duran® bottles (in which the soil was incubated) were opened by removing the Parafilm® for 15 minutes to allow free air circulation, thus ensuring that the headspace in each Duran bottle was equilibrated with ambient air. The Duran® bottles were then closed with modified lids that had rubber septa embedded within them to allow headspace gas sampling with a syringe. Before collecting the gas samples, the syringe and the needle was used to mix the air within the headspace of the Duran® bottles. This was done by filling and gently ejecting the gas from the syringe 3-4 times. After mixing, a 20 mL sample of headspace gas was taken for analysis. Each sample was injected into a 12 mL evacuated gas vial with a butyl rubber stopper for storage, resulting in a slightly higher than atmospheric pressure within the vial. Over-pressurisation of the gas vials was meant to prevent external air from diffusing in and contaminating the sample. Following removal of the first 20 mL sample, gas sampling from each Duran® bottle was repeated at 30, 60 and 90 minutes, to give a total of 4 gas samples per replicate Duran® bottle at each of

the sampling intervals. The vials were then stored for gas analysis using gas chromatography.

4.2.4 Gas analysis and calculations

The CO_2 concentrations were analysed using a gas chromatograph (GC-2014, Shimadzu, Japan) fitted with a thermal conductivity detector (TCD). Gas standards with concentrations of 500 ppm for CO_2, 50 ppm for CH_4 and 500 ppb for N_2O (BOC limited, Surrey, UK) were used. To start the gas analysis, the gas cylinder was opened to 0.2 bar and then the timer was started. Three standards were injected to flood the system. The first standard was injected for 90 seconds, and the subsequent standard injections were done for 20 seconds. Intermittent (after a run of 16 samples) and final standards were injected for 40 seconds. Then the syringe and needle were used to collect 5 mL samples of gas from the stored gas samples from each sampling interval and the gas was injected into the GC to measure the concentration of CO_2 in parts per million by volume (ppmv).

For each sample, the rate of CO_2 emission from soil in mg kg^{-1} hr^{-1} was then calculated as follows. The concentrations of CO_2 were measured in the headspace of Duran® bottles (where soils were incubated) in ppmv at fixed time intervals of 0, 30, 60 and 90 minutes. Concentrations (in ppmv) were plotted against measurement time and the slope (derived from the regression equation) was determined to give a rate of ppmv $minute^{-1}$ (example graph Figure 4-1). The slope from each graph represented one measured rate and the measurement were performed in quadruplicate (4 replicates).

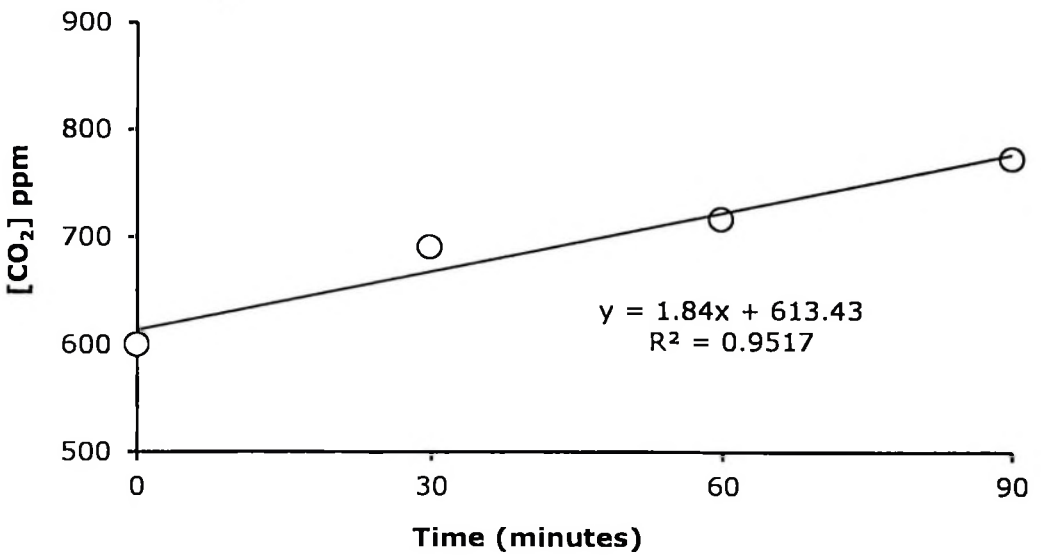

Figure 4-1: An example of the rate of CO_2 evolution with time from soil amended with fly ash.

The ppmv per minute value was then converted to mg CO_2 g^{-1} h^{-1} as follows: Each ppmv value was converted to litres and then to moles of CO_2 using the ideal gas equation PV=nRT where, P=pressure, V=volume, n=number of moles, R=the gas constant and T=temperature in Kelvin. Moles of CO_2 were then converted to milligrams of CO_2 by multiplying the moles by the molar mass of CO_2 (milligrams). Milligrams of CO_2 were then divided by the soil mass to give mg g^{-1}, which is the rate of CO_2 emission (mg g^{-1} released CO_2 per minute). The rate of CO_2 emission in mg g^{-1} min^{-1} was then converted to mg kg^{-1} h^{-1} by multiplying by 1000 and then by 60.

A separate additional experiment was also conducted in order to establish whether CO_2 evolution from the 'Duran-bottle incubation experiment with soil', was through a biological process as hypothesised, or a chemical process whereby CO_2 evolved from the ash itself; i.e. *via* a reaction with calcium (or another) carbonate to release CO_2 when ultra-pure water (pH 6.1) was added and the ash moistened. Here, UK1 ash was incubated in serum bottles (20 mL volume) crimped with silicone seals and CO_2 evolution was measured on days 1 and 7. Nine serum bottles were prepared where, 3 bottles were half filled with ultra-pure water, 3 bottles with the dry UK1 fly ash and 3 bottles with moistened UK1 fly ash. Ten glass beads were added to each bottle to insure the good air circulation within each bottle. In addition, 3 air samples from the laboratory

atmosphere were collected in gas vials (Exetainer® vial - Labco Ltd, UK) for comparison with the CO_2 gas evolving from the dry fly ash samples. Before air sample collection in the laboratory atmosphere, the gas vials were pre-evacuated as explained above (Section 4.2.3) and a 20 mL air sample of the laboratory atmosphere was then taken for analysis. A 5 mL sample of headspace air was taken from each serum bottle (following gentle mixing) and injected directly to the gas chromatography for CO_2 analysis.

4.2.5 Soil analysis for total C and total N

At the end of Experiment 2, soil samples amended with different fly ashes were analysed for total N and C concentrations in a CN analyser (Thermo Scientific FlashEA 1112 Nitrogen and Carbon analyser). For the analysis details please refer to Chapter 2 (Section 2.3.3).

4.2.6 Determination of extractable carbon and nitrogen

At each sampling interval (Experiment 1), extractable C and N were determined in the soil/ash mixtures using a CN analyser (Model Shimadzu TOC-VCPH, PC-controlled high-sensitivity model) after extracting the soil with 0.5 M K_2SO_4 solution in the ratio of 1:5 and diluting the extracted sample with ultrapure water in the ratio of 1:10. For the analysis details of the total extractable C, N, the inorganic C and organic carbon please refer to Chapter 2 (Section 2.3.4).

4.2.7 pH and elemental analyses

These analyses were performed following the procedures and formulas described in Chapter 2, Sections 2.3.2, 2.3.5, 2.3.6, 2.3.7 and 2.3.8.

4.2.8 Statistical analysis

Statistical analyses were performed using Genstat 17th Edition (VSN International, UK). A generalized two way analysis of variance (ANOVA) was conducted on all parameters (pH, CO_2 flux, extractable C, extractable N, total nutrients, total PTEs, extractable nutrients and extractable PTEs) using fly ash concentration and incubation time as factors for the long-term incubation data.

For the short-term incubation data, an unbalanced ANOVA was conducted for all parameters using fly ash types and fly ash concentrations as factors. Repeated measures ANOVA was used for the analysis of CO_2 flux data from the short-term incubation experiment. Normality was tested by plotting residuals against expected normal quantiles and post-hoc comparisons between means were based on least significant differences (LSD) tests at the 0.05 probability level.

4.3 RESULTS

4.3.1 Long-term effect of fly ash application on soil respiration, pH and extractable C and N (Experiment 1)

The addition of the alkaline UK1 fly ash to an acidic woodland soil induced changes in soil respiration, soil pH and extractable C and N following incubation for 24 months (Figure 4-2). Soil pH significantly increased with increasing fly ash concentration (0%, 4% and 16%) and this increase fluctuated with time, most notably within the unamended soil and least of all in the soil with the 16% ash amendment (Figure 4-2 and Table 4-1; ash concentration x time interaction; $p<0.001$).

Extractable C followed a similar trend in soil amended with 0% and 4% ash with few major differences occurring over the 24 month period, except for a spike at the penultimate sampling point (month 11). This spike in extractable C was also mirrored by the 16% ash amendment at the same sampling point (Figure 4-2). Overall, soil amendment with 16% fly ash significantly increased the extractability of C throughout the incubation time, although the trend fluctuated with time and the highest concentration was at month two and thereafter extractable C concentration lessened, although it always remained higher than the starting concentration (Figure 4-2 and Table 4-1; ash concentration x time interaction; $p<0.001$).

The 0% and 4% ash amendments resulted in similar extractable N concentrations. The 16% amendment resulted in a higher extractable N concentration than that observed for the other two treatments until the final sampling point (Figure 4-2 and Table 4-1; ash concentration x time interation;

p<0.001). There was a sharp increase in soil N for all three treatments from months 3-6 followed by a significant decrease in N from 11 to 24 months.

Respiration measured by the rate of CO_2 evolution was significantly higher from soils amended with the 16% ash than with either 4% or the 0% up to month 11 (Figure 4-2 and Table 4-1; ash concentration x time interaction; p<0.001). The 4% ash amended soil respired more than the control at only one time pont (month one).

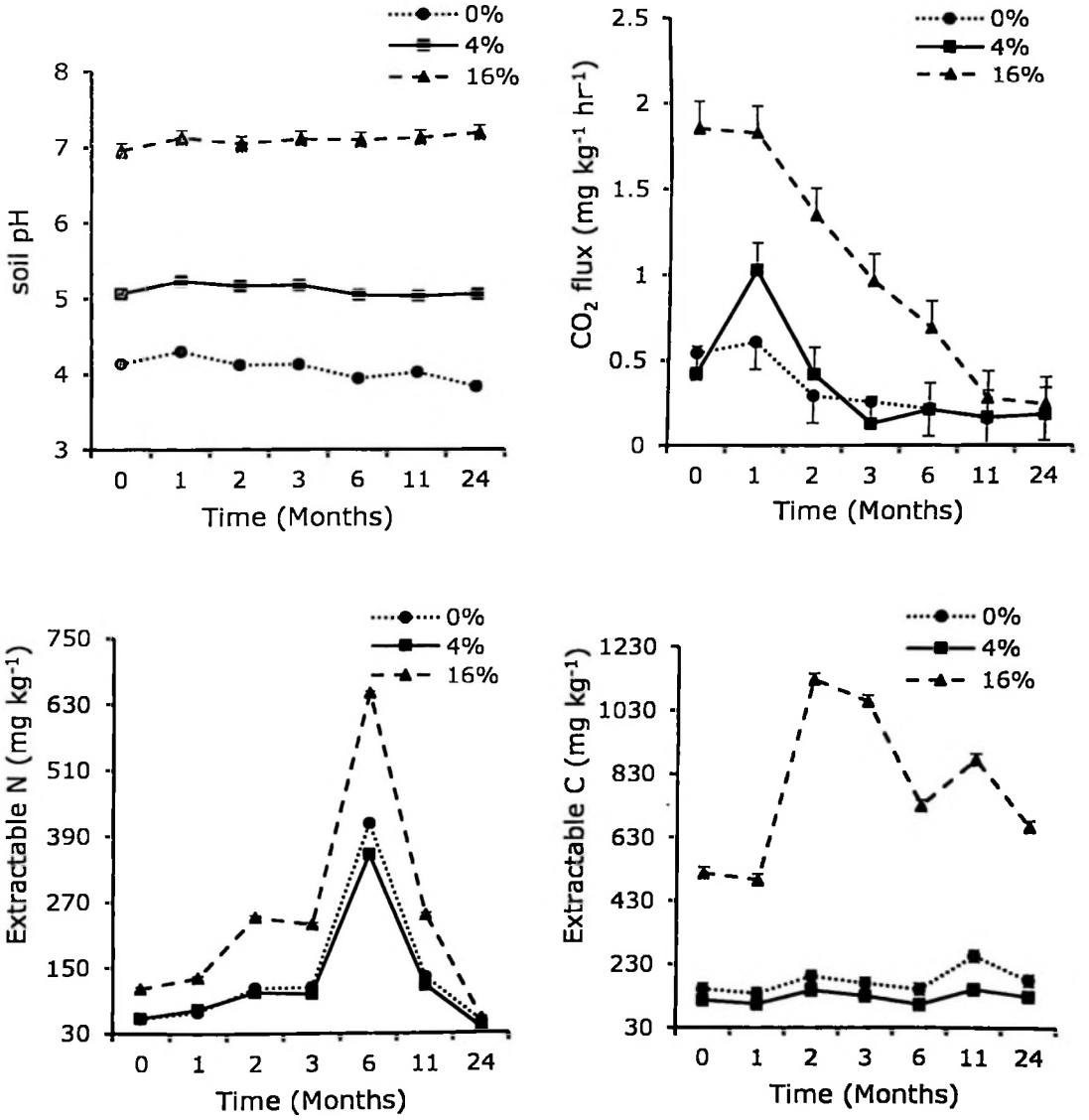

Figure 4-2: *Ash induced changes on soil pH, soil respiration (CO_2 flux), extractable N and C during soil incubation for 24 months. Individual error bars are based on the pooled variance estimate from the ANOVA with 60 (pH), 51 (extractable N) and 54 (for CO_2 flux and extractable C) degrees of freedom. LSD for pH=0.057, CO_2 flux=0.449, extractable N=10.52 and extractable C=53.24. Please note the scale differences on the Y-axes.*

After observing the highest CO_2 production at month 0 for the soil amended with 16% fly ash, it was decided to establish whether this was through a biological (respiration) or a physicochemical process. Therefore, quantification of CO_2 evolution from the fly ash (in the absence of soil) was measured to find out whether the evolving CO_2 in the soil/ash incubations was from the fly ash itself or due to stimulation of soil microbial activity following addition of the ash to soil. The atmospheric laboratory CO_2 concentration was used as a control for this after it was established that there was no significant difference between the atmospheric laboratory CO_2 concentration and the CO_2 concentration evolving from the dry fly ash samples. On day 1 of the physicochemical incubation (ash only), the CO_2 evolved from the moistened UK1 fly ash was significantly lower than that of the laboratory atmosphere where the experiment was conducted (Figure 4-3; CO_2 source x time interaction; $p<0.001$, $F_{2,12}=72.29$) and the general trend followed the order of laboratory atmospheric CO_2>CO_2 in headspace above water>CO_2 in headspace above UK1 ash. There were no significant differences in CO_2 evolution from the UK fly ash between days 1 and 7. A similar result was noted for CO_2 concentration from the laboratory atmospheric but, the CO_2 concentration decreased significantly in the headspace above the water sample on day 7 compared to day 1.

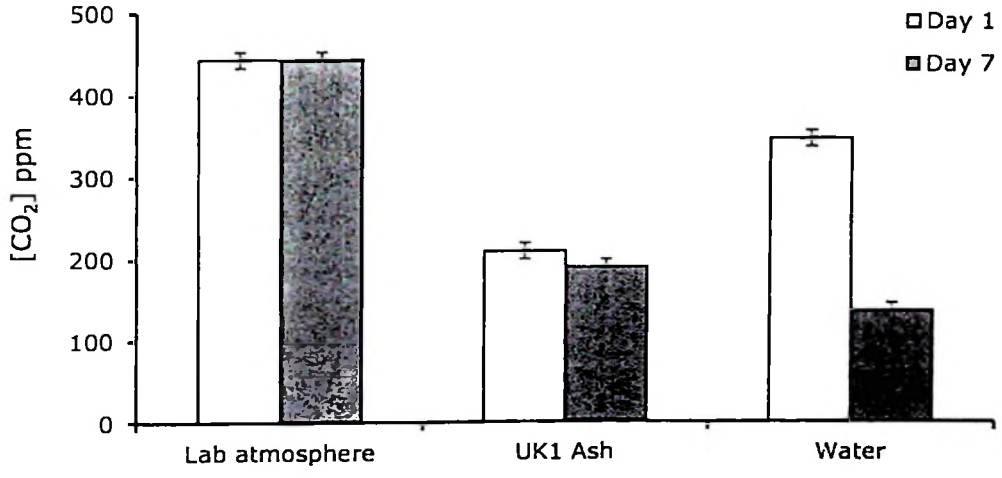

Figure 4-3: *CO_2 evolution from UK1 fly ash sample on day 1 and after 7 days of fly ash incubation in comparison to the CO_2 concentration in the laboratory atmosphere and in the headspace above water. Ash and water samples were maintained in closed airtight serum bottles. Individual error bars are based on the pooled variance estimate from the ANOVA with 12 degrees of freedom. LSD = 29.84.*

4.3.2 Long-term effect of fly ash application on total soil nutrients and PTE concentrations

Soil amendment with fly ash increased the total concentration of the nutrients P, K, Ca, Mg and Mn (Figure 4-4 and Table 4-2; ash concentration x time interaction; $p<0.001$, for P, Ca and Mg and $p=0.009$ for Mn). For almost all these nutrients in fly ash amended soils, an increasing trend was noted from month 0-1 and thereafter, the concentration decreased with increasing incubation time, most notably from months 11 to 24. The largest difference between ash concentrations was observed for total soil Ca (Figure 4-4).

With regard to time, the concentration of these PTEs varied across the incubation period with As, Ni, Cu, Zn, Cr and Co concentrations in month 24 being lower than at the start of the experiment. This was not the case for Cd or Pb. The PTE concentrations demonstrate a degree of noise within the data from month to month, but the various peaks and troughs for each individual PTE (apart from Pb) are consistent across all three ash concentrations for any particular PTE (Figures 4-5 and 4-6 and Table 4-2; ash concentration ×time interaction; $p<0.001$ for each PTE).

There was no interaction effect in ANOVA between fly ash concentration and incubation time for amount of total soil K. Fly ash as a single factor resulted in increased K concentration with the 16% ash amendment resulting in the highest K concentration ($p<0.001$; K concentration at 0%=944, 4%=999 and 16%=1066 mg kg^{-1}; data pooled across time).

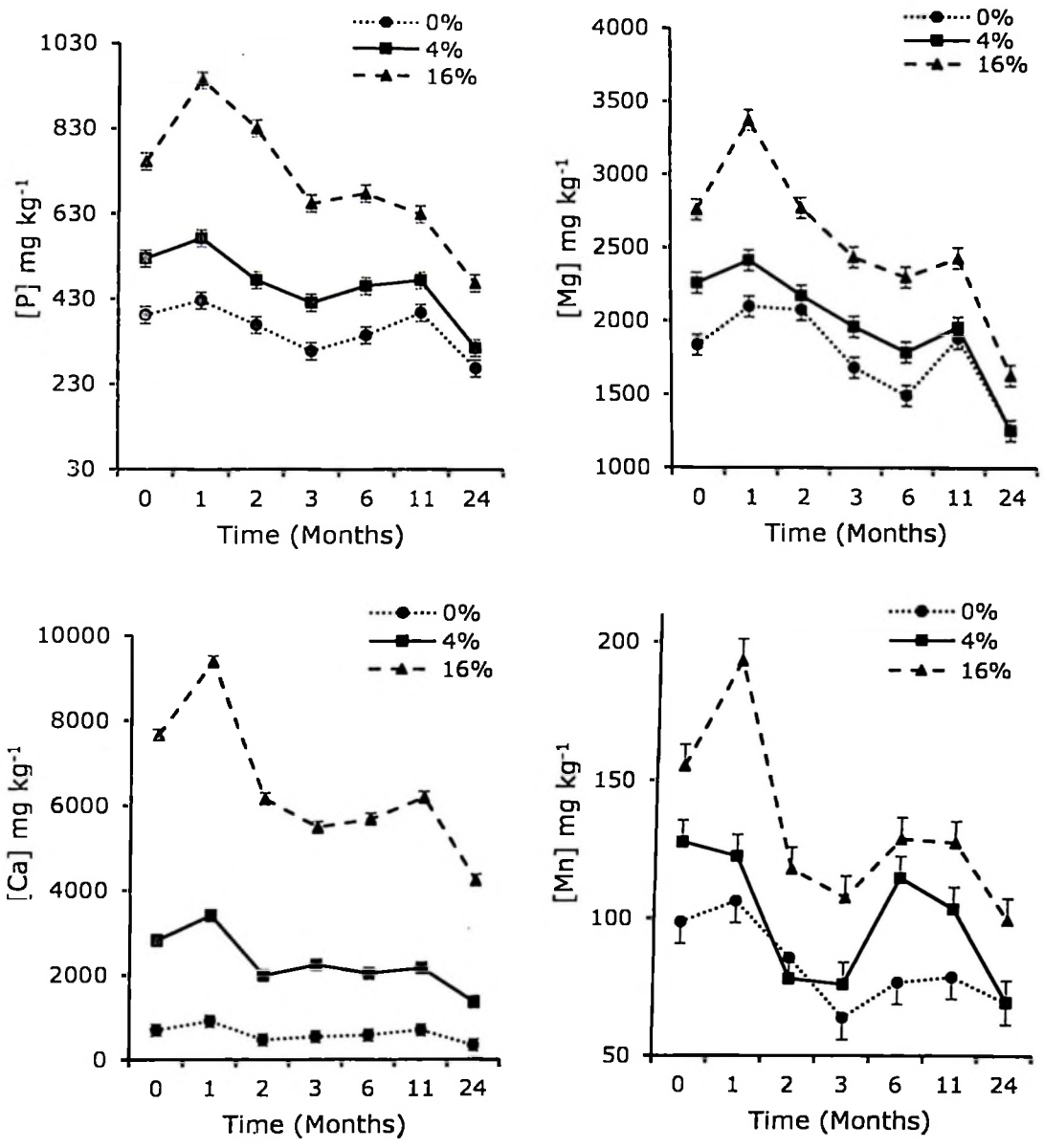

Figure 4-4: *Ash induced changes on total soil nutrient concentrations (P, Mg, Ca and Mn) following soil incubation for 24 months. Individual error bars are based on the pooled variance estimate from the ANOVA with 60 degrees of freedom. LSD for P=55.92, Mg= 201.9, Ca=400.1 and Mn=22.3. Please note the scale differences on the Y-axis.*

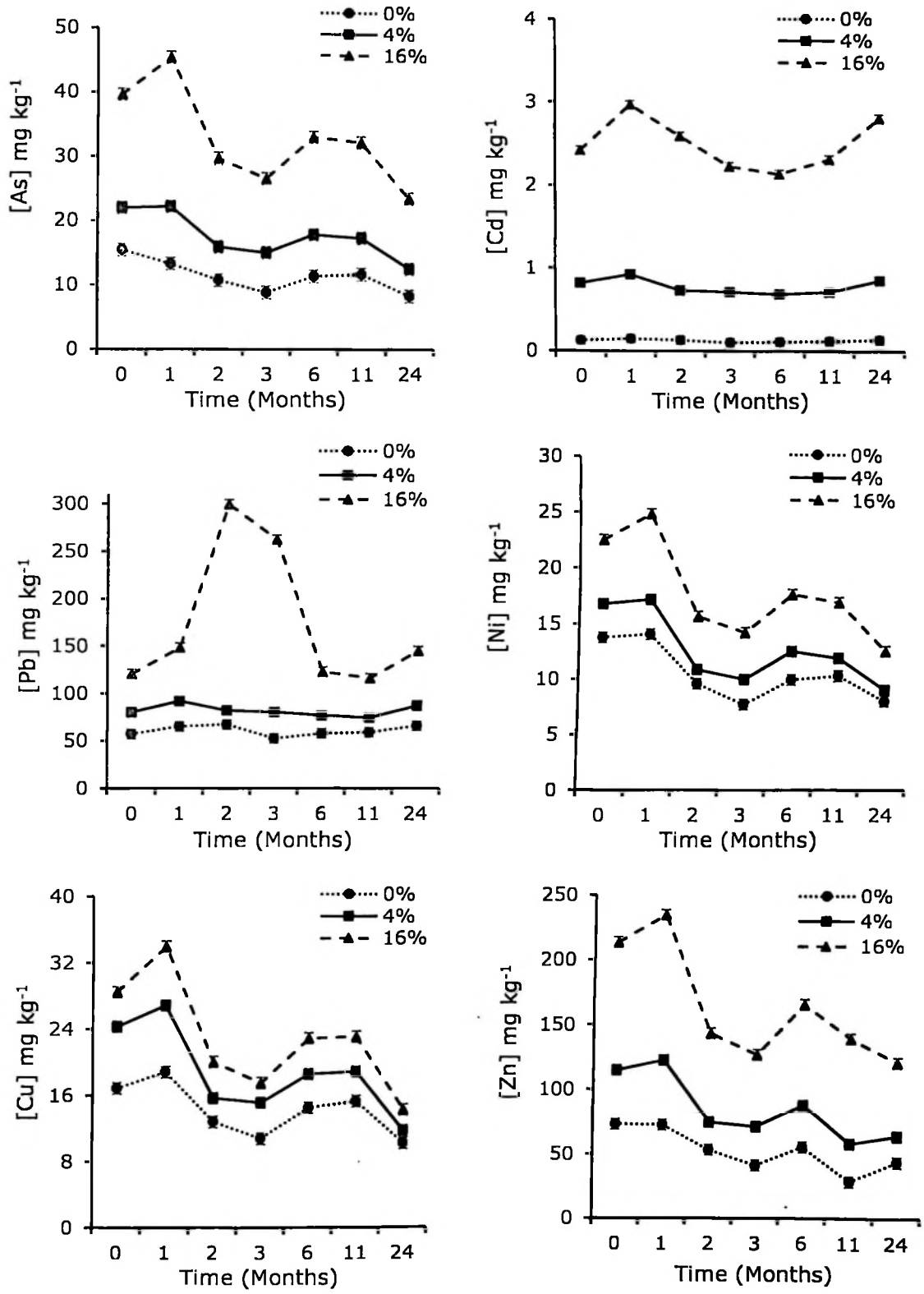

Figure 4-5: *Ash induced changes on total PTE concentrations (As, Cd, Pb, Ni, Cu and Zn) following soil incubation for 24 months. Individual error bars are based on the pooled variance estimate from the ANOVA with 60 degrees of freedom. LSD for As=2.722, Cd =0.1382, Pb=13.85, Ni=1.32, Cu=1.922 and Zn=11.48.*

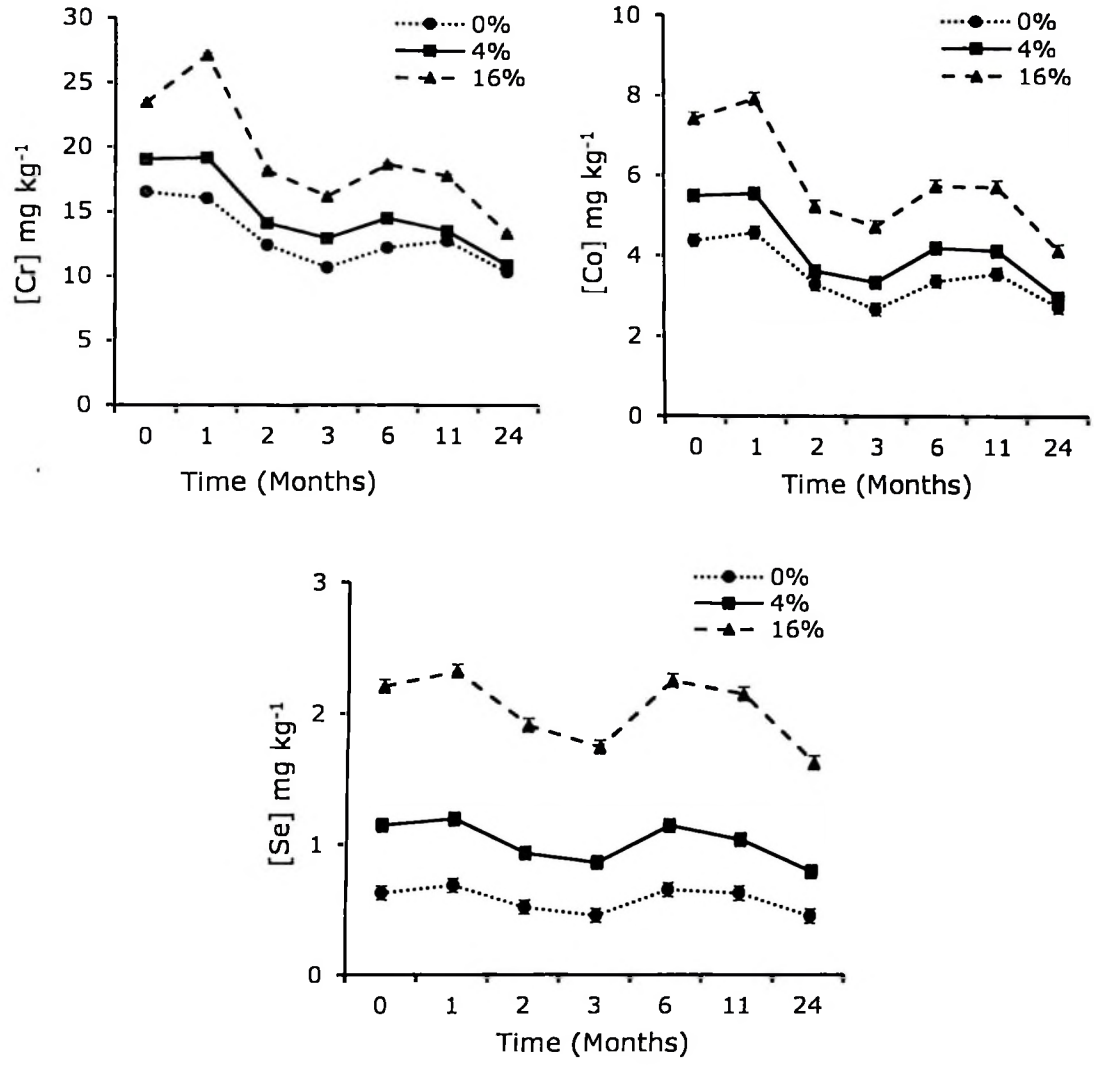

Figure 4-6: *Ash induced changes on total PTE concentrations (Cr, Co and Se) following soil incubation for 24 months. Individual error bars are based on the pooled variance estimate from the ANOVA with 60 degrees of freedom. LSD for Cr=1.647, Co=0.4524, and Se= 0.1512*

4.3.3 Long-term effect of fly ash application on exchangeable soil nutrient and PTE concentrations

Long-term application of fly ash induced some changes in the NH_4NO_3 extractability of nutrients from the soil. The concentrations of the exchangable (NH_4NO_3 extractable) Ca, B, Mg, and S increased with increasing concentration of the added fly ash (0%, 4% and 16%) throughout the incubation period, but the highest concentration was noted in month two (Figure 4-7 and Table 4-3; ash concentration x time interaction; $p<0.001$ for each nutrient). Application of fly ash decreased the concentration of exchangable Mn throughout the

incubation period (Figure 4-7 and Table 4-3; ash concentration x time interaction; $p<0.001$).

There were no interactions between fly ash concentration and incubation time for the exchangable concentration of K and P, but each factor individually exerted a significant effect. Ash concentration as a single factor significantly increased the exchangeable concentrations of these nutrients when the soils were amended with 16% fly ash (Table 4-3; K concentration at 0%=156, 4%=151 and 16%=187 mg kg^{-1}, $p<0.001$ and P concentration at 0%=0.64, 4%=0.16 and 16%=6.26 mg kg^{-1}, $p<0.001$; data are pooled across time). Regarding the incubation time as a single factor, the highest concentration of exchangable K was observed in month two (Figure 4-8; $p<0.001$) while the highest concentration of the exchangable P was recorded in month 3 (Figure 4-8; $p=0.022$).

Table 4-1: *Summary of two-factor ANOVA for pH, CO_2 flux and extractable C and N from the long-term experiment*

VARIATE	FACTOR	DF	F	P VALUE	LSD (95%)
pH	Ash (%)	2	40997	<0.001	0.022
	Time	6	36.04	<0.001	0.033
	Interaction	12	24.83	<0.001	0.057
	Residual	60			
CO_2 flux	Ash (%)	2	43.83	< 0.001	0.170
	Time	6	16.23	< 0.001	0.260
	Interaction	12	3.43	< 0.001	0.449
	Residual	54			
Extractable N	Ash (%)	2	2051.6	< 0.001	3.975
	Time	5	5303.9	< 0.001	6.072
	Interaction	10	204.31	< 0.001	10.52
	Residual	51			
Extractable C	Ash (%)	2	2629.9	< 0.001	20.12
	Time	6	77.23	< 0.001	30.74
	Interaction	10	62.37	< 0.001	53.24
	Residual	54			

Table 4-2: *Summary of two-factor ANOVA for total soil nutrients and PTEs concentration from the long-term experiment*

NUTRIENTS						PTEs					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**	**VARIATE**	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
P	Ash (%)	2	578.26	<0.001	21.14	**As**	Ash (%)	2	929.57	<0.001	1.029
	Time	6	65.15	<0.001	32.29		Time	6	63.27	<0.001	1.571
	Interaction	12	9.18	<0.001	55.92		Interaction	12	8.85	<0.001	2.722
	Residual	60					Residual	60			
K	Ash (%)	2	17.52	<0.001	41.36	**Cd**	Ash (%)	2	4389.27	<0.001	0.052
	Time	6	38.98	<0.001	63.18		Time	6	22.67	<0.001	0.080
	Interaction	12	1.26	0.267	109.42		Interaction	12	10.3	<0.001	0.138
	Residual	60					Residual	60			
Ca	Ash (%)	2	3118.16	<0.001	151.2	**Pb**	Ash (%)	2	1048.84	<0.001	5.23
	Time	6	102.21	<0.001	231		Time	6	81.88	<0.001	8
	Interaction	12	29.57	<0.001	400.1		Interaction	12	77.55	<0.001	13.85
	Residual	60					Residual	60			
Mg	Ash (%)	2	216.82	<0.001	76.3	**Ni**	Ash (%)	2	442	<0.001	0.499
	Time	6	93.22	<0.001	116.6		Time	6	155	<0.001	0.762
	Interaction	12	4.61	<0.001	201.9		Interaction	12	5.02	<0.001	1.32
	Residual	60					Residual	60			
Mn	Ash (%)	2	73.11	<0.001	8.43	**Cu**	Ash (%)	2	287.28	<0.001	0.726
	Time	6	24.58	<0.001	12.88		Time	6	163.86	<0.001	1.109
	Interaction	12	2.52	0.009	22.3		Interaction	12	7.67	<0.001	1.922
	Residual	60					Residual	60			
						Zn	Ash (%)	2	1391.27	<0.001	4.339
							Time	6	144.79	<0.001	6.628

	Interaction	12	15.36	<0.001	11.48
	Residual	60			
Cr	Ash (%)	2	214.41	<0.001	0.623
	Time	6	98.11	<0.001	0.951
	Interaction	12	4.92	<0.001	1.647
	Residual	60			
Co	Ash (%)	2	392.24	<0.001	0.171
	Time	6	125.15	<0.001	0.261
	Interaction	12	4.49	<0.001	0.452
	Residual	60			
Se	Ash (%)	2	1371.61	<0.001	0.057
	Time	6	31.72	<0.001	0.087
	Interaction	12	2.85	0.004	0.151
	Residual	60			

Long-term application of fly ash also induced some changes in the exchangeable potentially toxic elements in the soil. The concentrations of exchangable As and Cr were highest when soil was amended with 16% fly ash (Figure 4-9 and Table 4-3; ash concentration x time interaction; As, $p=0.003$; Cr, $p<0.001$) in comparison to the control and 4% ash treatment. Soil amendment with 4% fly ash did not have any significant effect on the extractability of these PTEs throughout the incubation period.

Application of 16% ash to the soil increased the exchangeable concentration of Cu, but conversly, 4% ash resulted in a lower exchangeable Cu concentration than either the control or the 16% ash amendment (Figure 4-9 and Table 4-3; ash concentration x time interaction; $p<0.001$). For all treatments, soil Cu increased in month one, then slowly (albeit at different rates) decreased throughout the incubation period. The exchangable concentrations of Cd and Zn were significantly higher throughout the incubation period with the 4% ash amendment and lowest with the 16% ash treatment (Figure 4-9 and Table 4-3; ash concentration x time interaction; $p<0.001$ for Cd and $p<0.001$ for Zn). With 4% ash, trends for Cd and Zn concentrations fluctuated with time throughout the incubation period while at 16% ash the trends were almost constant throughout the incubation period.

Application of fly ash to the soil resulted in significantly lower concentrations Co, Ni and Pb than in the control soil and this was enhanced with increasing fly ash concentration (Figure 4-10 and Table 4-3; ash concentration x time interaction; $p<0.001$, for Co, $p=0.009$ for Ni and $p<0.001$ for Pb).

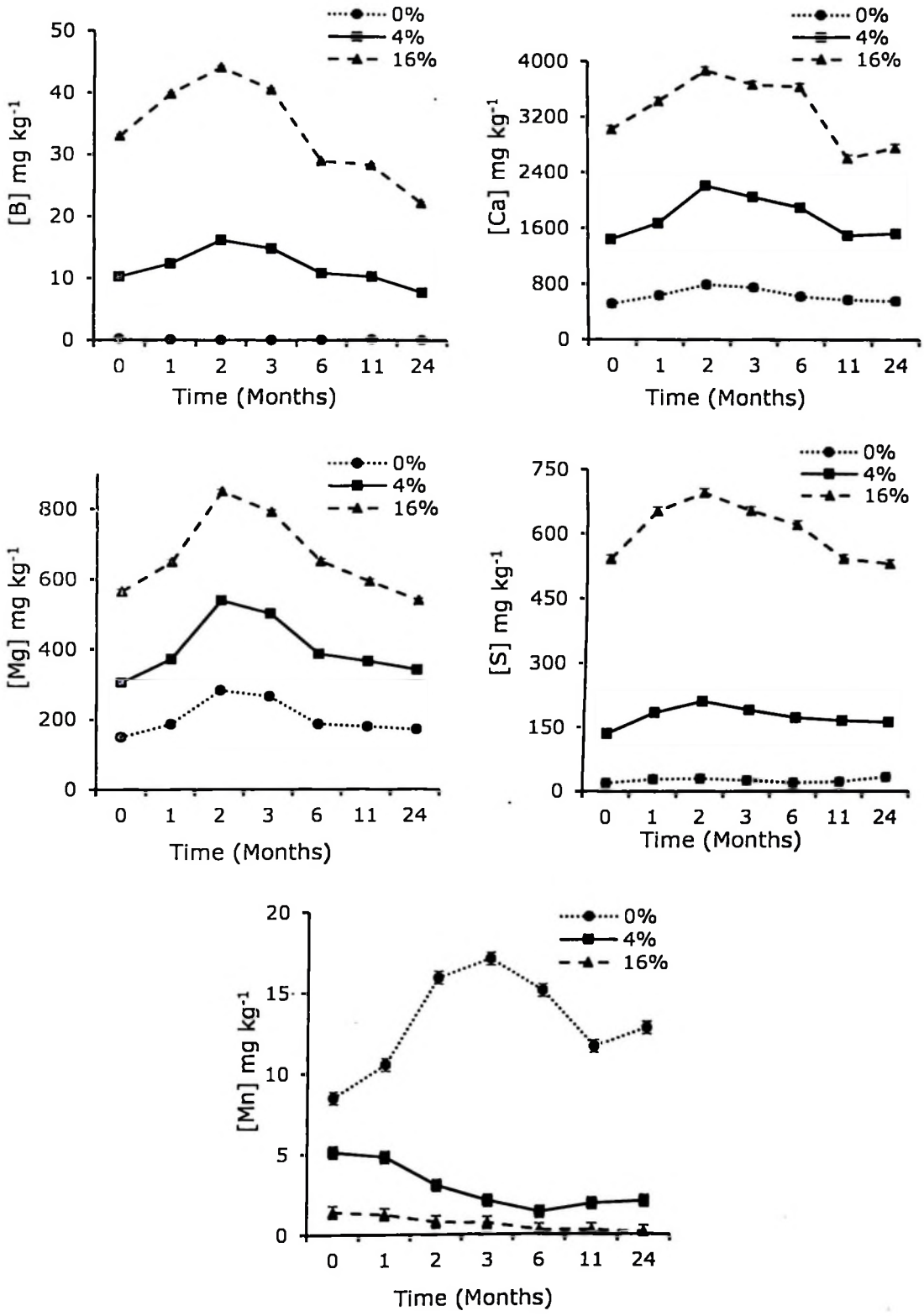

Figure 4-7: *Ash induced changes in exchangeable nutrient concentrations (B, Ca, Mg, S and Mn) following soil incubation for 24 months. Individual error bars are based on the pooled variance estimate from the ANOVA with 63 degrees of freedom. LSD for B=0.8063, Mg=20.16, Ca=149.1, S=27.97 and Mn=1.1005*

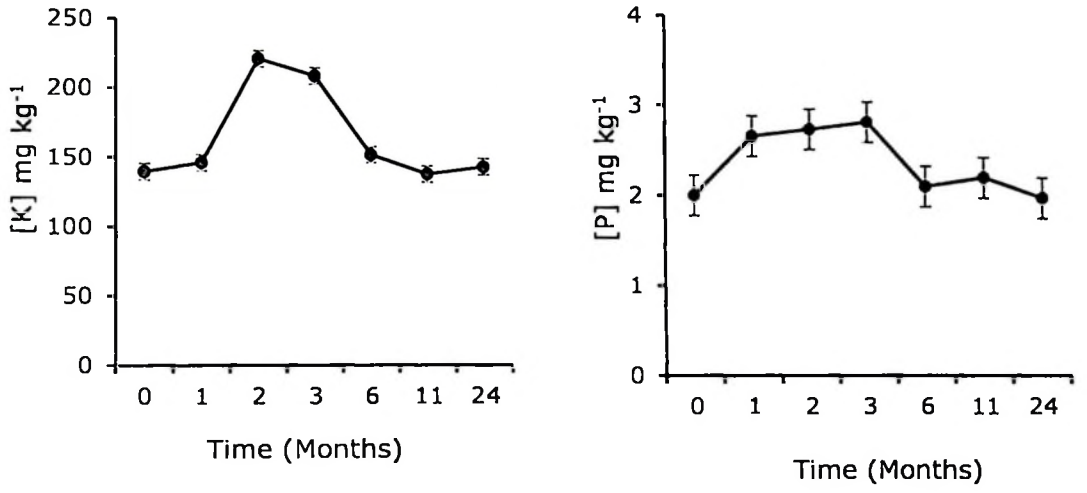

Figure 4-8: *Ash induced changes in exchangeable nutrient concentrations (K and P) following soil incubation for 24 months. Data for ash concentrations are pooled. Individual error bars are based on the pooled variance estimate from the ANOVA with 63 degrees of freedom. LSD for K=16.27 and P=0.63*

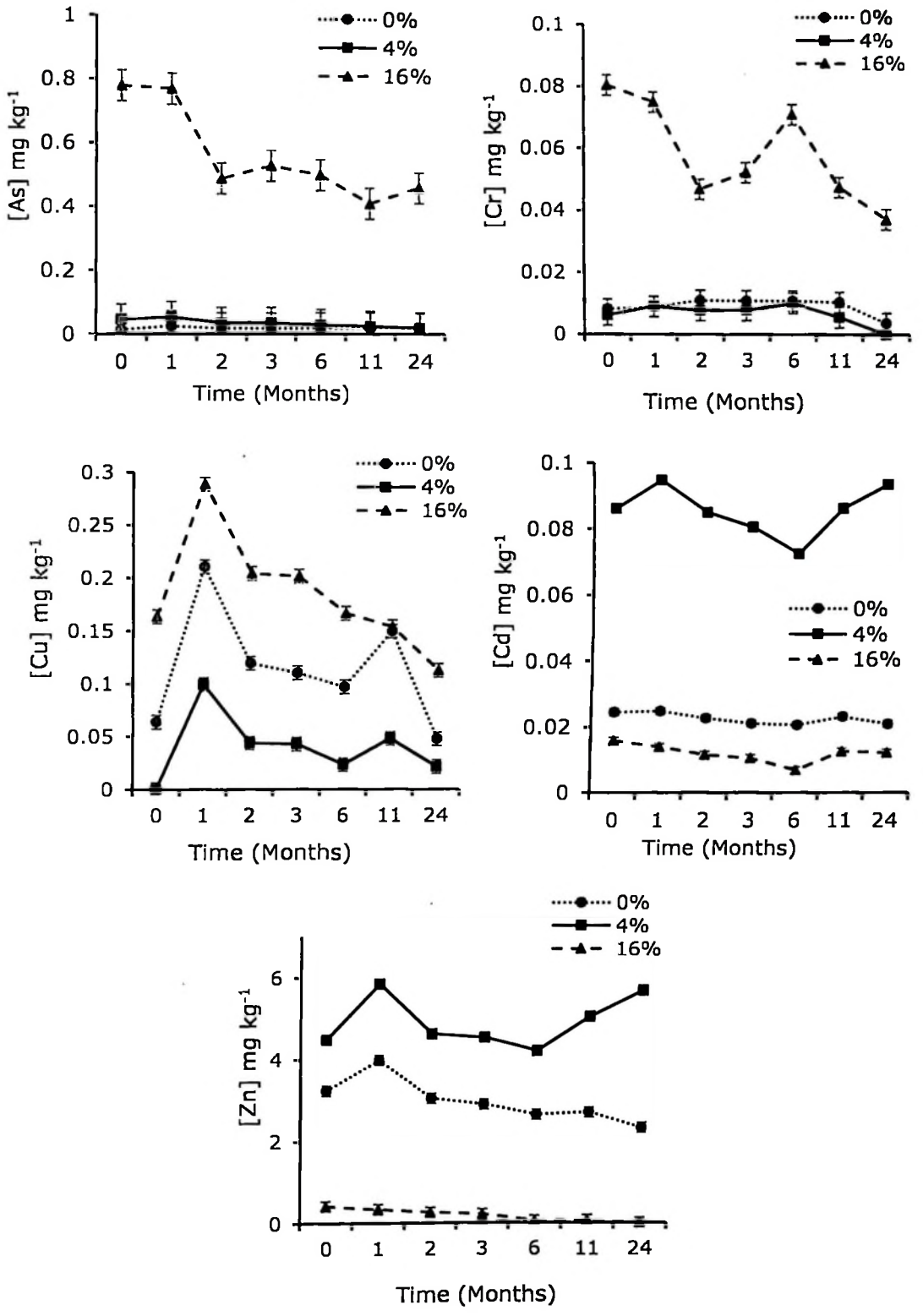

Figure 4-9: *Ash induced changes in exchangeable PTE concentrations (As, Cr, Cu, Cd and Zn) following soil incubation for 24 months. Individual error bars are based on the pooled variance estimate from the ANOVA with 63 degrees of freedom. LSD for As=0.1383, Cr= 0.009, Cu=0.018, Cd=0.0029, and Zn=0.3489*

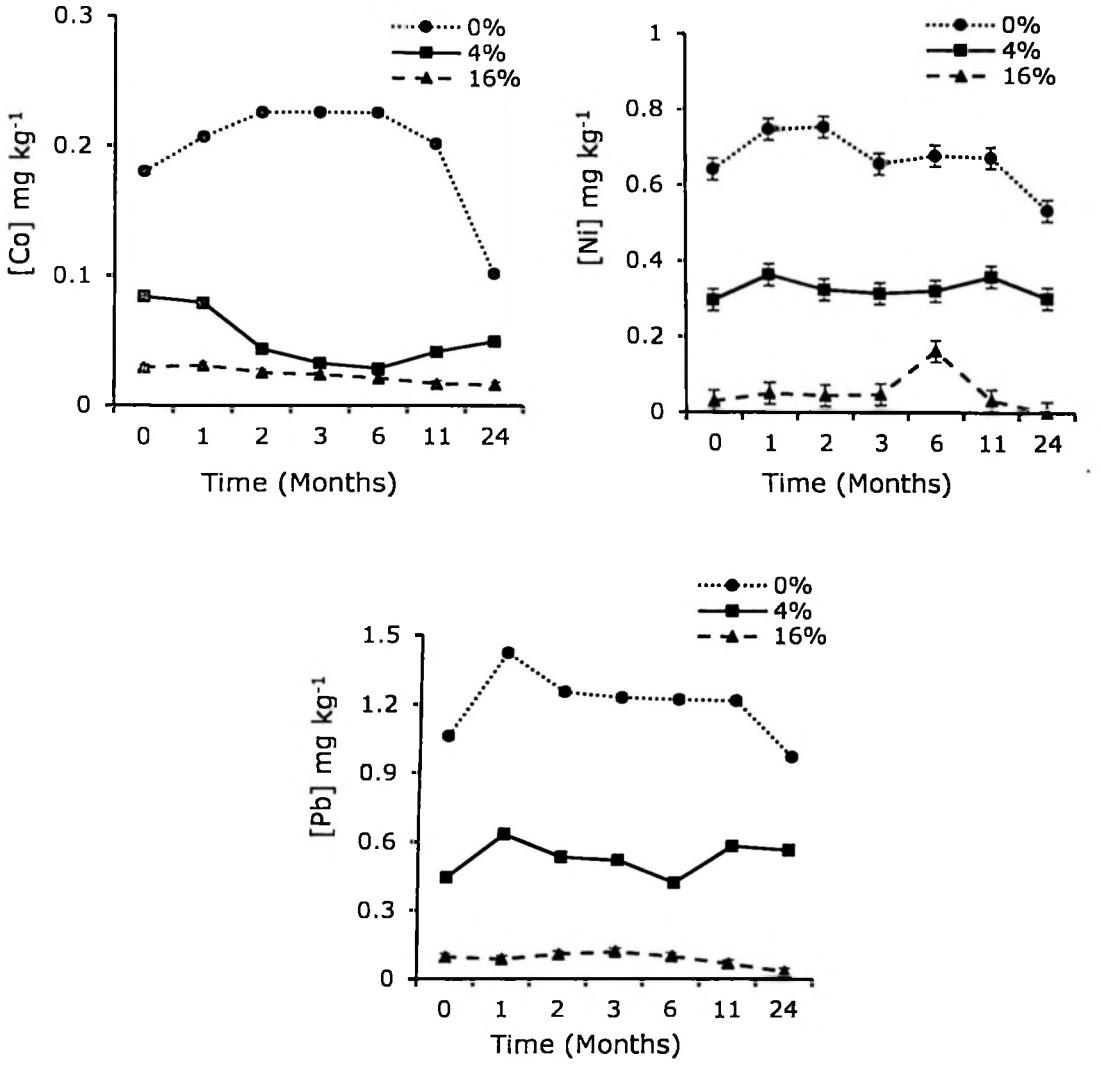

Figure 4-10: *Ash induced changes in exchangeable PTE concentrations (Co, Ni, and Pb) following soil incubation for 24 months. Individual error bars are based on the pooled variance estimate from the ANOVA with 63 degrees of freedom. LSD for Co=0.007, Ni=0.081 and Pb=0.044*

4.3.4 Long-term effect of fly ash application on water-extractable soil nutrients and PTE concentrations

Long term application of fly ash induced some changes in water extractability of nutrients (P, Mg, Ca, S, B, K and Mn) in the soil. The concentrations of P, Mg, Ca, S and B increased with increasing fly ash concentration (Figure 4-11 and Table 4-4; ash concentration x time interaction; $p<0.001$ for each nutrient), but the trend within the incubation period varied from one nutrient to another.

Table 4-3: *Summary of two-factor ANOVA for exchangeable soil nutrients and PTE concentrations from the long-term experiment*

Nutrients						PTEs					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**	**VARIATE**	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
P	Ash (%)	2	533.04	<0.001	0.415	As	Ash (%)	2	280.32	<0.001	0.052
	Time	6	2.69	0.022	0.635		Time	6	3.59	0.004	0.080
	Interaction	12	1.29	0.245	1.099		Interaction	12	2.87	0.003	0.138
	Residual	63					Residual	63			
K	Ash (%)	2	26.34	<0.001	10.65	Cr	Ash (%)	2	555.38	<0.001	0.004
	Time	6	36.65	<0.001	16.27		Time	6	12.33	<0.001	0.005
	Interaction	12	1.48	0.156	28.19		Interaction	12	7.43	<0.001	0.009
	Residual	63					Residual	63			
Ca	Ash (%)	2	4460.4	<0.001	56.4	Cd	Ash (%)	2	10814	<0.001	0.001
	Time	6	89.64	<0.001	86.1		Time	6	39.6	<0.001	0.002
	Interaction	12	16.47	<0.001	149.1		Interaction	12	13.28	<0.001	0.003
	Residual	63					Residual	63			
Mg	Ash (%)	2	7307.81	<0.001	7.62	Co	Ash (%)	2	10058	<0.001	0.003
	Time	6	409.84	<0.001	11.64		Time	6	129.49	<0.001	0.004
	Interaction	12	24.82	<0.001	20.16		Interaction	12	144.08	<0.001	0.007
	Residual	63					Residual	63			
B	Ash (%)	2	25515.2	<0.001	0.305	Cu	Ash (%)	2	895.74	<0.001	0.007
	Time	6	463.98	<0.001	0.466		Time	6	147.48	<0.001	0.010
	Interaction	12	202.04	<0.001	0.806		Interaction	12	12	<0.001	0.018
	Residual	63					Residual	63			
S	Ash (%)	2	6464.03	<0.001	10.57	Ni	Ash (%)	2	816.78	<0.001	0.031

	Time	6	27.38	<0.001	16.15		Time	6	5.77	<0.001	0.047
	Interaction	12	11.97	<0.001	27.97		Interaction	12	2.51	0.009	0.081
	Residual	63					Residual	63			
Mn	Ash (%)	2	2024.36	<0.001	0.416	Pb	Ash (%)	2	9267	<0.001	0.016
	Time	6	12.27	<0.001	0.635		Time	6	53.34	<0.001	0.025
	Interaction	12	33.99	<0.001	1.101		Interaction	12	30.46	<0.001	0.044
	Residual	63					Residual	63			
						Zn	Ash (%)	2	2598	<0.001	0.132
							Time	6	21.64	<0.001	0.201
							Interaction	12	12.1	<0.001	0.349
							Residual	63			

Despite the variability in the data across the 24 month incubation period, as for the NH_4NO_3 extractable concentrations, the water available nutrients broadly followed similar patterns. However, the 16% ash amendment resulted in noteable concentration peaks and troughs for some nutrients, e.g. P and Mg, whilst Mn concentrations increased almost linearly over the 24 months in the unamended soil, but not in the ash treatments (Figures 4-11 and 4-12 and Table 4-4; ash concentration x time interaction; $p<0.001$).

Long-term incubation of fly ash amended soil induced some changes in water extractability of the potentially toxic elements (As, Pb, Cd, Cr, Cu, and Zn). The concentration of water-extractable As was highest with the 16% ash amendment throughout the incubation period (Figure 4-13 and Table 4-4; ash concentration x time interaction; $p<0.001$), but the trends for As in soil amended with 4% and 16% fly ash were of a decrease with increasing incubation time. The incubation time did not affect As availability in unamended soil.

The concentration of water-extractable Pb was higher with increasing fly ash concentration and consistently higher in soil amended with 16% ash up to the month 24 sampling point. Water-extractable Pb concentrations remained most consistent in ash-free soil throughout the experiment (Figure 4-13 and Table 4-4; ash concentration x time interaction; $p<0.001$).

From months 2-24, there was no significant difference in Cr concentration between the 0% and 4% fly ash-amended soils, but higher concentrations of Cr were measured in soils amended with 16% ash. This followed a decrease in Cr availability across all ash concentrations after month one (Figure 4-13) and any significant differences were lost by month 24.

Soil amended with fly ash (4% and 16%) increased the concentrations of water-extractable Cd in comparison to the control at month one (Figure 4-13 and Table 4-4; ash concentration x time interaction; $p<0.001$), but there was no significant difference in Cd concentrations between 4% and 16% fly ash-amended soils. For the soil amended with 16% ash, the trend was almost constant throughout the incubation period but in the soil amended with 4% ash, the concentration of Cd dropped in month two and thereafter increased linearly.

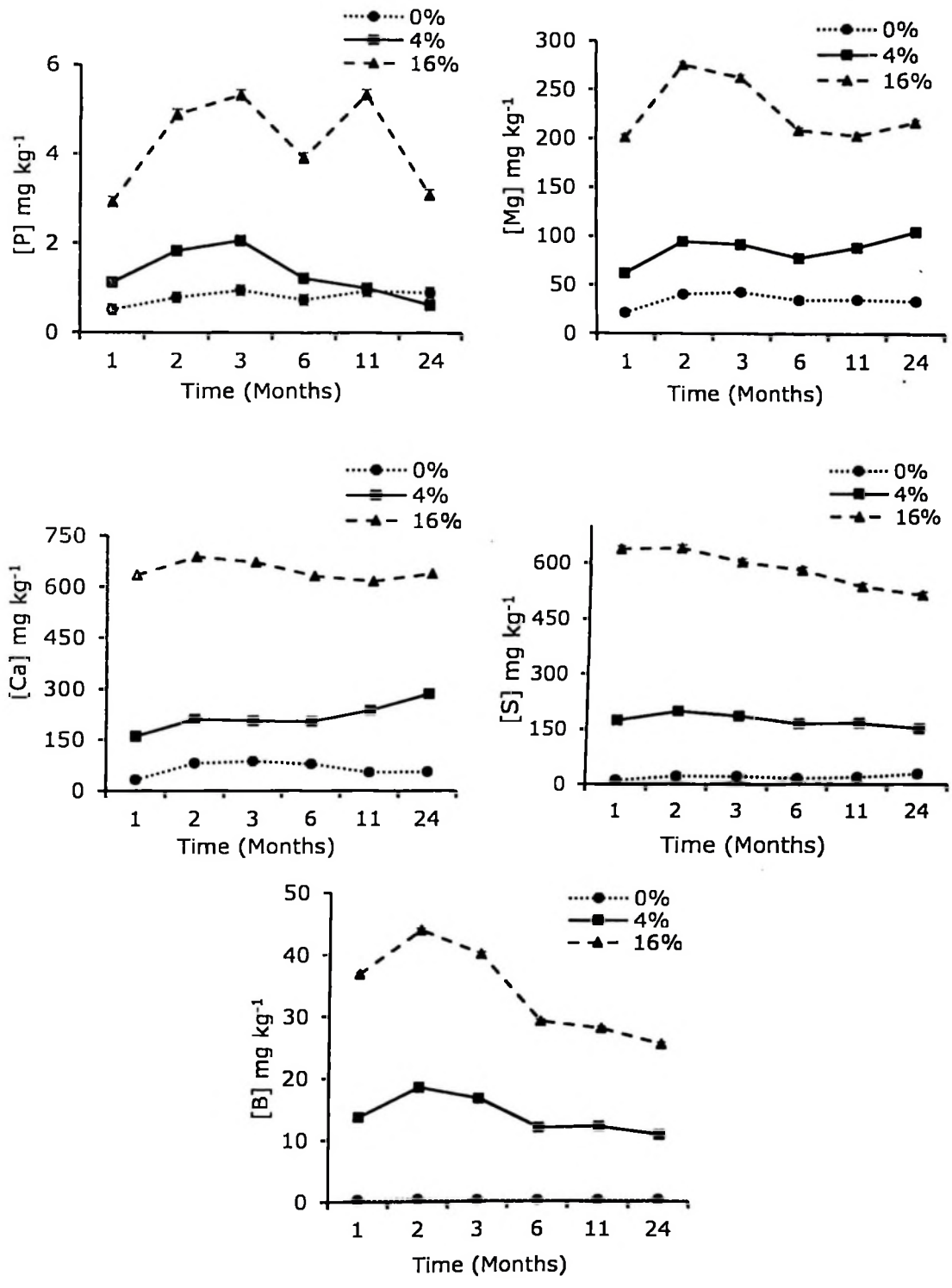

Figure 4-11: *Ash induced changes in water extractable nutrient concentrations (P, Mg, Ca, S, and Mn) following soil incubation for 24 months. Individual error bars are based on the pooled variance estimate from the ANOVA with 54 degrees of freedom. LSD for P= 0.337, Mg= 8.201, Ca= 32.36, S=27.97 and B= 0.8959*

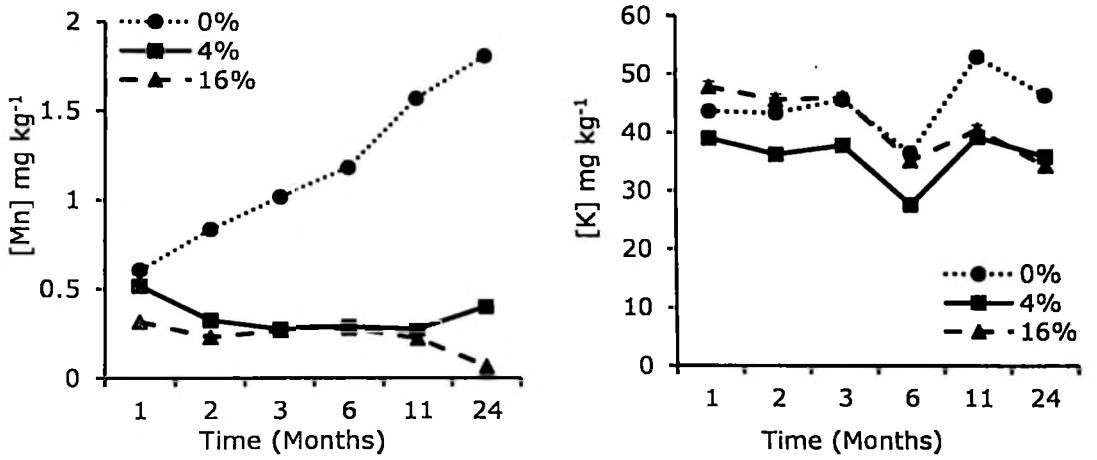

Figure 4-12: *Ash induced changes in water extractable nutrient concentrations (K and Mn) following soil incubation for 24 months. Individual error bars are based on the pooled variance estimate from the ANOVA with 54 degrees of freedom. LSD for K= 2.632 and Mn= 0.1453*

A similar linear increase in water available Zn was also measured in the soil amended with 4% ash, the opposite of the observed decrease when 16% ash was added (Figure 4-13).

Soil amendment with 16% ash increased the concentration of water-extractable Cu over the incubation period, while the 4% ash amendment significantly decreased Cu availability (Figure 4-13 and Table 4-4; ash concentration x time interaction; $p<0.001$). For all fly ash-amended soils and the control, decreasing trends in Cu concentration were observed from month 1-2; thereafter the trends were almost constant throughout the incubation period.

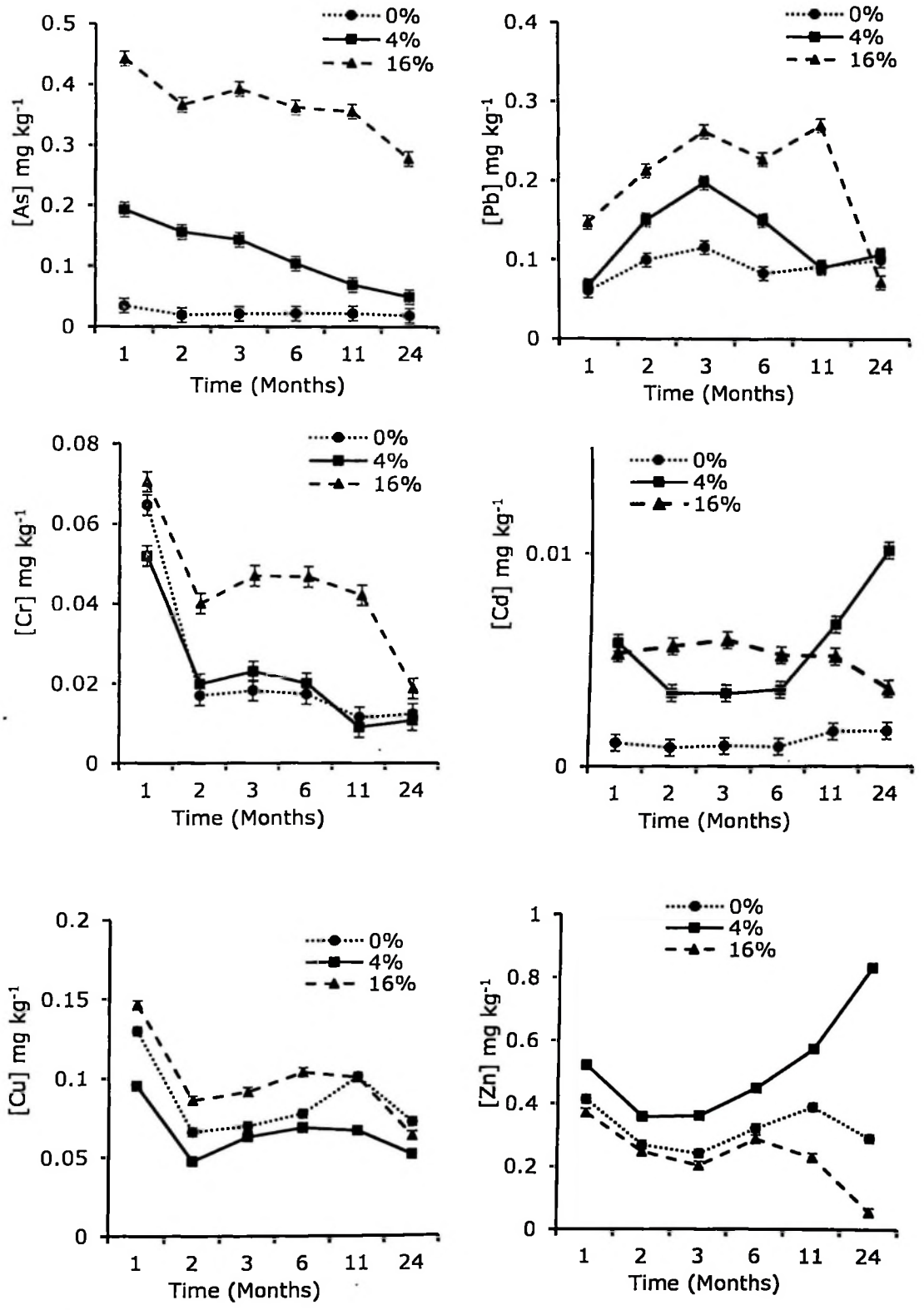

Figure 4-13: *Ash induced changes in water extractable PTE concentrations (As, Pb, Cr, Cd, Cu and Zn) following soil incubation for 24 months. Individual error bars are based on the pooled variance estimate from the ANOVA with 54 degrees of freedom. LSD for As=0.034, Pb= 0.0245, Cr= 0.007, Cd=0.001, Cu=0.008, and Zn=0.038*

Table 4-4: *Summary of two-factor ANOVA for water- extractable soil nutrients and PTEs concentration from the long-term experiment*

Nutrients						PTEs					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**	**VARIATE**	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
P	Ash (%)	2	1483.09	<0.001	0.138	As	Ash (%)	2	1320.93	<0.001	0.014
	Time	5	59.53	<0.001	0.195		Time	5	27.45	<0.001	0.020
	Interaction	10	23.99	<0.001	0.337		Interaction	10	6.59	<0.001	0.034
	Residual	54					Residual	54			
K	Ash (%)	2	137.49	<0.001	1.075	Cr	Ash (%)	2	139.58	<0.001	0.003
	Time	5	60.83	<0.001	1.52		Time	5	131.19	<0.001	0.004
	Interaction	10	16.22	<0.001	2.632		Interaction	10	6.35	<0.001	0.007
	Residual	54					Residual	54			
Ca	Ash (%)	2	4200.87	<0.001	13.21	Cd	Ash (%)	2	224.24	<0.001	0.0005
	Time	5	9.07	<0.001	18.68		Time	5	11.3	<0.001	0.0006
	Interaction	10	6.59	<0.001	32.36		Interaction	10	19.64	<0.001	0.0011
	Residual	54					Residual	54			
Mg	Ash (%)	2	7206.25	<0.001	3.348	Cu	Ash (%)	2	213.22	<0.001	0.003
	Time	5	92.44	<0.001	4.735		Time	5	189.17	<0.001	0.005
	Interaction	10	33.78	<0.001	8.201		Interaction	10	10.64	<0.001	0.008
	Residual	54					Residual	54			
B	Ash (%)	2	17249.26	<0.001	0.366	Pb	Ash (%)	2	237.86	<0.001	0.001
	Time	5	360.26	<0.001	0.517		Time	5	62.78	<0.001	0.014
	Interaction	10	140.23	<0.001	0.896		Interaction	10	25.35	<0.001	0.024
	Residual	54					Residual	54			
S	Ash (%)	2	6740.61	<0.001	10.10	Zn	Ash (%)	2	693.95	<0.001	0.016
	Time	5	17.54	<0.001	14.28		Time	5	69.77	<0.001	0.022

	Interaction	10	11.01	<0.001	24.73	Interaction	10	93.11	<0.001	0.038
	Residual	53				Residual	54			
Mn	Ash (%)	2	604.47	<0.001	0.059					
	Time	5	16.17	<0.001	0.084					
	Interaction	10	34.88	<0.001	0.145					
	Residual	54								

4.3.5 Short-term effect of ash application on soil respiration, pH and extractable C and N (Experiment 2)

The short-term ash induced changes in soil respiration, pH, total C and N following soil incubation for 16 weeks are presented in Figures 4-14 and 4-15. From weeks 0-16, soil amendment with different ash types at 4% and 16% did not significantly affect CO_2 production except when the soil was amended with 16% of the UK2 fly ash (Figure 4-14 and Table 4-5; ash concentration x ash type interaction; $p=0.031$). Generally, CO_2 production from all soils amended with different fly ash types decreased with increasing incubation time; this decrease was significant in soils amended with 4% of the TZ1 ash and 16% of the UK2 ash (Figure 4-14 and Table 4-5; ash concentration x time interaction; $p=0.031$).

Amendment with 4% of the Czech Republic and Tanzania 2 ashes decreased the soil pH significantly while higher ash concentrations up to 16% did not have any significant effect on soil pH (Figure 4-15 and Table 4-5; ash concentration x ash type interaction; $p<0.001$). Soil pH decreased significantly with increasing TZ1 ash concentration (4%-16%) (Figure 4-15 and Table 4-5; ash concentration x ash type interaction; $p<0.001$). A contrasting result was observed in soils amended with the UK2 ash when pH increased significantly with an increase in the fly ash concentration from 4%-16% (Figure 4-15 and Table 4-5; ash concentration x ash type interaction; $p<0.001$). Despite the statistical differences in soil pH, the key observation is that the UK2 ash (4% and 16%) resulted in soil with a higher pH than the control or the other ash treatments and this effect was heightened with the maximum ash concentration (16%).

Soil amendment with CR and UK2 ashes did not have any significant effect on the soil %C but, in soils amended with Tanzanian ashes (TZ1 and TZ2), the %C increased with increasing ash concentration. Application of the CR ash at 4% did not have any significant effect on the %N in the soil, but the 16% amendment significantly decreased the soil N in contrast to the soil containing 16% of the Tanzanian ashes (TZ1 and TZ2) which had an increased %N (Figure 4-15 and Table 4-5; ash concentration x ash type interaction; $p<0.001$). Application of the UK2 ash to the soil did not have any significant effect on soil N availability.

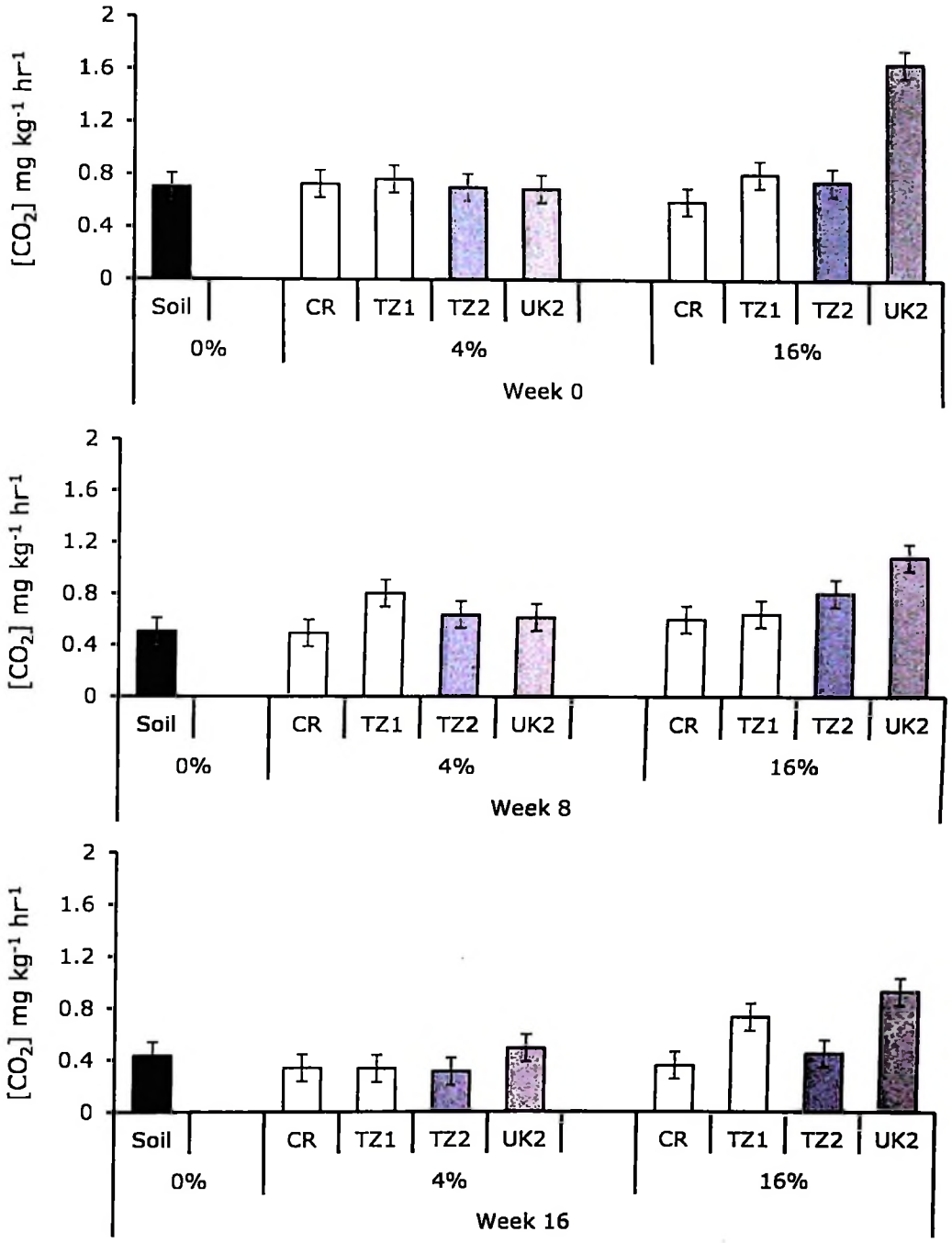

Figure 4-14: *The effect of different ashes on soil respiration (CO_2 evolution rate) during soil incubation for 16 weeks. Individual error bars are based on the pooled variance estimate from the ANOVA with 50 degrees of freedom. LSD for CO_2 flux =0.3642. CR, TZ1, TZ2 and UK2 are the Czech Republic, Tanzania batch 1, Tanzania batch 2 and UK batch 2 ash, respectively.*

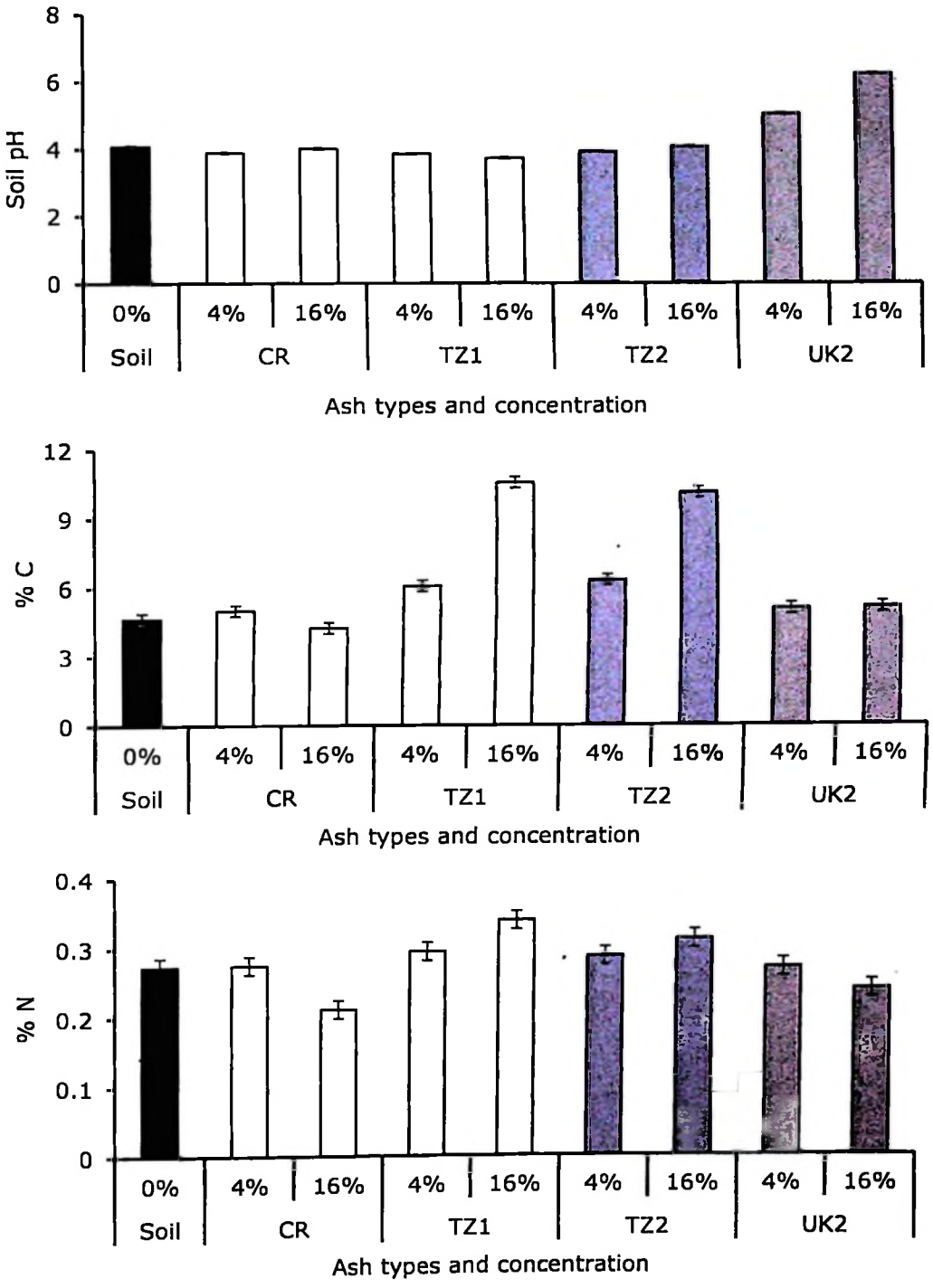

Figure 4-15: *The effect of different ashes on soil pH, total C and N following a short-term soil incubation. Individual error bars are based on the pooled variance estimate from the ANOVA with 27 degrees of freedom. LSD for pH=0.099, C=0.698, and N= 0.0377. CR, TZ1, TZ2 and UK2 are the Czech Republic, Tanzania batch 1, Tanzania batch 2 and UK batch 2 ash, respectively.*

Table 4-5: *Summary of the repeated measure ANOVA for CO_2 flux and two-factor unbalanced ANOVA for pH, %N and %C from the short-term experimental data.*

VARIATE	FACTOR	DF	F	P VALUE	LSD (95%)
CO_2 flux	SoilorAsh	1	1.81	0.19	
	SoilorAsh × Ash type	3	6.44	0.002	
	SoilorAsh × Ash %	1	9.92	0.004	
	SoilorAsh × Ash type × Ash %	3	4.52	0.011	
	Residual	27			
	Time	2	24.07	<0.001	
	Time × SoilorAsh	2	0.42	0.639	
	Time × SoilorAsh × Ash type	6	1.06	0.395	
	Time × SoilorAsh × Ash %	2	0.58	0.548	
	Time × SoilorAsh × Ash type × Ash%	6	2.65	0.031	0.364
	Residual	50			
pH	Ash (%)	2	133.49	<0.001	
	As type	3	1321.59	<0.001	
	Interaction	3	148.08	<0.001	0.099
	Residual	27			
N%	Ash (%)	2	0.34	0.713	
	As type	3	14.76	<0.001	
	Interaction	3	7.37	<0.001	0.038
	Residual	27			
C%	Ash (%)	2	90.02	<0.001	
	As type	3	134.11	<0.001	
	Interaction	3	59.57	<0.001	0.698
	Residual	27			

4.3.6 Short-term effects of ash application on total concentrations of nutrients and PTEs in the soil

Ash induced changes in the total concentrations of the soil nutrients (measured following acid digestion) are presented in Figure 4-16. Amendment with the 4% CR fly ash decreased the concentration of soil P relative to the unamended soil and the 16% ash addition enhanced this effect (Figure 4-16 and Table 4-6; ash concentration x ash type interaction; $p<0.001$). The TZ1 ash did not affect the total soil P irrespective of concentration whilst the 16% application of the TZ2 and UK2 ashes significantly increased the total soil P relative to both the control and the 4% ash treatment (Figure 4-16 and Table 4-6; ash concentration x ash type interaction; $p<0.001$).

Total Ca concentrations were unaffected by addition of 4% of the CR, TZ1 and TZ2 ashes relative to the control, but the 16% amendment of each ash significantly increased the total soil Ca (Figure 4-16 and Table 4-6; ash concentration x ash type interaction; $p<0.001$). The UK2 fly ash resulted in higher soil Ca concentrations at both levels of amendment, with the 16% ash treatment more than doubling the Ca content compared to the 4% addition and resulting in a 4-fold increase over the control (Figure 4-16 and Table 4-6; ash concentration x ash type interaction; $p<0.001$).

Neither the CR nor the TZ1 ash altered the soil Mg concentration but amendment with the TZ2 ash significantly decreased soil Mg (Figure 4-16 and Table 4-6; ash concentration x ash type interaction; $p=0.017$). Soil Mg was unaffected by 4% amendment of the UK2 fly ash, but 16% addition significantly increased soil Mg (Figure 4-16 and Table 4-6; ash concentration x ash type interaction; $p=0.017$).

Soil Mn followed a similar trend to Mg, except that application of both CR ash concentrations increased soil Mn (Figure 4-16 and Table 4-6; ash concentration x ash type interaction; $p<0.001$).

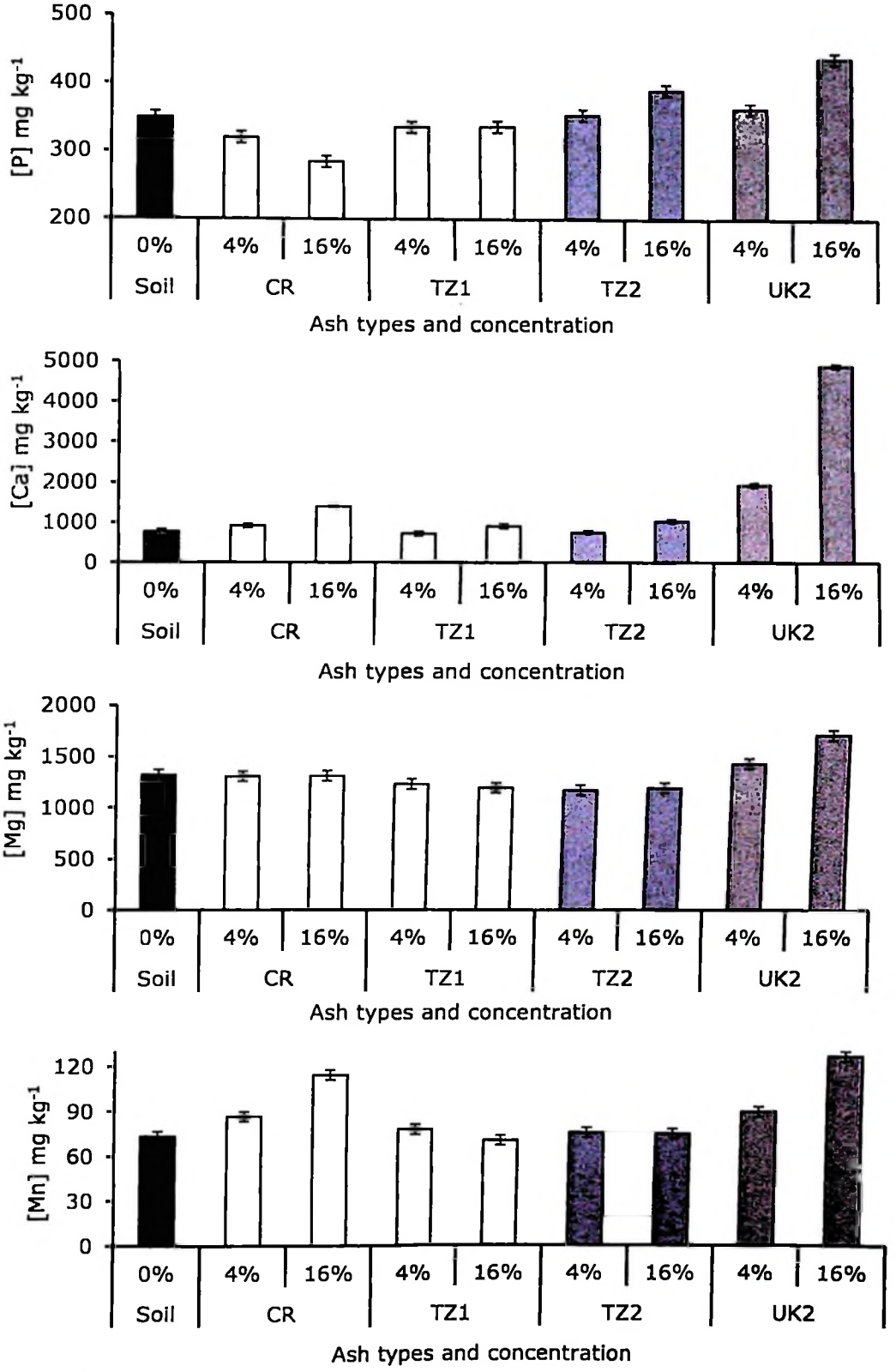

Figure 4-16: *The effect of different ashes on total soil nutrients following a short-term soil incubation. Individual error bars are based on the pooled variance estimate from the ANOVA with 27 degrees of freedom. LSD for P= 25.13, Ca= 180.5, Mg= 143.6, and Mn= 9.574. CR, TZ1, TZ2 and UK2 are the Czech Republic, Tanzania batch 1, Tanzania batch 2 and UK batch 2 ash, respectively.*

The short term incubation (16 weeks) of soils amended with different types of fly ashes induced some changes in the soil PTE concentrations (Figures 4-17 and 4-18). Soil amendment with the UK2 fly ash significantly increased the concentration of As and Pb in the soil (Figures 4-17 and 4-18 and Table 4-6; ash concentration x ash type interaction; As, $p<0.001$ and Pb, $p<0.001$) with the 16% treatment having the greatest effect. Other ashes used in this experiment did not have any significant effect on As or Pb concentrations in the soil. Similarly, soil Cd concentrations were low and relatively unaffected by ash amendment except that the 16% addition of TZ1 ash increased soil Cd and both concentrations of the UK2 ash enhanced soil Cd quite markedly (Figure 4-17 and Table 4-6; ash concentration x ash type interaction; $p<0.001$). Soil Zn followed the same pattern, with 16% application of the TZ1 and UK2 ashes increasing soil Zn concentrations (Figure 4-18 and Table 4-6; ash concentration x ash type interaction; $p<0.001$).

Application of 4% of the CR, TZ1 and TZ2 ashes did not affect soil Cu or Ni, but the 16% amendment significantly increased soil concentrations of both PTEs (Figure 4-17 and 4-18 and Table 4-6; ash concentration x ash type interaction; Cu, $p=0.005$ and Ni; $p<0.001$).

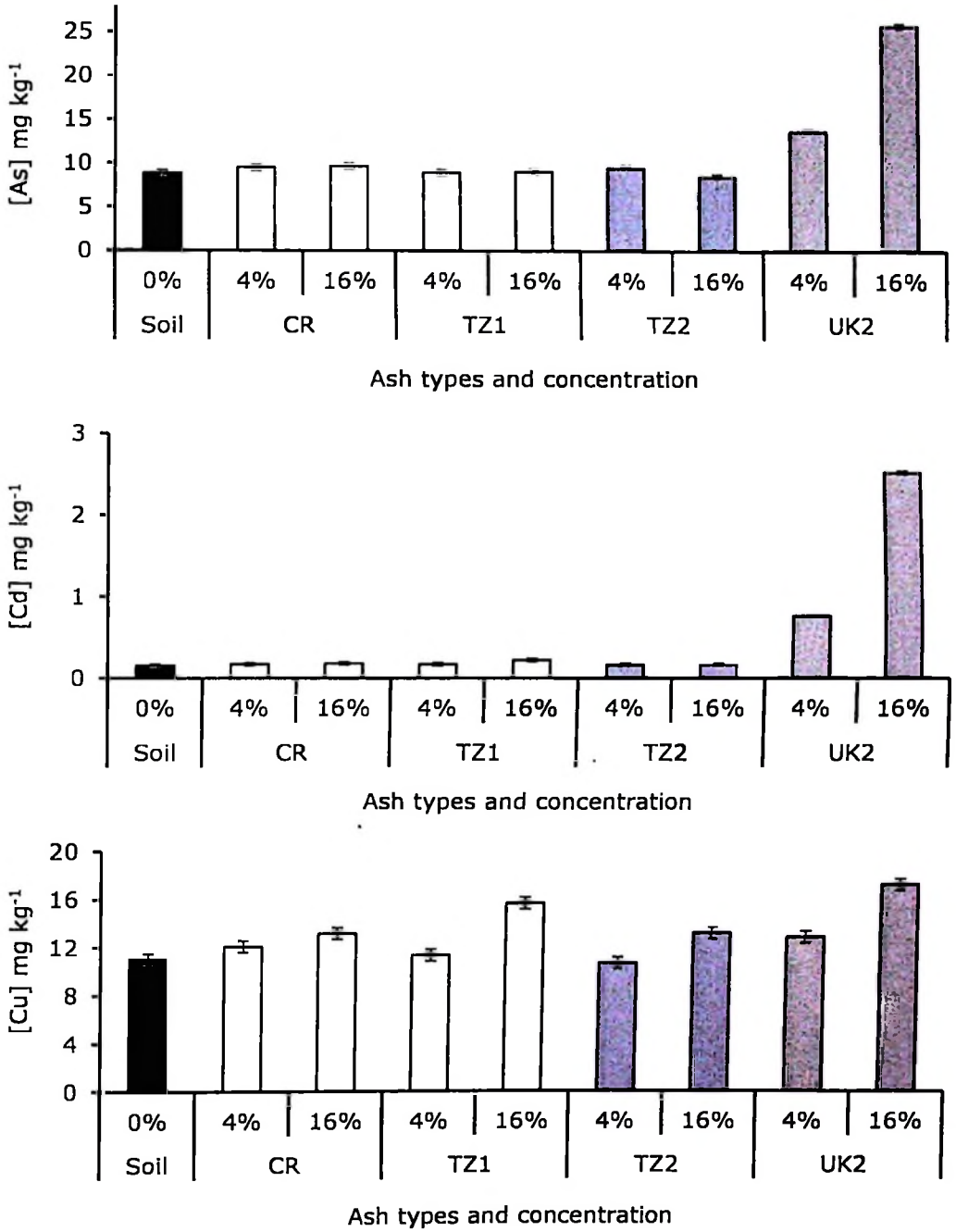

Figure 4-17: *The effect of different ashes on total soil PTEs following a short-term soil incubation. Individual error bars are based on the pooled variance estimate from the ANOVA with 27 degrees of freedom. LSD for As=0.997, Cd=0.065 and Cu=1.399. CR, TZ1, TZ2 and UK2 are the Czech Republic, Tanzania batch 1, Tanzania batch 2 and UK batch 2 ash, respectively.*

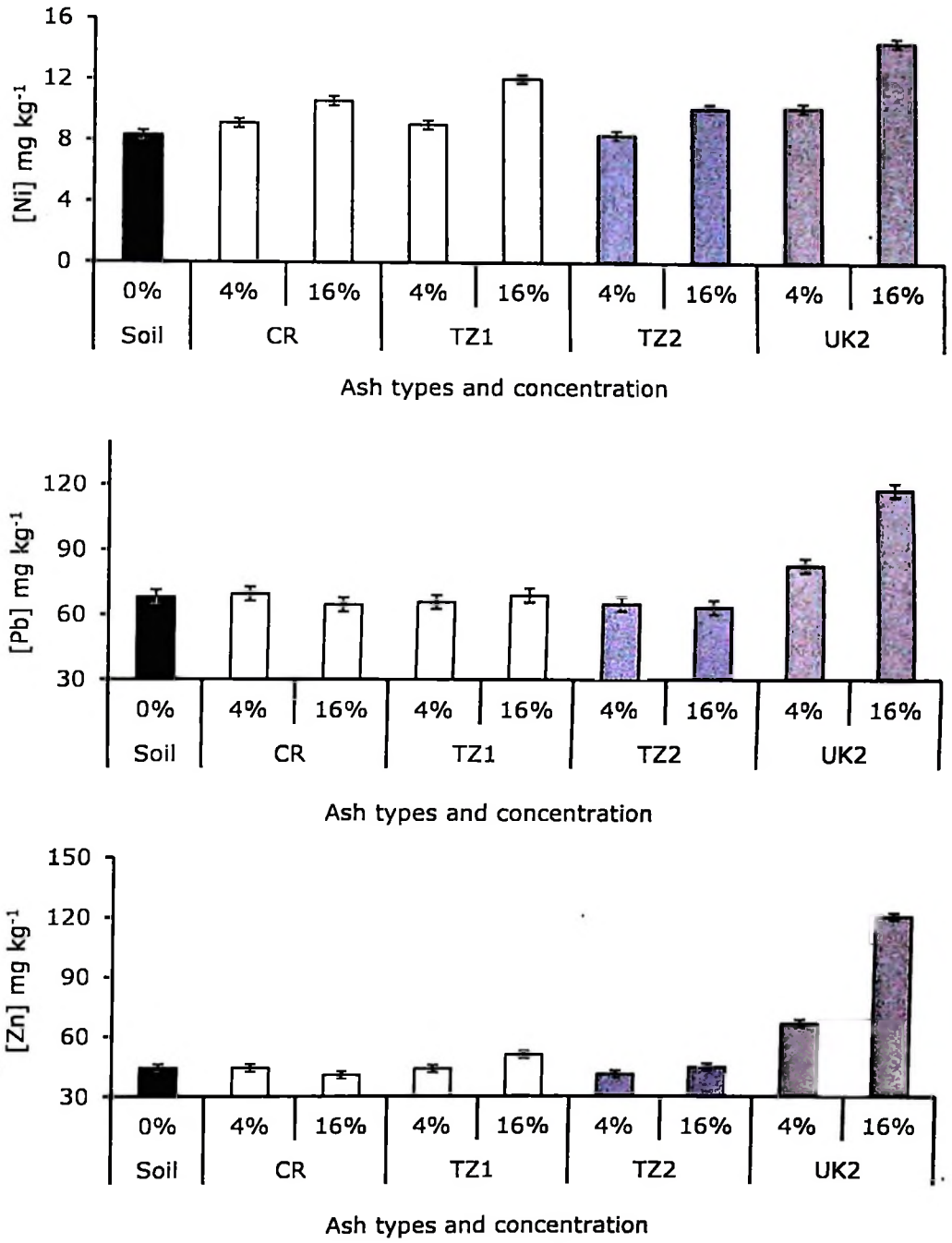

Figure 4-18: *The effect of different ashes on total soil nutrients following a short-term soil incubation. Individual error bars are based on the pooled variance estimate from the ANOVA with 27 degrees of freedom. LSD for Ni=0.862, Pb=9.291, and Zn=5.243. CR, TZ1, TZ2 and UK2 are the Czech Republic, Tanzania batch 1, Tanzania batch 2 and UK batch 2 ash, respectively.*

Table 4-6: *Summary of two-factor ANOVA for total soil nutrients and PTEs concentration from the short-term experiment*

VARIATE	FACTOR	DF	F	P VALUE	LSD interaction	LSD (95%) Factors Min	Average	Max
Nutrients								
P	Ash (%)	2	5.29	0.011		12.57	17.43	19.87
	Ash type	3	51.02	<0.001		17.77	19.37	21.77
	Interaction	3	14.99	<0.001	25.13			
	Residual	27						
Ca	Ash (%)	2	320.5	<0.001		90.2	125.2	142.7
	Ash type	3	800.15	<0.001		127.6	139.1	156.3
	Interaction	3	232.28	<0.001	180.5			
	Residual	27						
Mg	Ash (%)	2	1.82	0.181		71.78	99.59	113.49
	Ash type	3	25.18	<0.001		101.5	110.6	124.3
	Interaction	3	4.03	0.017	143.6			
	Residual	27						
Mn	Ash (%)	2	28.99	<0.001		4.787	6.642	7.569
	Ash type	3	55.39	<0.001		6.77	7.379	8.291
	Interaction	3	21.29	<0.001	9.574			
	Residual	27						
PTEs								
As	Ash (%)	2	106.05	<0.001		0.499	0.692	0.788
	Ash type	3	486.32	<0.001		0.705	0.769	0.864
	Interaction	3	166.31	<0.001	0.997			
	Residual	27						
Cd	Ash (%)	2	549.85	<0.001		0.032	0.045	0.051
	Ash type	3	2138.62	<0.001		0.046	0.050	0.056
	Interaction	3	757.25	<0.001	0.065			
	Residual	27						
Cu	Ash (%)	2	50.18	<0.001		0.340	0.473	0.539
	Ash type	3	15.33	<0.001		0.989	1.078	1.211
	Interaction	3	5.44	0.005	1.399			
	Residual	27						
Ni	Ash (%)	2	108.4	<0.001		0.431	0.5976	0.6811
	Ash type	3	42.49	<0.001		0.609	0.6639	0.7461
	Interaction	3	9.58	<0.001	0.862			
	Residual	27						
Pb	Ash (%)	2	7.95	0.002		4.646	6.445	7.345
	Ash type	3	56.7	<0.001		6.57	7.16	8.046
	Interaction	3	16.41	<0.001	9.291			
	Residual	27						
Zn	Ash (%)	2	91.34	<0.001		2.621	3.637	4.145
	Ash type	3	375.24	<0.001		3.707	4.04	4.54
	Interaction	3	104.02	<0.001	5.243			
	Residual	27						

4.3.7 Short-term effects of fly ash application on extractable nutrients and PTEs in the soil

The short-term incubation (16 weeks) of soils amended with different types of fly ashes induced some changes in the water extractability (availability) of nutrients in the soil (Figures 4-19 and 4-20). Application of the CR, TZ1 and UK2 ashes at 4% did not affect availability of P, but the 16% amendment significantly decreased available P concentrations. In contrast, the 16% additions of TZ2 and UK2 ash significantly increased available soil P (Figure 4-19 and Table 4-7; ash concentration x ash type interaction; $p<0.001$).

The water availability of Mg and Ca both significantly increased with the 16% TZ1 and UK2 ash amendments and decreased with the same concentration of TZ2 ash (Figure 4-19 and Table 4-7; ash concentration x ash type interation; $p<0.001$).

Soil amendment with CR, TZ1 and UK2 ash at 4% did not have any significant effect on the water extractable K in the soil relative to the control, but the 16% ash amendment increased K availability (Figure 4-19 and Table 4-7; $p<0.001$). The available K also significantly increased with the 16% TZ2 addition relative to both the control and the 4% treatment (Figure 4-19 and Table 4-7; ash concentration x ash type interation; $p<0.001$). The S availability increased with the 16% amendments of all ash types, particularly with the TZ1 and UK2 ashes (Figure 4-20 and Table 4-7; ash concentration x ash type interation; $p<0.001$).

The water available B most notably increased after addition of the CR and UK2 fly ashes (Figure 4-20 and Table 4-7; ash concentration x ash type interation; $p<0.001$).

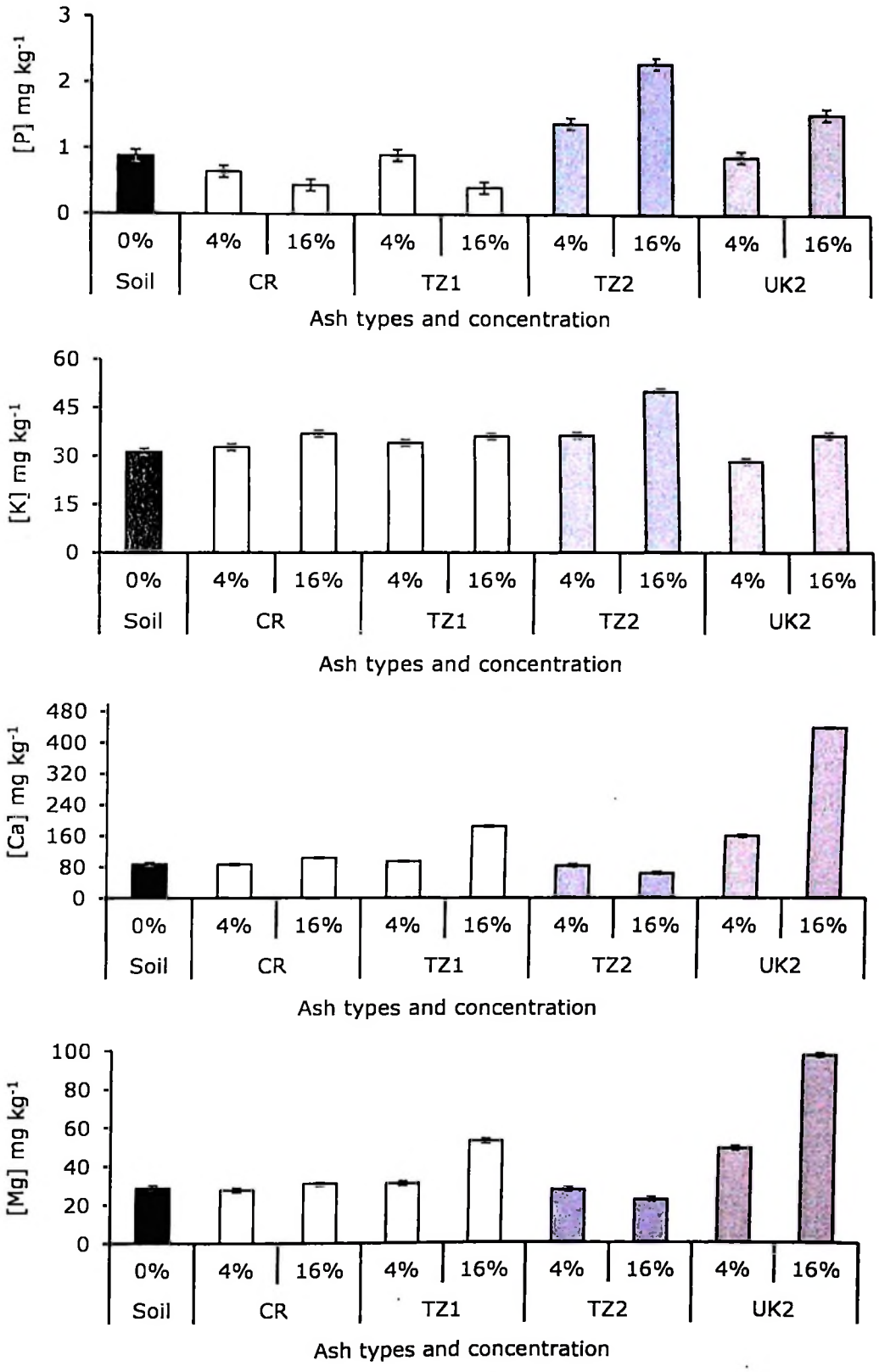

Figure 4-19: *The effect of different ashes on water extractable nutrients following a short-term soil incubation. Individual error bars are based on the pooled variance estimate from the ANOVA with 27 degrees of freedom. LSD for P= 0.261, K= 3.032, Ca= 14 and Mg=3.721. CR, TZ1, TZ2 and UK2 are the Czech Republic, Tanzania batch 1, Tanzania batch 2 and UK batch 2 ash, respectively.*

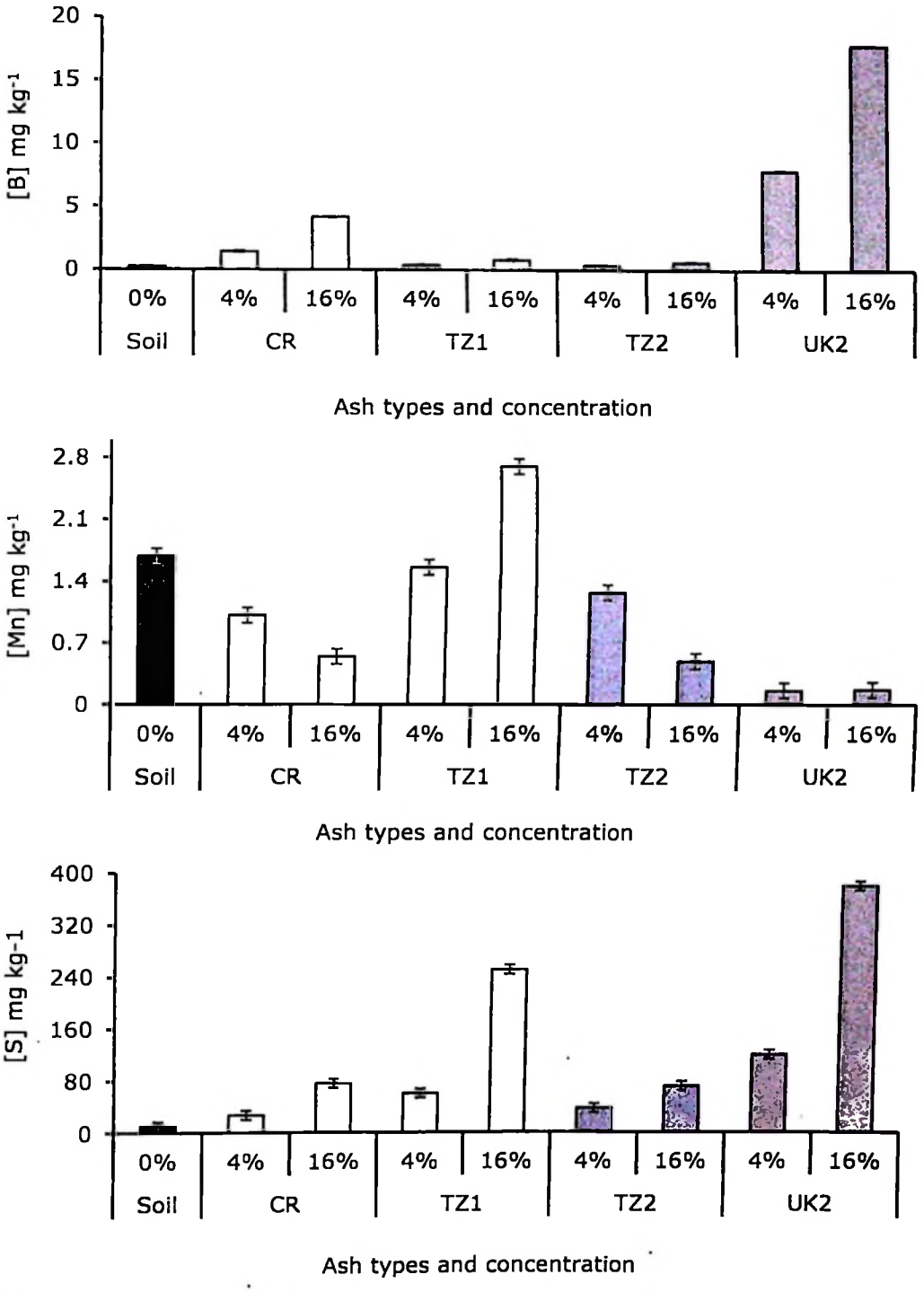

Figure 4-20: *The effect of different ashes on water extractable nutrients following a short-term soil incubation. Individual error bars are based on the pooled variance estimate from the ANOVA with 27 degrees of freedom. LSD for B= 0.295, Mn= 0.251, and S=20.19. CR, TZ1, TZ2 and UK2 are the Czech Republic, Tanzania batch 1, Tanzania batch 2 and UK batch 2 ash, respectively.*

The short-term incubation of soils amended with different types of ash also induced some changes in the water extractability of the potentially toxic elements in the soil (Figure 4-21). Soil amendment with the CR, TZ2, and UK2 fly ashes increased As availability in the soil, with the UK2 ash having the biggest effect (Figure 4-21 and Table 4-7; ash concentration x ash type interation; $p<0.001$). The 16% amendment of all ash types increased available As except for the TZ1 ash, which led to a reduction in As availability (Figure 4-21 and Table 4-7; ash concentration x ash type interation; $p<0.001$).

Available Cu and Pb followed similar trends with the 16% CR and TZ1 ash amendments lowering availability. Whilst this trend was also observed for available Cu after application of the TZ2 ash, this ash amendment did not alter Pb availability (Figure 4-21 and Table 4-7; ash concentration x ash type interaction; Cu, $p<0.001$; Pb, $p=0.001$).

Availability of Zn was unaffected by the 4% ash amendments irrespective of ash type. However, the 16% additions of all ashes lowered Zn availability apart from the TZ1 ash, which significantly increased concentrations of water extractable Zn (Figure 4-21 and Table 4-7; ash concentration x ash type interaction; $p<0.001$).

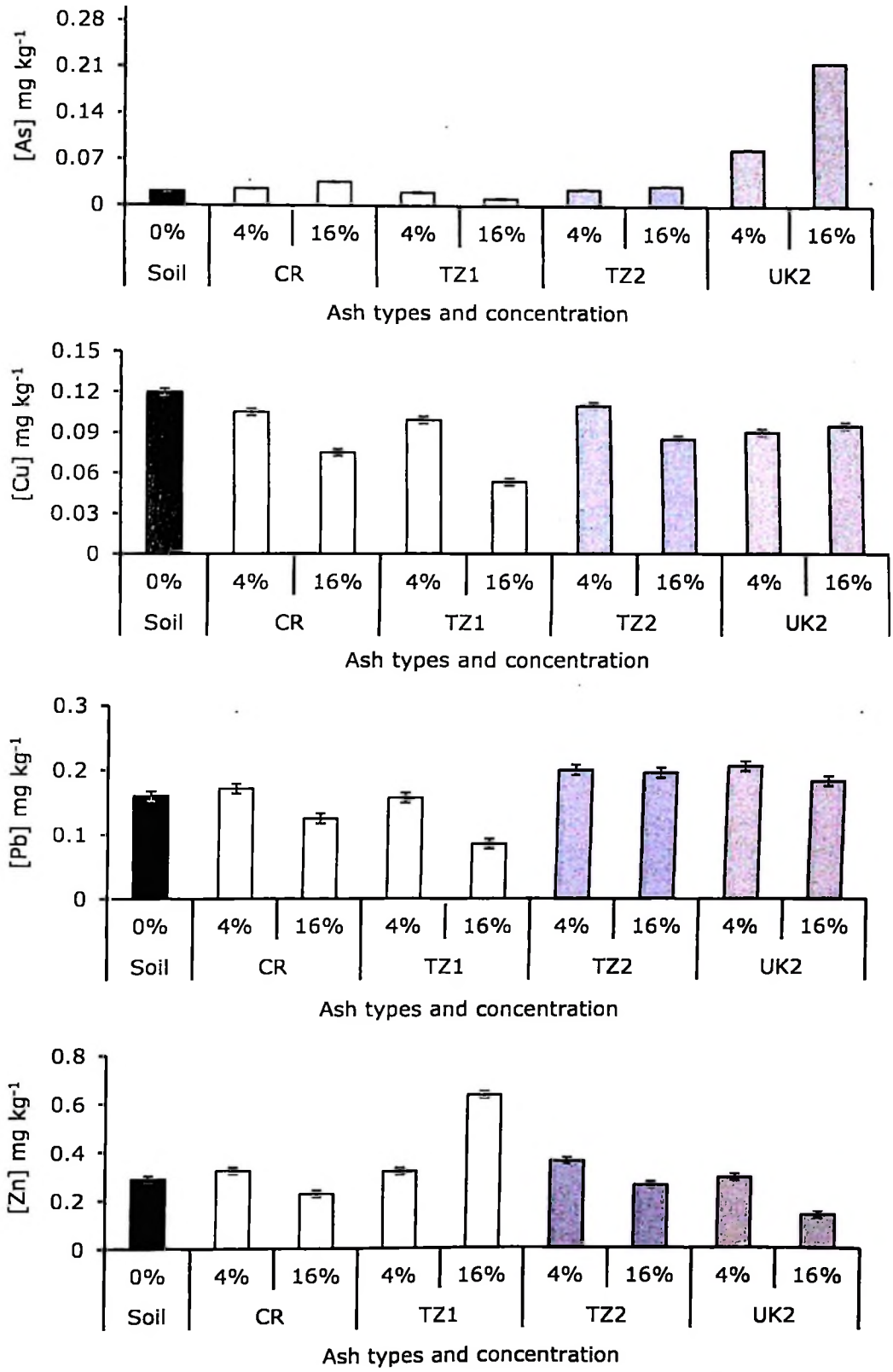

Figure 4-21: *The effect of different ashes on water extractable PTEs following a short-term soil incubation. Individual error bars are based on the pooled variance estimate from the ANOVA with 27 degrees of freedom. LSD for As= 0.004, Cu= 0.008, Pb 0.023= and Zn= 0.040. CR, TZ1, TZ2 and UK2 are the Czech Republic, Tanzania batch 1, Tanzania batch 2 and UK batch 2 ash, respectively.*

Table 4-7: *Summary of two-factor ANOVA for water-extractable soil nutrients and PTEs concentration from short-term experiment*

VARIATE	FACTOR	DF	F	P VALUE	LSD interaction	LSD (95%) Min	Average	Max
Nutrients								
P	Ash (%)	2	8.3	0.002		0.130	0.181	0.206
	Ash type	3	90.85	<0.001		0.184	0.201	0.226
	Interaction	3	28.54	<0.001	0.261			
	Residual	27						
K	Ash (%)	2	56.63	<0.001		1.516	2.104	2.397
	Ash type	3	41.14	<0.001		2.144	2.337	2.626
	Interaction	3	12.27	<0.001	3.032			
	Residual	27						
Ca	Ash (%)	2	438.57	<0.001		7.00	9.712	11.068
	Ash type	3	903.68	<0.001		9.90	10.79	12.12
	Interaction	3	380.64	<0.001	14.00			
	Residual	27						
Mg	Ash (%)	2	227.35	<0.001		1.861	2.582	2.942
	Ash type	3	577.91	<0.001		2.631	2.868	3.223
	Interaction	3	170.74	<0.001	3.721			
	Residual	27						
Mn	Ash (%)	2	28.81	<0.001		0.126	0.174	0.199
	Ash type	3	179.8	<0.001		0.178	0.194	0.218
	Interaction	3	47.05	<0.001	0.251			
	Residual	27						
B	Ash (%)	2	1788.4	<0.001		0.148	0.205	0.233
	Ash type	3	6836.7	<0.001		0.209	0.228	0.256
	Interaction	3	1031.6	<0.001	0.295			
	Residual	27						
S	Ash (%)	2	495.86	<0.001		10.09	14.00	15.96
	Ash type	3	372.58	<0.001		14.27	15.56	17.48
	Interaction	3	124.97	<0.001	20.19			
	Residual	27						
PTEs								
As	Ash (%)	2	793.78	<0.001		0.0022	0.0030	0.0035
	Ash type	3	3678.3	<0.001		0.0031	0.0034	0.0038
	Interaction	3	955.51	<0.001				
	Residual	27			0.0044			
Cu	Ash (%)	2	138.8	<0.001		0.0039	0.0054	0.0061
	Ash type	3	23.88	<0.001		0.0055	0.0060	0.0067
	Interaction	3	31.65	<0.001	0.0077			
	Residual	27						
Pb	Ash (%)	2	21.93	<0.001		0.011	0.016	0.018
	Ash type	3	45.64	<0.001		0.016	0.018	0.020
	Interaction	3	6.89	0.001	0.0228			
	Residual	27						
Zn	Ash (%)	2	2.63	0.091		0.020	0.028	0.032
	Ash type	3	129.59	<0.001		0.029	0.031	0.035
	Interaction	3	122.65	<0.001	0.040			

4.4 DISCUSSION

4.4.1 Long- and short-term effects of ash on soil pH, soil respiration and C and N concentrations

In both incubation experiments, application of fly ash induced some changes in soil chemical properties and the magnitude of these changes varied depending on the source of the ash, the concentration of the ash applied and the length of the incubation period. In the short-term incubation experiment, soil pH changes following soil amendment with fly ash varied depending on the characteristics and the concentration of the applied ash. The decrease in pH following soil amendment with TZ1 ash and the pH increase when the soil was amended with UK2 ash could be attributed to the pH of the added ash: TZ1 ash was very acidic (pH 4.2) while the UK2 ash was very alkaline (pH 10.6). Due to the dependence of soil pH on the content of carbonates and hydroxides of Ca and Mg present in fly ash (Nayak et al., 2015) the decrease in soil pH following amendment with 4% of the CR and TZ2 ashes could be linked to the decrease in the content of basic cations (Ca and Mg) noted in the soil. In the long-term incubation experiment, application of the UK1 fly ash to the soil increased the soil pH significantly and this can be attributed to the alkalinity (pH 12.3) of this ash. The influence of this ash on the alkalinity of the soil was observed throughout the incubation period (2 years) which implies the changes in soil reaction brought about by soil amendment with ash may be permanent. A similar finding was reported by Ciećko et al. (2015) who observed an increase in soil pH 29 years after the soil was amended with 100-600 Mg ha^{-1} (5-30%) of hard coal fly ash. Based on the long-term beneficial effect of alkaline ash on soil pH, Ciećko et al. (2015) suggested the use of fly ash as an alternative source to classical liming materials without any detrimental effect to the metabolic processes which influence soil quality. Even though the soil in the present study was incubated for only 2 years and was with 4-16% of fly ash, the results seems to confirm this suggestion.

In the first incubation experiment (long-term incubation for 2 years), a high rate of CO_2 evolution in month 0 was noted from the soil amended with 16% of the UK1 fly ash but there were no differences in CO_2 evolution rates between the control and the soil amended with 4% ash. The highest CO_2 evolution rate in 16% ash was maintained until month one. A rapid increase in CO_2 evolution

rate from month 0-1 was noted in the soil amended with 4% ash concentration. This implies that soil amendment with fly ash had a strong influence on soil mirobial activity, particularlly in the first month of the soil incubation.

Measurement of CO_2 from ash (in the absence of soil) was undertaken to find out whether the initial increase in the rate of CO_2 evolution in the soil amended with 16% was directly from the ash or whether observations from the soil incubations could be attributed to microbial activity in the soil. The CO_2 evolution rates from this measurement confirmed the stimulation of the microbial activities after fly ash amendment because there were very low CO_2 fluxes emanating from the UK1 fly ash in isolation. In both incubation experiments, soils were moistened to 30% w/w and allowed to stabilize (equilibrated) for 10 days which, evidently, was enough time to stimulate microbial activity at month 0, especially in the soil amended with 16% ash.

Pitchtel (1990) noted an increase in CO_2 evolution in the first 3 days after incubation of fly ash amended soil which was associated with the activation of microbial activity due to soil moistening. The initial increase in CO_2 evolution might also be due to the addition of nutrients to the soil after soil amendment with the fly ash (Wong and Wong, 1986). In this study, the initial increase in soil respiration in soils amended with ashes was noted when soils were amended with very alkaline ashes (UK2 and UK1), which could also be explained by the improvement in the soil pH which favoured the microbial activities. This result contradicts the findings reported by Pichtel (1990) who observed an initial inhibition of microbial activity linked to an increase in soil pH following soil amendment with 10-20% fly ash. This contrast might be due to the differences in the degree of pH increase. In Pichtel's (1990) study the soil pH increased from an original 6.4 to pH 9.1 and 9.4 when soils were amended with 10 and 20% ash respectively. In the current study, the soil pH increased from 4.1 to 5.1 and 7 when soil was amended with 4% and 16% of UK1 ash respectively, and from pH 4.1 to 5.1 and 6.3 when the soil was amended with UK2 ash, respectively. The optimal soil pH for most bacteria is at nearly neutral pH, while most fungi prefer an acidic pH range and for the actinomycetes a preferred pH ranging from 6.5-8 has been reported (Pitchel, 1990; Rousk et al. 2009; Calvino and Bååth, 2010; Sleutel et al., 2011). However, the decline of the CO_2 evolution rate noted from months 2-24 in the first incubation where UK1 ash

was used and from week 8-16 in the second incubation for UK2 ash amended soils could be associated with the exhaustion of substrates for microbes in the soil such as carbon and nitrogen (Wong and Wong, 1986) leading to utilization of more resistant organic matter like the humified organic substances formed during the decomposition process (Jenkinson, 1981). The reduced CO_2 evolution rate with time in soil amended with ash also might be due to the PTEs present in ashes which could be toxic to microbes in the soil. The toxicity of the PTEs to microorganisms, with particular effect on CO_2 evolution, has been reported from previous investigations (Wong and Wong, 1986; Hattori, 1992). The lack of a significant effect on soil respiration when the soil was amended with TZ1, TZ2 and CR ashes in the second incubation experiment may be attributed to the decrease in soil pH in soils amended with these ashes which probably inhibited the microbial activities. Nayak et al. (2014) reported no impact on heterotrophic microbial activity in soils amended with lower concentrations ($\leq$100 t ha^{-1}) of an acidic fly ash.

Fly ashes, being the by-products of coal combustion contain small/negligible amount of carbon and nitrogen (Carlson and Adriano, 1993; Matsi and Keramidas 1998). Nitrogen tends to be lost as oxides to the atmosphere during the combustion process and is thus very low in fly ashes; it can be discounted as an important source of N to the plants in the experiments reported here (Ciećko et al., 2010). From this study, the increase in C concentration in the soil following the soil amendment with 16% of the UK1 ash might be due to the higher concentration of C within the ash. The higher C concentration in the soil amended with ash than in the control soil throughout the incubation period implies the permanent change of this soil property due to the applied ash. Lim et al. (2017) also noted an increase in soil C at the end of the third season in a paddy field which was the residual effect of soil amendment with 10% fly ash. Besides the lower content of %N and extractable N in the UK1 ash than in the woodland soil (Figure 3-1 and Table 6-1), soil amendment with 16% of this ash significantly increased the concentration of extractable N in the soil. Although the concentration of extractable N increased in the first six months, then dropped up to the 24th month, throughout the incubation period the concentration of N in the fly ash amended soil was higher than in the control soil. This also implies that the positive change in soil nitrogen concentration induced by fly ash may be permanent besides its decrease with time. A similar

finding was reported by Ciećko et al. (2010) who observed a significant increase in total and extractable forms of nitrogen in soils amended with 0-400 Mg ha^{-1} of fly ash 19 years after application.

In the second experiment where the soil was incubated for 16 weeks with different ashes, soil amendment with Tanzanian ashes increased the concentrations of carbon and nitrogen in the soil while the CR ash reduced the concentration of C and N in the soil. UK2 ash did not have any effect at all. These effects may be linked to the concentrations of C and N in the ashes applied because Tanzanian ashes had higher concentrations of C and N than other ashes. Moreover, Tanzanian ashes were bottom ashes rich in C while UK and CR ashes were fly ashes characterized by a low/negligible quantity of C (Tharaniyil, 2013). From this study, it was noted that the effect (long- or short-term) of ash application on soil characteristics, particularly the concentrations of C and N, varied depending on the characteristics and the concentration of the ash applied. Application of 4% of most ashes did not have any significant effect on soil C and N concentrations, except CR ash which reduced them.

4.4.2 Long- and short-term effects of ash on total soil nutrient and PTE concentrations

From the short-term incubation experiment, the influence of fly ash on total nutrient concentrations varied depending on the particular nutrient and the type and concentration of the ash applied. The decrease in P concentration in soils amended with the CR ash is likely to be due to a 'dilution effect' when ash was added to the soil. In contrast, the increases observed when the UK2 and TZ2 ashes were added to soil were due to the high P concentration of both ashes leading to an additive effect. Moreover, low contents of Ca and Mg in soils amended with these ashes might also be due to similarly low contents of these nutrients in ashes. The positive influence of TZ2 and UK2 ashes on soil P concentration could also be linked to the high content of P in these ashes and the alkalinity of these ashes.

Even though higher concentrations of P, Ca, Mg and Mn were noted in the UK2 ash than in other ashes used in this experiment, the influence of this ash on the soil nutrient concentrations varied depending on the amount of ash applied.

The concentration of these nutrients generally increased when soils were amended with 16% compared with 4% of the UK2 fly ash. The direct, positive influence of fly ash on total concentrations of nutrients in soils has been reported due to the presence of these nutrients in fly ashes (Adriano and Weber, 2001; Kalra et al., 2000; Yeledhalli et al., 2007). However, from this study, it was noted that the effect of fly ash application on soil nutritional status varied depending on the type and amount of ash applied because of the differences in ash elemental concentrations already discussed. From the long-term incubation experiment (Experiment 1), the increase in total concentrations of most nutrients (P, K, Ca, Mg and Mn) following soil amendment with the UK1 fly ash could also be attributed to the higher content of these nutrients in fly ashes (Carlson and Adriano, 1993). The increased trend of most nutrient concentrations associated with the 16% ash amendment from months 0-1 and the subsequent decreasing trend from months 2-24 may be linked to the increased initial microbial stimulation and the decreased microbial activity with time noted through the measured CO_2 evolution. However, since this was a closed system, it is difficult to explain why these trends were obtained, because one would not expect any net increases or decreases in elemental concentrations unless losses were due to volatilisation. The most parsimonius explanation is therefore likely to be that of a Type I error. Soil amendment with 4% ash concentration in the current study did not show a marked significant effect which supports the suggestion of a Type I error for the 16% amendment at month 1. However, a similar finding was reported by Wyszkowski et al. (2014) who observed a significant increase in total concentrations of nutrients in soils amended with 100-800 Mg ha^{-1} of fly 19 years after the application of ash, although this was a field study and therefore not a closed system as described here. Wyszkowski et al. (2014) also observed an increase in soil nutrients in proportion to the concentration of the applied fly ash, which supports the findings of the current incubation study.

Besides the positive effect of fly ash on soil nutrients, soil amendment with fly ashes also increased the concentrations of PTEs in the soil. In the short incubation experiment, the effect of fly ash on PTE concentrations in the soil varied depending on the PTE and the type and concentration of the ash applied. The greatest increase in PTEs was due to soil amendment with the UK2 ash than other ashes and this increase was proportional to the concentration of the

ash applied. This could be linked to the higher content of PTEs noted in this ash than in other ashes. However, the effect of CR, TZ1 and TZ2 ash on most soil PTEs was noted only when the soil was amended with 16% of each ash and not at 4% which could probably be linked to the low concentrations of PTEs in these ashes. A direct effect of fly ash application on soil PTE concentrations has been reported by several workers (Carlson and Adriano, 1993; Singh et al., 2008; Seshadri et al., 2010) and has been linked to the presence of PTEs in ashes. In the long-term incubation (2 years), soil amendment with the UK1 ash also increased the concentrations of PTEs in the soil, which might also be linked to the high content of PTEs noted in this ash. However, after 2 years, the concentrations of PTEs were still higher in fly ash amended soils than in control soils, implying a long-time effect of ash on soil PTE concentrations. A similar finding was reported by Ciećko et al. (2015) who observed an increase in the total concentrations of PTEs (Cd, Cr, Cu, Mn, Fe, Zn and Pb) as a residual effect of soil amendment with fly ash (100-800 Mg ha^{-1}) 29 years after ash was applied.

4.4.3 Long- and short-term effect of ash on extractability of soil nutrient and PTE concentrations

From the short-term incubation experiment, the water extractability of nutrients following soil amendment with different ashes (UK2, TZ1, TZ2 and CR) varied depending on the source and concentration of the ash applied and the nutrient type. Soil amendment with the UK2 ash increased the availability of most nutrients in the soil which might be due to the high content of nutrients observed in this ash. Low extractability of P noted in soils amended with CR and TZ1 ashes could be attributed to the decrease in the total concentration of P in the soil amended with these ashes and the presence of insoluble P forms in fly ash (Gupta et al., 2012). The decreasing trend of Mn extractability in fly ash amended soils which followed the order of TZ1<CR<TZ2<UK2, despite the high total content of this nutrient in UK2 and CR ashes (data not shown), might be linked to the pH of these ashes (which increased following the same order) and changes in the soil pH induced by these ashes. Mn extractability tends to be high under very acidic conditions and the extractability decreases with each unit increase of the soil pH (Miller, 2016). In the long-term incubation experiment, the extractability (exchangeable and water-extractable) of nutrients P, K, Ca, Mg, S and B increased significantly following the soil amendment with the UK1

ash. This might be linked to the increased total concentrations of these nutrients (Banin et al., 1987); however, the extractability of Mn decreased with increasing ash concentration and throughout the incubation period. The reduced extractability of Mn may be ascribed to the alkalinity induced by fly ash application to the soil (Jala and Goyal, 2006). The higher extractability of most nutrients in fly ash amended soils than in control soil after 24 months implies a long-term positive effect of ash on soil nutritional status. A similar result was reported by Ciećko et al. (2015) who observed an increase in extractable nutrients (N, P, K and Mg) in arable soil 29 years after soil amendment with fly ash. Rautaray et al. (2007) also noted an increase in soil nutrient extractability as a residual effect after four seasons of rice -based cropping when the soil was fertilized with organic materials, mineral fertilizers and 10 t ha^{-1} of fly ash.

In addition to the increase in nutrient extractability in soils amended with fly ash, the extractability of PTEs also increased in fly ash amended soil which might be linked to the increase in total concentrations of these PTEs in the soil (Banin et al., 1987). The increased extractability of As and Cr following the amendment of soil with the UK1 ash could be attributed to the increase in soil pH as these PTEs are highly mobile in alkaline conditions (Hooda, 2010). Furthermore, increased Cd and Pb solublity may be associated with the ash-related increase in Ca concentration, since Ca tends to compete with these PTEs for soptive sites (Christensen, 1984). The higher extractability of PTEs in soil amended with ash than in controls throughout the long-term incubation experiment implies a long-term risk of contaminating the soils with these PTEs. A similar finding was reported by Ciećko et al. (2015) who noted increased extractability of Zn, Cu, Mn and Fe in arable soil 29 years after soil amendment with fly ash. Therefore, long-term availability of PTEs like As, Se and Mo in soils amended with ash has been reported as a limiting factor for use of fly ash as a soil amendment (Adriano and Weber, 2001).

4.5 CONCLUSIONS

Based on the long-term soil incubation results, the use of an alkaline ash may be a promising way of improving the soil pH of acidic soils thus ameliorating the problem of soil acidity permanently. Application of an alkaline fly ash at lower concentrations may also help to improve soil microbial activity and the

soil fertility status in the long-term, particularly when applied to problematic soils like the acidic soil used in this experiment. However, the effect of ash on the long-term accumulation of potentially toxic elements in the soil needs to be considered by either controlling the amount of ash added to the soil or by application of ash only to problematic soils. Based on the short-term soil incubation results, the effect of fly ash on soil characteristics varies depending on the characteristics and the amount of ash added to the soil. Since the results from the current study was based on single application of fly ash to the soil, further research to evaluate the long-term effect of fly ashes and the effects of multiple applications of fly ashes on soil characteristics are recommended

5 ENZYME ACTIVITIES AND WHEAT GROWTH RESPONSE IN ASH AMENDED SOILS

5.1 INTRODUCTION

Fly ash is one of several coal combustion by-products considered to be beneficial in improving soil characteristics and crop productivity, due to the presence of essential plant nutrients and the alkaline nature of most ashes (Kolbe et al., 2011; Gupta et al., 2012; Singh et al., 2014). However, being an industrial waste product, fly ash also contains potentially toxic elements (PTEs) which may be toxic to microorganisms (Wong et al., 1986; Hattori, 1992). Several studies have reported the improvement of physical and chemical soil characteristics following soil amendment with fly ash (Adriano and Weber, 2001; Pathan et al., 2003; Yunusa et al., 2011; Singh et al., 2014; Shaheen et al., 2014); however, to date, few studies have investigated the effect of fly ash on soil biological characteristics, particularly soil enzyme activities.

Soil enzymes are a small but very important fraction of soil organic matter controlling all the biochemical actions in the soil (Dahm et al., 2011). Soil enzymes play an important role of regulating ecosystem functioning by controlling nutrient cycling and fertilizer use efficiency, reflecting the microbiological activities in soils and acting as indicators of any changes in soil conditions (Dick and Wang 2000; Makoi and Ndakidemi, 2008). The primary source of enzymes is the soil microbiome, but enzymes may also originate from plants and animals (Dahm et al., 2011). The sources of phosphatase enzymes in the soil, which hydrolyse organic P to inorganic P, are soil bacteria, plant roots and fungi (Kramer and Green 2000; Makoi and Ndakidemi 2008). Alkaline phosphatase is derived solely from microorganisms (Tabatabai, 1994) though acid phosphatase can be derived from either microbes or plants. The source of the enzyme dehydrogenase, which provides a direct measure of microbial activity in soil and an indication of soil health, is the microbes (Utobo and Tewari, 2014). Glucosidase is an enzyme that catalyses the hydrolysis of β-glucosides present in organic matter; it tends to originate from microbes, plants and animals (Utobo and Tewari, 2014). The main sources of urease, an enzyme that hydrolyses urea fertilizer to NH_3 and CO_2 and increases soil pH, are microbes and plants (Makoi and Ndakidemi, 2008).

Soil management by the application of fly ash has been noted to inhibit soil respiration and enzyme activities (Wong and Wong, 1986; Pitchel 1990; Pati and Sahu 2004). This inhibition has been linked to fly ash characteristics such as low availability of C and N, high pH and salinity, high concentration of soluble salts and the presence of PTEs in ashes. Therefore, studying the effect of fly ash on soil enzymes, an important index used in assessing the effects of soil contamination on microbial activities and fertility status of soils (Utobo and Tewari 2014), will help us to understand the impact of fly ash amendments on the biological soil health.

The present study was carried out with the aim of evaluating the effect of coal ash from the UK and Tanzania on soil pH, selected soil enzyme activities (dehydrogenase, acid phosphatase, alkaline phosphatase, urease and β-glucosidase) and on vegetative growth of wheat grown in woodland and arable soils. The study was carried out on two soils (woodland and arable), amended with different concentrations of the UK1 and TZ1 ashes; wheat plants were grown for 50 days and harvested pre-grain development. The specific objectives of this study were:

i) To evaluate the effect of increasing concentrations of each coal ash on growth and biomass production of wheat.

ii) To evaluate the effect of increasing concentrations of each coal ash on enzyme activities (dehydrogenase, acid phosphatase, alkaline phosphatase, urease and β-glucosidase),

iii) To establish whether similar effects of each coal ash occur in two contrasting soils.

5.2 MATERIAL AND METHODS

5.2.1 Experimental approach

Two pot experiments were conducted in which spring wheat (*Triticum aestivum*) var. Willow was grown in woodland and arable soils amended with fly ash. In the first experiment, soils were amended with the fly ash collected from the UK (first batch = UK1) at concentrations of 0, 2, 4, 8 and 16%; in the second experiment, soils were amended with the ash collected from Tanzania (first batch = TZ1) at the same concentrations. In both experiments, the plants were grown for 50 days (pre-grain development). Both experiments were designed

to evaluate the effect of fly ash application in woodland and arable soils on soil enzymatic activities (dehydrogenase, phosphatase, glucosidase, and urease) and wheat (*T. aestivum*) growth.

5.2.2 Experimental set up

5.2.2.1 Experiment 1; UK ash 1 in woodland and arable soils

The experiment involved five concentrations of fly ash 0, 2, 4, 8 and 16 % on a dry weight basis. The equivalent fresh weight of 250 g dry weight of arable and woodland soil was mixed thoroughly in a plastic bag with each concentration of fly ash and then the mixture was used to fill the required number of plant pots. Four replicates of each fly ash treatment plus soil mixture were prepared. All pots were placed in a designated growth room arranged in a randomized block design (with 4 replicate blocks), watered with deionized water and maintained at 20°C/18°C day/night, 16h/8h day/night duration (including a 1 hour dawn and a 1 hour dusk period). Each pot was watered with deionized water and allowed to equilibrate for 24 hours before sowing the wheat seed. The settling period avoided 'surface sealing' of the germinating seeds, especially in pots treated with higher concentrations of fly ash. Six seeds of spring wheat var. Willow were sown in each pot at a depth of about 1 cm. The pots were watered with deionized water. All plants were maintained up to 50 days, following normal agronomic requirements including watering, thinning to 1 plant per pot after germination, removal of weeds and monitoring the occurrence of any disease and phytotoxic symptoms to the plant following the ash amendment. No fertilizer was added to these plant pots.

5.2.2.2 Experiment 2; Tanzania ash 1 in woodland and arable soil

The experiment was set up as for the UK-ash experiment above, except that ash amendments were mixed thoroughly into the soil using a food processor prior to filling the pots. Four replicates of each fly ash treatment + soil mixture were prepared. All pots were placed in a different growth room from that used for the UK-ash trial, but the temperature and daylength settings were the same. Pots were arranged in a randomized block design (with 4 replicate blocks). Six seeds of spring wheat var. Willow were sown in each pot at a depth of 1 cm and plants were thinned to 1 per pot following germination. Maintenance of plants in pots was as described for the UK-ash trial above.

5.2.3 Plant harvesting and analysis

All plants from both experiments were harvested 50 days after the sowing date. Before harvesting, numbers of tillers and leaves were counted. The shoot biomass was determined by harvesting the shoots and oven drying them at 60°C until constant weight and recording the weight of shoots per plant per pot. The roots were extracted from the soil, washed thoroughly with tap water, oven dried at 60°C until constant weight, and root biomass recorded for each treatment.

5.2.4 Soil analysis after harvesting plants

After harvesting, all soils from each pot were homogenized and frozen at -20°C pending enzyme analysis. For the first experiment, soils were frozen for 18 months prior to enzyme analysis because of a leave of absence and for 4 months for the second wheat experiment.

Before assaying enzyme activities in the experimental soils, all methods to be used were tested by assaying urease, dehydrogenase, acid and alkaline phosphatases and glucosidase enzymes in fresh soil collected under actively growing grasses on the Sutton Bonington campus (results not shown). Apart from method testing, this enabled broad comparison (in terms of same order of magnitude) with the data from the experimental soils to ensure that freezing had not detrimentally affected the results and that comparisons between treatments were valid.

Enzyme assays were performed on the experimental samples after thawing in a cold room (4°C) for 2 days and then at room temperature (about 20°C) for 15 hours.

5.2.5 Determination of urease activity

The soil assay for urease was performed following the procedure reported by Kandeler and Gerber (1988). Five grams of soil were weighed into a 50 mL 'DigiTUBE' (non RackLock, no Cap, Code: 010-500-264) and wetted with 2.5 mL of 79.9 mM urea solution. The tubes were stoppered and incubated at 37°C for 2 hours. After incubation, 2.5ml of utra-pure water and 50 mL of a 1:1 ratio of 1M KCl and 1M HCl were added and the mixtures were shaken using an end-

over-end vertical rotary shaker at 30 rpm for 30 minutes. The resulting suspensions were filtered using qualitative filter papers (Fisher brand) and the filtrates analysed for the ammonium released following the calorimetric procedure at 690 nm wavelength. For photometric analysis, 1 mL of filtrate was diluted to 10 mL with ultrapure H_2O and, successively, 5 mL of Na salicylate solution and 2 mL of 39.1 mM Na dichloroisocyanurate were added. The Na salicylate solution was prepared by dissolving a mixture of 17 g of sodium–salicylate and 120 mg sodium nitroprusside in 100 mL deionised water. The diluted filtrates were allowed to stand for 30 minutes at room temperature for colour development and then the optical density was determined at 690 nm wavelength. The controls were prepared as above with 2.5 mL of utra-pure H_2O and the substrate (2.5 mL urea) was added at the end of the incubation and immediately before KCl/HCl addition.

To prepare the standard stock solution, 3.8207 g of NH_4Cl was dissolved in 1000 mL of deionised water (1000 µg NH_4^+-N mL^{-1}). To prepare the standard calibration curve, 0, 1, 1.5, 2 and 2.5 mL of standard stock were diluted to 100 mL with KCl/HCl solution. This calibration standards were equivalent to 0, 10, 15, 20 and 25 µg NH_4^+-N mL^{-1}.

The calibration graph was plotted and the NH_4-N content in the filtrate was calculated from the regression equation. Further calculation was performed using the formula;

$$\mu gN/g\ DM/2h = (S - C) * 10 * 55 * \frac{100}{5 * \%DM} \qquad Equation\ 5-1$$

Where:
S = value for each sample (µg mL^{-1})
C = mean value for 'analytical' controls (µg mL^{-1})
10 = dilution factor
55 = volume of extract (mL)
5 = initial soil weight
% DM = percentage dry matter

Four replicates were prepared for each treatment sample with the urease activity being expressed as µg N g^{-1} dm $2h^{-1}$.

5.2.6 Determination of dehydrogenase activity

The soil assay for dehydrogenase was performed following the modified procedure by Thalman (1968). Five grams of soil were weighed into test tubes and wetted with 5 mL of the substrate (1, 2, 3 and 5% triphenyltetrazolium chloride (TTC) solution). This concentration range of the substrate was selected because the experimental soils were loamy soils. The substrates were prepared by dissolving TTC in Tris buffer at pH 7.6 for neutral soil samples (pH 6-7), pH 7.4 for alkaline soil samples (pH >7) and pH 7.8 for acidic soil samples (pH <6). The samples were mixed well, closed with the rubber stoppers and then incubated for 16h at 25°C.

The triphenyl formazan (TPF) produced by the dehydrogenase enzyme was extracted by adding to the samples 25 mL of acetone, mixing well and shaking the tubes for 2 h in the dark. Subsequently, the samples were filtered in a semi-dark room and the extinction of the filtrate and calibration standards were measured photometrically at 546 nm within 1 h.

To prepare the standard stock solution (10 mg TPF mL^{-1}), 1 g of TPF was dissolved in 100 mL of acetone. To prepare the working standard (0.1 mg TPF mL^{-1}), 1 mL of the standard stock solution was diluted to 100 mL with acetone in a volumetric flask. The calibration standards were prepared by pipetting 0, 1, 2, 5 and 10 mL of working standard into test tubes and then diluting them to 30 mL with acetone. These calibration standards corresponded to 0, 100, 200, 500 and 1000 µg TPF. A calibration graph was plotted and the µg TPF content in filtrates were calculated from the regression equation. Further calculation was performed using the formula;

$$\mu gTPF/g\,DM/16h = (S - C) * \frac{100}{5 * \%DM} \qquad Equation\ 5-2$$

Where: S = value of each sample (µgTPF)
C = mean value for 'analytical' controls (µgTPF)
5 = initial soil weight (g)
% DM = percentage dry matter

5.2.7 Determination of phosphatase (alkaline and acid phosphatase) activities

Phosphatase activities in soils were assayed following the original method of Tabatabai and Bremner (1969) modified by Eivazi and Tabatabai (1977). One gram of soil was weighed into 50 mL Falcon tubes and wetted with 1 mL of the desired substrate (appropriate for determination of alkaline or of acid phosphatase) and 4 mL of the corresponding working buffer solution (either for determination of alkaline or acid phosphatase). The tubes were shaken briefly, stoppered and incubated for 1 h at 37°C. The substrates for acid and alkaline phosphatases were prepared by dissolving 4.268 g of disodium p-nitrophenyl phosphate hexahydrates in 1000 mL working buffer solutions of appropriate pH for the enzyme being assayed.

The preparation of the modified universal buffer (MUB) stock solution was performed by dissolving 12.1 g of tris (hydroxymethyl) amino methane, 11.6 g of maleic acid, 14 g of citric acid, and 6.3 g of boric acid in 500 ml of 1M NaOH and made to 1000 mL with ultrapure water. The working buffer solution for alkaline phosphatase was prepared by mixing 200 mL of MUB and 500 mL of ultrapure water, adjusting the pH to 11 with NaOH and then adjusting the volume to 100 mL with ultrapure water. The working buffer solution for acid phosphatase was prepared by mixing 200 mL of MUB and 500 mL of ultrapure water, adjusting the pH to 6.5 with HCl and then adjusting the volume to 100 mL with ultrapure water.

After incubation, 1 mL of 0.5 M $CaCl_2$, and 4 mL 0.5 M NaOH were added to the samples which were then diluted to the ratio of 1:10 with ultrapure water, shaken briefly and then filtered with qualitative filter papers (Fisher brand). Then the extinction of the yellow colour intensity of calibration standards, controls and samples was measured photometrically at 400 nm against the reagent blank. The calibration curve for the standards was plotted and the µg p-nitrophenol (pNP) in filtrates was calculated from the regression equation of the plotted calibration curve. Further calculations were performed using the formula;

$$\mu g\ NP/gDM/h = (S - C) * 10 * \frac{100}{1 * \%DM} \qquad Equation\ 5-3$$

Where: S = value of each sample (µg pNP)

C = mean value for 'analytical' controls (µg pNP)

1 = initial soil weight (g)

10= factor for dilution of the extract

% DM = percentage dry matter

5.2.8 Determination of β-glucosidase activity

Glucosidase activities in soils were assayed following the modified method published by Hoffmann and Dedeken (1966). Five grams of moist soil was weighed into a 50 mL 'DigiTUBE'. Two controls and four replicates from each experimental treatment were weighed. Twenty mL of acetone were added to both samples and controls followed by 10 mL of substrate solution (salicin) which was added only to the samples. Ten mL of ultrapure water were added to controls instead of substrate. The substrate was prepared by dissolving 1 g of salicin in a 100 mL volumetric flask with ultrapure water and diluting it to volume with the same water. All the tubes were well sealed and incubated for 3h at 37°C. After incubation, samples and controls were filtered using qualitative filter papers (Fisher brand) and then 3 mL of each filtrate were mixed with 5 mL of the borate buffer (0.2 M, pH 10) and 0.5 mL of the colour reagent into 50 mL volumetric flasks. The borate buffer was prepared by mixing 12.404 g of boric acid with 100 mL of 1 M sodium hydroxide solution and 600 mL of ultrapure water in a 1000 mL volumetric flask and then diluting to volume with ultrapure water. The colouring reagent was prepared by dissolving 2, 6-dibromchinon-4-chlorimide in 100 mL volumetric flask with ethanol (60 % v/v) and diluting to volume with ethanol. All test solutions in 50 mL volumetric flasks were allowed to stand for 1 h at room temperature for colour development and afterward made up to volume with ultrapure water. Then the extinction was measured at 578 nm with a spectrophotometer against the reagent blank within 90 minutes.

To prepare the standard stock solution (758 µg phenol mL^{-1}), 0.758 g of phenol was dissolved in ultrapure water in a 1000 mL volumetric flask and made up to volume with the same water (758 µg phenol mL^{-1} corresponding to 1 µg saligenin mL^{-1}). The working standard (7.58 µg phenol mL^{-1}) was prepared by pipetting 10 mL of the standard stock solution in a 1000 mL volumetric flask and diluting to volume with ultrapure water (7.58 µg phenol mL^{-1} corresponding

to 10 µg saligenin mL^{-1}). The calibration curve was then prepared by pipetting 0 (reagent blank), 1, 2, 5, 10 and 15 mL of the working standard into 50 mL volumetric flasks. Then the same procedures for dilution, colour development and extinction measurement were followed as for the soil filtrates. The calibration curve for the standards was plotted and the µg of saligenin content in filtrates was calculated from the regression equation of the plotted calibration curve. Further calculation was performed using the formula;

$$\mu g\ \mathbf{saligenin/gDM/3h} = (S - C) * 30 * \frac{100}{3 \cdot 5 \cdot \%DM} \qquad Equation\ 5-4$$

Where: S = value for each sample (µg saligenin)
C = mean value for 'analytical' controls (µg saligenin)
30 = volume of incubation mixture (mL)
5 = initial soil weight (g)
3= aliquot of filtrate
% DM = percentage dry matter

5.2.9 Statistical analysis

Statistical analyses were performed using Genstat 17th Edition (VSN International, UK). A generalized two way analysis of variance (ANOVA) was conducted on all parameters (enzyme activities and plant growth data) using fly ash concentration and soil type as factors. Normality was tested by plotting residuals against expected normal quantiles and post-hoc comparisons between means were based on a least significant differences (LSD) test at 0.05 probability level.

5.3 RESULTS

5.3.1 Effects of ash on soil pH

Results of the effect of the UK and Tanzania ashes on soil pH are presented in Figure 6-1. The application of UK1 ash to both soils (woodland and arable) increased the soil pH (Figure 5-1a; ash concentration x soil type interaction; $p<0.001$, Table 5-1). The pH in both soils increased with increasing fly ash concentration but the pH of the arable soil was higher than in the woodland

soil. Soil amendment with the Tanzanian ash reduced the pH of both soils (Figure 5-1b; ash concentration x soil type interaction; $p<0.001$, Table 5-1) but the extent of this decrease was higher in the arable soil than in the woodland soil. The pH of the arable soil decreased from 6.76-5.92 and in the woodland soil from 4.27-4.06 following soil amendment with 0-16 % ash, respectively.

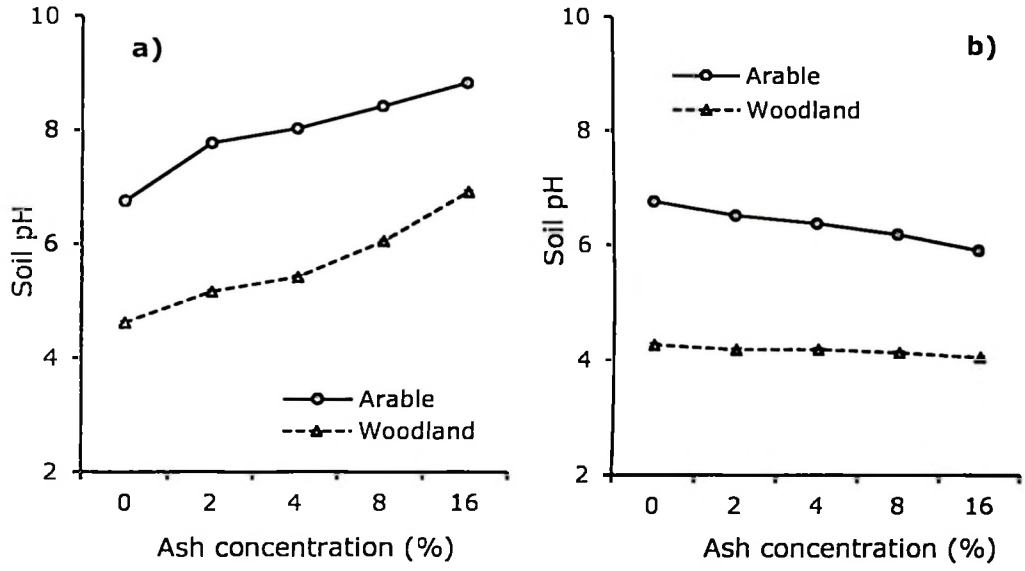

Figure 5-1: *Effect of ash application on soil pH.* ***a)*** *= The soil treated with the UK1 ash, LSD=0.095, SE=0.033 and* ***b)*** *= the soil treated with Tanzanian ash, LSD=0.068, SE=0.024. The individual error bars are based on the pooled variance estimate from the ANOVA with 30 degrees of freedom.*

5.3.2 Enzyme activities in soils amended with the UK1 ash

In Experiment 1, application of the UK1 ash in both experimental soils influenced the activities of all the enzymes determined (Figure 5.2). In woodland soil, application of UK1 ash from 0-4 % and at 16 % significantly increased dehydrogenase activity in comparison to the control, but this activity decreased significantly at 8 % fly ash concentration (Figure 5-2 and Table 5-1; ash concentration x soil type interaction; $p=0.023$). Soil amendment with this ash to the arable soil did not significantly affect dehydrogenase activity. Glucosidase activity increased significantly when the woodland soil was amended with 2 % UK1 fly ash and then decreased significantly with increasing ash concentration from 4-16 % (Figure 5-2 and Table 5-1; ash concentration x soil type interaction; $p<0.001$). Application of the UK1 fly ash to the arable soil

did not significantly affect glucosidase activity. Urease activity in the woodland soil increased significantly with increasing concentration of the UK1 fly ash (Figure 5-2 and Table 5-1; ash concentration x soil type interaction; $p<0.001$). A similar trend was noted in the arable soil amended with this ash from 0-8 % but at 16 % ash concentration, the urease activity in the arable soil decreased significantly (Figure 5-2 and Table 5-1; ash concentration x soil type interaction; $p<0.001$). Fly ash concentration as an individual factor did not produce any significant effect in alkaline phosphatase activity when both soils were amended with 0-8 % ash, but the alkaline phosphatase activity decreased significantly in soils amended with 16 % fly ash concentration (Figure 5-2 and Table 5-1; $p=0.002$). Soil type as an individual factor also influenced the alkaline phosphatase activity; the activity was significantly higher in the arable soil than in woodland soil (arable soil=262.4 and woodland soil=161.2 μg NP g^{-1} h^{-1}; $p<0.001$ data not shown).

Acid phosphatase activity was determined only in the woodland soil (which was very acidic) and not in the arable soil (which was slightly acidic/near neutral) due to the predominance of acid phosphatase in acid soils and alkaline phosphatase in neutral or alkaline soils (Dick and Tabatabai, 1984; Dick et al., 2000).

Application of 0-4 % of UK1 fly ash to the woodland soil did not have any significant effect on acid phosphatase activity, while further increase in ash concentration from 8-16 % decreased the activity of this enzyme significantly in comparison to the control (Figure 5-3 and Table 5-1; $p=<0.001$).

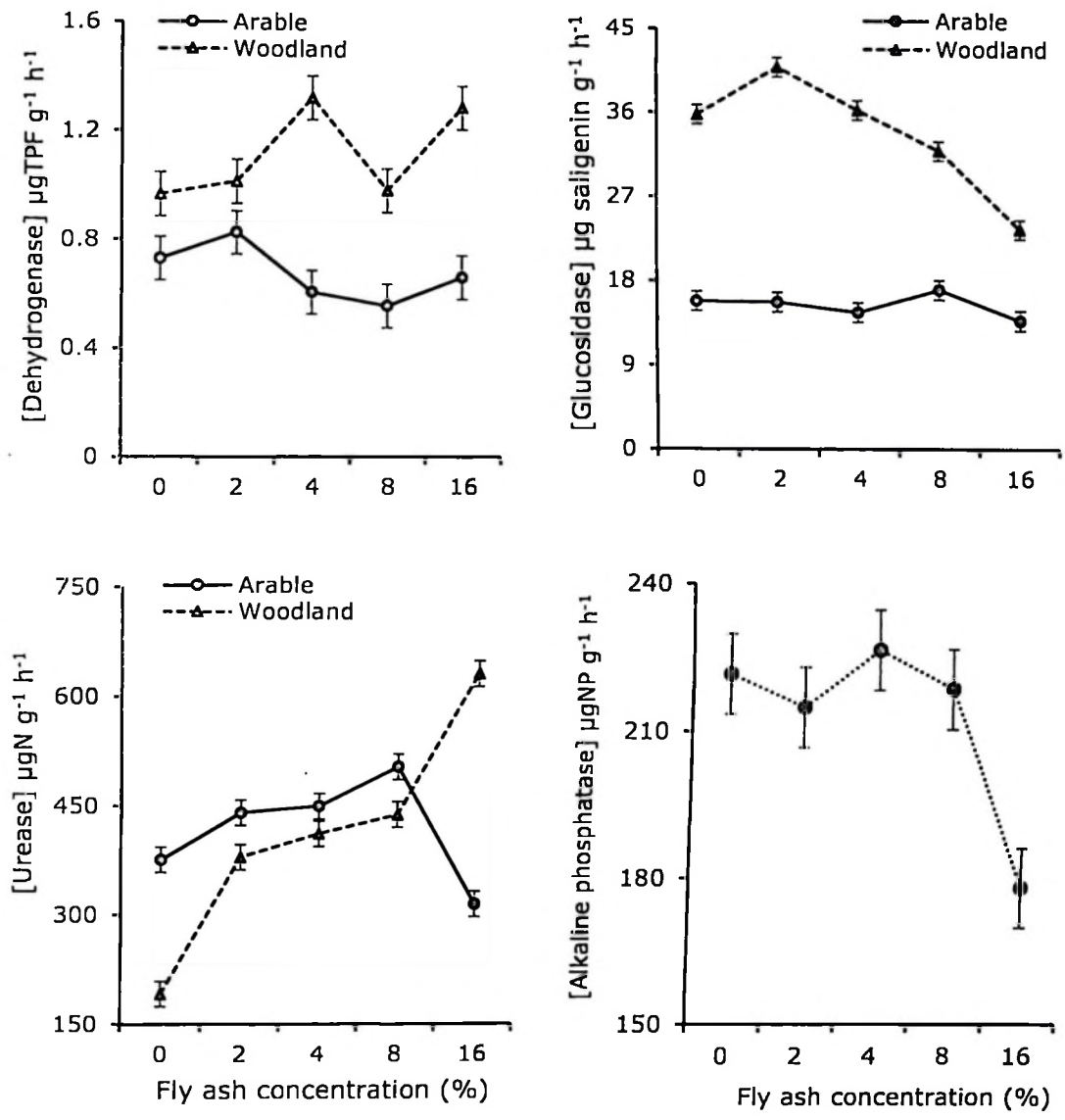

Figure 5-2: *Enzyme activities in UK1 fly ash amended soils, under wheat plants for 50 days. LSD for dehydrogenase=0.261, glucosidase=2.97, urease=50.4, and alkaline phosphatase= 23.52. The individual error bars are based on the pooled variance estimate from the ANOVA with 30 degrees of freedom. Please note the scale differences on the Y-axes. For alkaline phosphatase, data are means pooled across the woodland and arable soils.*

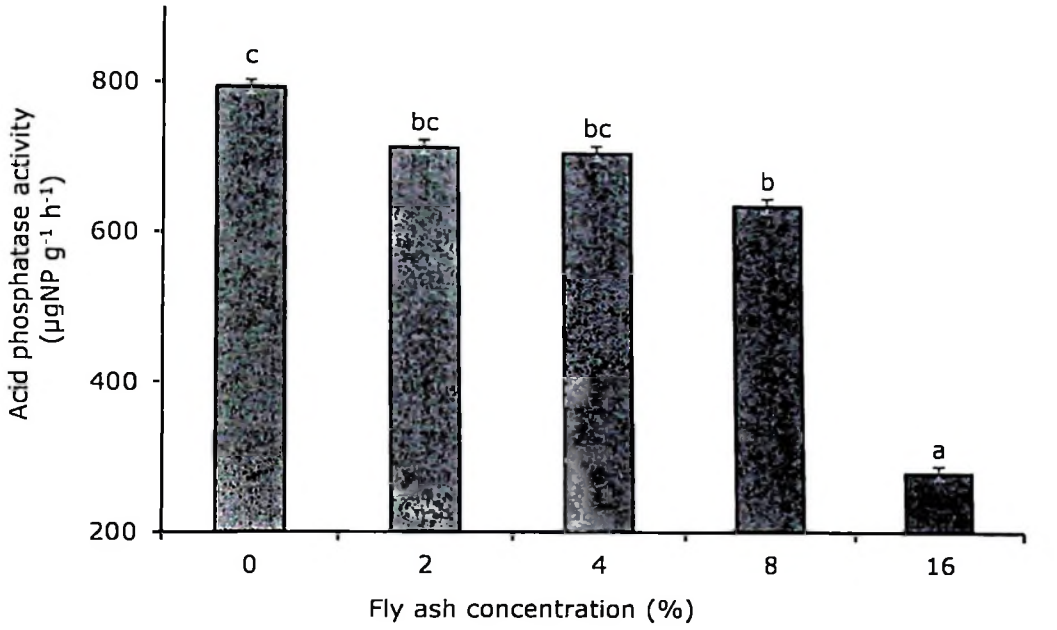

Figure 5-3: *Acid phosphatase in woodland soil amended with different concentrations of the UK1 fly ash. Columns with the same letters are not significantly different according to Tukey's multiple comparison test, p<0.001.*

5.3.3 Effect of the UK1 fly ash on wheat growth

Soil amendment with the UK1 fly ash improved all growth parameters of spring wheat which was grown for 50 days (Figure 5-4). In woodland soil, the shoot biomass and number of leaves increased significantly with increasing concentration of the fly ash from 4-16 % while in the arable soil, both parameters increased significantly for the plants grown in 0-4 % ash and thereafter (from 8-16 % fly ash) there were no further significant increases in these parameters (Figure 5-4 and Table 5-1; ash concentration x soil type interaction; $p<0.001$ for shoot biomass and $p=0.01$ for number of leaves). In woodland soil, the root biomass increased with increasing concentration of the fly ash while in the arable soil a significant increase in the root biomass was noted in plants grown in soil amended with 4 % ash and there was no further significant increase in root biomass with the 8-16 % amendments (Figure 5-4 and Table 5-1; ash concentration x soil type interaction; $p=0.002$). Fly ash as a single factor also influenced tiller formation in plants grown in both soils; the number of tillers increased significantly with an increasing concentration of fly ash from 4-16 % (Figure 5-4 and Table 5-1; $p<0.001$).

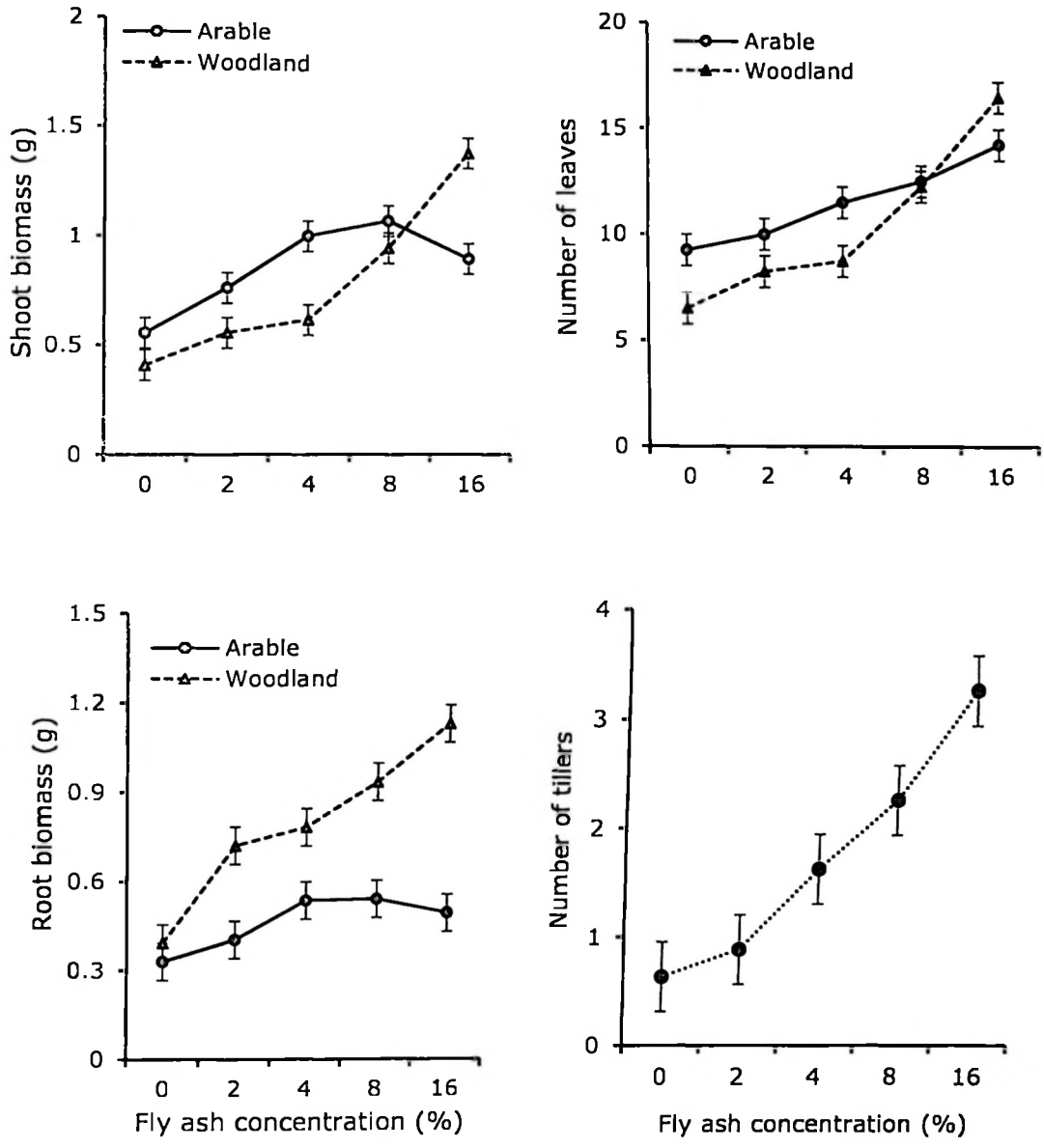

Figure 5-4: *The effect of the UK1 fly ash on wheat growth parameters after 50 days. LSD for shoot biomass=0.2017, Number of leaves=2.138, root biomass=0.1807, and number of tillers=0.923. The individual error bars are based on the pooled variance estimate from the ANOVA with 30 degrees of freedom.*

Table 5-1: *Summary of two-factor ANOVA for soil enzyme activities and wheat growth parameters from the Experiment 1*

ENZYME ACTIVITIES						WHEAT GROWTH PARAMETERS					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**	**VARIATE**	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
Dehydrogenase	Ash (%)	4	1.83	0.15	0.1846	**Shoot biomass**	Ash (%)	4	28.6	<0.001	0.1426
	Soil type	1	59.25	<0.001	0.1167		Soil type	1	2.88	0.1	0.0902
	Interaction	4	3.31	0.023	0.261		Interaction	4	11.1	<0.001	0.2017
	Residual	30					Residual	30			
Urease	Ash (%)	4	39.33	<0.001	35.64	**Number of leaves**	Ash (%)	4	32.01	<0.001	1.512
	Soil type	1	0.34	0.566	22.54		Soil type	1	5.03	0.032	0.956
	Interaction	4	58.81	<0.001	50.4		Interaction	4	4.06	0.01	2.138
	Residual	30					Residual	30			
Glucosidase	Ash (%)	4	24.47	<0.001	2.103	**Root biomass**	Ash (%)	4	15.51	<0.001	0.1278
	Soil type	1	791.63	<0.001	1.33		Soil type	1	69.52	<0.001	0.0808
	Interaction	4	17.27	<0.001	2.974		Interaction	4	5.62	0.002	0.1807
	Residual	30					Residual	30			
Alkaline phosphatase	Ash (%)	4	5.69	0.002	23.52	**Number of tillers**	Ash (%)	4	22.26	<0.001	0.653
	Soil type	1	193.27	<0.001	14.88		Soil type	1	1.53	0.226	0.413
	Interaction	4	1.86	0.143	33.27		Interaction	4	0.46	0.765	0.923
	Residual	30					Residual	30			
Acid phosphatase (WL soil)	Ash (%)	4	95.65	<0.001							
	Residual	14									

5.3.4 Enzyme activities in soils amended with Tanzanian ash (TZ1)

In Experiment 2, soil amendment with the Tanzanian ash (TZ1) also influenced activity of all enzymes measured (Figure 5-5). In woodland soil, a slight increase in the dehydrogenase activity was noted when the soil was amended with 2 % of the TZ1 ash, but higher ash concentrations up to 16 % decreased dehydrogenase activity significantly (Figure 5-5 and Table 5-2; ash concentration x soil types interaction; $p=0.024$). In the arable soil, a decreasing trend of dehydrogenase activity was noted, although this trend fluctuated (Figure 5-5 and Table 5-2; ash concentration x soil types interaction; $p=0.024$).

Glucosidase activity in the woodland soil decreased significantly with increasing ash concentration from 0-8 % but higher ash concentrations up to 16 % did not result in further significant decreases in activity (Figure 5-5 and Table 5-2; ash concentration x soil types interaction; $p=0.008$). However, in the arable soil, glucosidase activity decreased significantly with increasing ash concentration from 4-16 % (Figure 5-5 and Table 5-1; ash concentration x soil types interaction; $p=0.008$). Soil amendment with the TZ1 fly ash did not affect urease activity in the woodland soil while in the arable soil, activity increased significantly in the soil amended with 2 % ash concentration (Figure 5.5 and Table 5-2; ash concentration x soil types interaction; $p=0.024$). There was no further increase in urease activity in the arable soil amended with 4-8 % ash and 16 % decreased urease activity in the arable soil (Figure 5-5 and Table 5-2; ash concentration x soil types interaction; $p=0.024$).

A decreasing trend in acid phosphatase activity in both soils was observed following ash amendment, but in the woodland soil, the activity decreased significantly with addition of 2-16 % ash in comparison to the control, while in the arable soil, activity decreased significantly with 4-16 % ash amendment (Figure 5-5 and Table 5-2; ash concentration x soil types interaction; $p<0.001$).

Alkaline phosphatase activity was only determined in the arable soil which was slightly acidic/neutral and not in the woodland soil (which was very acidic) due to the predominance of alkaline phosphatase in neutral or alkaline soils and acid phosphatase in acidic soils (Dick and Tabatabai, 1984; Dick et al., 2000). Application of the TZ1 ash (ash as an individual factor) from 0-4 % did not affect alkaline phosphatase, while 8-16 % ash addition resulted in decreaded

alkaline phosphatase activity compared to the control (Figure 5-6 and Table 5-2; p=<0.001).

Tanzanian (TZ1) ash did not affect any of the measured wheat growth parameters when applied to either the woodland or to the arable soil.

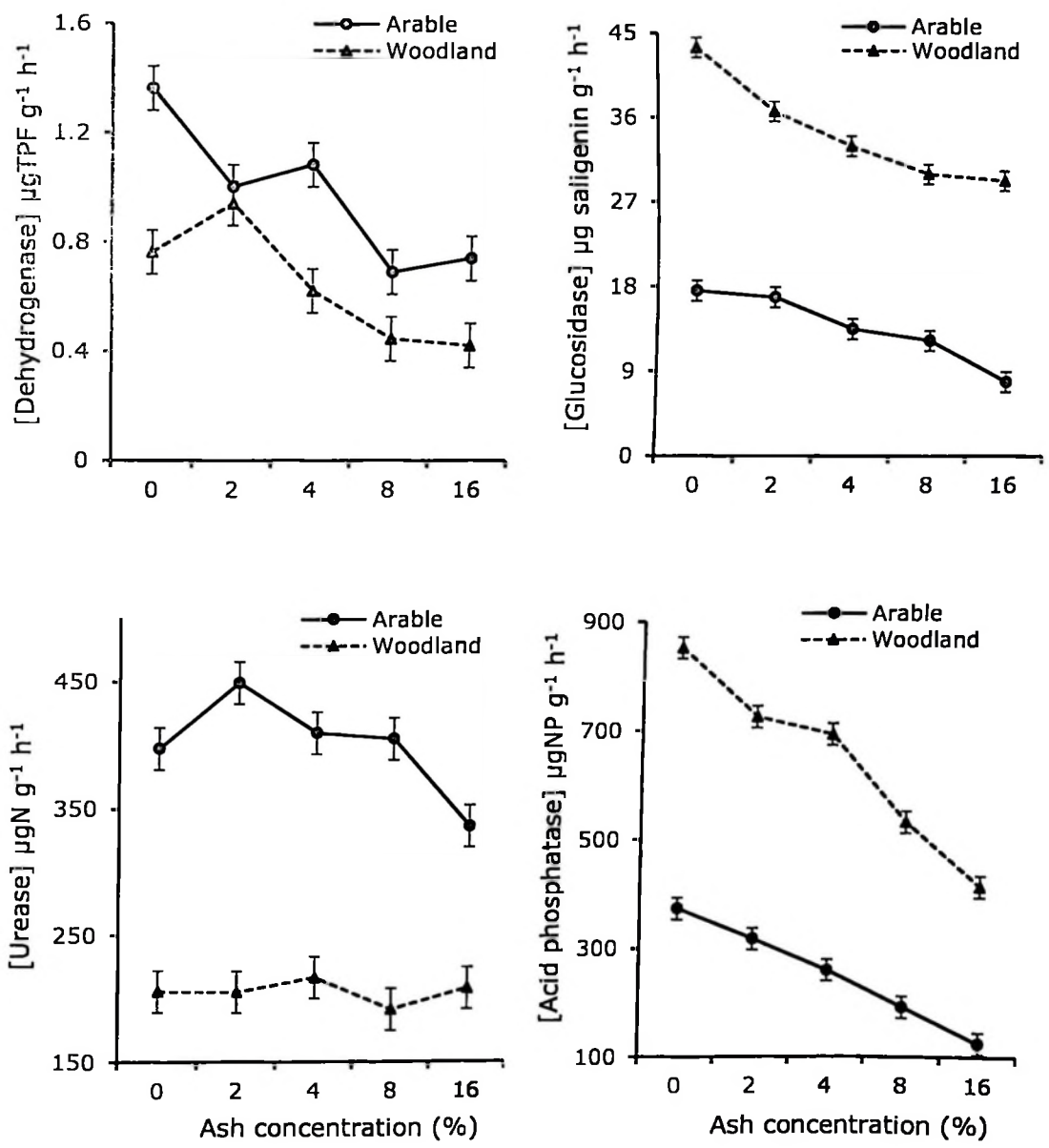

Figure 5-5: *Enzymatic activities in soils amended with the Tanzanian ash (TZ1) under wheat plants after 50 days. LSD for dehydrogenase=0.232, glucosidase=3.1, urease=47.96, and acid phosphatase=57.89. The individual error bars are based on the pooled variance estimate from the ANOVA with 30 degrees of freedom. Please note the scale differences on the Y-axes.*

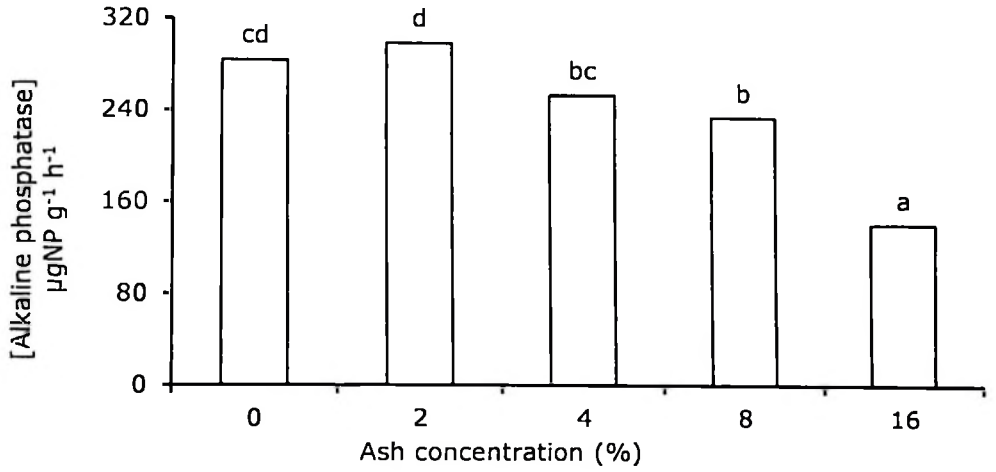

Figure 5-6: *Alkaline phosphatase in the arable soil amended with different concentrations of the Tanzanian ash. Columns with the same letters are not significantly different according to Tukey's multiple comparison test, $p<0.001$, $F_{4, 15}=42.41$*

Table 5-2: *Summary of two-way ANOVA for enzyme activities from the Experiment 2*

VARIATE	FACTOR	DF	F	P VALUE	LSD (95%)
Dehydrogenase	Ash (%)	4	15.59	<0.001	0.164
	Soil type	1	43.59	<0.001	0.1037
	Interaction	4	3.28	0.024	0.232
	Residual	30			
Urease	Ash (%)	4	3.02	0.033	33.91
	Soil type	1	342.11	<0.001	21.45
	Interaction	4	3.29	0.024	47.96
	Residual	30			
Glucosidase	Ash (%)	4	37.92	<0.001	2.19
	Soil type	1	943.34	<0.001	1.385
	Interaction	4	4.24	0.008	3.097
	Residual	30			
Acid phosphatase	Ash (%)	4	91.09	<0.001	40.94
	Soil type	1	948.73	<0.001	25.89
	Interaction	4	7.2	<0.001	57.89
	Residual	30			
Alkaline phosphatase (Arable soil)	Ash (%)	4	42.41	<0.001	
	Residual	15			

5.4 DISCUSSION

In this study, the activities of the enzymes dehydrogenase, urease, phosphatase and β-glucosidase were determined in woodland and arable soils amended with fly ashes and cropped with wheat for 50 days. Soil samples from both experiments were frozen before analysis immediately after completing the pot experiments. According to ISO 2009, storage of temperate soils for 3-12 months at -20, -80 or -180°C does not inhibit microbial activities. Kendeler and Gebger (1988) found no significant effect of freezing soil for 5 months on urease activities. Sample storage by freezing has also been recommended as a better method than air drying by Wallenius et al. (2010) due to its small effect on enzymatic activities particularly in clay loam and forest humus soils. Differences in soil enzymatic activities in control soils (soils without fly ash amendments) between the two experiments were noted which suggests there were variations in the conditions under which wheat plants were grown. Indeed the two growth rooms were lit by different bulb types and had different ventilation systems; one was illuminated with 400W BLV Signion duro bulbs whilst the other was fitted with banks of OSRAM Lumilux HO 54W/840 bulbs, resulting in noticeably different light levels (although these were not measured).

5.4.1 Effects of the UK1 ash on soil pH, enzyme activities and wheat growth

Soil amendment with the UK1 fly ash increased the pH of both soils. This trend might be linked to the higher pH (12.3) of the applied ash. The liming effect of fly ash may be associated with the presence of the considerable amounts of CaO and MgO in fly ashes reported previously (Adriano et al., 1980; Pati and Sahu, 2004).

In Experiment 1, application of the UK1 ash at lower concentrations (0-4 %) increased dehydrogenase activity in the woodland soil but not in the arable soil, which might imply the beneficial effect of this fly ash in improving microbial activity in very acidic soil. However, at higher fly ash concentrations (8-16 %), there were no clear trends of dehydrogenase activity in the woodland soil. Similar findings were reported by Sarangi (2001) and Pati and Sahu (2004) who observed a positive influence of fly ash on dehydrogenase activities for soils amended with 2.5 % ash but an inhibitory effect at ash concentrations greater than 2.5 %. Wong and Wong (1986) also noted a positive effect of fly

ash on dehydrogenase activity in soil amended with 10 % ash but an inhibitory effect at ash concentrations greater than 10 %, which was linked to the ability of fly ash to supply nutrients to microbes to perform their metabolic activities and the toxicity of ash to microbes when applied at higher concentration. Since soil pH has been suggested as the best predictor of soil dehydrogenase activities (Moeskops et al., 2010), the variation in dehydrogenase activity between the woodland and arable soils after being amended with UK1 ash may be associated with changes in the soil pH. Siddaramappa et al. (1994) and Pati and Sahu, (2004) also associated the influence of fly ash on soil enzymatic activity with its effect on soil pH because the activities of all enzymes are strongly pH-dependent. However, even though the pH of both soils here increased following soil amendment with the UK1 ash, this increase did not have any effect on the dehydrogenase activity in the arable soil. Variation in dehydrogenase activities between the soils before and after amendment with ash might also be linked to differences in the organic matter (OM) content between the soils; the woodland soil had a higher OM content than the arable soil. OM in the soils provides a substrate for microbial biomass and is likely to increase enzymatic activities (Yuan and Yue, 2012). Indeed, glucosidase activity was higher in woodland than in arable soil across all ash concentrations, although increasing ash content lowered the enzyme activity. This suggests that nutrient availability in woodland soil was sufficiently high to drive biotic decomposition of the organic matter, although production of phosphatase indicated that P may have been limiting. High ash concentrations in woodland soil lowered glucosidase and phosphatase activity, suggesting that ash amendment resulted in a toxic effect (perhaps because of PTE addition), or that N became a limiting factor, which is evidenced by increased urease production with high concentrations of the UK1 ash. Plant growth benefited by addition of high ash amendments to the woodland soil, again suggesting that nutrients were not limiting and were likely to have been released in plant- and microbe-available forms. It is known that nutrient elements affect decomposition of soil organic matter and that N, P and C cycles are coupled (Galloway et al., 2008). However, the key effect of adding the UK1 ash to woodland soil was that of enhancing the soil pH. It is known that microbial biomass is lower in acidic soils and that a positive relationship between pH and soil microbial activity exists (Treseder, 2008). That plant biomass was not increased by high additions of UK1 ash to arable soil signifies a more complex scenario; in this case it is possibly that PTEs adversely affected

growth. If this is the case, it is feasible that the higher organic matter content of the woodland soil limited PTE availability due to increased cation exchange capacity. Xiao et al. (2017) demonstrated that organic matter addition to paddy fields reduced Cd transfer to rice grains, but not As.

The increase in dehydrogenase activity in woodland soil may also be linked to the increase in the root biomass and associated rhizosphere microbes. Urease activity in control soils was lower in the woodland soil than in the arable soil, which might be linked to the history of fertilizer application to the arable soil (which is not known) and the lower pH of the woodland soil since urease activity tends to increase with increasing soil pH (Makoi and Ndakidemi 2008). Soil amendment with the UK1 fly ash increased the urease activity at all concentrations (0-16 %) in the woodland soil and from 0-8 % in the arable soil. The increase in urease activity might be linked to the increase in soil pH and Ca content in soils (Blonska, 2010) following soil amendment with this fly ash (refer to the Ca data reported in Chapters 4 and 6). A similar finding regarding the positive effect of fly ash on urease activities was noted by McCarty et al. (1994); in their study, increased urease activity was also linked to the soil liming effect of the fly ash. The decline in urease activity in the arable soil amended with 16 % ash might be due to the high pH of the ash which probably created unfavourable conditions for microbial activities (Lai et al., 1999). This reduction might also be due to the accumulation of potentially toxic elements in fly ash amended soil which tend to inhibit soil enzymatic activities (Sarangi et al., 2001; Pati and Sahu 2004; Yang et al., 2006). Since the urease enzyme originates from soil microbes and plants (Burns, 1986; Makoi and Ndakidemi 2008), the increase in activity of this enzyme in fly ash amended soil coincided with the increase in plant growth (root and shoot biomass), suggesting a beneficial effect of the applied ash on nutrient cycling, particularly that of N.

Application of the UK1 fly ash at low concentrations did not affect phosphatase activity in comparison with the control soil, although at high ash concentration (16 %), phosphatase activity declined significantly. Since the source of alkaline phosphatase in the soil is the microbiome (Tabatabai 1994), application of this ash to both soils probably did not provide any beneficial effect to the microbes producing this enzyme and they were, therefore, inhibited at high ash concentration. The inhibition of this enzyme at higher ash concentration may

be attributed specifically to the accumulation of PTEs in the soil amended with ash (Lai et al., 1999). Acid phosphatase, which was only determined in the woodland soil due to the dominance of this activity in acidic soil (Dick and Tabatabai, 1984; Dick et al., 2000), was also unaffected by low ash concentrations, but declined significantly with higher ash amendments (8-16 %). Despite the increase in the root biomass noted in plants grown in woodland soil, which could be another source of acid phosphatase in addition to that produced by microbes (Makoi and Ndakidemi 2008), acid phosphatase activity was still inhibited in soil amended with the high ash concentration. The reduction of phosphatase activities (acid and alkaline) in both soils is probably linked to the high pH, low availability of P and the toxicity of PTEs from fly ash (Pan and Yu, 2011; Sanchez et al., 2015).

In this study, the activity of β-glucosidase increased in woodland soil amended with 2 % of the UK1 ash in comparison to the unamended soil but, above this concentration, the activity declined significantly. However, application of this ash to the arable soil did not have any significant effect on the glucosidase activity. The higher glucosidase in the unamended woodland soil compared to the arable soil (controls) could be attributed to the presence of higher organic matter in the woodland soil as this enzyme is involved in catalysing the hydrolysis and biodegradation of various β-glucosides found in decomposing organic matter (Makoi and Ndakidem 2008; Sing et al., 2016). The increase in glucosidase activity in the woodland soil with 2 % ash amendment was probably due to the higher carbon content of the ash; however, inhibition of activity at higher ash concentrations might be linked to the sensitivity of this enzyme to the changes in pH brought about by the applied ash (Acosta-Martinez and Tabatabai (2000). The reduction of β-glucosidase activities may also be associated with the high pH and lower availability of C from the ash (Sanchez et al., 2015), as well as the adverse effect of trace elements in fly ash amended soil (Fang et al., 1998).

Besides the variation in soil enzymatic activity in both woodland and arable soil amended with the UK1 ash, wheat growth responded positively to this amendment. Almost all the growth parameters determined (shoot biomass, number of leaves, root biomass and number of tillers) increased with increasing fly ash concentration, but the rate of increase was higher in the woodland soil

than in the arable soil. This might be linked to the increase in dehydrogenase activity, which is an indicator of gross soil biological activities (Lai et al., 1999; Makoi and Ndakidemi 2008) and high organic matter in this soil. In the arable soil, the root biomass increased significantly only when the soil was amended with 0-4% ash; there were no further significant increase when ash concentration was greater than 4 %. Improvement in wheat dry matter yield (shoot and root biomass) might also be linked to the liming effect of fly ash (Lai et al., 1999; Fang et al., 1998 and Pati, 2004) and the nutrient-supplying ability of the fly ash (Garg et al., 2005; Tripathi et al., 2009; Tsadilas et al., 2014).

5.4.2 Effects of the TZ1 ash on soil pH, enzyme activities and wheat growth

Soil amendment with the TZ1 ash decreased the pH of both soils due to the relatively low pH (4.2) of the applied ash. Soil acidification due to the application of this ash may be associated with the presence of low concentrations of basic cations (e.g. Ca) and the high S content of the fly ash (see data presented in Chapter 3). When soil S content is increased, soil acidification is often linked to the negative relationship between S and soil pH (Basu et al., 2009; Singh et al., 2016).

The higher dehydrogenase activity in the arable than in woodland soil might be due to the pH of arable soil being slightly acidic (pH 6.8) thus being within the optimum pH range of 5.17 to 7.27 reported for dehydrogenase activities in previous studies (Brzezińska et al., 2001; Natywa et al., 2011). It is also possibly due to the history of fertilizer application to the arable soil, although this is unknown. Besides the presence of organic matter in the woodland soil and the positive correlation between the organic matter and dehydrogenase activities reported earlier (Yuan and Yue, 2012), low dehydrogenase activity in this soil could be associated with its lower pH.

However, the higher glucosidase and acid phosphatase in the woodland soil than in the arable soil might be due to higher organic matter in the former since β-glucosidase in involved in cycling C by catalysing the conversion of disaccharides to glucose (Moeskops et al., 2010). The lower pH of the woodland soil favoured the acid phosphatase because this activity tends to dominate in acidic soils (Shaw and Read, 1989; Dick et al., 2000). Soil amendment with fly ash at lower concentrations (<10%) has been noted by others to have no

significant effect, or even a positive effect, on soil enzymatic activities and at higher concentrations to inhibit enzymatic activities (Lai et al., 1999; Pati and Sahu, 2004; Sanchez et al., 2015). However, in this study almost all enzymes were inhibited even by lower concentrations of the TZ1 ash. Since application of the TZ1 ash decreased the pH in both soils (from 6.76 to 5.93 in arable soil and from 4.27 to 4.06 in the woodland soil), inhibition of enzyme activities in both soils may be linked to soil acidification. Even though the pH in woodland soil amended with TZ1 ash changed by <1 pH unit (from 0-16 % ash), this change was statistically significant and its impact on almost all enzymatic activities was apparent. The decrease in dehydrogenase activity in both soils amended with TZ1 ash might be associated with inhibition of this enzyme in acidic soils (Levyk et al., 2007). Alkaline phosphatase tends to dominate in neutral or alkaline soils (Dick et al., 2000), thus soil acidification due to ash application probably inhibited activity.

Microbes are the main source of urease in the soil and N is the nutrient required to synthesise urease in microbial cells (Singh et al., 2016). Therefore, soil acidification due to ash application (which tends to inhibit some microbial activities) and the lower content of N in fly ash might be the reasons for the reduction in urease activity in the arable soil.

Despite the dominance of acid phosphatase in acidic soils (Shaw and Read, 1989; Dick et al., 2000) and the increase of its activity in soils with P stress (Makoi and Ndakidemi, 2008), further acidification of both soils by addition of high concentrations of the TZ1 ash, inhibited acid phosphatase activity. Moreover, the dramatic decrease in enzyme activities in both soil types amended with TZ1 ash might also be attributed to increased concentrations of potentially toxic elements in the soil (as reported in Chapters 4 and 6). Pan and Yu (2011) associated reduced enzyme activities in soil contaminated with heavy metals to the interaction between metals and the enzyme-substrate complex, denaturation of the enzyme and the effect of the metals on enzyme synthesis by microbial cells. Fang et al. (1998) and Sanchez et al. (2015) also associated the reduction of soil enzyme activities to accumulation of PTEs in soil following the soil amendment with coal ash.

Soil amendment with the TZ1 ash did not have any effect on wheat growth up to the stage when the plants were harvested, despite the ability of fly ash to supply nutrients (Tripathi et al., 2009; Tsadilas et al., 2014). This may be linked to inhibition of soil enzyme activities which plays an important role in the cycling of nutrients in the soil.

5.5 CONCLUSIONS

This study has shown that soil amendment with fly ash may result in either a beneficial effect akin to 'liming' acidic soils or a detrimental effect in which acidic soils are further acidified. However, these effects will depend on the pH and the concentration of the applied ash. Application of the UK1 ash increased dehydrogenase activity in woodland soil and urease activities in both soils, suggesting a beneficial 'liming' effect of fly ash on acidic soils, which in turn created favorable conditions for microbes and a positive growth response of wheat. Since some enzymes were inhibited in soils amended with high concentrations of this ash, despite its potentially beneficial liming effect, only concentrations of <4 % of alkaline ashes (similar to that of the UK1 ash) may be recommended. However, application of acidic ash like the TZ1 to acidic soils is not recommended due to its effect on soil acidification and inhibition of microbial activities. Further research to investigate the effect of fly ash on soil enzymatic activities, particularly testing the effects of acidic ashes on very alkaline soils is recommended.

6 EFFECTS OF COAL ASH APPLICATION ON GROWTH, YIELD AND ACCUMULATION OF POTENTIALLY TOXIC ELEMENTS IN SOILS AND WHEAT PLANTS

6.1 INTRODUCTION

Wheat (*Triticum aestivum*) is a staple cereal crop, produced in many countries of the world. Based on 2013 data, world production of wheat was 713 million tons, making it the third most-produced cereal after maize (1,016 million tons) and rice (745 million tons) (FAO 2015).

Coal fly ash is an industrial bi-product of coal combustion produced by power plants. Chemically, it is defined as an amorphous ferroalumino silicate with a matrix similar to soil (Shaheen et al., 2014). The major building block of fly ash is mainly composed of silica, alumina and iron oxides together with other constitutes which always vary in their amount, such as carbon, calcium, magnesium and sulphur (Shaheen et al., 2014). Physically, fly ash consists of fine, powdery particles and its particle size distribution ranges from 0.01-100 µm (Pandey and Singh, 2010). From the perspective of plant nutrition, fly ash comprises almost all the essential plant nutrients (macro- and micro-nutrients; Ca, P, Mg, Na, K, Cu, Fe, Mn, Mo, Zn and B) except nitrogen which tends to oxidize during the coal combustion process (Singh et al., 2014). Most fly ash is alkaline in nature, though acidic fly ashes may also exist if formed from parent coal with low lime content and higher sulphur content. Generally, fly ash pH ranges from 4.5-13.5 (Shaheen et al., 2014).

The use fly ash in agriculture as a soil conditioner has been reported in the literature (Yeledhalli et al., 2007; Gupta et al., 2012; Saraswat and Chaudhary, 2014). This may be an acceptable and viable technology for large scale disposal of fly ash because fly ash comprises almost all the essential plant nutrients (Singh et al., 2014); thus, it can be used to supplement nutrients when plants are grown in nutrient deficient soils. In addition, since most fly ashes are alkaline (Shaheen et al., 2014), they can be used to raise the pH of acidic soils in agricultural, horticultural and forest fields. However, fly ash also contains several potentially toxic substances such as heavy metals and metalloids (Singh et al., 2008; Aggarwal et al., 2009) which may affect the soil environment, crop productivity and human health. Moreover, inconsistent results regarding the effect of fly ash on plant growth and yields for different crops have been

reported (Sikka and Kansal 1994; Kalra et al., 1997; Manoharan et al., 2007; Aggarwal et al., 2009). Fly ash application to the soil in fields where wheat is grown has been reported to induce both positive (Totawat et al., 2002; Sharma et al., 2002; Kalra et al., 2003; Aggarwal et al., 2009) and negative responses (Singh et al., 2014; Aggarwal et al., 2009) on growth and yields of this crop. Due to inconsistent results from many studies, there is no clear recommendation regarding the use of fly ash as a soil amendment to improve plant growth. Reported inconsistencies in crop response could be related to a number of factors such as: i) Diverse fly ash characteristics derived from different power plants due to variable composition of the parent coal, combustion conditions, efficiency of emission control, storage and handling of fly ash (Jala and Goya 2006); ii) variations in soil characteristics to which ash was added; iii) variations between plant species and varieties grown in fly ash amended soils (Wong and Wong, 1990). Therefore, further research must be conducted to determine the capability of fly ash as a soil amendment and the fate of potentially toxic trace elements present in fly ash when applied to soil-plant systems. In Tanzania, despite the ongoing increase in fly ash production from industries using coal as a source of fuel, no information is available regarding the use of fly ash as a soil amendment.

In view of the above, the present study was conducted with the aim of evaluating the potential of two distinct coal ashes (collected from Tanzania and the UK) to enhance the yield of wheat grown in pots containing two contrasting soils (woodland and arable) under controlled conditions.

The specific objectives of this study were to:

i) Evaluate the fertiliser effect of increasing concentrations of each coal ash on growth and yield of wheat.

ii) Quantify phytotoxic effects of each ash.

iii) Determine whether ash-derived potentially toxic elements are transferred from ash-soil-wheat grain.

iv) Establish whether similar effects occur in two contrasting soils.

6.2 MATERIALS AND METHODS

6.2.1 Coal ash used

For logistical reasons, two separate trials were undertaken, the first using UK ash and the second, using Tanzanian ash. The fly ash used in the 1st wheat experiment (UK ash batch 1) was collected from Ratcliffe-on-Soar power station, Nottingham, while the fly ash used in the 2nd experiment (Tanzania ash batch 1) was collected from 21st Century Textile Industry, Morogoro, Tanzania. These ashes were selected for use from the 5 ash samples obtained in total (see Chapter 2 (Section 2.2) and Chapter 3), because of their contrasting characteristics, e.g. pH and elemental concentrations.

In brief, Tanzania ash batch 1 (TZ1) contained a higher %C and %N than the UK ash batch 1 (UK1), although the C in the UK1 ash was more readily extractable. The TZ1 ash was relatively acidic whilst the UK1 ash was alkaline (Figure 1, Chapter 3). The UK1 ash had higher total concentrations of P, Mg and Ca than the TZ1 ash which contained more total S (Figure 2, Chapter 3), although these were not necessarily reflected in the water extractable fractions (Figure 3, Chapter 3). Concentrations of Zn, Cr, As, Cd and Pb were higher in the UK1 ash than in the TZ1 ash (Table 2, Chapter 3). Please refer to Chapter 3 for full analytical differences between the two ash types.

6.2.2 Soil sampling and preparation

The two soils used (arable and woodland soil) were collected from the Sutton Bonington Campus Farm, University of Nottingham as detailed in Section 2.1 (Chapter 2). The arable soil was taken from 'field 6' next to Domleo's Spinney and the woodland soil was collected from within the spinney. The soils were sieved to 4mm prior to establishing the experiments.

6.2.3 Soil analysis

Please see Chapter 2 for full analytical details. Analyses were carried out on all experimental soil and soil/ash combinations. These included: i) Moisture content (Section 2.3.1); ii) pH (Section 2.3.2); iii) total C and N (Section 2.3.3); (iv) extractable C and N (Section 2.3.4); v) analysis of water-extractable elemental concentrations (Sections 2.3.5 and 2.3.8); vi) analysis of total elemental concentrations following acid digestion (Sections 2.3.7 and 2.3.8).

6.2.4 Experimental approach

Two pot experiments were conducted where spring wheat var. Willow was grown in both woodland and arable soil amended with one of 0, 2, 4, 8, 16 or 32% fly ash (on a dry weight basis). UK1 ash was used in experiment 1 and TZ1 ash in experiment 2. Both soil types were used in experiments 1 and 2. Due to a growth-room malfunction a different room was used for each experiment, therefore the data from each experiment were analysed separately. In both experiments, the plants were grown until maturity (seed set).

6.2.5 Experimental set up

6.2.5.1 Experiment 1; UK ash 1 in woodland and arable soil

Woodland and arable soils were each amended with the following concentrations of fly ash on a dry weight basis: 0, 2, 4, 8, 16 and 32%. Ash was manually mixed into 150 g dry weight equivalent batches of field moist soils and then used to fill pots prior to sowing the seeds. Three replicates of each fly ash concentration + soil mixture were prepared. All pots were placed in a designated growth room arranged in a randomized block design (with 3 replicate blocks). Each pot was watered with deionized water and allowed to equilibrate/settle for 24 hours before sowing the wheat seeds. The settling period avoided 'surface sealing' of the germinating seeds, especially in pots treated with higher concentrations of fly ash. Four seeds of spring wheat var. Willow were sown in each pot at a depth of 1cm. The pots were watered with deionized water and maintained at 20°C/18°C day/night, 16h/8h day/night duration (including a 1 hour dawn and a 1 hour dusk period). Following germination, plants were thinned to one per pot and watered as required until seed set and ripening. Plants were fertilised with NPK + micronutrients 5 weeks after germination when symptoms of manganese deficiency occurred across all treatments and P deficiency in plants growing with the 16% and 32% ash amendments. Plants did not require additional fertiliser following the first application. Plants were harvested after 4 months when grain was hard (GS92), but before loosening began.

6.2.5.2 Experiment 2; Tanzania ash 1 in woodland and arable soil

The experiment was set up as for the UK-ash experiment above, except that 450 g dry weight equivalent of arable and woodland soils were used in order to

avoid nitrogen deficiency symptoms observed in the UK trial with the lower soil weight. Appropriate ash amendments were mixed thoroughly into the soil using a food processor prior to filling the pots. Four replicates of each ash treatment + soil mixture were prepared. All pots were placed in a different growth room from that used for the UK-ash trial, but the temperature and daylength settings were the same. Pots were arranged in a randomized block design (with 4 replicate blocks). Six seeds of spring wheat var. Willow were sown in each pot at a depth of 1cm and plants were thinned to 1 per pot following germination. Maintenance was as described for the UK-ash trial, although in this experiment no nutrient deficiencies were observed and therefore no additional fertilisation took place. Plants were harvested after 6 months when grain was hard (GS92), but before loosening began.

6.2.6 Plant harvesting and analysis

Before harvesting, number of tillers and leaves were counted and the shoot lengths (from the stem-soil surface to the beginning of the head) were measured. Then all heads were removed and oven dried at 60°C until constant weight and biomass recorded. The total grain yield was determined by shredding the wheat heads and counting the number of grains per plant. The grain weight was determined by oven drying the grains at 60°C until constant weight and weighing the total number of grains per plant. Shoot biomass was also determined after harvesting the shoots and oven drying at 60°C until constant weight. The roots were extracted from the soil, washed thoroughly with tap water and oven dried at 60°C until constant weight. All the three parts of the plant (grains, shoots and roots) were ground in an ultra-centrifugal mill (Retch model ZM 200) at 1200 rpm ready for microwave digestion. The finely ground shoots, roots and grain samples (0.2 g) were then digested in pressurized PFA vessels with 6.0 mL of 70% Fisher 'trace analysis grade' (TAG) HNO_3 with microwave heating (Anton Paar, 'Multiwave' fitted with a 48-place carousel). Digested samples were made up to 20 mL with ultra-pure water and then diluted 1-in-10 with ultra-pure water in preparation for ICP-MS analysis. The multi-element analysis was performed following the procedure explained in Section 2.3.8 (Chapter 2). All elemental concentrations were converted to mg kg^{-1} following the Equation 6-2 below;

$$Cplant = \frac{Csol - Cblank}{Wplant} X\, Vol \qquad Equation\ 6-2$$

Where, C_{plant} is the elemental concentration (mg kg^{-1}) in the plant tissue; C_{sol} and C_{blank} are the concentrations (µg L^{-1}) in the plant and blank digests, corrected for dilution, Vol is the digest volume (20 mL) and W_{plant} is the mass of plant tissue digested (0.2 g).

6.2.7 Soil analysis after plant harvesting

After harvesting, soil from each pot was homogenized, and analyses undertaken as described in Section 6.2.3.

6.2.8 Statistical analysis

Statistical analyses were performed using Genstat 17th Edition (VSN International, UK). A generalized two-way analysis of variance was conducted on all ash, soil, plant growth and yield data (pH, %C, %N, extractable C, extractable N, total nutrients, total PTEs, extractable nutrients and extractable PTEs, shoot length, number of tillers, number of leaves, number of heads/plant, weight of heads, number of grains, total weight of grains, root weight, shoot weight, shoot chemistry, root chemistry and grain chemistry) using ash concentration and soil type as a factors for each experiment. Due to lack of grain production by plants grown in arable soil amended with the UK ash (32% treatment), a one-way ANOVA was also conducted on plant chemistry data. Normality was tested by plotting residuals against expected normal quantiles and post-hoc comparisons between means were based on least significant differences (LSD) at 0.05 probability level for two-way ANOVAs and by Tukey's honestly significant difference (HSD) for one-way ANOVAs.

6.3 RESULTS: EXPERIMENT WITH UK FLY ASH

6.3.1 Initial characteristics of soils and UK and TZ ashes

The chemical characteristics and elemental composition of soils and fly ash used in both wheat experiments are presented in Table 6-1. The fly ashes used were UK batch 1 (UK1) and Tanzania batch 1 (TZ1) and their pH values were 12.32 and 4.2 respectively (Table 6-1). The two soils used were Domleo spinney

(referred to as woodland) and arable soil with pH values of 3.81 and 6.43 respectively (Table 6-1). The lowest percentage total nitrogen (TN) was recorded in UK1 ash but generally, the trend followed the order of woodland soil>Tanzania ash>arable soil>UK ash, while the highest percentage total carbon (TC) was recorded in Tanzania ash and the trend followed the order of Tanzania ash>UK ash>woodland soil>arable soil. The concentration of extractable C (mg kg^{-1}) in soils and ashes followed the order of woodland soil>UK ash>arable soil>Tanzania ash while the total extractable N followed the order of arable soil>woodland soil>Tanzania ash>UK ash (Table 6-1). Regarding elemental composition of soils and ashes measured by ICP-MS, concentrations of Ca, Mg, P, B, and S were higher in the UK fly ash than in the two soils, while the concentration of these nutrients in Tanzania ash was lower than in the two soils except S. The concentration of the PTEs Pb, Cu, Co, Cd, Ni, Zn and Se were higher in both ashes than in the two soils (Table 6-1).

6.3.2 Post-harvest soil pH following amendment with UK fly ash

A significant increase in soil pH with each increase in ash concentration was observed in both soils. The pH of the woodland soil without ash was 3.8, whilst that of the arable soil minus ash was pH 6.5. The 32% ash amendment resulted in little differentiation between the pH of the two soils relative to the difference observed with lower ash amendments (Figure 6-1; ash concentration × soil type interaction, $p<0.001$, Table 6-2).

6.3.3 Wheat growth and yield in soils amended with the UK fly ash

Results from two-way ANOVA showed a significant interaction between the ash concentration and soil type on all growth and yield parameters (Table 6-2), primarily because plants grown in the woodland soil responded to ash amendment whilst those grown in arable soil did not (Figures 6-2 and 6-3).

Leaf number increased following 2% ash amendment in wheat grown in woodland soil relative to the control, but greater additions of ash did not result in further increases in number of leaves (Figure 6-2a). Leaf number was unaffected by ash amendments to arable soil.

Neither tiller number (stems arising from the original shoot) nor root biomass were significantly affected by ash treatment of arable soil. However, tillering

was greater in wheat grown in the woodland soil with 2-16% ash amendments (Figure 6-2b; ash concentration × soil type interaction, p=0.005; Table 6-2). Root biomass of wheat grown in woodland soil was generally enhanced by the 4-32% ash amendments (Figure 6-2c; ash concentration × soil type interaction, p=0.025; Table 6-2). The ash-related enhancement of root growth, leaf production and tillering in wheat growing in woodland soil resulted in larger plants relative to those growing in arable soil and this was reflected in yield.

Table 6-1: *Initial chemical properties and elemental composition of fly ashes and soils*

Parameter	UK1 ash	Tanzania1 ash	Arable soil	Woodland soil
pH	12.32 ±0.02	4.2 ±0.01	6.43 ±0.01	3.81 ±0.012
TC (%)	8.6 ±0.1	28.2±1.1	0.4±0.03	5.8 ±0.3
TN (%)	0.03±0.002	0.45 ±0.02	0.12 ±0.1	2.3 ±0.1
Extractable C *(mg kg^{-1})*	261.3 ±6	28.21 ±1.10	254.1 ±6	527 ±2
Extractable N *(mg kg^{-1})*	4.6 ±1.02	86.2 ±1.8	341 ±3	245 ±3
% moisture	9.44 ±0.03	3.56 ±0.02	16.7 ±0.1	22.5 ±0.1
Nutrients (mg kg^{-1})				
P	1023.4 ±14	237 ±6.3	801 ±94	411 ±3.85
K	893 ±7	837 ±19	1520 ±145.1	987 ±32.56
Mg	2774 ±42	201 ±9	1931 ±194	1807±53.11
Ca	14835 ±195	1054 ±51	2249 ±235	1326.4 ±58
S	449 ±18	1889 ±100	BDL	75.1 ±14
B	115.1 ±2	BDL	5.42 ±0.18	5.51 ±0.18
Mn	187.3 ±2.1	38.5 ±1.2	232 ±2 22	97.52 ±9.1
PTEs (mg kg^{-1})				
Zn	331.4±2.7	74.3 ±2.3	54.27 ±4.10	55.74 ±1.83
Cu	27 ±0.7	36 ±1.4	17.17 ±1.8	13.44 ±0.43
As	66 ±1	6 ±0.1	9.97 ±1	10.49 ±0.35
Co	8.29 ±0.1	20.6 ±0.3	4.25 ±0.11	3.31 ±0.13
Cd	16.7 ±0.5	0.5 ±0.02	0.27 ±0.01	0.17 ±0.00
Ni	24.2 ±0.2	31.1 ±0.6	9.08 ±0.61	9.57 ±0.47
Pb	546 ±15.2	17.7 ±0.6	39.01 ±1.6	59.22 ±2.11
Cr	23.2 ±0.3	11.1 ±0.2	13.85 ±1	11.31 ±0.28
Se	5.7 ±0.1	3.7 ±0.1	0.37 ±0.02	0.60 ±0.02

Values given are means of four replicates ± standard errors. BLD=below detectable limit during ICP analysis. TN = total nitrogen; TC = total carbon.

Total shoot biomass, number of grains and grain weight per plant increased significantly with fly ash concentrations of 2-4% relative to the ash-free (0%) treatment in wheat grown in woodland soil, but further increases in ash amendment did not result in further growth or yield enhancements, nor was there any apparent detrimental effect on yield or on biomass (Figure 6-3; Table 6-2). However, several plants grown in arable soil with 32% ash, died before grain production occurred. Despite differences in grain number and weight per plant, the 100-grain weight remained constant irrespective of soil type or ash amendment (grand mean 3.1 g for plants grown in each soil type).

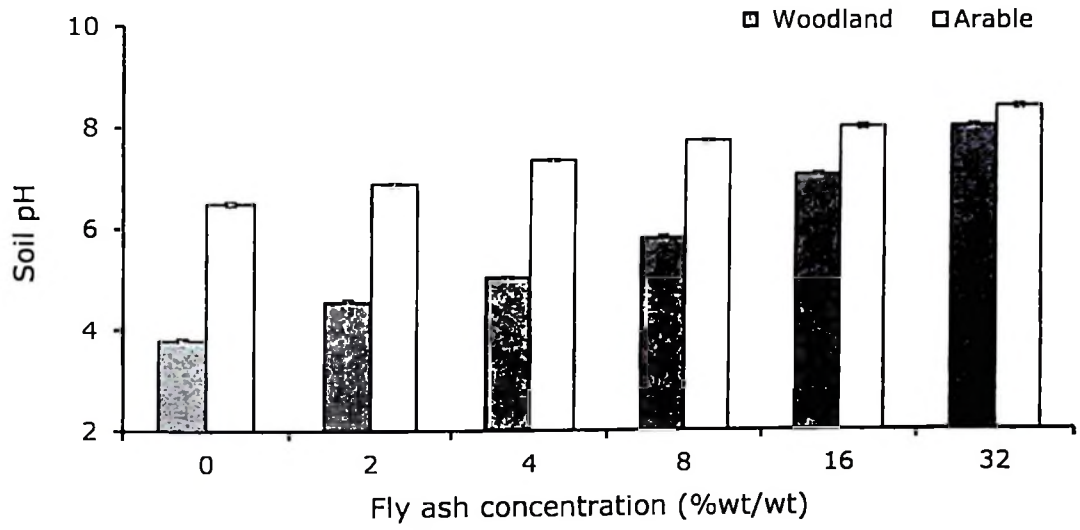

Figure 6-1: *The effect of UK fly ash application on pH of woodland and arable soils after harvesting. Individual error bars are based on the pooled variance estimate from the ANOVA with 24 degrees of freedom. LSD=0.17*

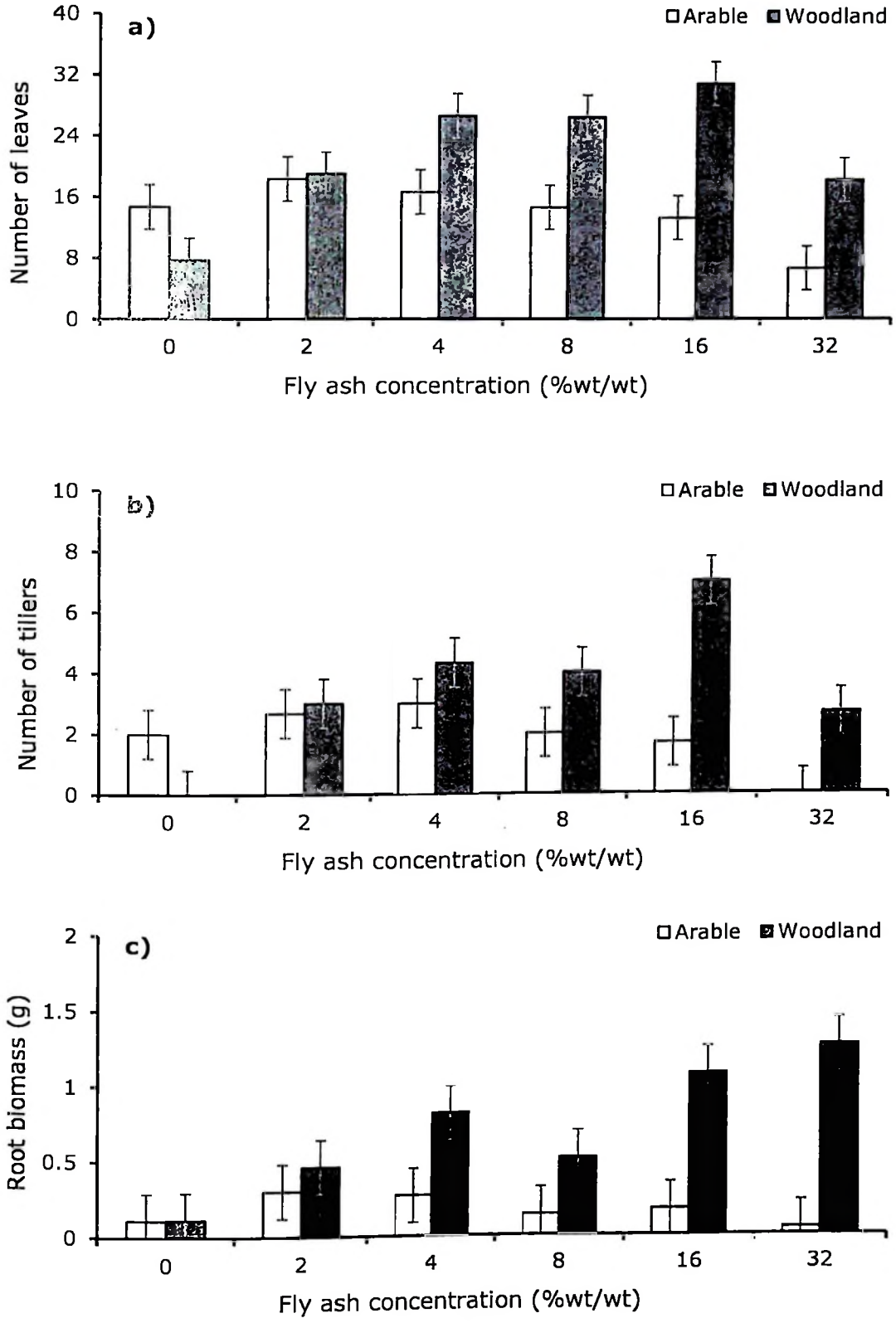

Figure 6-2: *Effect of UK ash application on a) number of leaves, b) number of tillers and c) root biomass of wheat grown in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 23 degrees of freedom. LSD for number of leaves =8.47, number of tillers =2.35 and root biomass =0.53*

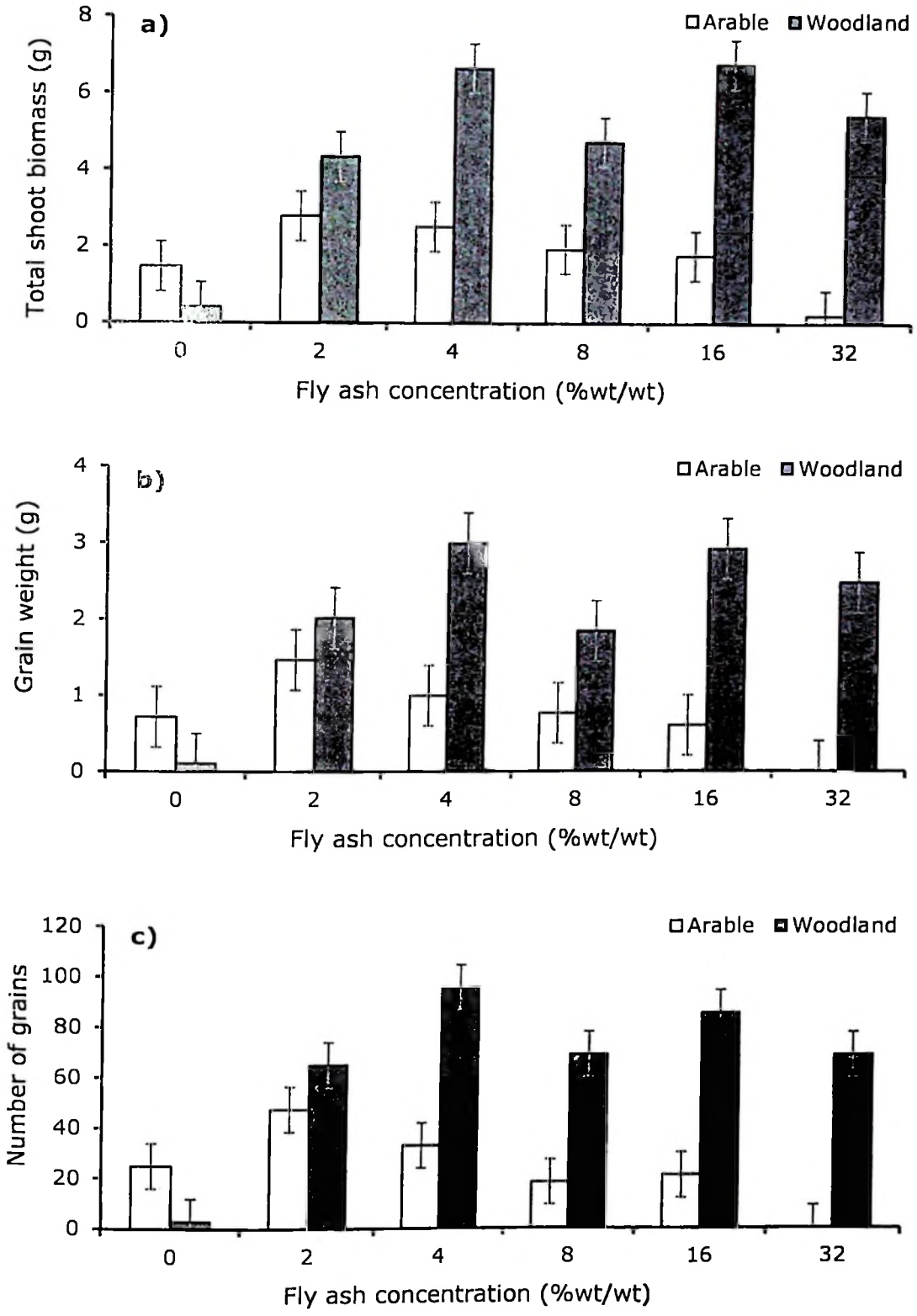

Figure 6-3: *Effect of UK ash application on a) shoot biomass, b) grain weight and c) grain number of wheat grown in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 23 (for total shoot biomass), 19 (for grain number) and 18 (for grain weight) degrees of freedom. LSD for total shoot biomass = 1.89, grain weight =1.18 and grain number = 26.56.*

Table 6-2: Summary of 2-factor ANOVA for pH, and wheat growth and yield parameters from the experiment with UK1 fly ash

VARIATE	FACTOR	DF	F	P VALUE	LSD (95%)
pH	Ash (%)	5	815.87	<0.001	0.118
	Soil type	1	2882.9	<0.001	0.0681
	Interaction	5	125.34	<0.001	0.1669
	Residual	24			
Number of leaves	Ash (%)	5	5.47	0.002	5.99
	Soil type	1	19.98	<0.001	3.458
	Interaction	5	4.8	0.004	8.471
	Residual	23			
Number of tillers	Ash (%)	5	5.23	0.002	1.664
	Soil type	1	12.03	0.002	0.961
	Interaction	5	4.61	0.005	2.354
	Residual	23			
Root biomass	Ash (%)	5	2.58	0.054	0.3722
	Soil type	1	26.25	<0.001	0.2149
	Interaction	5	3.19	0.025	0.5264
	Residual	23			
Total shoot biomass	Ash (%)	5	8.14	<0.001	1.338
	Soil type	1	62.88	<0.001	0.772
	Interaction	5	6.96	<0.001	1.892
	Residual	23			
Grain weight	Ash (%)	5	4.53	0.008	0.835
	Soil type	1	21.66	<0.001	0.482
	Interaction	4	4.37	0.012	1.181
	Residual	18			
Number of grains	Ash (%)	5	8.15	<0.001	18.78
	Soil type	1	60.5	<0.001	10.84
	Interaction	5	7.93	<0.001	26.56
	Residual	19			

6.3.4 Post-harvest total nutrient content of soils amended with UK fly ash

Increasing amounts of fly ash resulted in greater concentrations of total soil nutrients (Figure 6-4). Both ash concentration and soil type were significant single factors within the two-way ANOVA for P, K, Mg, Ca, Mn and Fe, but there

was no interaction between these factors. Ash amendments of 8-32% increased total soil P, Mg and Fe relative to the 0-4% additions, whilst soil Ca concentration was enhanced by 4-32% fly ash (Figure 6-4; Table 6-4). Soil amendment with 32% fly ash resulted in the largest increase in soil concentrations of these particular elements, but it was the only concentration to enhance soil total Mn (Figure 6-4).

The total concentrations of P, K, Mg, Ca and Mn were significantly higher in the arable soil than in the woodland soil irrespective of ash concentration (Table 6-3, soil as a single factor in ANOVA).

Table 6-3: *Total soil nutrients and potentially toxic elements in woodland and arable soils at harvest. Data are pooled means from ANOVA (soil as a significant single factor).*

Elements	*Woodland soil	*Arable soil	DF	F ratio	P-value	SED
P	398	730	1,24	962.11	<0.001	10.72
K	542	868	1,22	183.35	<0.001	24.0
Mg	1523	1741	1,24	47.31	<0.001	31.6
Ca	2513	3615	1,24	105.97	<0.001	107.0
Mn	157	238	1,23	86.20	<0.001	8.7
Fe	14354	12481	1,24	11.63	< 0.001	549.1
Cr	12.6	14.09	1,24	21.55	<0.001	0.33
Co	3.7	4.20	1,24	7.28	=0.013	0.19

*mg kg^{-1}

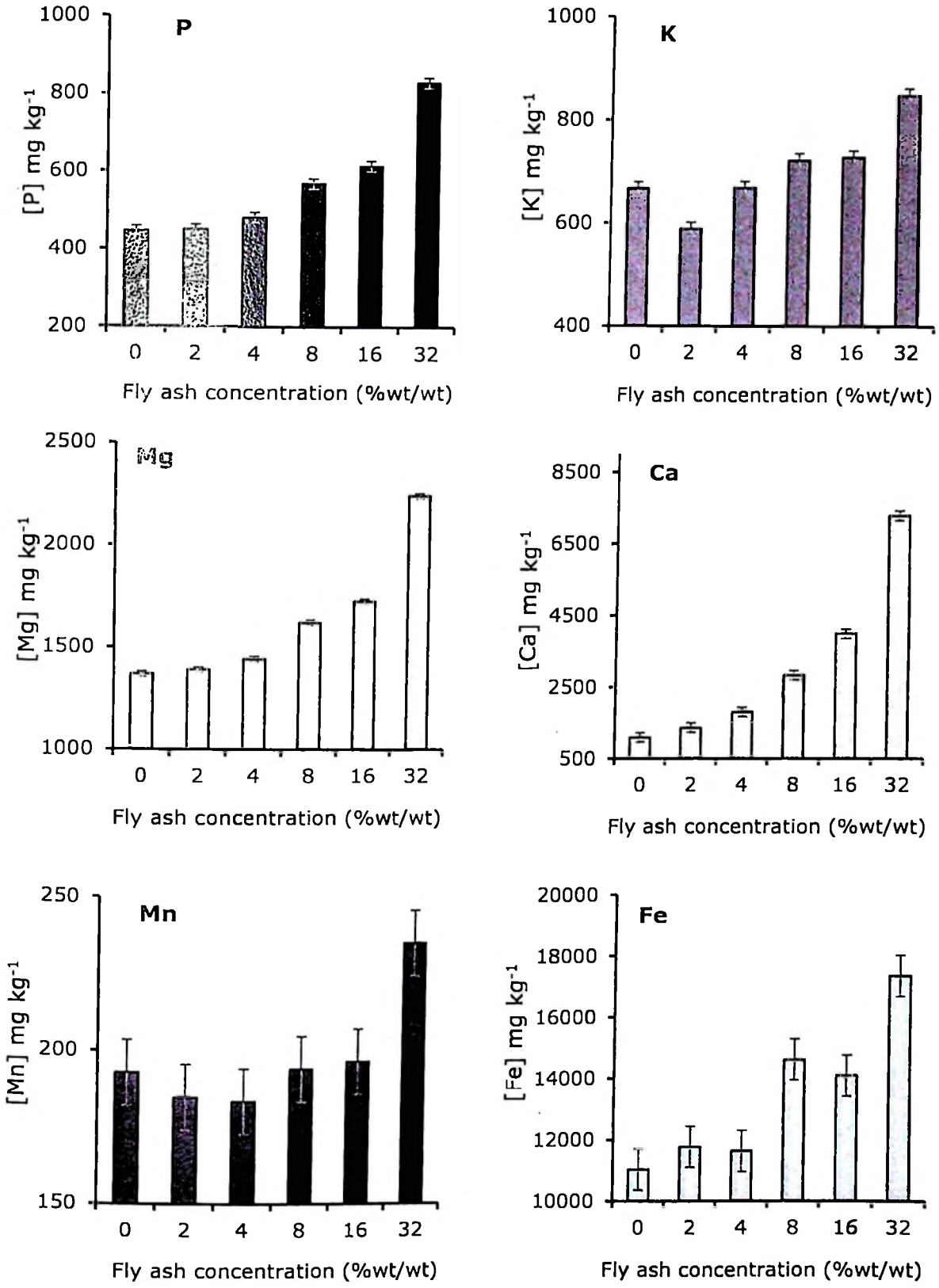

Figure 6-4: *Effect of UK fly ash application on total soil nutrient concentrations in woodland and arable soils after harvesting wheat. Data are pooled means from ANOVA (fly ash as a significant single factor). Individual error bars are based on the pooled variance estimate from the ANOVA with 24 (for P, Ca, Mg and Fe), 22 (for K) and 23 (for Mn), degrees of freedom. LSD for P = 38.3, K= 86.7, Mg= 113.0, Ca = 382.6, Mn = 31.2 and Fe= 1962.9*

6.3.5 Total PTE concentrations in UK fly ash amended soils

Fly ash amendment increased the total concentration of Zn, Cu, Co, Ni, Cr and Cd (Figure 6-5; ash concentration as a significant single factor within the two-way ANOVA; Table 6-4). Cu, Co and Cd concentrations were significantly higher with 8% ash amendments compared to the 0-4% treatments, whilst 4% ash increased soil Ni and Cr concentrations relative to that of the lower amounts of ash. Soil Zn concentration increased with just 2% ash amendment. Each subsequent increase in ash content raised the total concentrations of these elements (Figure 6-5).

Besides the effect of ash, soil as a single factor also showed an effect on the total concentration of Cr and Co, where the concentration of Cr in the arable soil was significantly higher than that in the woodland soil (arable, 14.09 mg kg^{-1}; woodland, 12.58 mg kg^{-1}; $p<0.001$). The concentration of Co in the arable soil was also significantly higher than that in the woodland soil (arable, 4.20 mg kg^{-1}; woodland, 3.69 mg kg^{-1}; $p=0.013$).

As, Pb and Se concentrations also increased with ash amendment in both soils, although the arable soil contained lower concentrations than the woodland soil up to the 16-32% additions when the trend flipped. At 32% ash amendment, As, Pb and Se concentrations in the arable soil were higher than those in the woodland soil (Figure 6-6; ash concentration × soil type interaction, $p=0.018$ for As and $p<0.001$ for Pb and Se).

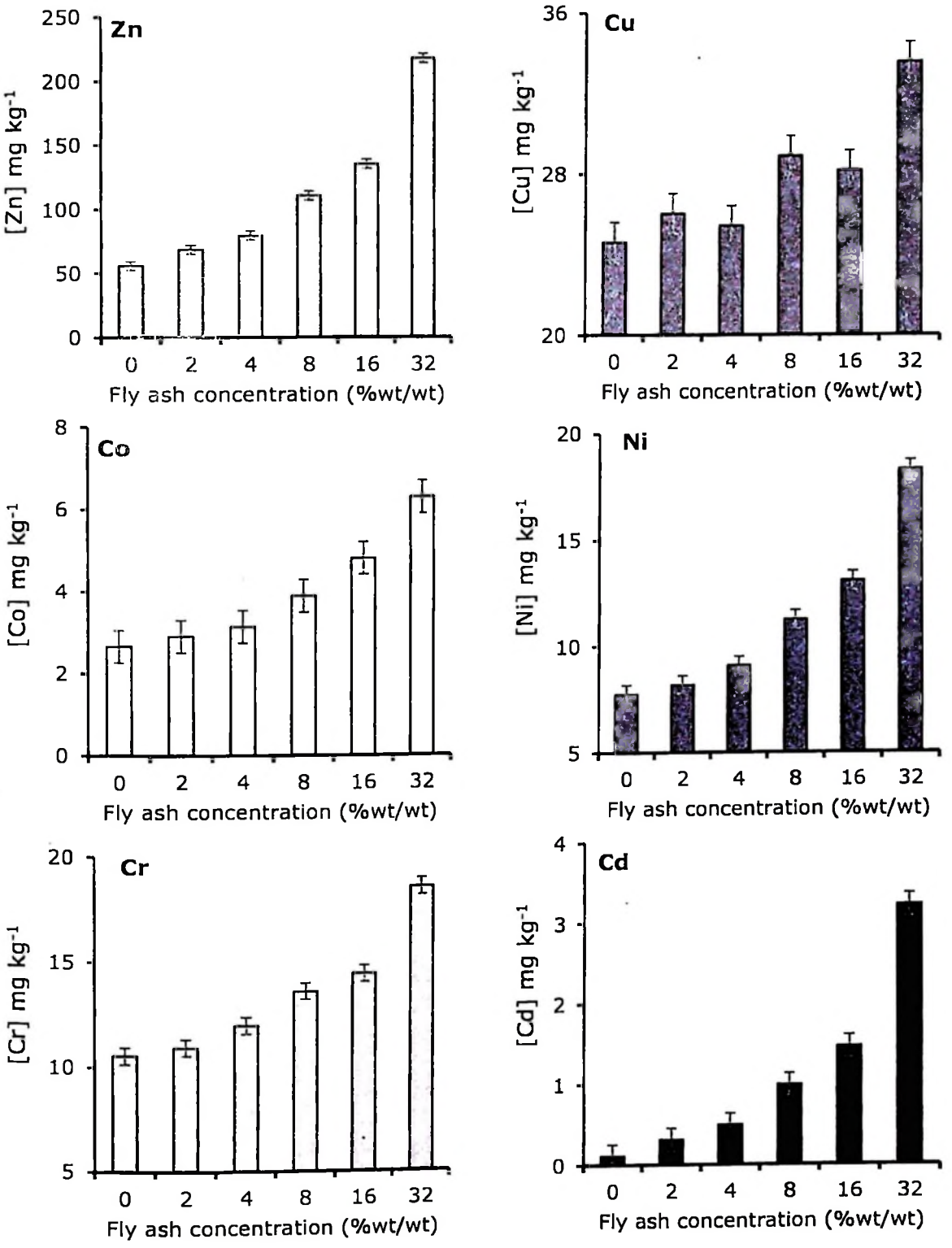

Figure 6-5: *Effect of UK fly ash application on total soil concentration of the potentially toxic elements in woodland and arable soils (ash as a single factor in ANOVA). Individual error bars are based on the pooled variance estimate from the ANOVA with 24 degrees of freedom. LSD for Zn= 10.24, Cu= 2.93, Co= 0.68, Ni= 1.27, Cr= 1.16 and Cd= 0.411*

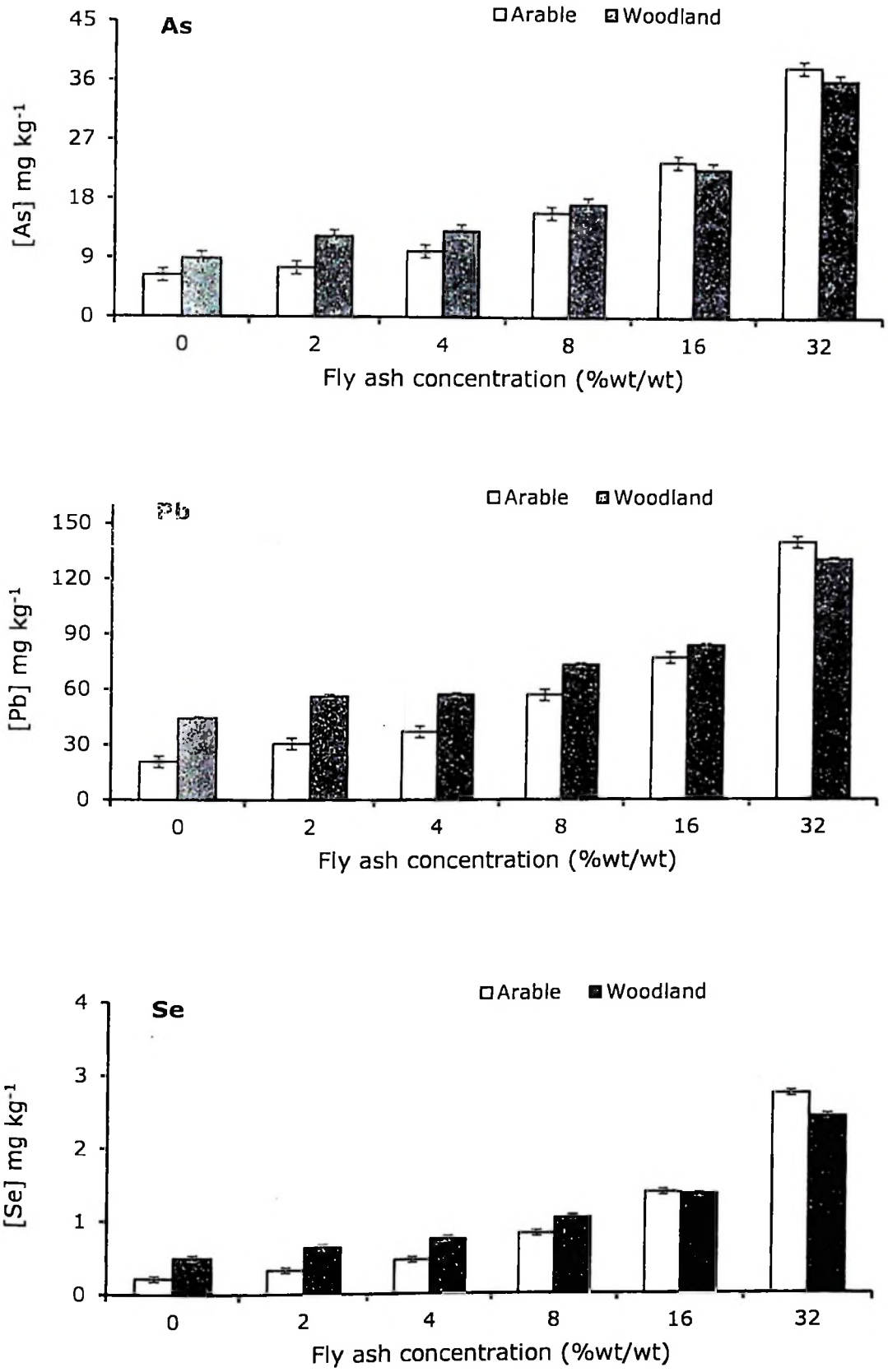

Figure 6-6: *Effect of UK fly ash application on total soil concentration of the potentially toxic elements, As, Pb and Se in woodland and arable soils (ash concentration × soil type interaction). Individual error bars are based on the pooled variance estimate from the ANOVA with 24 degrees of freedom. LSD for As=2.89, Pb=9.06 and Se=0.11.*

Table 6-4: *Summary of 2-factor ANOVA from post harvest total nutrient and PTEs content of soils amended with UK1 fly ash*

NUTRIENTS						PTEs					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**	**VARIATE**	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
P	Ash (%)	5	122.94	<0.001	38.33	**Zn**	Ash (%)	5	289.3	<0.001	10.24
	Soil type	1	962.11	<0.001	22.13		Soil type	1	0.15	0.702	5.91
	Interaction	5	0.62	0.689	54.21		Interaction	5	2.46	0.062	14.48
	Residual	24					Residual	24			
K	Ash (%)	5	8.82	<0.001	86.7	**Cu**	Ash (%)	5	3.71	0.013	6.6
	Soil type	1	183.35	<0.001	50.1		Soil type	1	1.93	0.177	3.811
	Interaction	5	1.19	0.347	122.6		Interaction	5	0.55	0.736	9.334
	Residual	22					Residual	24			
Mg	Ash (%)	5	72.13	<0.001	113	**Co**	Ash (%)	5	35.86	<0.001	0.677
	Soil type	1	47.31	<0.001	65.2		Soil type	1	7.28	0.013	0.3909
	Interaction	5	0.46	0.799	159.8		Interaction	5	1.19	0.343	0.9575
	Residual	24					Residual	24			
Ca	Ash (%)	5	316.98	<0.001	382.6	**Ni**	Ash (%)	5	84.11	<0.001	1.271
	Soil type	1	105.97	<0.001	220.9		Soil type	1	0.11	0.741	0.734
	Interaction	5	0.23	0.944	541.1		Interaction	5	1.65	0.186	1.797
	Residual	24					Residual	24			
Mn	Ash (%)	5	3.15	0.026	31.19	**Cr**	Ash (%)	5	55.77	<0.001	1.161
	Soil type	1	86.21	<0.001	18.01		Soil type	1	21.55	<0.001	0.67
	Interaction	5	1.11	0.383	44.1		Interaction	5	0.5	0.772	1.642
	Residual	23					Residual	24			

Fe	Ash (%)	5	12.78	<0.001	1962.9
	Soil type	1	11.63	0.002	1133.3
	Interaction	5	1.55	0.212	2776
	Residual	24			
Cd	Ash (%)	5	66.69	<0.001	0.4111
	Soil type	1	0.21	0.648	0.2373
	Interaction	5	0.09	0.993	0.5813
	Residual	24			
As	Ash (%)	5	253.7	<0.001	2.045
	Soil type	1	6.34	0.019	1.181
	Interaction	5	3.43	0.018	2.892
	Residual	24			
Pb	Ash (%)	5	295.3	<0.001	6.408
	Soil type	1	60.09	<0.001	3.699
	Interaction	5	9.04	<0.001	9.062
	Residual	24			
Se	Ash (%)	5	914	<0.001	0.0801
	Soil type	1	30.92	<0.001	0.0463
	Interaction	5	20.73	<0.001	0.1133
	Residual	24			

6.3.6 Water-extractable nutrients in UK fly ash amended soils

Both the arable and woodland soils (without ash amendment) contained a similar concentration of water-extractable boron (6.2 and 3.6 mg kg^{-1} respectively). Addition of increasing concentrations of ash resulted in higher B availability within both soils, although this was most marked in the arable soil (ash concentration × soil type interaction, p=0.001; Figure 6-7; Table 6-5). Four per cent to 32% ash amendment to arable and woodland soils respectively, resulted in a significantly greater B availability than that of the control (unamended) soil.

Water-extractable P was significantly lower in the arable soil after just 2% ash amendment relative to the unamended control soil. The concentration of available P broadly remained the same thereafter, irrespective of ash concentration. However, there was an apparently significant increase in P availability following addition of the 16% ash treatment, although this is most likely to be a Type 1 error (Figure 6-7). In contrast, water-extractable P in the woodland soil increased with both 16% and 32% ash amendment, relative to all the other ash treatments (ash concentration × soil type interaction, p=0.005; Figure 6-7; Table 6-5). Overall, the arable soil contained four times the concentration of water extractable P as the woodland soil.

In contrast to P, water-available Mn was present in the woodland soil at higher concentrations than in the arable soil. Ash amendment did not affect Mn availability in arable soil, but addition of 2% ash to woodland soil significantly decreased water-available Mn relative to the unamended control soil. Higher ash content resulted in a consistently lower Mn availability than for the control soil (apart from a spike with the 16% amendment which, as for P, may be a Type 1 error) (ash concentration × soil type interaction, p<0.001; Figure 6-7; Table 6-5).

Available Fe content was lowered by ash addition in both soils (ash as a single factor within the two-way ANOVA, p<0.001, LSD = 1014). Fe was less available in soils amended with 16% and 32% ash (512 and 173 mg kg^{-1} respectively, data pooled across both soils) compared to the 0% treatment (1646 mg kg^{-1}).

Ash amendment did not influence the concentration of other key nutrients within the soils at the time of harvest; e.g., Ca, Mg and S (grand means, 4435 mg kg^{-1}, 1382 mg kg^{-1} and 5125 mg kg^{-1} respectively). Water-available K was also unaffected by ash amendment, although a lower concentration was measured in the woodland soil (164 mg kg^{-1}) than in the arable soil (1451 mg kg^{-1}) (soil as a single factor, $p<0.001$).

6.3.7 Water-extractable PTEs in UK fly ash amended soils

Water extractable Co, Cr and Cu did not follow a pattern with regard to ash amendment, but significantly ($p<0.001$) higher concentrations of Co were available in arable (1.72 mg kg^{-1}) than in woodland (0.82 mg kg^{-1}) soil when data were pooled across all ash concentrations. The same trend was observed for Cr and Cu which were both significantly ($p=0.002$) higher in the arable soil (0.42 and 41.2 mg kg^{-1} respectively) than in the woodland soil (0.28 and 21.4 mg kg^{-1} respectively). Available Zn concentrations were higher ($p<0.001$) in arable (151.7 mg kg^{-1}) than in woodland (77.5 mg kg^{-1}) soil, as was available Cd ($p=0.046$; arable and woodland soil, 2.63 and 1.88 mg kg^{-1} respectively).

Both Zn and Cd also responded to increasing ash concentrations as a single factor, as did Pb (all $p<0.001$; data not shown). These elements followed the same trend as Se (Figure 6-8).

Available Ni within the arable soil increased with the 2% and 4% amendments relative to the 0% control, but thereafter, concentrations remained similar irrespective of increasing ash concentration. A similar trend was observed for Ni in the woodland soil, except that significant increases were not observed at ash amendments lower than 8%. At the lower ash concentrations (0%-4%), Ni was more readily available in the arable soil, but this trend changed on application of 8% ash (ash concentration × soil type interaction, $p=0.031$; Table 6-5; Figure 6-8).

Available As concentrations were similar across both soils and all ash treatments up to the 16% and 32% amendments after which availability significantly increased in both soils, but more so in the arable soil (ash concentration × soil type interaction, $p=0.006$; Table 6-5; Figure 6-8).

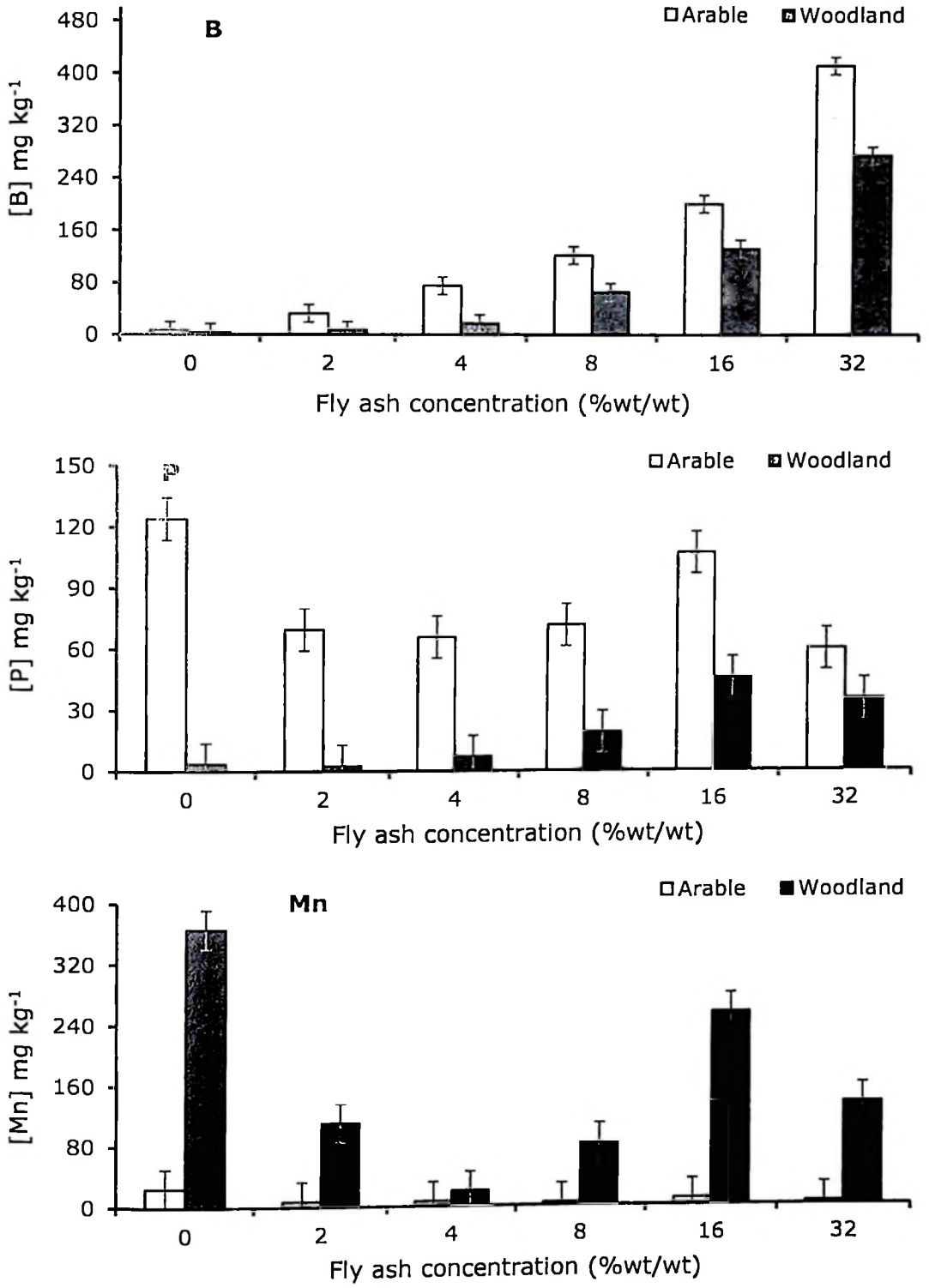

Figure 6-7: *The effect of fly ash on water extractable B, P and Mn in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 22 degrees of freedom. LSD for B= 39.59, P= 30.32 and Mn= 74.86. Please take note of scale differences on the Y axes.*

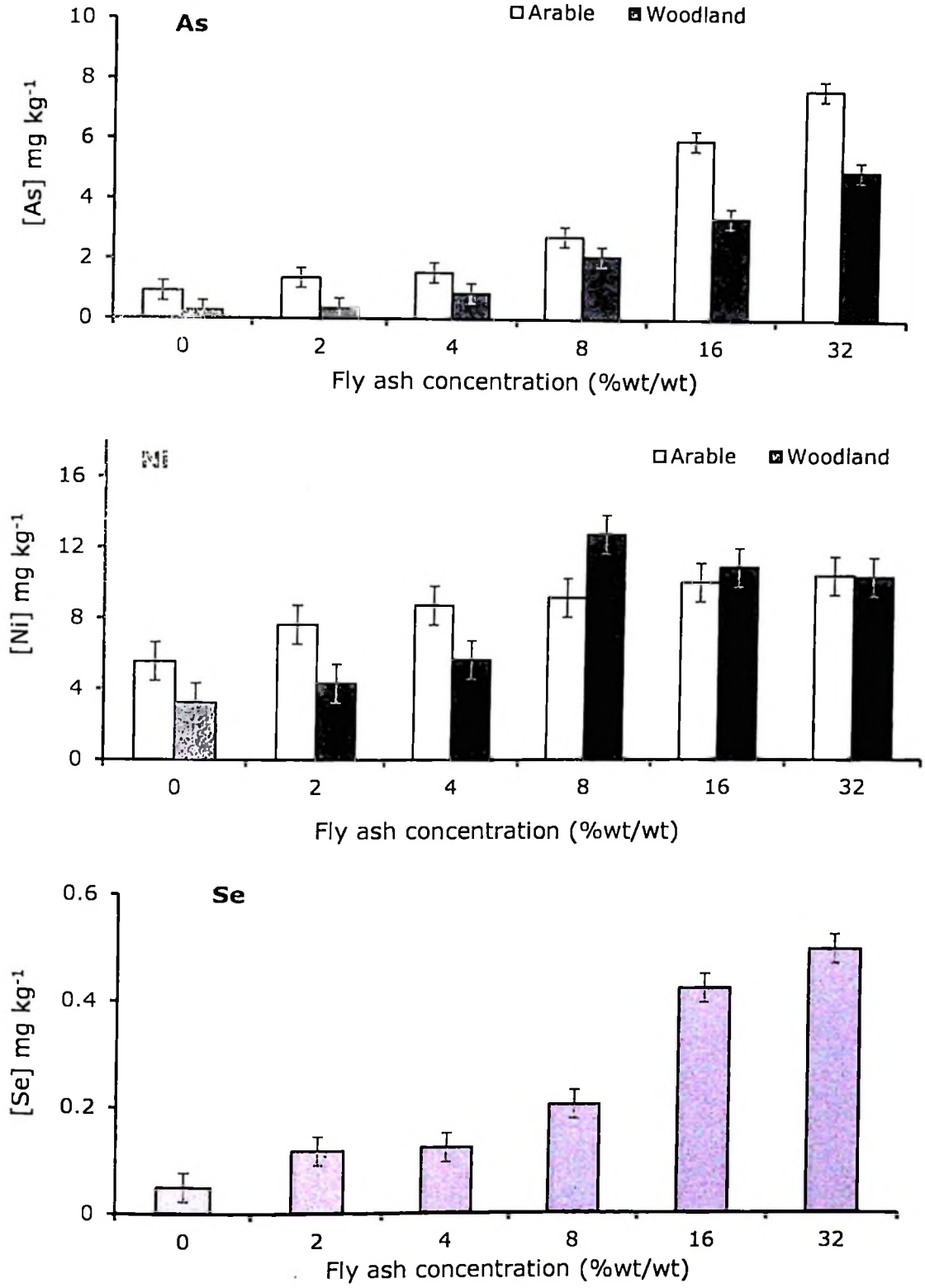

Figure 6-8: *Effect of fly ash application on water extractable concentration of the potentially toxic elements As, Ni and Se in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 22 degrees of freedom. LSD for As= 0.98, Ni= 3.20, Se= 0.080. Please take note on scale differences in Y axis. Data for Se are pooled means for both soil types because ash concentration was significant as a single factor (see Table 6-5).*

Table 6-5: *Summary of 2-factor ANOVA from post-harvest water extractable nutrient and PTEs content of soils amended with UK1 fly ash*

NUTRIENTS					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
B	Ash (%)	5	181.38	<0.001	27.99
	Soil type	1	56.14	<0.001	16.16
	Interaction	5	5.92	0.001	39.59
	Residual	22			
P	Ash (%)	5	4.83	0.004	21.44
	Soil type	1	115.89	<0.001	12.38
	Interaction	5	4.57	0.005	30.32
	Residual	22			
Mn	Ash (%)	5	13.6	<0.001	52.93
	Soil type	1	106.92	<0.001	30.56
	Interaction	5	11	<0.001	74.86
	Residual	22			

PTEs					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
As	Ash (%)	5	99.52	<0.001	0.6916
	Soil type	1	52.25	<0.001	0.3993
	Interaction	5	4.43	0.006	0.9781
	Residual	22			
Ni	Ash (%)	5	12.93	<0.001	2.265
	Soil type	1	1.33	0.262	1.308
	Interaction	5	3.05	0.031	3.204
	Residual	22			
Se	Ash (%)	5	44.66	<0.001	0.0795
	Soil type	1	0.14	0.711	0.0459
	Interaction	5	1.13	0.376	0.1125
	Residual	22			

6.3.8 PTE content of grains, roots and shoots of wheat grown in UK fly ash amended soil

Due to the death of most replicate plants grown in the arable soil amended with 32% ash prior to grain fill, data for elemental concentrations within different plant parts (roots, shoots and grain) were analysed by one-way ANOVA using ash concentration as the main factor; data are shown in Tables 6-6 and 6-7 for plants grown in woodland and arable soil respectively. A two-way ANOVA was also conducted on data for plants grown with 0%-16% ash. There were no interactions between ash concentration and soil type for grain chemistry, thereby endorsing the decision to utilise one-way ANOVAs. However, soil type was a significant single factor for some elemental concentrations; where appropriate, these are highlighted in the text for grain PTE content, since this is the most important portion of the plant from a dietary perspective.

Ash concentration had little effect on the macronutrient content of the grains irrespective of soil type, although 4-32% ash lowered the grain S concentration in wheat grown in the woodland soil relative to the 0-2% ash amendment (e.g. 0% ash=1661 mg kg^{-1}, 4%=709 mg kg^{-1} and 32%=492 mg kg^{-1}; $p=0.002$; LSD=454.9). Ash had no effect on grain S content of plants grown in the arable soil. Grain from wheat grown in the arable soil had higher concentrations overall (data pooled across ash concentrations, two-way ANOVA) of Ca (arable=383 mg kg^{-1}, woodland=338 mg kg^{-1}; $p=0.022$, pooled SE= 12.48) and P (arable=3783 mg kg^{-1}, woodland=2490 mg kg^{-1}; $p<0.001$, pooled SE= 287), but lower Mn content than grain from woodland soil-grown plants (arable=31.4 mg kg^{-1}, woodland=57.8 mg kg^{-1}; $p<0.001$, pooled SE= 1.92). No other macronutrients were affected by treatments. Grain Fe content was significantly lower in plants grown with all ash concentrations relative to the control (e.g. 0%=124.9 mg kg^{-1}, 2% ash=62.0 mg kg^{-1} and 16%=55.7 mg kg^{-1}; ash as a single factor in two-way ANOVA, $p=0.001$, LSD=32.45). For the purposes of this investigation, other micronutrients will be considered as potentially toxic elements (PTEs) and this is the focus here.

For plants grown in woodland soil, Ni and Pb concentrations in roots were generally higher following soil amendment by 8-32% fly ash relative to roots of the control plants (Table 6-6; Ni, $p=0.03$; Pb, $p<0.001$), but there were no significant effects of ash on shoot Ni and Pb concentrations. In grains, the concentration of Ni decreased significantly with increasing fly ash concentration

from 2-32% ($p<0.001$), but there was no significant effect of ash on grain Pb content.

Root, shoot and grain Se concentrations were significantly enhanced by 16% and 32% ash amendments to the woodland soil (Table 6-6; $p<0.001$ for all three parameters). Similar trends for Se concentrations were also observed for roots, shoots and grains of plants grown in the arable soil (Table 6-7). Relative to the control, amendment of woodland soil with 32% fly ash significantly increased the concentration of Cr in roots and shoots (Table 6-6; roots, $p=0.012$; shoots, $p=0.022$), but there was a much clearer trend within the grain, where all ash amendments reduced Cr concentration to a similar level ($p=0.004$). In contrast, 32% ash amendment increased Cr in roots of plants grown in the arable soil, but not of shoots or grain (Table 6-7).

In roots, the concentration of As increased significantly following woodland soil amendment with 16-32% fly ash (Table 6-6; $p<0.001$) but in shoots and grains, the concentration of As increased when the woodland soil was treated with 8-16% fly ash (Table 6-6; shoots, $p<0.001$; grains, $p=0.004$). The highest levels of ash addition to arable soil enhanced As concentration of roots and shoots; no grain was obtained from wheat grown with 32% ash, but the apparent increase in grain As concentration in plants grown with 16% ash was not significant (Table 6-7).

Root concentrations of Cd and Zn increased when plants were grown in woodland soil amended with 16-32% ash (Table 6-6; Cd, $p=0.016$; Zn, $p=0.012$), but ash treatment did not affect shoot Cd and Zn concentrations. In contrast, grain Zn content decreased significantly with increasing fly ash amendment ($p<0.001$; Table 6-6). All ash amendments to the arable soil resulted in a similar decrease in grain Zn relative to the 0% control ($p=0.020$; Table 6-7). The trend for Cd in plants grown in woodland soil was different from that of Zn, with the highest grain concentrations recorded following the 4% ash treatment and subsequent significant reductions in concentration when plants were grown with 8-32% ash (Table 6-6). When plants were grown in the arable soil, root Cd concentrations were significantly higher when subjected to the 32% treatment relative to all others, but ash supplementation did not affect shoot or grain Cd (Table 6-7).

Woodland soil amendment with fly ash did not significantly affect shoot Co concentration, although root Co content was approximately 1.5 times higher when plants were grown with ash amendments of 8-16% than when subjected to 0-4% ash ($p=0.008$; Table 6-6). Grain Co concentration generally decreased with increasing ash content in the woodland soil; an order of magnitude difference in concentration was recorded in grain from plants grown in unamended soil to that of plants subjected to the 32% ash treatment ($p<0.001$; Table 6-6).

6.3.9 Transfer ratios of PTEs from the soil to the plant parts

The soil-to-root, root-to-shoot and shoot-to-grain transfer ratios were calculated to determine the content of PTEs expected to enter the plant (Table 6-8). These were calculated from the ratio of the elemental concentration in each plant part relative to that of the preceeding plant part (or of soil) following the equation:

$$TR = \frac{Cp}{Cs} \qquad Equation\ 6-3$$

Where TR = PTE transfer ratio, Cp and Cs are concentrations of PTEs in plant and soil respectively on a dry weight basis (Duressa et al., 2015), in the case of soil-to-root transfer. TRs of >1 generally indicate accumulation of the element, whilst those <1 show exclusion.

Analysis of the calculated PTE transfer ratios from soil-to-roots of wheat plants grown in woodland soil showed significant transfer of As and Se following soil amendment with 16-32% fly ash ($p=0.002$ for As and $p<0.001$ for Se, one-way ANOVA; Table 6-8), but the TRs were most markedly >1 after spiking soil with 8% ash. Whilst ash amendment did not significantly increase the TR from woodland soil-to-roots of the remaining PTEs, the TR for Cd was >1 across all treatments (grand mean, 1.97). TRs for Co, Cr, Ni and Pb were 0.94, 0.92, 1.06 and 0.82 respectively and this did not change significantly with ash treatment.

From roots-to-shoots (i.e. stem and leaves, not including the seed head), the transfer ratios of As and Zn decreased when the woodland soil was amended with 16-32% ash (Table 6-8; $p=0.01$ for As and $p=0.03$ for Zn), although since

TR values were generally <1, no accumulation in the shoot material was obvious. Other PTEs had low TRs (e.g. Cd, 0.72; Cr, 0.04, Se, 0.14).

Table 6-6: *Average concentration of PTEs in roots, shoots and grains of wheat (mg kg^{-1}) based on different UK fly ash dosage applied to woodland soil*

Ash content	Potentially toxic elements							
	As	Cd	Co	Cr	Ni	Pb	Zn	Se
Root								
0%	4.05^{a}	0.26^{a}	2.70^{ab}	0.71^{a}	8.60^{a}	34.30^{a}	81.50^{a}	0.51^{a}
2%	6.84^{a}	0.41^{a}	2.88^{ab}	11.41^{ab}	10.50^{ab}	35.06^{ab}	77.10^{a}	0.78^{a}
4%	7.08^{a}	0.60^{a}	2.42^{a}	11.00^{ab}	8.91a	32.76^{a}	76.3^{a}	0.80^{a}
8%	20.39^{ab}	1.43^{a}	4.01^{b}	9.64^{ab}	13.80^{b}	67.04^{bc}	112.2^{a}	1.57^{a}
16%	42.24^{bc}	4.43^{a}	3.96^{ab}	13.55^{ab}	13.88^{b}	109.93^{d}	244^{a}	4.20^{b}
32%	59.12^{c}	4.52^{a}	4.11^{b}	16.7^{b}	12.52^{ab}	93.95^{cd}	251^{a}	6.08^{c}
P value	<0.001	0.016	0.008	0.012	0.003	<0.001	0.012	<0.001
$F_{5,11}$	19.42	4.60	5.69	5.01	7.27	24.99	4.99	81.58
Shoot								
0%	ND	ND	ND	ND	ND	ND	ND	ND
2%	1.27^{a}	0.37	0.18	0.12^{a}	2.04	1.16	52.05	0.07^{a}
4%	1.75^{a}	0.64	0.20	0.46^{ab}	2.44	1.85	80.14	0.09^{a}
8%	4.59^{bc}	0.53	0.55	0.47^{ab}	3.03	6.96	50.22	0.20^{a}
16%	4.94^{c}	1.17	0.50	0.69^{ab}	3.44	23.02	62.11	0.73^{b}
32%	3.00^{ab}	2.40	0.53	0.52^{b}	3.88	29.21	102.5	1.08^{c}
P value	<0.001	NS	NS	0.022	NS	NS	NS	<0.001
$F_{4,8}$	17.43	2.97	2.24	5.25	0.84	3.60	1.50	96.36
Grain								
0%	0.03^{a}	0.01^{a}	0.10^{c}	0.55^{b}	1.31^{c}	0.06	77.81^{d}	0.01^{a}
2%	0.21^{ab}	0.06^{b}	0.05^{ab}	0.15^{a}	0.46^{b}	0.04	32.99^{c}	0.06^{a}
4%	0.22^{ab}	0.10^{c}	0.02^{a}	0.05^{a}	0.30^{ab}	0.03	29.93^{c}	0.09^{a}
8%	0.53^{b}	0.04^{ab}	0.08^{bc}	0.07^{a}	0.29^{ab}	0.09	20.20^{b}	0.26^{a}
16%	0.56^{b}	0.02^{a}	0.03^{a}	0.07^{a}	0.14^{ab}	0.06	13.60^{a}	0.93^{b}
32%	0.36^{ab}	0.02^{ab}	0.01^{a}	0.05^{a}	0.09^{a}	0.09	14.44^{a}	1.37^{c}
P value	0.004	<0.001	<0.001	0.004	<0.001	NS	<0.001	<0.001
$F_{5,10}$	7.10	20.04	18.98	7.08	40.32	0.76	584.51	48.82

ND= Not determined, NS=non-significant within column, means with the same letter are not significantly different (Tukey's test p<0.05) within a column, p and F values derived from one-way ANOVA.

Table 6-7: *Average concentration of PTEs in roots, shoots and grains of wheat (mg kg^{-1}) based on different UK fly ash dosage applied in arable soil*

Ash content	Potentially toxic elements							
	As	**Cd**	**Co**	**Cr**	**Ni**	**Pb**	**Zn**	**Se**
Root								
0%	3.43[a]	2.02	18.34	9.68[a]	26.57	79.28	419.1	0.49[a]
2%	8.08[a]	1.04	5.63	9.06[a]	9.65	46.87	151.6	1.18[a]
4%	15.72[a]	2.42	7.39	9.75[a]	9.47	41.44	208	1.24[a]
8%	12.65[a]	1.92	6.29	6.36[a]	8.37	43.82	159	2.90[a]
16%	38.69[a]	17.98	13.30	8.83[a]	18.12	108.66	1052	5.51[a]
32%	47.46[a]	5.57	6.81	18.87[b]	16.61	95.24	298	12.50[b]
P value	0.041	NS	NS	<0.001	NS	NS	NS	< 0.001
$F_{5,11}$	3.44	1.59	1.29	10.52	0.94	0.81	1.22	19.12
Shoot								
0%	0.99[a]	2.62[a]	23.20	0.50[ab]	44.29	92.01	704.5	0.11[a]
2%	1.12[a]	3.29[a]	8.83	0.36[ab]	17.33	106.36	551.6	0.20[a]
4%	1.31[a]	2.28[a]	5.47	0.35[ab]	14.21	30.68	295.5	0.25[a]
8%	1.28[a]	2.08[a]	2.01	0.32[ab]	8.50	22.38	209.2	0.47[ab]
16%	3.1[2a]	5.62[a]	8.17	0.26[a]	27.90	35.24	405.4	0.89[b]
32%	4.71[a]	31.08[b]	6.93	1.56[b]	50.78	165.3	1441	3.01[c]
P value	0.030	0.001	NS	0.021	NS	NS	NS	<0.001
$F_{5,12}$	3.69	8.17	0.78	4.12	1.06	1.42	2.63	140.40
Grain								
0%	0.06	0.01	0.20	0.26	0.49	0.22	28.38[b]	0.02[a]
2%	0.16	0.01	0.08	0.09	0.14	0.13	14.99[a]	0.10[a]
4%	0.15	0.01	0.08	0.12	0.24	0.11	12.49[a]	0.19[a]
8%	0.15	0.01	0.05	0.09	0.18	0.05	14.68[a]	0.38[a]
16%	0.4	0.02	0.17	0.15	0.55	0.21	13.96[a]	0.88[b]
32%	ND	ND	ND	ND	ND	ND	ND	ND
P value	NS	NS	NS	NS	NS	NS	0.020	<0.001
$F_{4,7}$	1.78	1.07	0.83	1.66	0.79	0.76	6.05	19.13

ND= Not determined, NS=non-significant within column, means with the same letter are not significantly different (Tukey's test p<0.05) within a column, p and F values derived from one-way ANOVA.

Whilst there were ash-related significant differences in transfer ratio for some PTEs from shoot-to-grains when plants were grown in woodland soil (Table 6-5), these TR values were all <1, as were the TRs for PTEs that were not significantly affected by ash addition (e.g. TR for As, 0.13 and Co, 0.11).
In arable soil, ash amendment did not significantly affect transfer ratios of PTEs from soil-to-root or from root-to-shoot. However, all PTEs (apart from Cr) had TRs from soil-to-root of >1, with Cd, Se and Zn having the highest TRs (6.4, 3.4 and 4.0 respectively); Ni (1.52) and Pb (1.57) had the lowest. Only Cd, Ni, and Zn accumulated in the shoot from the roots (TRs 2.38, 1.82 and 2.25 respectively).

Shoot to grain transfer ratios of PTEs when plants were grown in arable soil were all <1. TR values ranged from 0.006 for Pb to 0.81 for Se and only the TR for Cd was significantly affected by ash amendment to arable soil ($p=0.002$, Table 6-8), with the values suggesting exclusion of Cd from the grains.

Separate one-way ANOVAs were conducted on each soil because of some plant losses when grown in the arable soil with 32% ash. However, a two-way ANOVA using a restricted data set (2%-16% ash amendments for woodland and arable soil) indicated that shoot-to-grain TRs were around an order of magnitude higher ($p<0.01$) in plants grown in the woodland soil, although all TR values were <1 (e.g. TR for Zn: arable soil, 0.06; woodland soil, 0.43).

Table 6-8: *Transfer ratios of PTEs from soil to plant parts for wheat plant grown in soils amended with UK fly ash*

	Fly ash concentration (% dry weight)							
Woodland soil	0	2	4	8	16	32	**F ratio**	**p value**
Soil to Root								
As	0.46^{a}	0.55^{a}	0.56^{a}	1.22^{ab}	1.88^{b}	1.63^{b}	$F_{5,11}=7.81$	0.002
Se	1.00^{a}	1.08^{a}	1.20^{a}	1.56^{ab}	$2.52b^{c}$	3.11^{c}	$F_{5,11}=17.43$	<0.001
Root to shoot								
As	ND	0.21^{ab}	0.27^{b}	0.22^{b}	0.13^{ab}	0.05^{a}	$F_{4,8}=7.04$	0.01
Zn	ND	0.74^{ab}	1.10^{b}	0.45^{ab}	0.30^{a}	0.45^{ab}	$F_{4,8}=4.55$	0.03
Shoot to grain								
Cd	ND	0.15^{bc}	0.16^{c}	0.08^{ab}	0.02^{a}	0.014^{a}	$F_{4,8}=21.16$	<0.001
Cu	ND	1.40^{c}	1.03^{bc}	1.08^{bc}	0.37^{a}	0.71^{ab}	$F_{4,8}=8.61$	0.005
Ni	ND	0.26^{b}	0.14^{ab}	0.08^{a}	0.05^{a}	0.03^{a}	$F_{4,8}=13.4$	0.001
Pb	ND	0.03^{b}	0.02^{b}	0.014^{ab}	0.003^{a}	0.004^{a}	$F_{4,8}=12.96$	0.001
Zn	ND	0.67^{b}	0.38^{ab}	0.41^{ab}	0.24^{a}	0.20^{a}	$F_{4,8}=5.67$	0.018
Arable soil								
Shoot to grain								
Cd	0.018^{b}	0.008^{a}	0.005^{a}	0.007^{a}	0.003^{a}	ND	$F_{4,7}=14.69$	0.002

Shoot includes the stem and leaves, ND=Not determined, ratios with the same letter within a row are not significantly different (Tukey's test $p<0.05$), p and F values derived from one-way ANOVA for each soil type separately.

6.4 RESULTS: EXPERIMENT WITH TANZANIA ASH

6.4.1 Post-harvest soil pH following amendment with Tanzania ash

Ash application lowered the pH of both soils, with the largest effect observed in the arable soil where pH ranged from 6.77 in the control to pH 5.88 when 32% ash was added. Whilst the pH of the woodland soil also fell with ash amendment, the decrease was not as large, with the difference between the control and the 32% ash amendment being just 0.2 pH units (Figure 6-9; ash concentration × soil type interaction, $p<0.001$; Table 6.9. In woodland soil, application of 8% ash significantly reduced the soil pH relative to that of the control soil, but higher ash amendments did not show any further decreases beyond that. In arable soil, the pH decreased significantly when amended with 8% ash and thereafter with each increase in ash concentration.

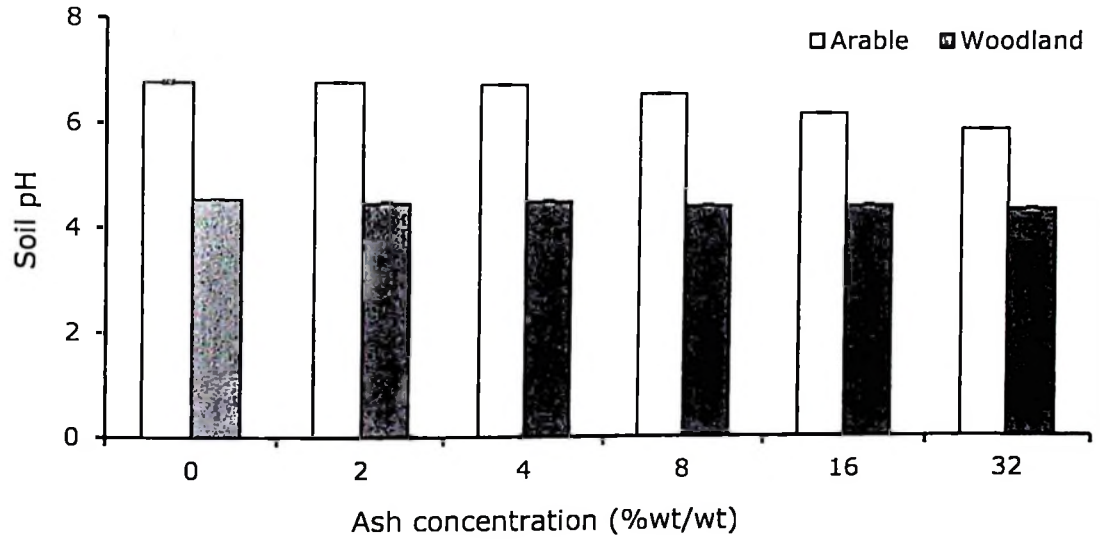

Figure 6-9: *The effect of coal ash application on soil pH after harvesting, $p<0.001$ (ash concentration × soil type interaction), LSD= 0.11.*

6.4.2 Wheat growth and yield in soils amended with Tanzania ash

There was a significant interaction effect between ash concentration and soil type for all wheat growth and yield parameters (number of leaves, tillers, grains, total shoot biomass, root biomass and grain weight); Table 6.9.

Ash amendment did not significantly affect leaf number, or tiller number, or root biomass in plants grown in the arable soil (Figure 6-10). Numbers of leaves and tillers were lower in arable soil-grown plants, as was root biomass

compared to wheat grown in woodland soil (Figure 6-10, Table 6.9). In contrast to arable soil, application of 2% ash to woodland soil significantly increased the number of leaves, tillers and root biomass (Figure 6-10; Table 6.9) with maximum leaf number recorded in plants grown with 4% and 8% ash. The general trend for total shoot biomass was of decreasing weight with increasing ash concentration when grown in arable soil, but with the opposite effect when grown in woodland soil (Figure 6-11a). This was also reflected in the grain weight which would have been a large proportion of the shoot component and also the number of grains (Figure 6-11b&c; Table 6.9).

There was no significant difference in yield (grain weight per plant) between woodland and arable soil before ash application, but in woodland soil, application of 16% ash increased the grain weight significantly. In contrast, ash amendment of arable soil, resulted in significantly decreased grain weight (Figure 6-11b; Table 6.9).

Grain number followed a similar trend to grain weight per plant (Figure 6-11c; Table 6.9, although whilst ash amendment to arable soil decreased the number of grains, the effect on grain production when wheat was grown in woodland soil was not significantly different across the ash concentrations. There is a strong linear relationship between grain number and weight for arable soil-grown plants, but the relationship is weaker for woodland grown grains (data not shown). This is particularly interesting since the calculated weight of 100 grains was not significantly different in any plant, irrespective of soil type or ash concentration (grand mean 4.18 g).

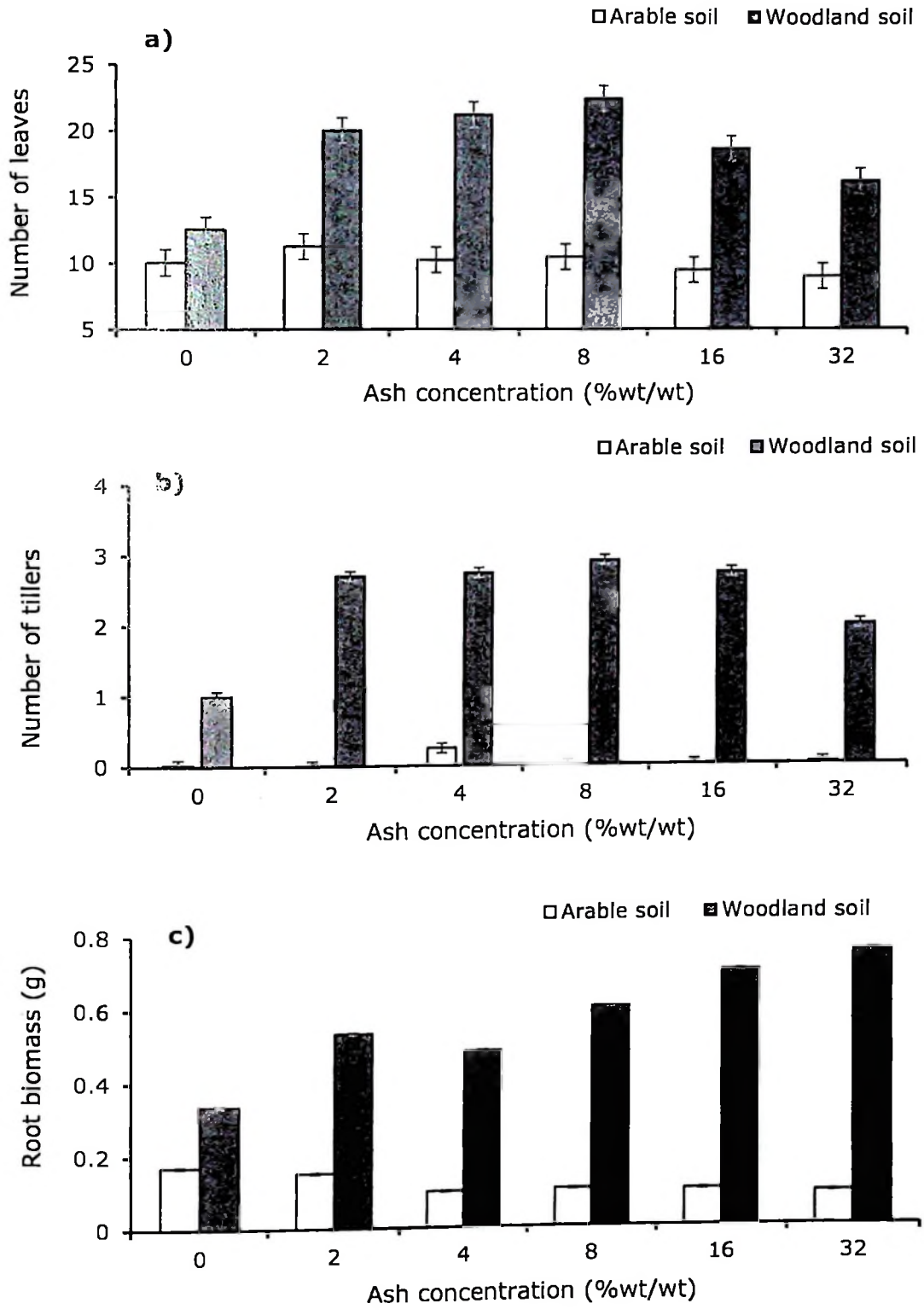

***Figure 6-10**: Effect of coal ash application on a) number of leaves, b) number of tillers and c) root biomass of wheat grown in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 29 degrees of freedom. LSD (for the interaction terms) for number of leaves =2.85, number of tillers =0.77, and root biomass =0.16*

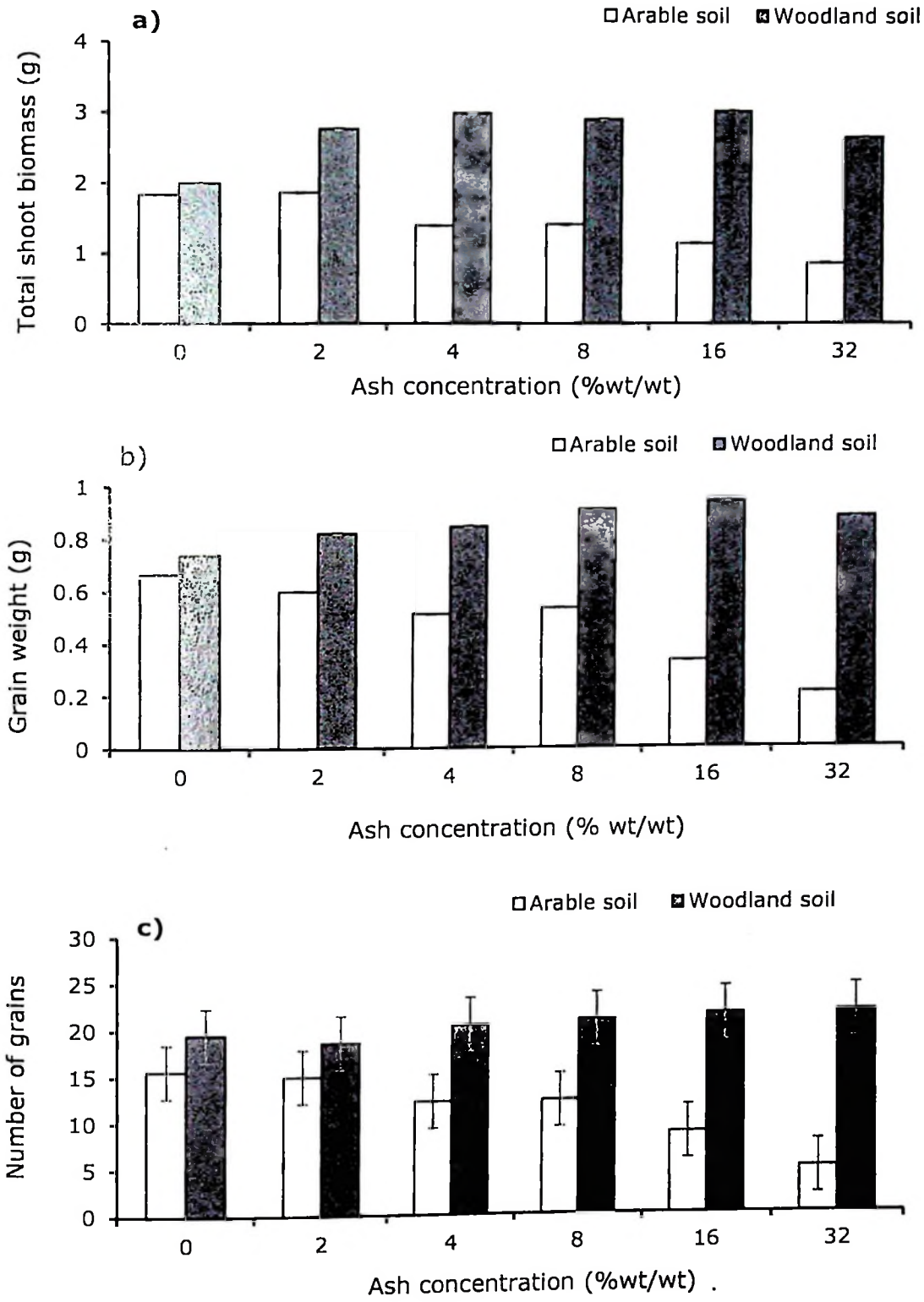

Figure 6-11: *Effect of coal ash application on a) shoot biomass, b) grain weight and c) grain number of wheat grown in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 28 (for grain weight and grain number) and 29 (for total shoot biomass) degrees of freedom. LSD (for the interaction terms) for total shoot biomass = 0.35, grain weight =0.17, and grain number = 4.92.*

Table 6-9: *Summary of 2-factor ANOVA for pH, and wheat growth parameters from the experiment with Tanzania 1 ash*

VARIATE	FACTOR	DF	F	P VALUE	LSD (95%)
pH	Ash (%)	5	56.57	<0.001	0.0833
	Soil type	1	7419.49	<0.001	0.0481
	Interaction	5	28.02	<0.001	0.1178
	Residual	33			
Number of leaves	Ash (%)	5	8.57	<0.001	2.016
	Soil type	1	220.92	<0.001	1.164
	Interaction	5	5.85	<0.001	2.851
	Residual	29			
Number of tillers	Ash (%)	5	4.12	0.006	0.5424
	Soil type	1	226.92	<0.001	0.3131
	Interaction	5	3.76	0.01	0.767
	Residual	29			
Root biomass	Ash (%)	5	2.77	0.036	0.1103
	Soil type	1	208.43	<0.001	0.0637
	Interaction	5	5.5	0.001	0.156
	Residual	29			
Total shoot biomass	Ash (%)	5	5.55	0.001	0.2464
	Soil type	1	353.99	<0.001	0.1423
	Interaction	5	14.92	<0.001	0.3485
	Residual	29			
Grain weight	Ash (%)	5	2.61	0.046	0.1172
	Soil type	1	133.97	<0.001	0.0677
	Interaction	5	8.04	<0.001	0.1658
	Residual	28			
Number of grains	Ash (%)	5	1.58	0.199	3.481
	Soil type	1	84.08	<0.001	2.01
	Interaction	5	4.53	0.004	4.922
	Residual	28			

6.4.3 Post-harvest total nutrient content of soils amended with Tanzania ash

Results of total concentrations of selected soil nutrients after harvesting are presented in Figure 6-12. Total soil P in woodland soil was unaffected by ash amendment, but in arable soil P was significantly decreased by application of 8% ash and thereafter, each successive increase in ash concentration resulted in a significantly lower P content relative to the preceeding amendments (Figure 6-12; ash concentration × soil type interaction, $p=0.014$).

In contrast, Ca concentrations in arable soil were unaffected by ash amendment, while in woodland soil, application of 16% and 32% ash significantly increased the total concentration of Ca in comparison to the control (Figure 6-12; ash concentration × soil type interaction, $p=0.041$). Overall, there was a significantly greater concentration of both Ca (1.8×) and P (2.4×) in the arable compared to the woodland soil (Table 6-10).

Mg and Mn concentrations were both reduced overall by increasing ash concentration (Figure 6-12; ash concentration as a single factor). Mg concentrations were significantly decreased by the 32% amendment and Mn by the 8%, 16% and 32% ash additions relative to the control soil (Figure 6-12).

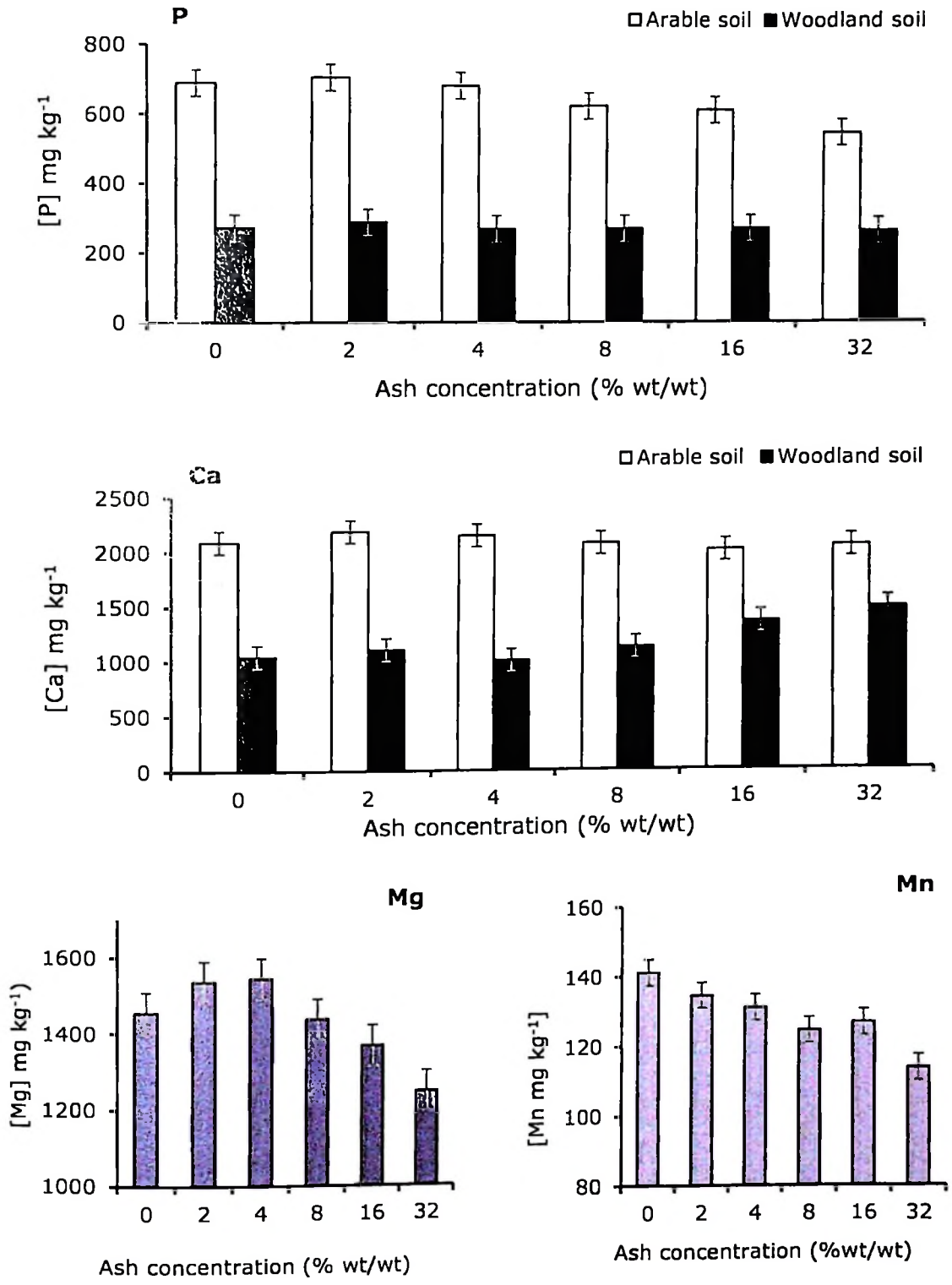

Figure 6-12: *Effect of coal ash application on total nutrients concentration (mg kg^{-1}) in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 33 degrees of freedom. LSD (for interaction terms) for P = 59.19 and Ca =297.3; LSD (ash concentration as a single factor) for Mg=153.7 and Mn =10.71.*

6.4.4 Total PTE concentrations in Tanzania ash amended soils

Results for total PTEs from soil analysis after harvesting (Figure 6-13) showed a trend of increasing PTE concentrations in soils following ash application. Soil type was also a significant single factor (Table 6-10) for some PTEs, but there were no ash concentration × soil type interactions.

The total concentrations of Se and Co increased significantly with an increasing ash concentration from 2-32% (Figure 6-13; $p<0.001$ for Se and $p<0.001$ for Co; Table 6-11, ash as a single factor). Ni and Cu increased significantly with 2% ash relative to the control treatment and then again with 16-32% ash amendments (Figure 6-13; $p<0.001$ for Ni and $p<0.001$ for Cu). Cd and Zn concentrations only increased with the 16-32% ash amendments (Figure 6-13; $p<0.001$ for Cd and $p=0.01$ Zn, Table 6-11).

Besides the effect of ash on these PTEs, the total concentration of Cd, Co and Cu was significantly higher in arable soil than in woodland soil, whilst the total concentration of Se and Zn was significantly higher in woodland soil than in arable soil (Table 6-10, soil type as a single factor).

Table 6-10: *Average total soil concentration (mg kg^{-1}) of nutrients and the potentially toxic elements in woodland and arable soils (soil as a single factor; data are pooled across ash concentrations)*

Elements	Woodland soil	Arable soil	DF	F ratio	P- value	SED
Mg	1294	1568	1,33	39.44	<0.001	43.6
Mn	81.1	176.2	1,33	977.3	<0.001	3.04
Cd	0.22	0.37	1,33	427.09	<0.001	0.007
Co	4.14	4.70	1,33	39.31	<0.001	0.089
Cu	12.05	17.55	1,33	151.42	<.001	0.45
Se	0.75	0.57	1,33	136.01	<0.001	0.015
Zn	48.41	44.53	1,33	10.22	0.003	1.21

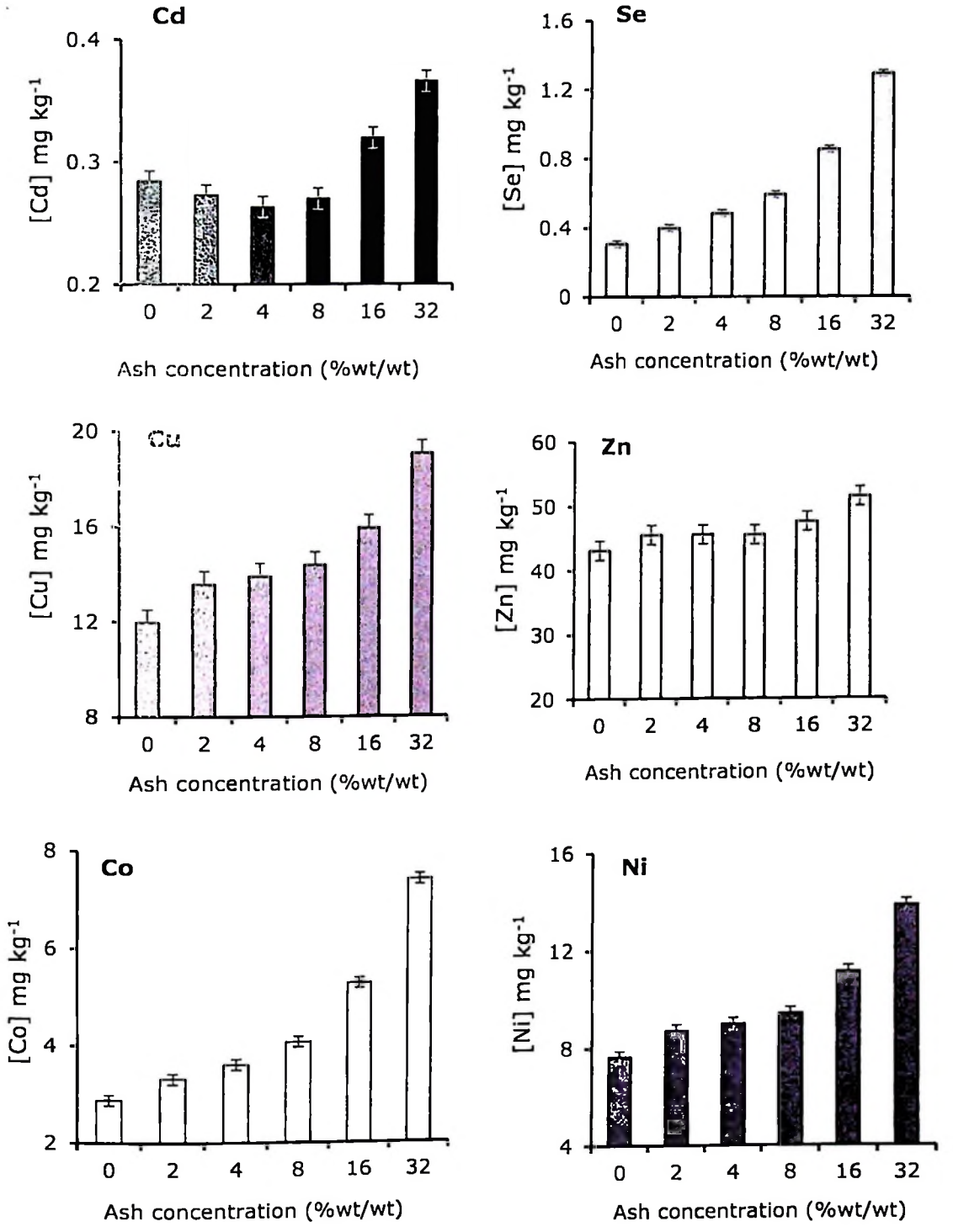

Figure 6-13: *Effect of coal ash application on total soil concentration (mg kg^{-1}) of the potentially toxic elements in woodland and arable soils (ash as a single factor, Table 10-11). Individual error bars are based on the pooled variance estimate from the ANOVA with 33 degrees of freedom. LSD for Cd=0.025, Se=0.054, Cu=1.57, Zn=4.28, Co=0.31 and Ni=0.74. Data are pooled across both soil types.*

Table 6-11: *Summary of 2-factor ANOVA from post harvest total nutrient and PTEs content of soils amended with Tanzania1 ash*

NUTRIENTS					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
P	Ash (%)	5	5.09	0.001	41.86
	Soil type	1	972.9	<0.001	24.17
	Interaction	5	3.39	0.014	59.19
	Residual	33			
Ca	Ash (%)	5	1.11	0.375	210.2
	Soil type	1	231.19	<0.001	121.4
	Interaction	5	2.64	0.041	297.3
	Residual	33			
Mg	Ash (%)	5	4.33	0.004	153.7
	Soil type	1	39.44	<0.001	88.7
	Interaction	5	0.57	0.725	217.4
	Residual	33			
Mn	Ash (%)	5	6.36	<0.001	10.71
	Soil type	1	977.3	<0.001	6.18
	Interaction	5	1.69	0.165	15.15
	Residual	33			

PTEs					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
Cu	Ash (%)	5	20.02	<0.001	1.574
	Soil type	1	151.42	<0.001	0.909
	Interaction	5	1.71	0.16	2.227
	Residual	33			
Co	Ash (%)	5	235.7	<0.001	0.3139
	Soil type	1	39.31	<0.001	0.1812
	Interaction	5	0.46	0.801	0.4439
	Residual	33			
Ni	Ash (%)	5	74.98	<0.001	0.736
	Soil type	1	1.02	0.319	0.425
	Interaction	5	0.46	0.799	1.041
	Residual	33			
Cd	Ash (%)	5	21.07	<0.001	0.02485
	Soil type	1	427.09	<0.001	0.01434
	Interaction	5	1.36	0.265	0.03514
	Residual	33			
Se	Ash (%)	5	384.22	<0.001	0.05387
	Soil type	1	136.01	<0.001	0.0311
	Interaction	5	0.2	0.993	0.07619
	Residual	33			
Zn	Ash (%)	5	3.63	0.010	4.277
	Soil type	1	10.22	0.003	2.469
	Interaction	5	0.82	0.543	6.049
	Residue	33			

6.4.5 Water extractable nutrients in Tanzania ash amended soils

An increasing trend of water extractable Ca and S was observed in both soils with increasing ash concentration, although this was only significant with the 32% amendment for Ca and for the 8-32% additions for S ($p<0.001$ for both elements, ash as a single factor, Figure 6-15).

However, an interaction effect between ash concentration and soil type was observed for K, Mg, P, Mn and B (Figures 6-14 and 6-15). In arable soil, water extractable K increased significantly with 4% ash ($p=0.038$, ash x soil type interaction) and no further significant increase was noted with the higher ash concentrations. In contrast, in woodland soil there was no significant effect of ash on K extractability.

Water extractable Mg increased in both soils amended with 8-32% ash; the highest ash addition resulted in a significantly greater soluble Mg concentration in the woodland soil (Figure 6-14; $p=0.037$). A similar trend was observed with B availability although the differences between soil types were recorded at the lower ash concentrations and these disappeared with the 32% ash amendment ($p=0.007$, Figure 6-15). In contrast to Mg and B, water soluble P within the arable soil decreased significantly with increasing ash concentration, but ash did not affect soluble P in the woodland soil (Figure 6-14; $p<0.001$, Table 6-12).

6.4.6 Water extractable PTEs in Tanzania ash amended soils

The results for the water extractable PTEs following soil amendment with ash are shown in Figures 6-16, 6-17 and 6-18.

A decreasing trend was observed for water extractable As, Cr, Cu and Pb within both soils with increasing ash concentration (Figures 6-16 and 6-17). In contrast, available Se increased with increasing ash amendment in both soils, whilst water extractable Cd, Se, Zn and Ni were significantly higher in woodland (but not in arable) soil when 8%-32% ash were added, with Co only responding to 16% and 32% additions (Figures 6-17 and 6-18; Table 6-12).

Whilst low, intermediate and high ash amendments to arable soil resulted in lower water availability of As, Cr and Cu, the elements in woodland soil only

responded to higher ash concentrations, with As being significantly less available with the 32% amendment of woodland soil than with other ash treatments (Table 6-12 for ash concentration × soil type ANOVA output).

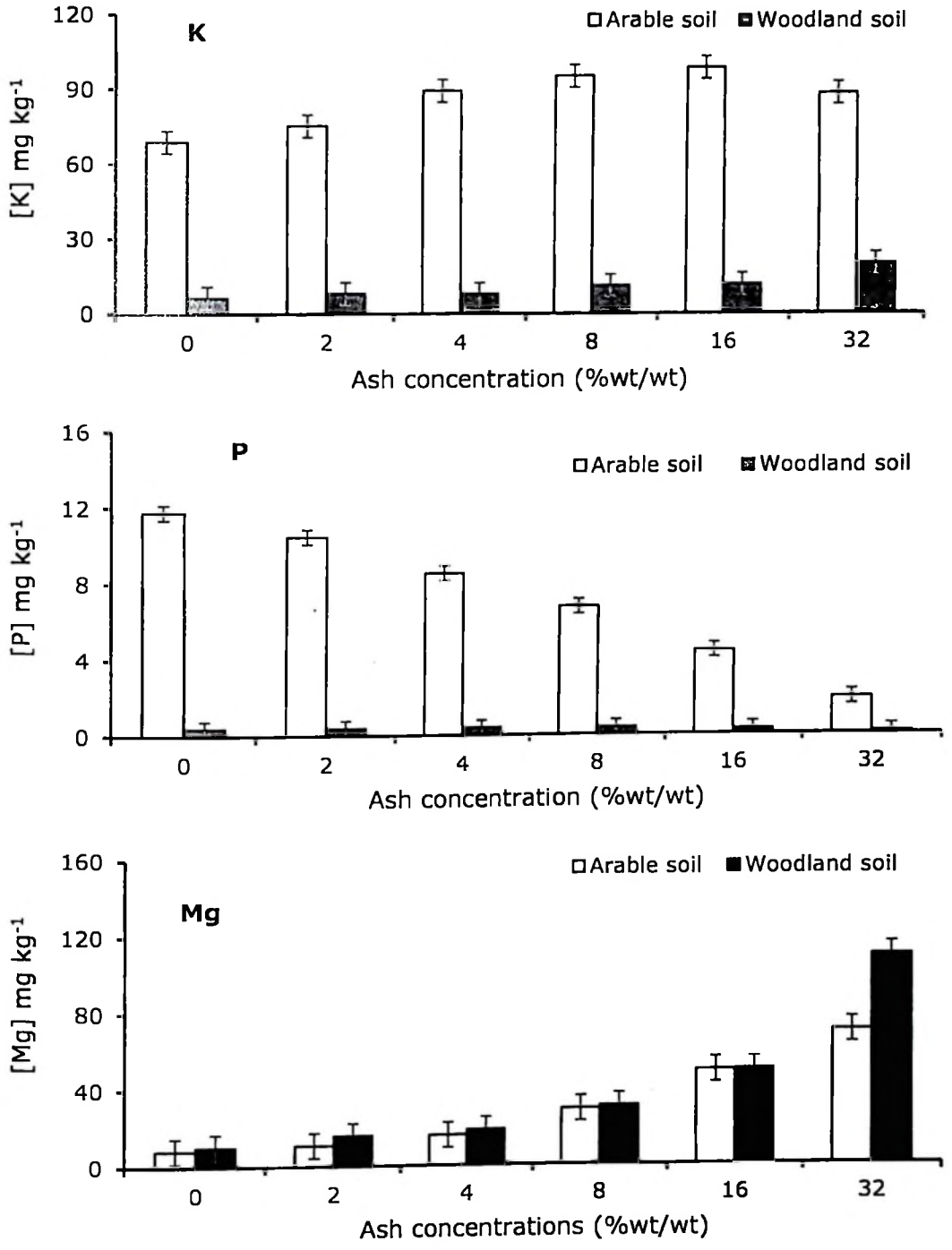

Figure 6-14: *The effect of coal ash on water extractable nutrients in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 33 degrees of freedom. LSD (for interaction terms) for K= 12.99, P= 1.12 and Mg= 18.88. Please take note of scale differences on Y axes.*

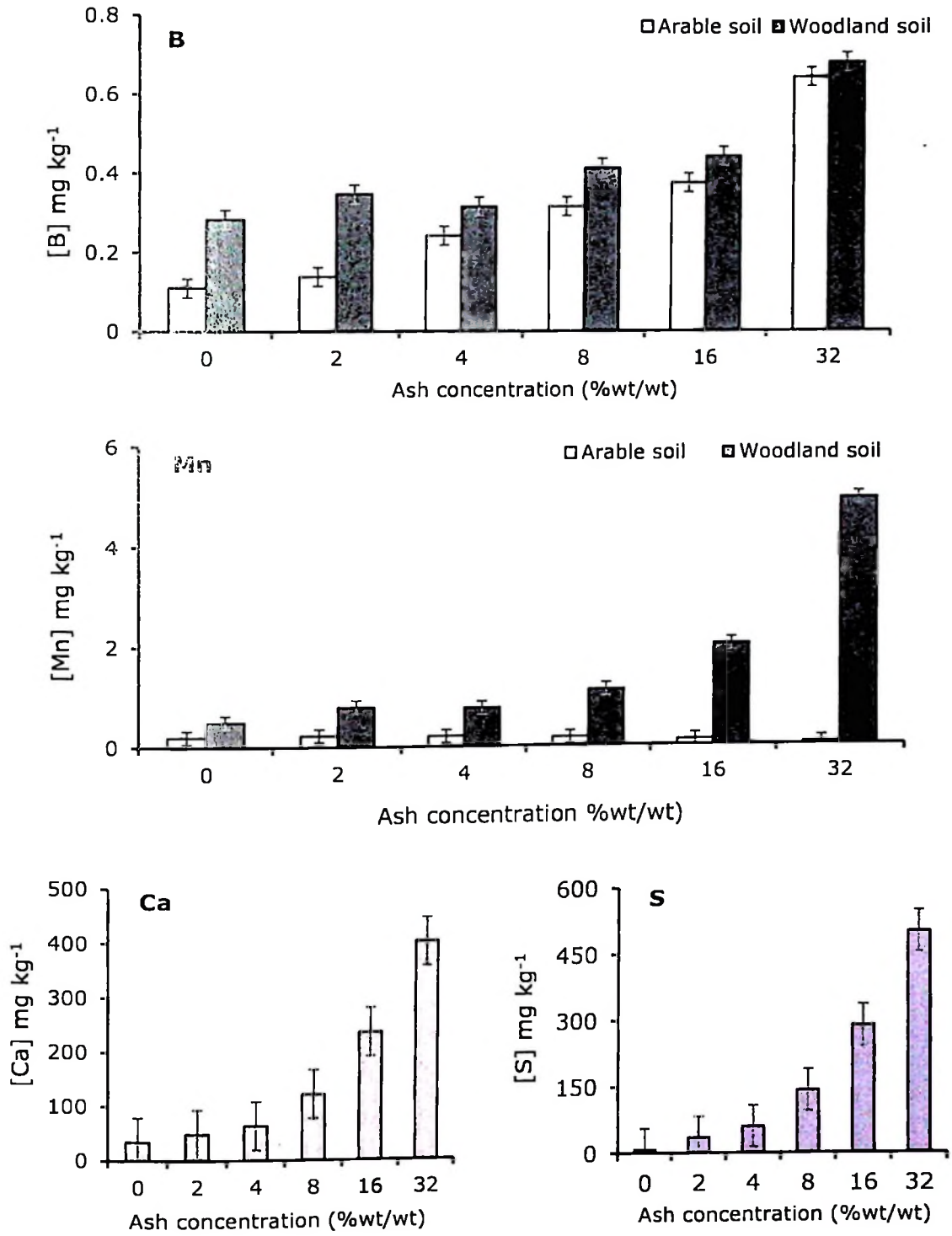

Figure 6-15: *Effect of coal ash on water extractable nutrients in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 33 degrees of freedom. LSD (for interaction terms) for B=0.069 and Mn=0.38; LSD for ash as a single factor for Ca=128.9, and S=136.2. Please take note of scale differences on Y axes.*

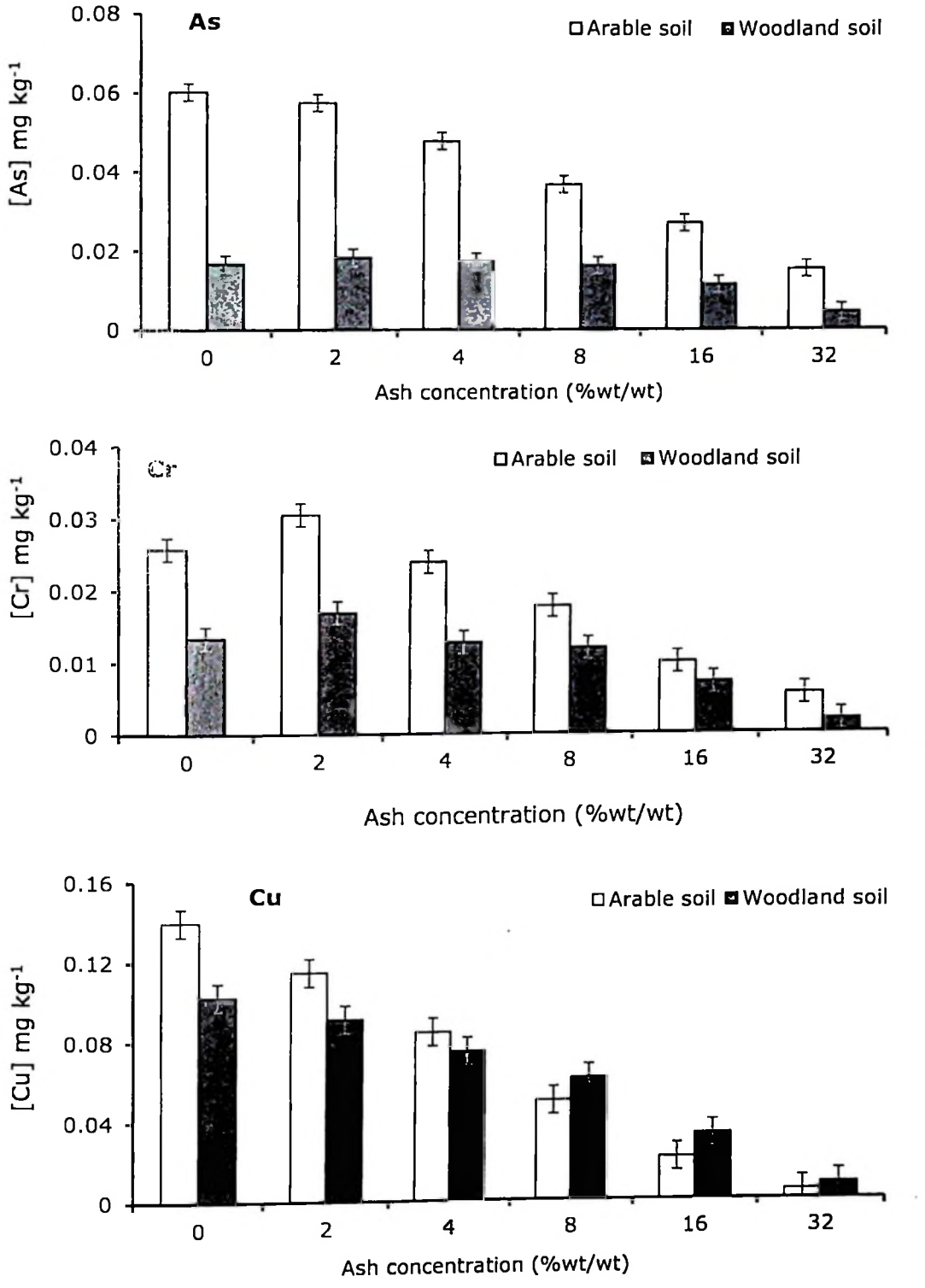

Figure 6-16: *Effect of coal ash application on water extractable concentration of the potentially toxic elements in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 33 degrees of freedom. LSD for As= 0.006, Cr= 0.005, Cu= 0.020. Please take note of scale differences on Y axes. See Table 6-12 for corresponding ANOVA output.*

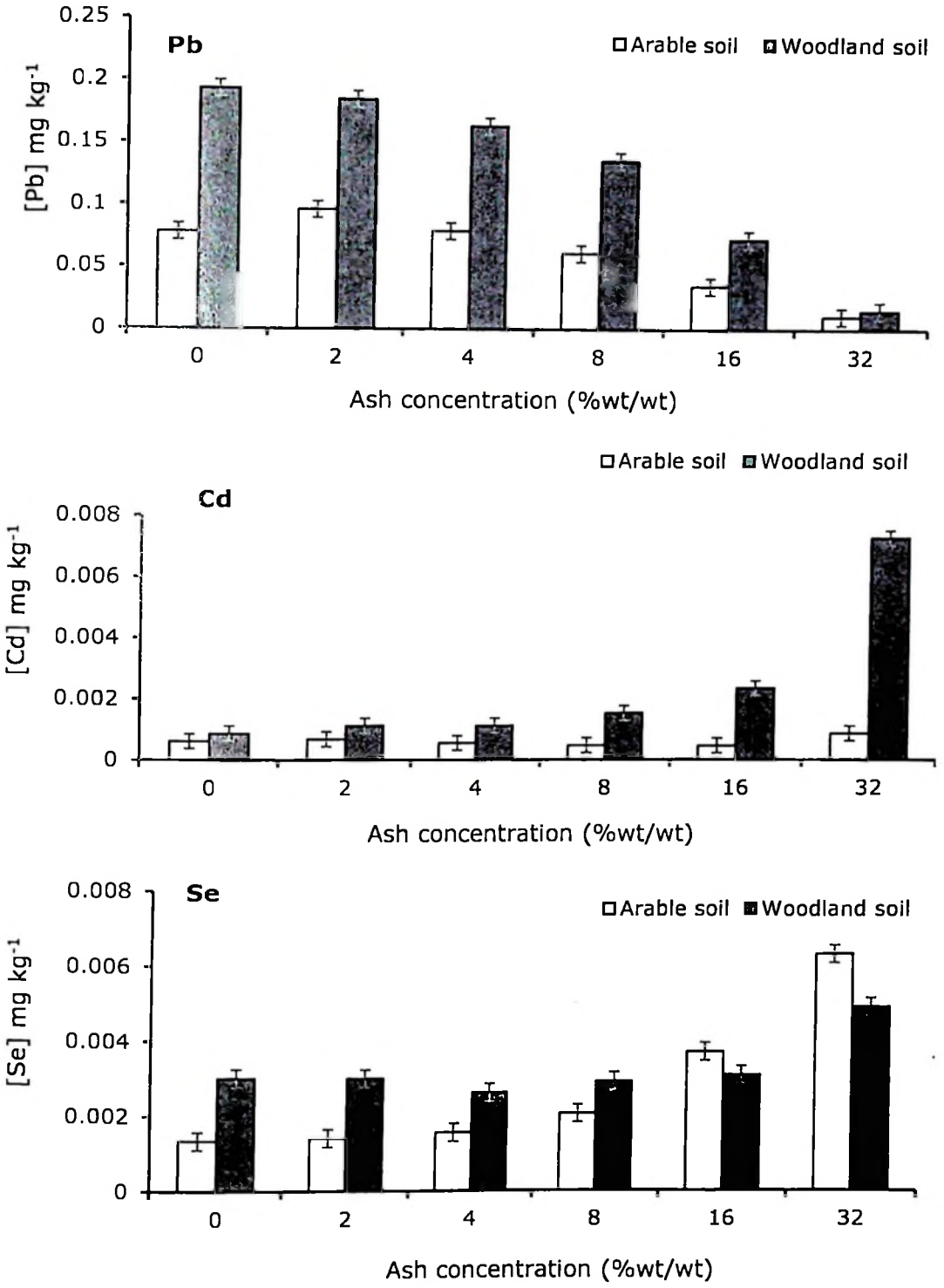

Figure 6-17: *Effect of coal ash application on water extractable concentration of the potentially toxic elements in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 33 degrees of freedom. LSD for Pb= 0.019, Cd= 0.0007, Se=0.0007.*

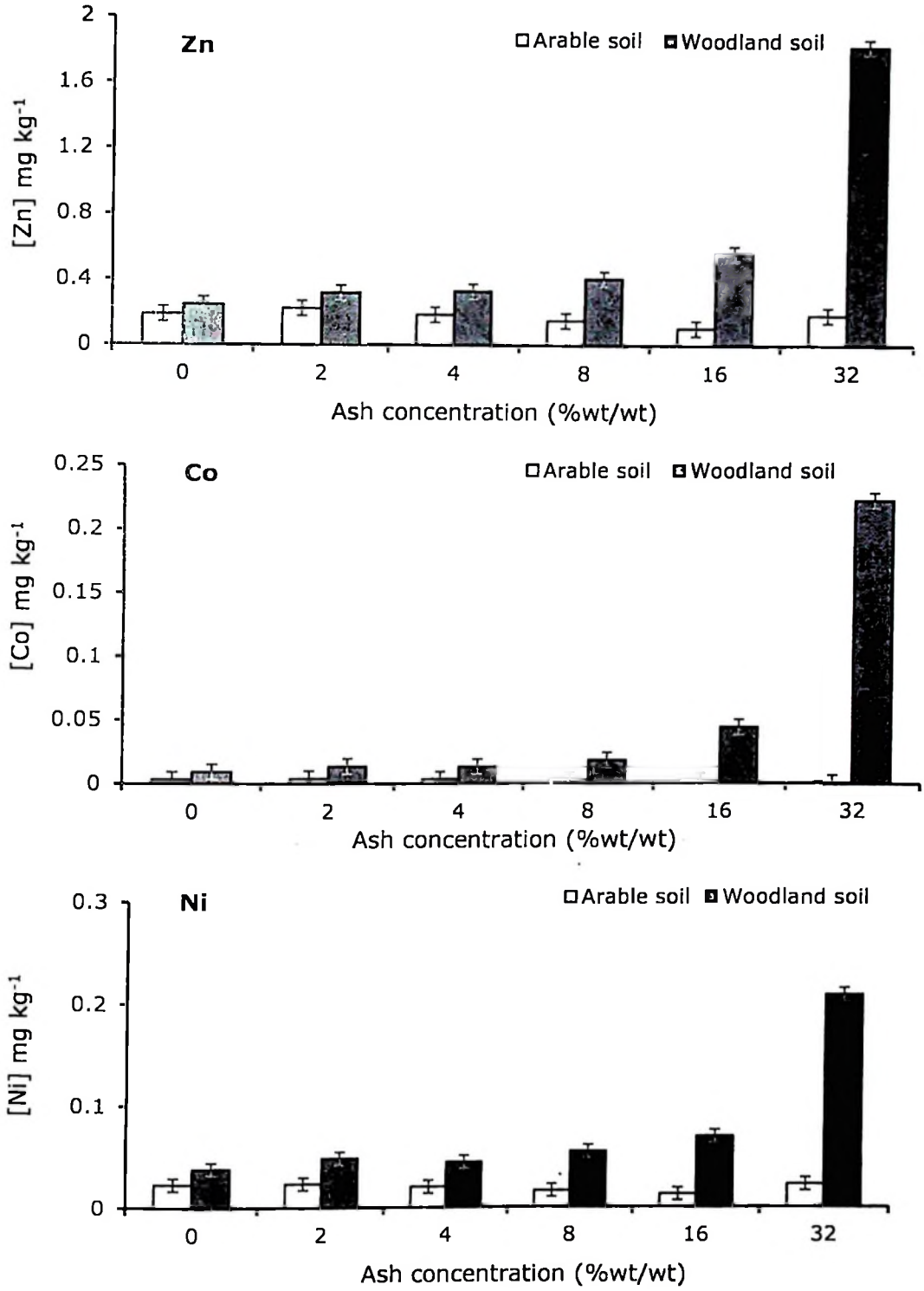

Figure 6-18: *Effect of coal ash application on water extractable concentration of the potentially toxic elements in woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 33 degrees of freedom. LSD for Zn=0.13, Co= 0.017 and Ni= 0.018.*

Table 6-12: *Summary of two-factor ANOVA from post-harvest water extractable nutrient and PTEs content of soils amended with the Tanzania 1 ash*

NUTRIENTS						PTEs					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**	**VARIATE**	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
K	Ash (%)	5	5.35	0.001	9.18	**As**	Ash (%)	5	54.4	<0.001	0.004
	Soil type	1	836.84	<0.001	5.3		Soil type	1	464.42	<0.001	0.003
	Interaction	5	2.69	0.038	12.99		Interaction	5	18.51	<0.001	0.006
	Residual	33					Residual	33			
P	Ash (%)	5	48.08	<0.001	0.794	**Co**	Ash (%)	5	96.25	<0.001	0.012
	Soil type	1	966.59	<0.001	0.458		Soil type	1	216.33	<0.001	0.007
	Interaction	5	43.02	<0.001	1.122		Interaction	5	100.3	<0.001	0.017
	Residual	33					Residual	33			
Ca	Ash (%)	5	10.23	<0.001	128.9	**Cr**	Ash (%)	5	44.54	<0.001	0.003
	Soil type	1	0.33	0.57	74.4		Soil type	1	81.66	<0.001	0.002
	Interaction	5	11	1.17	182.2		Interaction	5	4.44	0.003	0.005
	Residual	33					Residual	33			
Mg	Ash (%)	5	43	<0.001	13.35	**Cu**	Ash (%)	5	82.55	<0.001	0.014
	Soil type	1	5.04	0.032	7.71		Soil type	1	3.46	0.072	0.008
	Interaction	5	2.72	0.037	18.88		Interaction	5	4.16	0.005	0.020
	Residual	33					Residual	33			
B	Ash (%)	5	100.79	<0.001	0.048	**Cd**	Ash (%)	5	56.24	<0.001	0.0005
	Soil type	1	63.76	<0.001	0.028		Soil type	1	160.36	<0.001	0.0003

	Interaction	5	3.9	0.007	0.069
	Residual	33			
Mn	Ash (%)	5	74.29	<0.001	0.27
	Soil type	1	402.82	<0.001	0.1559
	Interaction	5	86.67	<0.001	0.3819
	Residual	33			
S	Ash (%)	5	16.12	<0.001	136.2
	Soil type	1	0	0.987	78.6
	Interaction	5	1.17	0.343	192.6
	Residual	33			
	Interaction	5	47.08	<0.001	0.0007
	Residual	33			
Ni	Ash (%)	5	54.58	<0.001	0.013
	Soil type	1	248.28	<0.001	0.007
	Interaction	5	52.05	<0.001	0.018
	Residual	33			
Pb	Ash (%)	5	113.85	<0.001	0.014
	Soil type	1	304.67	<0.001	0.008
	Interaction	5	17.5	<0.001	0.019
	Residual	33			
Zn	Ash (%)	5	87.61	<0.001	0.0934
	Soil type	1	280.41	<0.001	0.0539
	Interaction	5	87.83	<0.001	0.1321
	Residual	33			

6.4.7 PTE content in wheat roots, shoots and grains

Results from two-way ANOVA showed no interaction effect between ash concentration and soil type on PTE accumulation in roots, but ash concentration as a single factor significantly increased Cr, Ni, Co, Cd and Se concentrations with different ash treatments affecting root uptake of some PTEs more than others. For instance, Ni and Cr uptake was significantly increased by 2% ash, whilst Cd by 32% (Figure 6-19, Table 6-13). Pb was largely unaffected, although root concentrations were lower in plants grown with the 32% ash amendment (Figure 6-19).

In shoots, ash as a single factor significantly decreased the concentration of Cr and Ni following soil amendment with 16% and 32% ash. Ash led to an increase in Cr from 7.7 mg kg^{-1} in roots grown in control soil to 20.2 mg kg^{-1} in roots grown with 16% ash ($p=0.008$, data not shown). Ni content increased from 5.7 mg kg^{-1} in control roots to 15.4 mg kg^{-1} in those subjected to 16% ash-amended soil ($p<0.001$, data not shown).

Interaction effects between ash concentration and soil type were observed for Se, Pb, Cu, Co, Cd and As content in shoots (Figures 6-20 and 6-21). Shoot uptake of Se, Co and Cd was significantly enhanced when ash concentation in woodland soil increased (from 8% upwards). This effect was also observed for Se in shoots of arable soil-grown plants, but only the 32% ash treatment increased shoot Cd. Shoot Co was largely unaffected by ash amendment of arable soil (Figure 6-20; Table 6-14 for ANOVA output)

In woodland soil, a significant decrease in Cu concentration in shoots occurred following ash applications of 2-32%; but only 16-32% ash reduced shoot Cu in plants grown in arable soil (Figure 6-21; $p<0.001$, ash concentration x soil type interaction). Shoot Pb concentration decreased significantly following ash application from 4-32% to woodland soil, but was unaffected when plants were grown in arable soil (Figure 6-21; $p<0.001$; Table 14). In contrast, shoot As concentration did not respond to ash in woodland soil, but decreased with increasing ash concentration (from 4-32%) when applied to arable soil (Figure 6-21; $p<0.001$, ash concentration x soil type interaction).

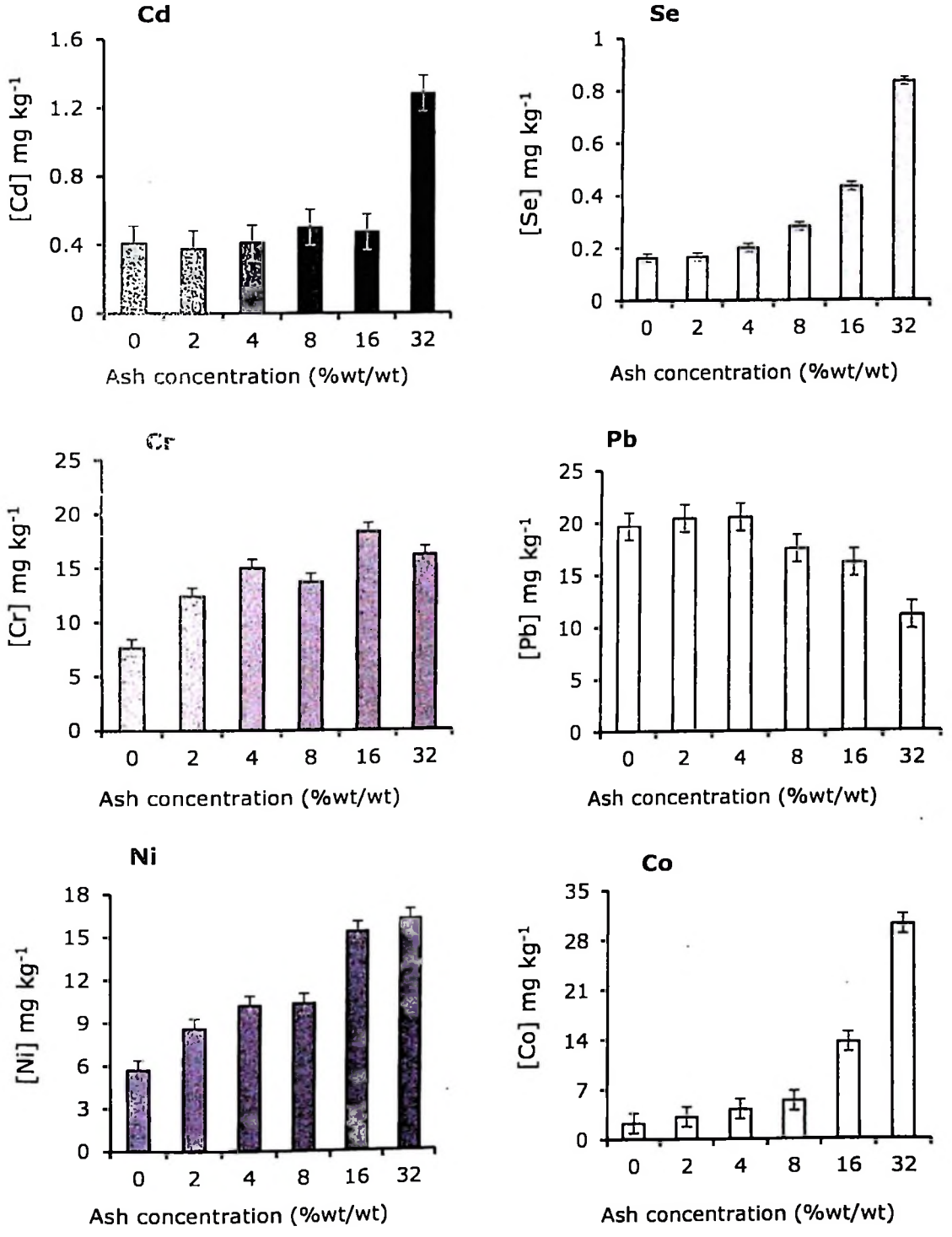

Figure 6-19: *Total concentration of PTEs in wheat roots grown in soil amended with ash. Data are means pooled across woodland and arable soils. Individual error bars are based on the pooled variance estimate from the ANOVA with 33 degrees of freedom. LSD (for ash as a single factor) for Cd=0.301, Se=0.046, Cr=2.30, Pb=3.77, Co=4.03 and Ni=1.98.*

Table 6-13: *Summary of two-factor ANOVA for PTEs in roots of wheat after harvesting plants from both woodland and arable soils ammended with the Tanzania 1 ash.*

PTEs					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
Cd	Ash (%)	5	11.15	<0.001	0.301
	Soil type	1	0	0.963	0.174
	Interaction	5	0.02	1	0.426
	Residual	33			
Co	Ash (%)	5	58.98	<0.001	4.033
	Soil type	1	0.01	0.909	2.328
	Interaction	5	0.04	0.999	5.703
	Residual	33			
Cr	Ash (%)	5	21.37	<0.001	2.298
	Soil type	1	1.83	0.187	1.327
	Interaction	5	1.32	0.284	3.250
	Residual	30			
Ni	Ash (%)	5	34.22	<0.001	1.981
	Soil type	1	0	0.969	1.144
	Interaction	5	1.19	0.337	2.802
	Residual	31			
Pb	Ash (%)	5	7.62	<0.001	3.770
	Soil type	1	0.63	0.432	2.177
	Interaction	5	0.54	0.743	5.332
	Residual	33			
Se	Ash (%)	5	267.08	<0.001	0.046
	Soil type	1	0.02	0.898	0.026
	Interaction	5	2.87	0.029	0.065
	Residual	33			

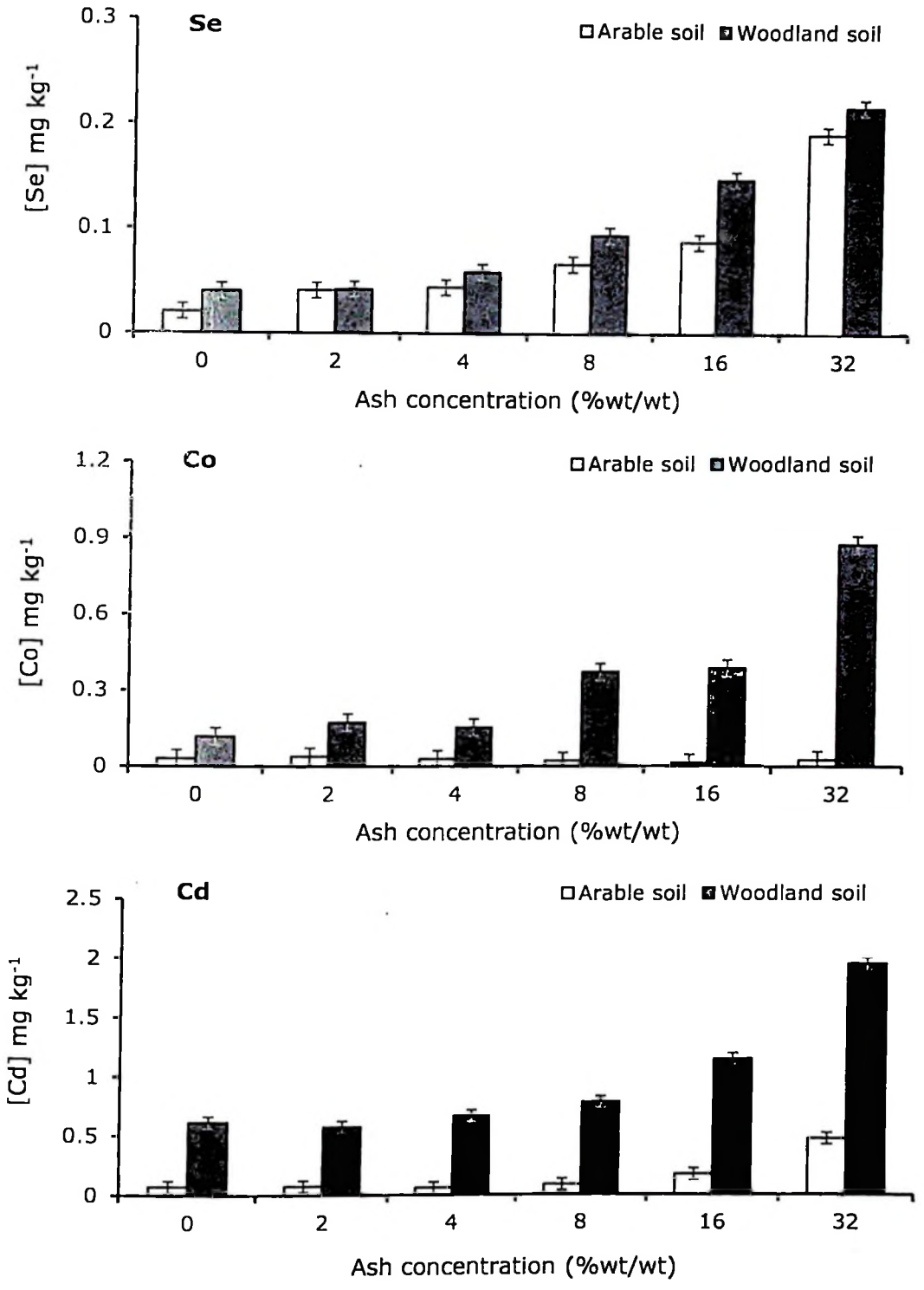

Figure 6-20: *Total concentration of PTEs in wheat shoots grown in woodland and arable soil amended with ash. Individual error bars are based on the pooled variance estimate from the ANOVA with 33 degrees of freedom. LSD (for interaction term) for Se=0.022, Co=0.097 and Cd=0.14.*

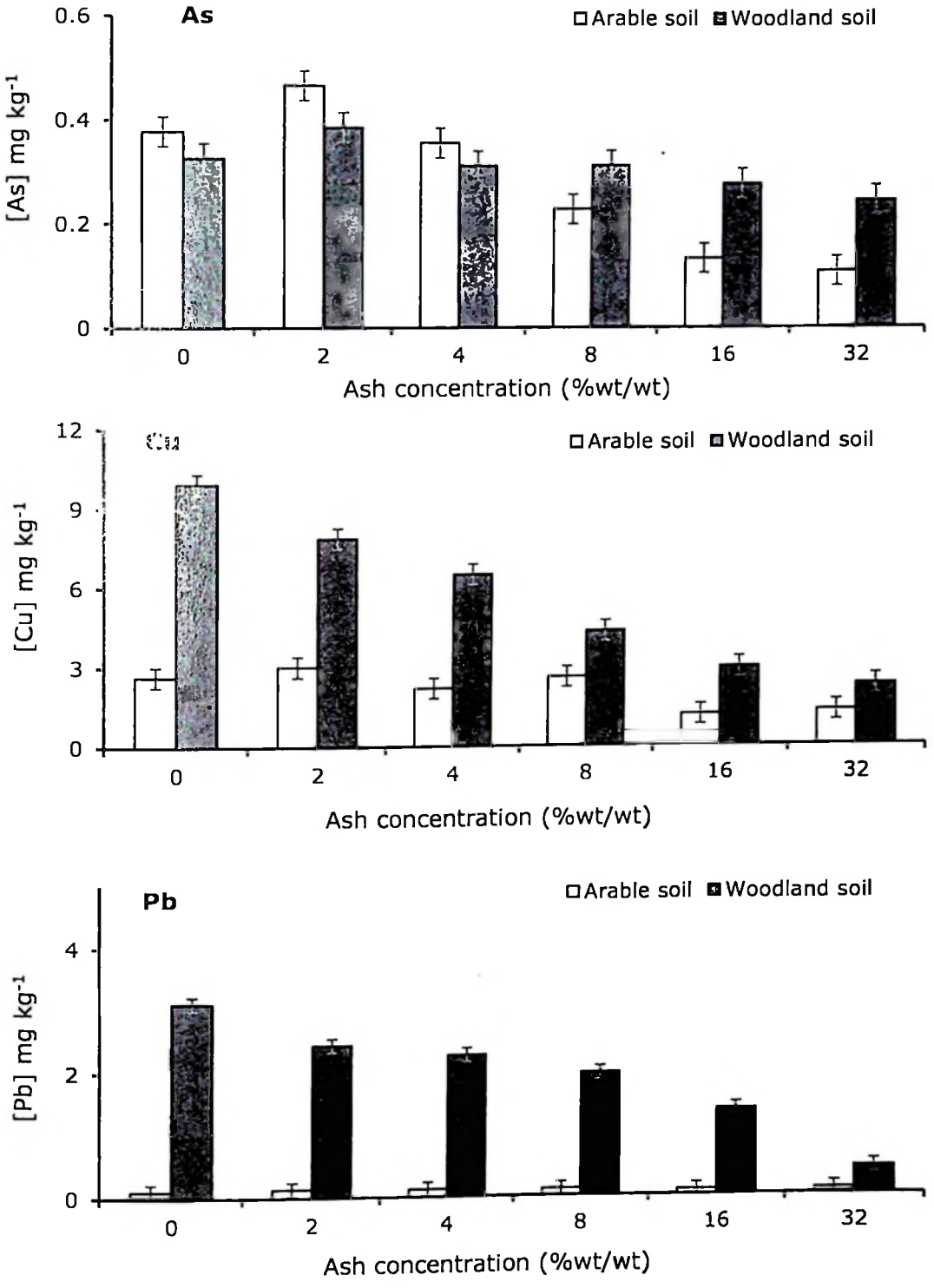

Figure 6-21: *Total concentration of PTEs in wheat shoots grown in woodland and arable soil amended with ash. Individual error bars are based on the pooled variance estimate from the ANOVA with 33 degrees of freedom. LSD (for interaction term) for As=0.082, Cu=1.12 and Pb=0.32.*

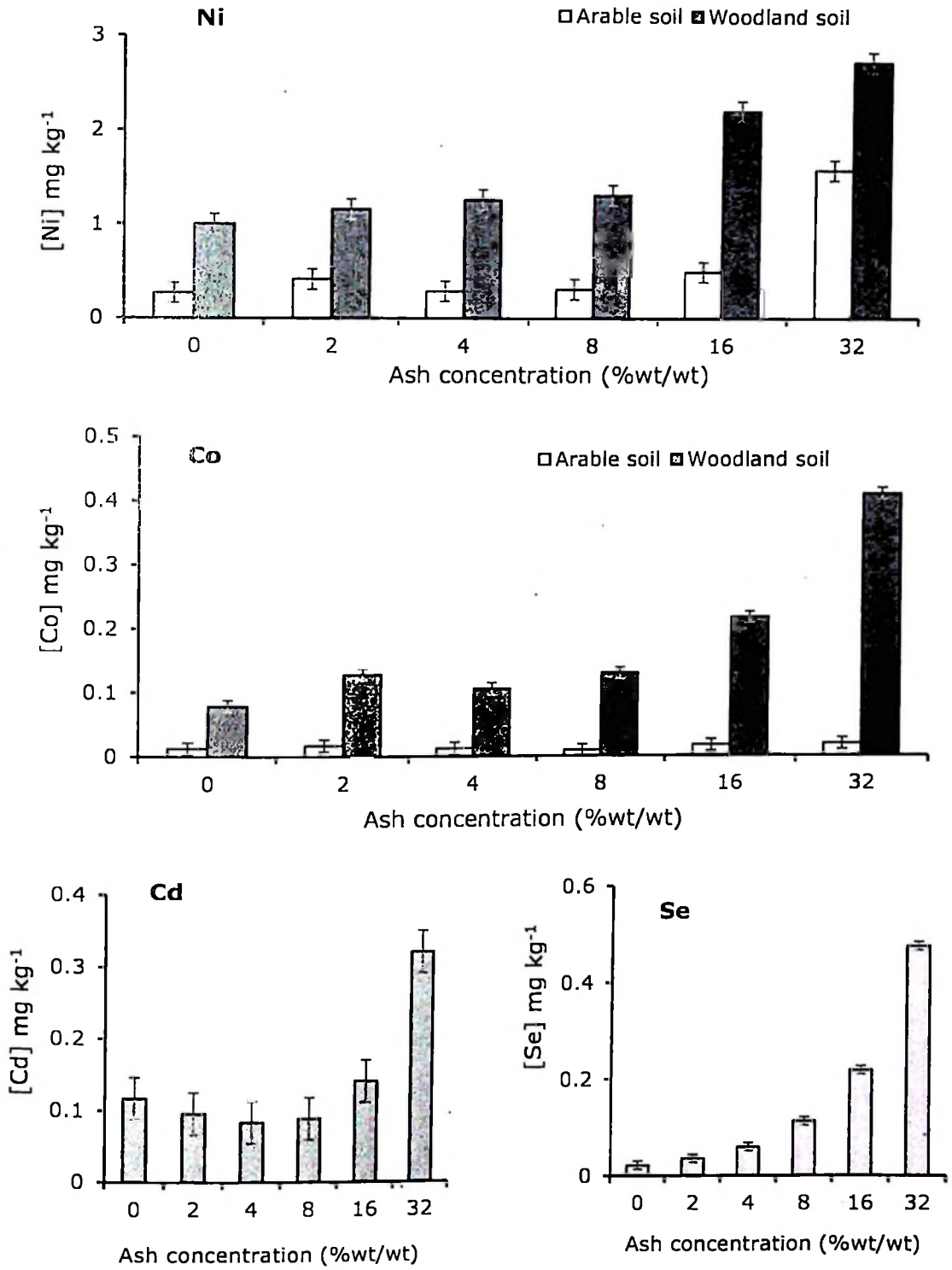

Figure 6-22: *Total concentration of PTEs in grains of wheat grown in woodland and arable soil amended with ash. Individual error bars are based on the pooled variance estimate from the ANOVA with 29 degrees of freedom. LSD (for interaction term) for Ni=0.31, C0=0.027, Cd=0.085 and Se=0.025.*

In grains, a significant interaction between ash concentration and soil type was noted for the accumulation of Ni and Co; where in woodland soil, Ni increased significantly when the soil was amended by 16-32% while in arable soil, Ni concentration in grain was only significant at 32% ash concentration (Figure 6-22; $p<0.001$, ash concentration × soil type interaction; Table 6-14). The concentration of Ni in grains from wheat grown in the woodland soil was consistently higher, irrespective of ash amendment. Grain Co content followed the same trend as grain Ni concentration when plants were grown in the woodland soil, but was unaffected by ash treatment of the arable soil (Figure 6-22; $p<0.001$). Pb concentration was higher in grains from woodland soil-grown plants (0.10 mg kg^{-1}) compared to those grown in arable soil (0.007 mg kg^{-1}) in the absence of ash, but with the 32% ash amendment this was modified to 0.67 and 0.02 mg kg^{-1} for arable and woodland soil-grown grain respectively ($p<0.001$, ash concentration × soil type interaction, data not shown).

Ash as a single factor also increased significantly the concentration of Se and Cd in grains following soil amendment with 8-32% and 32% ash concentration respectively (Figure 6-22; $p<0.001$ for both elements, ash as a single factor).

Irrespective of ash amendment, Cd, Cr, Cu, Fe, Mn, S and Zn were all present in significantly higher concentrations in the grains of woodland-grown plants (data not shown).

With regard to grain macro-nutrients, Ca content was increased ($p<0.001$) by the 32% ash amendment to arable soil (0% ash, 406.5 mg kg^{-1}; 32% ash, 524.3 mg kg^{-1}) whilst it remained similar in grain from woodland-grown plants (0%, 423.8 mg kg^{-1}; 32% ash, 430.0 mg kg^{-1}). K, Mg and P concentrations remained consistent irrespective of ash or soil treatment.

Table 6-14: *Summary of two-factor ANOVA for PTEs in shoots and grains of wheat after harvesting plants from both woodland and arable soils ammended with the Tanzania 1 ash*

PTEs IN SHOOTS					
VARIATE	**FACTOR**	**DF**	**F**	**P VALUE**	**LSD (95%)**
As	Ash (%)	5	21.87	<0.001	0.058
	Soil type	1	3.76	0.061	0.033
	Interaction	5	6.41	<0.001	0.082
	Residual	33			
Cd	Ash (%)	5	98.64	<0.001	0.099
	Soil type	1	802.94	<0.001	0.057
	Interaction	5	28.85	<0.001	0.141
	Residual	33			
Co	Ash (%)	5	34.88	<0.001	0.068
	Soil type	1	273.73	<0.001	0.039
	Interaction	5	36.44	<0.001	0.097
	Residual	33			
Cu	Ash (%)	5	42.77	<0.001	0.789
	Soil type	1	243.28	<0.001	0.456
	Interaction	5	19.32	<0.001	1.116
	Residual	33			
Pb	Ash (%)	5	37.44	<0.001	0.223
	Soil type	1	835.88	<0.001	0.129
	Interaction	5	34.99	<0.001	0.315
	Residual	33			
Se	Ash (%)	5	155.21	<0.001	0.015
	Soil type	1	33.73	<0.001	0.009
	Interaction	5	3.5	0.012	0.022
	Residual	33			
PTEs IN GRAINS					
Cd	Ash (%)	5	9.51	<0.001	0.085
	Soil type	1	49.93	<0.001	0.049
	Interaction	5	1.87	0.13	0.120
	Residual	29			
Co	Ash (%)	5	93.32	<0.001	0.009
	Soil type	1	948.47	<0.001	0.005
	Interaction	5	85.66	<0.001	0.013
	Residual	29			
Ni	Ash (%)	5	57.88	<0.001	0.222
	Soil type	1	284.59	<0.001	0.128
	Interaction	5	5.69	<0.001	0.313
	Residual	29			
Se	Ash (%)	5	416.04	<0.001	0.025
	Soil type	1	2.04	0.164	0.014
	Interaction	5	2.25	0.076	0.035
	Residual	29			

6.4.8 Transfer ratios of PTEs from the soil to the plant parts

For ease of comparison with the transfer ratios (TRs) obtained when plants were grown with UK ash (Section 6.3.9), data are presented separately for the arable and woodland soils. In addition to the one-way ANOVAs carried out on TRs for soil-to-root, root-to-shoot and shoot-to-grain (Table 6-15), data were analysed by two-way ANOVA and any interactions or effects of soil as a single factor which are relevant to shoot-to-grain transfer are described in the text.

Transfer ratios of potentially toxic elements from soil-to-root were <1 for As, Pb and Se. Whilst there were some significant effects of ash amendment, these were trivial in real terms, since the grand means for TRs were 0.15 for As, 0.23 for Pb and 0.42 for Se. Amendment of soil with 4% ash raised the Ni transfer ratio to >1 (Table 6-15). All ash amendments increased the Co transfer ratio from 0.80 (control) to >1, with the highest ash amendment raising the TR more than five fold, to 4.41 (Table 6-15). The 32% ash treatment increased the Cd and Zn transfer ratios to 4.42 and 3.00 respectively; although the TRs for both elements were >1 in the control (2.07 for Cd and 1.90 for Zn).

The transfer ratios from roots-to-shoots (stem and leaves) were generally all <1 with the exception of Mo and Cd which had a TR of 1.46 and 1.53 respectively in control plants. Ash amendment reduced the TR of Mo to an average of 0.53 across all ash treatments ($p<0.001$), whilst the TR for Cd remained consistant across all treatments (grand mean of 1.86). Where trends were significant, this resulted in a lower TR with higher ash addition (Table 6-15).

When plants were grown in woodland soil, shoot-to-grain transfer ratios were all <1 irrespective of ash treatment, with the exception of Cu, Ni and Se which significantly accumulated in the grain when ash was present in the soil (Table 6-15).

Table 6-15: *Transfer ratios of PTEs from soil-to-plant parts for wheat plants grown in soils amended with Tanzania ash*

PTEs	Fly ash concentration (% dry weight)							
	0	2	4	8	16	32	F ratio	P value
Woodland soil								
Soil to Root								
Co	0.80^{a}	1.02^{a}	1.21^{ab}	1.44^{ab}	2.72^{b}	4.41^{c}	$F_{5,18}$=15.95	<0.001
Ni	0.61^{a}	0.97^{ab}	1.30^{b}	1.11^{ab}	1.42^{b}	1.23^{ab}	$F_{5,18}$=4.36	0.009
Se	0.34^{a}	0.34^{a}	0.32^{a}	0.42^{ab}	0.47^{b}	0.64^{c}	$F_{5,18}$=21.44	<0.001
Root to shoot								
As	0.42^{b}	0.36^{b}	0.31^{ab}	0.28^{ab}	0.17^{a}	0.17^{a}	$F_{5,18}$=7.72	<0.001
Cu	0.98^{d}	0.63^{cd}	0.56^{bc}	0.21^{ab}	0.19^{ab}	0.12^{a}	$F_{5,18}$=16.51	<0.001
Ni	0.24^{b}	0.12^{ab}	0.076^{a}	0.09^{a}	0.027^{a}	0.03^{a}	$F_{5,18}$=7.19	<0.001
Pb	0.17^{d}	0.13^{cd}	0.12^{bc}	0.12^{bc}	0.08^{ab}	0.04^{a}	$F_{5,18}$=19.20	<0.001
Shoot to grain								
Cu	0.64^{a}	0.71^{a}	0.92^{a}	1.14^{a}	1.98^{b}	2.24^{b}	$F_{5,18}$=22.23	<0.001
Ni	0.97^{a}	1.22^{a}	1.58^{a}	1.92^{a}	5.43^{b}	5.41^{b}	$F_{5,18}$=16.31	<0.001
Se	0.62^{a}	1.00^{ab}	1.09^{bc}	1.07^{bc}	1.45^{c}	2.05^{d}	$F_{5,18}$=24.66	<0.001
Arable soil								
Soil to root								
Cd	1.11^{a}	1.12^{a}	1.24^{a}	1.44^{ab}	1.23^{a}	2.95^{b}	$F_{5,18}$=4.22	0.010
Co	0.81^{a}	0.88^{a}	1.12^{a}	1.22^{ab}	2.45^{b}	3.81^{c}	$F_{5,18}$=16.46	<0.001
Root to shoot								
As	0.35^{bc}	0.35^{c}	0.34^{abc}	0.19^{abc}	0.09^{ab}	0.08^{a}	$F_{5,18}$=5.02	0.005
Co	0.01^{b}	0.01^{b}	0.01^{ab}	0.003^{a}	0.001^{a}	0.001^{a}	$F_{5,18}$=11.37	<0.001
Cu	0.23^{b}	0.25^{b}	0.20^{ab}	0.13^{ab}	0.08^{a}	0.07^{a}	$F_{5,18}$=6.92	<0.001
Shoot to grain								
Pb	0.09^{a}	0.11^{a}	0.14^{a}	0.12^{a}	0.19^{ab}	0.78^{b}	$F_{5,14}$=4.14	0.016
Se	0.73^{a}	0.88^{a}	1.24^{ab}	1.88^{bc}	2.45^{cd}	2.59^{d}	$F_{5,14}$=29.43	<0.001

Transfer ratios from soil-to-root for As, Cu and Pb when plants were grown in the arable soil were unaffected by ash amendment and were all <1. Mo, Ni and Zn accumulated within the root irrespective of ash treatment (average TRs, 2.30, 1.18 and 3.40 respectively) and Cr accumulated in the root of plants grown with ash concentrations including and greater than 4% (0% ash, TR 0.79; average TR of 4%-32% ash treatments, 5.6; p=0.020, data not shown).

Cd and Co both significantly accumulated in the root tissue when grown in the presence of increasing ash concentrations (Table 6-15).

Apart from Mo (overall average TR, 2.10), none of the elements classed as PTEs accumulated within the shoots, although ash amendment significantly reduced the TR for As, Co and Cu (Table 6-15).

Grains did not accumulate As, Cd, Co, Cr, Mo or Pb since all TRs were <1; however, ash amendment of the arable soil significantly increased the TR value of Pb (Table 6-15). Se accumulation in grain was enhanced to >1 by 8% ash addition, with 32% ash raising the TR to 2.59 ($p<0.001$; Table 6-15). Ni and Cu were accumulated by grains when plants were grown with 32% ash relative to those grown in the control soil (Ni: 0% ash, TR 1.15; 32% ash, TR 9.68, $p<0.001$. Cu: 0% ash, TR 1.80; 32% ash, TR 3.09, $p=0.003$).

Shoot-to-grain transfer ratios followed the same trend in both arable and woodland soils when ash affected accumulation; therefore within two-way ANOVA, ash and soil were often significant as single factors. Although shoot-to-grain transfer ratios for Cd and Pb were significantly greater in wheat grown in arable compared to woodland soil, the pooled values (across all ash treatments) were <1. The pooled averages for Cu and Se were >1 ($p<0.001$ in both cases. Cu: arable, TR 2.41; woodland, 1.27. Se: arable, TR 1.63; woodland, 1.22). The greatest difference between the two soils was with Zn ($p<0.001$); here, the shoot-to-grain TR was 0.68 for woodland soil grown plants and 2.08 for those grown in arable soil. In contrast, Cr accumulation in grains associated with woodland soil was higher (TR 1.79) than in those grown in arable soil (0.78) ($p=0.017$, soil type as a single factor). Neither As nor Co shoot-to-grain TRs were affected by soil type.

6.5 DISCUSSION

6.5.1 Soil and ash characteristics

The UK1 fly ash was used in the 1st wheat experiment; this ash was alkaline (pH 12.3), with lower total %N, higher %C and enriched with higher concentrations of nutrients (except K) compared to the experimental soils. The Tanzania1 ash was used in the 2nd wheat experiment; this ash was acidic (pH 4.2) with lower total %N, higher %C and lower in nutrient concentrations (except S) compared to the experimental soils. Both ashes were enriched with higher PTE concentrations than the experimental soils except for As and Pb concentrations which were lower in the Tanzania ash than in the soils. Although fly ash is usually alkaline (pH 10-12) due to the presence of Ca and Mg hydroxides and carbonates, ash may also be acidic (pH 3-4) as reported by Matsi and Keramidas (1998). The alkalinity and acidity of ash may also be linked to the amount of Ca and S present (Adriano et al., 2002; Izquierdo and Querol 2012). Being the by-product of coal combustion, the low %N found in both ashes used within this study, could be related to the oxidation of N during the combustion process (Shaheen et al., 2014). The woodland and arable soils used in these experiments were acidic and slightly acidic (pH 3.8 and 6.8 respectively). Woodland soil had higher total %N and %C than arable soil, but the concentration of key nutrients was higher in arable soil than in woodland soil. Due to the presence of higher nutrient concentrations and the alkalinity of the UK1 ash, application of this ash may enhance the pH and fertility of both soils, whilst application of the acidic ash (Tanzania1) may lower the soil pH, although it may also enhance the S content of both soils. However, due to the presence of higher concentrations of potentially toxic elements in both ashes than in the experimental soils, application of these ashes may result in accumulation of PTEs in soils. Therefore, the main aim of these experiments was to determine the costs and benefits of adding each ash type to both soils in order to establish their potential as a soil improved/fertiliser.

6.5.2 Effect of ash application on soil pH

In this study, the significant increase in pH of woodland and arable soils noted in the first wheat experiment and the significant decrease of soil pH noted in the second experiment following ash applications, which could be ascribed to

the alkalinity (pH 12.32) and acidity (pH 4.2) of the applied ash. These findings corroborate those of others, e.g. Kalra et al. (2000) and Shaheen et al. (2014).

In the first experiment where the UK ash was used, the higher pH of arable than woodland soil across the fly ash concentrations (0-32%) may further be attributed to differences in starting pH of each soil prior to ash addition (pH 6.4 and 3.8 for arable and woodland soils respectively). However, the loss of the pH difference between the two soils with the highest ash amendments could be linked to the buffering capacity of the soils (Matsi et al., 1998). At the highest fly ash concentration (32%), woodland soil pH increased by 4.25 units relative to initial soil pH, compared to an increase of 1.94 units in arable soil, thus implying a higher pH buffering capacity in the arable than in the woodland soil. However, addition of alkaline ash, increased the pH of both soils.

In contrast, in the second experiment, pH significantly decreased with increasing ash concentration; this was most notable in the more alkaline arable soil. Whilst ash amendments slightly lowered the pH of the woodland soil, in this instance it appeared to be more resistant to ash amendment than the arable soil, most likely because of the similar pH of both ash and soil. The observed decrease may be explained by the high amount of the acidic fly ash applied. Similar findings have been reported where land application with an acidic fly ash rich in S decreased the soil pH (Pathan et al., 2003). However, the results from the second wheat experiment do not corroborate those of Manoharan et al. (2007) who reported that application of acidic ash increased the pH (of an acidic soil) by 0.2-0.3 pH units. This variation may be due to the quantity of the ash used since Manoharan et al. (2007) applied 0, 12, 36 and 108 Mg ha^{-1} while in the current study, soils were amended with 0-32% fly ash, which is approximately in the range of 0-800 Mg ha^{-1}, assuming a bulk density of 1250 kg m^{-3} and a depth of 20 cm. They attributed their observation to proton utilisation during dissolution of silicate minerals in the ash. The mineralogy of the ashes used here was not determined; however, according to Ward and French (2006), silicate mineral patterns vary depending on the quality of the coal from which the ash originated. Manoharan et al. (2007) did not state the origin of their coal and the contradictory findings between their study and this one could largely be due to different feedstock origin and ash mineralogy. Therefore, changes in soil pH induced by application of fly ash to

soils will depend on the pH of the applied ash, the amount of ash, pH of the soil and pH buffering capacity of soils (Yao et al., 2015) in addition to the mineralogy of the ash.

6.5.3 The effect of ash on nutrient availability, growth and yield of wheat

In both experiments, application of ash to soils significantly affected the growth and yield of wheat; however, the magnitude of response varied depending on the type of soil (woodland/arable), the type of ash (UK/Tanzania) and the concentration (0%, 2%, 4%, 8%, 16% and 32%) of the ash applied.

In first experiment where the UK fly ash was used, a significant interaction between soil type and fly ash concentration was noted for most growth and yield parameters (number of leaves, number of tillers, number of grains, grain weight, total shoot biomass and root biomass), implying the dependence of ash-response to the soil type and soil characteristics (Sikka and Kansal 1995).

Application of 2% and 4% fly ash to woodland soil increased the grain yield by 21 and 31 fold, grain weight by 17 and 26 fold and the shoot biomass by 9 and 15 fold respectively. Generally, better response of all growth and yield parameters in plants grown in the woodland soil with 0-4% ash may be linked to the improvement of soil pH and P extractability. Studies by Pathan et al. (2003) and Manoharan et al. (2007) also showed an increase in P extractability, P uptake by plants and better yields following fly ash application to soil. Moreover, better growth and yield in this investigation may also be ascribed to the significant increase in total nutrient concentrations (P, Mg, Ca, Mn and Fe) and the increased extractability of B, noted from soil analysis after harvesting. Similar results regarding the influence of coal fly ash application on wheat growth and grain yield parameters were reported by Garg et al. (2005), Tripathi et al. (2009) and Tsadilas et al. (2014).

However, lack of further significant increases in grain yield and shoot biomass following application of higher ash concentrations (8-32%) to woodland soil may be attributed to a significant decrease in Mn extractability and the corresponding Mn deficient symptoms noted in the plants amended with UK ash during experiment 1. Moreover, lack of further significance increases in grain and shoot biomass might be due to accumulation of PTEs (As, Ni, Zn, Cr, Cd,

Pb and Se) in the soil and plant parts which may impair biochemical and physiological activities of the plants, thus reducing the growth and yield (Singh et al., 2008).

Even though the total nutritional composition and pH of arable soil were both significantly higher than in woodland soil (before and after ash amendment), the growth and yield response of wheat following ash application was poor. Grain yield and shoot biomass appeared to increase following application of 2% UK fly ash, but these increases were not statistically significant. The decreasing pattern of most growth and yield parameters was noted in arable soil in comparison to woodland soil following UK ash application from 4-32%. This may be ascribed to the significant reduction of P and Mn extractability due to the alkalinity induced by fly ash application to the soil (Moliner and Street, 1982; el-Mogazi et al., 1988; Jala and Goyal, 2006). Since the total P concentration increased significantly in the arable soil following amendment with 8-32% ash, limited P availability may have been due to the presence of insoluble P forms in the fly ash, thus being unavailable to the plants (Gupta et al., 2012). Moreover, the decrease in these parameters may also be attributed to the increased total concentration of PTEs (As, Cu, Zi, Cr, Co, As, Pb and Se) and the increased extractability of Se, Ni and As following soil amendment with fly ash.

When ash-free (control soils), the growth response was higher in arable than in woodland soil, possibly because of the greater nutrient concentrations present (P, K, Mg, Ca, Mn and Fe). Furthermore, the arable field is regularly fertilised with ammonium nitrate as well as other nutrients as required and the pH was also more suited to wheat growth than the pH of the woodland soil. The pH of the arable soil (6.8) was slightly acidic/near neutral, thereby enabling availability of most key nutrients (Jensen, 2010), while the acidic woodland soil was not conducive to nutrient availability. Even though the total %N was higher in the woodland than in the arable soil, plant availability would likely be limited by the lower pH (3.8) of this soil. Much of the N in the woodland soil may have been in the form of organic matter or microbial biomass; the higher extractable C/N ratio of the woodland soil compared to that of the arable soil is indicative of potentially limited N availability.

In the second experiment, application of the Tanzania ash induced a positive response in wheat grown in woodland soil and a negative response in wheat grown in arable soil.

In the woodland soil, application of 2% Tanzania ash increased almost all the growth parameters except for grain yield. A similar finding was reported by Manoharan et al. (2007) where application of acidic ash to acidic soil increased the dry matter yield and this was associated with improved P extractability. In this current study, ash application to woodland soil did not influence P extractability, therefore, the improvement in growth may be linked to the increased extractability of Ca, S, Mg, Mn and B.

However, lack of significant increase in grain yield might be due to low nutritional status and pH of the woodland soil and low pH of the applied ash. The optimum pH for wheat growth is 6.5 (Technical Bulletin Series No. 2, 2016, The Fertiliser Association of Ireland/Teagasc), mainly because of limited nutrient availability and root damage due to Al toxicity at acidic pH values. Moreover, lack of further significant increase in leaf number, tiller number, root and shoot biomass in the soil amended with 4-32% ash might be due to the low concentration and availability of P and K which are the primary nutrients for plant growth. Even though there were no observable nutrient deficiencies or phytotoxic symptoms throughout the growing period, the growth rate of the plants was reduced relative to those in the first experiment, resulting in a longer growing period (4 months in experiment 1 versus 6 months in experiment 2). The reduced growth rate of plants in this experiment relative to experiment 1 may be linked to differences in growth room conditions where the plants were grown for each trial. Moreover, the reduced growth and yields at higher ash concentrations here may be attributed to accumulation of PTEs (Ni, Cd, Co, Cu, Se, and Zn) in soil which tends to impair the biochemical and physiological activities of plants thus reducing the plant growth and yield (Singh et al., 2008) as hypothesised earlier for the similar effect observed in experiment 1.

Retarded growth and poor yield of wheat grown in arable soil following amendment with Tanzania ash can be linked to a significant decrease in total and extractable P and also in total Mg and Mn. Moreover, reduction of growth and yield of wheat could be linked to poor root growth (reflected by the

decreased root biomass) which may result from soil compaction in fly ash amended soil (Singh et al., 2008), Al toxicity due to high Al content in fly ash (Gunse et al., 2000) and the toxicity of the PTEs in fly ash amended soil (Tripathi et al., 2004). In this project, the total Al concentration did not increase significantly following soil amendment with ash and the water extractable Al decreased significantly ($p=0.001$) with increasing fly ash concentrations. For example, in the woodland soil, with 0% and 32% ash amendments, water extractable Al concentrations were 11.5 and 3.5 mg kg^{-1} respectively and a simiar trend was observed with the arable soil. Therefore, Al toxicity is unlikely to be significant here.

There were no significant differences in growth and yield of the plants grown in unamended woodland and arable soils (controls). These results are different from those of experiment 1, thus implying that variations in growth room conditions influenced growth.

Fly ash applications to agricultural soils of up to 40% have been suggested as beneficial for most crops, but higher concentrations may adversely affect crop yield (Khan and Khan 1996; Sigh and Siddique, 2003; Agrawal et al., 2004). Results from the current experiments would not countenance this recommendation since application of ash above 4% resulted in detrimental effects, particularly to wheat grown in the arable soil. Moreover, increased accumulation of most PTEs in both soils following ash amendment from 16% and the uptake of some PTEs by wheat plants implies a detrimental effect of high ash concentrations on soil and plant quality.

6.5.4 Accumulation and extractability of PTEs in soils amended with ash

From both experiments, application of ash to woodland and arable soils increased the total concentration of PTEs (Zn, C, Ni, Cd, Cr, Pb, As and Se), but the magnitude of increase varied depending on the soil type, the ash type and the ash concentration. Application of fly ash also increased the water extractability of these PTEs from both soils, but the magnitude of increase varied depending on the type of the ash added (UK or Tanzania ash).

In the first experiment where the UK ash was used, total Zn, Cu, Cr, Cd, Co and Ni concentrations increased significantly in both soils following soil amendment from 4-32%. Also, As, Se and Pb increased in both soils following amendment with 2-32% ash, but the rate of increase was higher in the arable soil than in woodland soil, particularly for Ni at the lower ash amendments. One possible reason for this is that Ni may have adsorbed onto organic matter in the woodland soil. At higher ash concentrations, pH would become a larger driver of Ni availability than the organic matter, thus at high ash concentrations, Ni in woodland soil would follow the same trend as that in the arable soil (Weng et al., 2004). Besides the increase in the total concentration of these PTEs following addition of the UK ash, only As, Se and Ni were extractable in water. Limited extractability of most PTEs in both soils from this experiment might be linked to the increased soil pH induced by the alkalinity of the applied ash (el-Mogazi et al., 1988). However, the increase in extractable As, Se and Ni beside the increase in soil alkalinity might be attributed to the increase in their total concentrations (Banin et al., 1987) following the soil amendment with fly ash.

In the second experiment where the Tanzania ash was applied, the total concentration of Zn, Cd, Cu, Ni, Co and Se increased following soil amendment with fly ash, but the extractability of these PTEs varied depending on the type of PTE. Fly ash application increased the water extractability of Zn, Cd, Ni, Co and Se, in both soils, meanwhile decreasing the availability of As, Cr, Cu, Se and Pb in woodland soil. Soil pH is the principal factor determining the solubility of metals in soil and availability to plants (Brallier et al., 1996) and since solubility increases at lower pH and decreases at higher pH (Rieuwerts et al., 1998), the enhanced PTE extractability observed in both soils may be linked to the significant ash-related decrease in soil pH. However, the decrease in PTE extractability in woodland soil which was rich in organic matter could be attributed to the further increase in organic carbon from the added ash and the tendency of organic matter to fix metals in the soil solid phase (Maskall et al., 1996). Moreover, the application of Tanzania ash did not increase the concentration of As, Cr, Cu and Pb in soils, thus the decreased extractability of these PTEs could also be linked to their low total concentration in the soil (Banin et al., 1987).

Besides the ash-related increase in PTE concentrations in both soils, in both experiments, all PTE concentrations were below the maximum permissible limit according to the EU, UK, USA and Tanzania standards, except As in UK fly ash amended soils (Table 6-16). Therefore, As may be a metalloid of concern for land application of an alkaline fly ash.

Table 6-16: *The maximum permissible limit of PTEs in soil (soil depth 0-30 cm) and the content of PTEs in the experimental soils (woodland and arable soil)*

Standards	**Potentially toxic elements concentration (mg kg^{-1})**						
	As	Cd	Cr	Cu	Zn	Ni	Pb
EU standard	*	3	180	140	300	75	300
UK standard	10	1.4	6.4	63	200	*	70
USA standard	14	3	400	80-200	200-300	*	300
Tanzania STD	1	1	100	200	150	100	200
Soils + UK ash	7.6-37.5	0.1-3.2	11-19	25-34	56-218	8.0-18.3	33-136
Soils + TZ ash	7.6-7.2	0.3-3.6	10.6-11	12-19	43.1-52	7.6-13.8	74-61

Sources: Haliru et al., (2014) and Simon et al., (2016). The concentration range of PTEs in the experimental soils corresponds to the 0-32% ash concentrations applied.

6.5.5 Uptake of PTEs by wheat plants grown in ash amended soils

In the first experiment, UK fly ash application to both soils resulted in plant contamination with PTEs. Most PTEs accumulated in the roots, particularly in those grown in woodland soil amended by 8-32%. Since the extractability of most PTEs in this soil decreased after fly ash application, accumulation of most PTEs in roots may be attributed to the better root development as reflected by the increased root biomass.

Se, As and Cr also accumulated in all shoots (for plants grown in both soils) and in grains for the wheat grown in woodland soil; but only Se accumulated in grains from plants grown in arable soil. This might be due to the increased extractability of these PTEs noted in both soils following the fly ash application. However, fly ash application reduced the concentration of some PTEs in grains, such as Zn, Ni, Cr and Co, particularly in woodland soil. Zn is a micronutrient and the decreased concentration in grains implies lower grain quality for wheat

grown in fly ash amended soils. Elseewi at al. (1980) noted the reduction of P and Zn content in maize plants grown in fly ash amended soils, thus the need for supplemental fertilization of plants with these nutrients was suggested. Sikka and Kansal (1994) also reported reduced Zn content in rice following soil amendment with 4-8% fly ash.

In the second experiment, application of the Tanzania ash to both soils at high concentrations (8-32%) also resulted in plant contamination with PTEs. Most PTEs (Cd, Co, Cr, Ni, Zn and Se) accumulated in the roots of the wheat grown in both soils. The accumulation of most PTEs in roots probably could be attributed to the increased extractability of these PTEs noted in both soils following the ash applications. As and Pb accumulation in almost all parts decreased with increasing ash concentration, probably because of the low content of these PTEs in Tanzania ash. In woodland soils, wheat plants accumulated Cd, Co and Se in their shoots and Cd, Co, Se and Ni in grains, while in arable soil increased accumulation of Cd and Se was measured in shoots and Cd, Ni, Pb and Se in grains following soil amendment with high ash concentrations (16-32%). Similar findings regarding PTE uptake by plants grown in soils amended with high concentrations of fly ash have been previously reported (Jala and Goya 2006; Pandey et al., 2009; Nayak et al., 2015). Zn and Cu are also micronutrients, but application of the Tanzania ash did not affect uptake of Zn and Cu, which may lower the grain quality of wheat grown in fly ash amended soil. Sharma et al. (2009) noted insignificant uptake of Zn and Cu by wheat plants grown in fly ash amended soil which was attributed to the occurrence of these PTEs in oxide forms in fly ash, thus becoming insoluble in water and unavailable for uptake. Low uptake of Cu by plants in both experiments may be associated to the low content of Cu in both ashes and the decreased extractability of Cu noted following soil amendment with the Tanzania ash. Similar results were reported by Sikka and Kansal (1994), where application of fly ash did not affect Mn or Cu uptake by rice plants and this was attributed to low availability of these nutrients.

In the present investigation, the concentrations of Se, As, Cd, Co, Ni and Pb in grains from wheat grown in both soils amended with 0-32% were below the maximum safe limit recommended for cereals by FAO/WHO, except As and Cd in grains from woodland soil amended with high concentrations of UK and

Tanzania fly ash respectively. Therefore, As and Cd may be elements of great concern for land application of coal ash.

6.5.6 Translocation of PTEs into different plant parts

In the first experiment, the soil-to-root transfer ratio for As and Se (both >1) increased significantly in plants grown in woodland soil amended with 16-32% ash. This suggests accumulation of these PTEs by wheat plants grown in fly ash amended soils. No transfer ratios of >1 were observed for root-to-shoot or for shoot-to-grain in plants grown in woodland soil with UK ash, except for Cu with a shoot-to-grain TR >1 at low ash concentrations. In this case, increasing ash amendments resulted in Cu exclusion (TR <1) from the grain rather than accumulation. A similar result was reported by Rautaray et al. (2003) where soil amendment with fly ash reduced Ni and Cd concentrations in rice grains and straw and these authors linked their finding to increased soil pH. Observing higher TRs in roots relative to foliage is often reported and depends on the species, the PTE, soil and environmental factors (Mirecki et al., 2015).

Brunetti et al. (2011) grew durum wheat at a contaminated site to test the phytoremediation potential of the plant. These authors calculated root-to-shoot transfer factors of <1 for a range of potentially toxic elements and concluded that wheat excluded the PTEs. Similar results were obtained for both soils with the UK ash amendment in the current experiment although interestingly, when Tanzanian ash was added to woodland soil, Mo and Cd had root-to-shoot TRs of >1 in control plants, although ash amendment resulted in Mo exclusion; increasing ash concentration also encouraged exclusion of As, Co and Cu from shoots of plants grown in arable soil. Mirecki et al. (2015) demonstrated a decrease in TRs when plants were grown with higher concentrations of PTEs. They also found that TFs differed between locations.

In contrast to the findings of the experiment with the alkaline UK ash, the acidic Tanzanian ash resulted in increased shoot-to-grain TRs (>1) for Pb, Se, Ni and Cu in plants grown in the arable soil, and Cu, Ni and Se in those grown in woodland soil. It should be noted that only the highest ash concentration elicited the response. Since the shoot-to-grain transfer ratios were similar for both soil types, it is reasonable to conclude that a component of the ash (e.g. pH modification) is the main driver and not soil type.

Whilst the transfer ratios give a valid indication of the translocation potential of the PTEs and whether fly ash amendment modifies that potential or not, it is important to consider the PTE concentration within the grains since this is the main dietary component.

Comparing the PTE concentrations in grains for the wheat grown in both UK and Tanzania fly ash amended soils to the maximum safe limit of PTEs in cereal grains recommended by FAO/WHO, all the PTEs were below the recommended safe standard (Table 6-17) except Cd for the grains from woodland soil amended with high concentrations of Tanzania ash and As for both soils after being amended with the UK fly ash.

Table 6-17: *Average concentration of PTEs in grains for wheat grown in woodland and arable soils amended by UK and Tanzania coal ashes in comparison with the FAO/WHO safe limit*

PTEs	Woodland soil +UK ash	Arable soil + UK ash*	Woodland soil + TZ ash	Arable soil + TZ ash	FAO/WHO safe limit
Cu	9.2-3.8	10.7-4.7	6.3-5.12	4.3-3.7	73.3
Zn	77.81-14.44	22.38-13.96	48.8-48.07	26.6-45.8	99.4
Co	0.1-0.01	0.2-0.17	0.08-0.41	0.01-0.02	50
Ni	1.31-0.09	0.49-0.55	0.10-2.74	0.25-1.57	67
Cr	0.55-0.05	0.26-0.15	0.67-0.40	0.18-0.26	2.3
Pb	0.06-0.09	0.22-0.21	0.1-0.02	0.01-0.03	0.3
Cd	0.01-0.02	0.01-0.02	0.19-0.49*	0.03-0.15	0.2
As	0.03-0.36*	0.07-0.4*	0.02-0.03	0.03-0.01	0.2
Se	0.01-1.37	0.03-0.87	0.02-0.45	0.02-0.5	NP

*PTE concentrations are in mg kg^{-1} and the range in grains corresponds to 0-32% fly ash amendment in each soil. Source: FOA/WHO safe limit in cereals cited by Tenegne et al., 2015. NP = not presented, * = values exceeding the FAO/WHO safe limit.*

6.6 CONCLUSIONS

The application of an alkaline fly ash at the range used in this experiment (0-32%) to acidic or near neutral soils (woodland and arable soil) will help in increasing the soil pH, essential nutrient concentrations and growth and yield of wheat; however, lower concentrations (0-4%) can be recommended to limit soil and wheat plant contamination with PTEs. Applications of high concentrations (16-32%) of either a very acidic or a very alkaline ash resulted in As and Cd accumulation in wheat grains, which may pose some health risks.

Low concentrations (0-2%) of an acidic ash can also be applied to an acidic soil rich in organic matter (like the woodland soil in this experiment), to improve nutrient availability and plant growth; however, application of this ash to very alkaline soils with the intention of lowering the soil pH and supplementing soils with S would probably be the best option. Application of either an alkaline or acidic ash must only increase/decrease soil pH to the optimal level favourable for nutrient availability and plant growth in order to avoid negative or unintended effects on nutrient and PTE availability. Following the decrease in P availability and reduced growth and yield in arable soil when amended with fly ash, application of fly ash to soil with similar characteristics to the one used in this study is not recommended. However, based on this investigation, the strategic agronomic use of fly ash particularly in problematic soil is recommended. The co-application of ash with other amendments rich in P, Cu and Zn or fertilizer supplementation for these nutrients is also recommended. Despite the concentrations of As, Cd, and Zn in various 'soil plus ash' mixes being outside the maximum permissible limits for Tanzania and As, Cr, Pb and Zn falling outside the UK permissible limits, the PTE transfer ratios from shoot-to-grain when the UK ash was used, suggest that wheat excluded the potentially harmful elements, although this was not the case for the grains from plants grown with the Tanzanian ash. Despite this, all the grain PTE concentrations were within the FAO/WHO safe limits for ingestion, except for As concentration of grains from plants grown in woodland soil amended with the highest UK ash concentrations and Cd content of grains associated with woodland soil and most of the Tanzania ash treatments.

These findings will be used to evaluate the risks involved with making a positive recommendation for use of ash for food production (Chapter 7).

7 RISK ASSESSMENT OF PTE CONTAMINATION IN SOIL, WHEAT GRAIN AND HUMAN INGESTION FOLLOWING LONG-TERM APPLICATION OF COAL ASH TO AGRICULTURAL SOILS

7.1 INTRODUCTION

In Chapter 6, positive effects were observed on nutrient concentrations and plant growth in coal ash-amended soils. However, these beneficial effects were accompanied by an increase in PTE concentrations in the soil and uptake by wheat plants. In this Chapter, a risk assessment is presented which evaluates the probable risks of increased contamination of soil and plant material and ingestion by humans of PTEs when repeated applications of fly ash are made to arable soils. Soil amendment with coal ash, particularly in the long term, may result in increased soil and plant contamination with PTEs due to the presence of these elements in ash (Moreno et al., 2005; Nalbandian, 2012). Soil contamination with PTEs reduces the suitability of the land for agricultural use because PTEs tend to decrease soil microbial activities (Pati and Sahu, 2004; Yang et al., 2006); they also interfere with nutrient uptake by plants (McGrath et al., 1997) and thus decrease crop yields. Uptake of PTEs by plants grown in contaminated soils varies depending on their solubility and the total concentration of these PTEs present in the soil (Marwa et al., 2012). Accumulation of PTEs in plant parts, particularly in edible parts such as grains, will eventually pose some health risks to humans ingesting the contaminated food. For instance, long-term consumption of food with high Cd concentrations causes kidney damage (Ministry of Environment, New Zealand, 2011). The consumption of food with high Pb concentrations tends to affect the brain, nervous system and the dietary uptake of Ca (Lockitch, 1993; Marwa et al., 2012). Cr in the soil can occur in trivalent or hexavalent forms, both of which are toxic when they are absorbed by plants and consumed at high concentrations (Ministry of Environment, New Zealand, 2011). A low dose of Cr (III) is essential in the human diet (being important in glucose and lipid metabolism), but Cr in hexavalent form (Cr-IV) is highly toxic and when consumed by humans via contaminated food it is known to cause cancer (Zayed and Terry, 2003). Arsenic can exist in organic or inorganic forms; both forms when consumed at high doses are toxic and carcinogenic (Marwa et al., 2012) but the inorganic forms (arsenic V and arsenic III) are more toxic and plant available in soil solution (Meharg and Hartley-Whitaker, 2002).

The direct effect of fly ash on soil and plant contamination with PTEs in soils amended with ash has been extensively studied (Singh et al., 2008; Pandey et al., 2009; Nayak et al., 2015); however, little is known regarding the long-term effects of PTE accumulation in soil, plants and the risks associated with human consumption following repeated addition of fly ash to agricultural soils. Therefore, modelling was performed with the aim of assessing the risks of PTE accumulation in the soil and plants and the associated risks of human consumption of PTEs following repeated annual application of coal ash to arable soil for five consecutive years. The residual effects of ash application on PTE accumulation were then modelled up to 30 years after the fifth year of consecutive annual applications.

The specific objectives were:

i) To calculate the concentration of PTEs expected to accumulate in the arable soil following the application of 2% of TZ1 ash for five consecutive years.

ii) To calculate the concentration of PTEs expected to accumulate in wheat grains grown in the arable soil amended with 2% of TZ1 ash for five consecutive years.

iii) To calculate the concentration of PTEs expected to be ingested by humans from the consumption of wheat grains grown in the arable soil amended with 2% of TZ1 ash for the five consecutive years

iv) To calculate the residual effects of ash application on PTE accumulation in soil, wheat plants and potential PTE consumption by humans 25 years after the final application of 2% of TZ1 ash to arable soil in year 5.

The model used (FRACAS - Fate of Repeated Applications of Coal Ash to Soils) was an adaptation of a simple analytical model designed to assess the impacts of sewage sludge applications to agricultural soils (Shaw, unpublished). The FRACAS model was used to calculate the contamination of soil, plant tissues (specifically grain) and human ingestion of selected PTEs following the repeated application of coal ash to an agricultural soil. Five PTEs (As, Cd, Cr, Pb and Zn) were selected based on their differing mobilities and bio availabilities in the soil. Cd and Zn were selected to represent mobile/bioavailable elements and Cr and Pb were selected to represent less mobile elements. Arsenic was also included as a metalloid

which is commonly found in fly ash. Calculated PTE contamination of soil, wheat grain and the rate of ingestion of PTEs expected to be consumed by humans were compared to guidelines on maximum permissible limits published previously by FAO/WHO, JECFA, UNEP and DEFRA-UK.

7.2 MODEL DESCRIPTION

The FRACAS model, described in Appendix 7-1, was used to assess the contamination of soil, plants and human ingestion of selected PTEs following repeated application of coal ash to agricultural soils. As a test case, the calculations considered a neutral arable soil (pH 6.8) represented by the Sutton Bonington soil described in Chapter 2. A soil depth of 0.2 m (i.e. a 'plough layer' of 20 cm) was selected and a bulk density of 1200 kg m^{-3} assumed. A soil moisture content of 20 % (0.2 g $g^{-1)}$ and an average annual infiltration rate (precipitation minus evaporation) of 0.44 m y^{-1} were assumed, the latter based on average precipitation and evaporation rates for England and Wales. The soil was amended with 2% w/w (dry) of either the UK or Tanzanian coal ash (equivalent to 5 kg m^{-2} or 50 tonnes ha^{-1} when mixed uniformly within the plough layer). The initial metal concentrations in the arable soil and in each ash were determined before mixing the soil and ash (see Chapter 3). The tendency of each metal to adhere to the soil solids in the arable soil after being amended with 2% ash was represented by the solid-liquid distribution coefficient (K_d, L kg^{-1}). K_d values were determined by dividing the total (acid-extractable) concentration (mg kg^{-1}) by the water-extractable concentration (mg L^{-1}) of each metal in the soil. All the K_d values were converted to m^3 kg^{-1} to ensure consistency of units in the model. All K_ds for the selected PTEs were compared to the K_ds for the same elements in soils suggested by the IAEA (2009). K_ds of all the selected PTEs in soil amended with 2% of the Tanzanian ash were within the range suggested by IAEA (2009) but, for soil amended with the UK ash, K_ds of the selected PTEs were below the range suggested by IAEA (2009). The Baes and Sharp (1983) equation is used within FRACAS to calculate the metal leaching coefficient (λ_s), which is subsequently used to calculate soil contamination $[S]_t$ at any time, t, after application of the coal ash to the soil. Since K_d is the only parameter which was varied in the modelling undertaken it was critical to the sensitivity of the model calculations; therefore, only K_d values derived for the Tanzanian ash-soil mixtures were used since these were within

the expected range, based on IAEA (2009). Wheat was used as a reference crop in the model calculations, with an assumed density of grain production of 0.25 kg m^{-2}. The soil-plant transfer factor for each metal from the soil to the wheat grain was calculated by taking the ratio of each metal concentration in grain to the concentration in the soil (Chapter 6). The initial interception of coal ash by wheat leaves (F in the model) was assumed to be zero because fly ash is likely to be applied between cropping cycles. The plant loss coefficient (λ_p in the model) was, therefore, assumed to be un-applicable because the ash was to be applied directly to the soil before seed sowing and any risk of direct plant shoot contamination was considered to be negligible. The human consumption of PTEs in wheat grain was calculated based on an assumed daily intake of 0.25 kg of grain for an adult with 70 kg body weight. The descriptions of model parameters are presented in Table 7-1 and 7-2. All equations used are shown in Appendix 7-1.

Table 7-1: *List of parameters used to calculate the contamination of soil, wheat grain and human consumption of PTEs, following repeated application of Tanzanian coal ash to an arable soil.*

Parameter	Description	Value	Unit			
I_{tot}	Total application rate of coal ash (dry solid basis)	5	kg m^{-2}			
F	Fraction of ash initially retained by wheat foliage	0	-			
d	Rooting depth of wheat/plough layer	0.2	m			
θ	Soil moisture content ('typical' UK arable soils)	0.2	g g^{-1}			
V_w	Soil water infiltration velocity ('typical' for England and Wales)	0.44	m y^{-1}			
ρ	Soil bulk density ('typical' arable soil UK)	1200	kg m^{-3}			
C_i (mg kg^{-1})	Initial concentration of PTEs in untreated soil	**As**	**Cd**	**Cr**	**Pb**	**Zn**
		7.42	0.37	11.8	67.7	43.2
C_s (mg kg^{-1})	Concentration of PTEs in Tanzanian (TZ1) ash	**As**	**Cd**	**Cr**	**Pb**	**Zn**
		5.98	0.46	11.1	17.7	74.3
K_d (L Kg^{-1})	Solid-liquid distribution coefficient of PTEs in soil	**As**	**Cd**	**Cr**	**Pb**	**Zn**
		1130	4510	3860	5150	1930
TF	Soil to wheat grain transfer factor of PTEs	**As**	**Cd**	**Cr**	**Pb**	**Zn**
		0.0047	0.0723	0.0417	0.0002	0.76
CR	Human consumption rate of wheat grain	0.25	kg d^{-1}			

Table 7-2: *List of variables calculated by the FRACAS model.*

Parameters	Description	Year 1	Year 2	Year 3	Year 4	Year 5
		As	**Cd**	**Cr**	**Pb**	**Zn**
$[G]_i$	Initial wheat contamination (mg kg^{-1})	0	0	0	0	0
λ_s	Soil leaching coefficient (y^{-1}) of PTEs	4.45×10^{-6}	1.11×10^{-6}	1.30×10^{-6}	9.76×10^{-7}	2.60×10^{-6}
λp	Plant loss rate coefficient (d^{-1}) of PTEs	0	0	0	0	0
$[S]_t$	Soil contamination at time t, (mg kg^{-1})	Refer to table 7.3				
$[G]_t$	Wheat contamination at time t, (mg kg^{-1})	Refer to table 7.3				
HC	Human consumption of PTEs (mg kg^{-1})	Refer to table 7.3				

7.3 RESULTS

The calculated PTE concentrations in the soil, wheat grain and the PTEs expected to be consumed by humans from the model were plotted against time (Figures 7-1, 7-2 and 7-3). Only two PTEs (Zn and Cd) have been presented as sample graphs, but all the calculated concentrations of each PTE are summarized in Table 7.3.

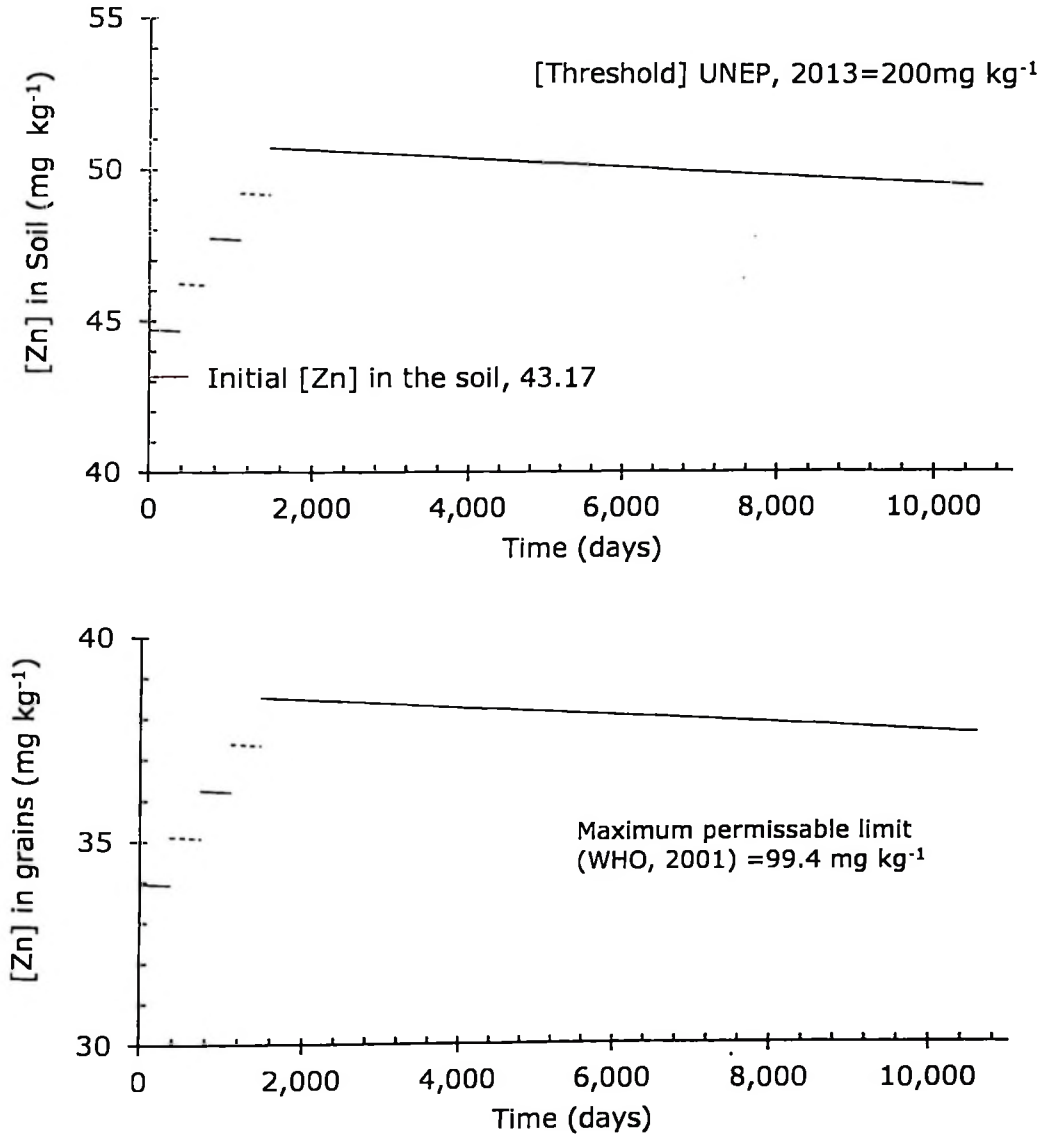

Figure 7-1: *Zn concentrations in the soil and wheat grains after the amendment of arable soil with 2% of the Tanzanian (TZ1) ash for 5 consecutive years (1825 days) and then calculating the residual effects of ash on Zn concentrations up to 30 years (10950 days).*

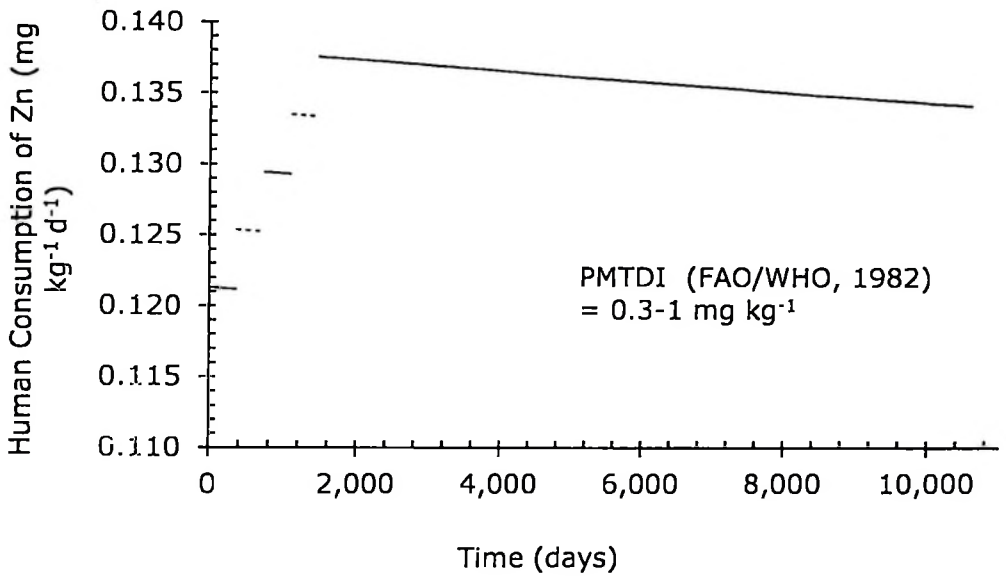

Figure 7-2: *Zn concentrations expected to be ingested by humans consuming contaminated wheat grain following the amendment of arable soil with 2% of the Tanzanian (TZ1) ash for 5 consecutive years (1825 days) and then calculating the residual effects of ash on Zn concentrations up to 30 years (10950 days). PMTDI= Provisional Maximum Tolerable Daily Intake.*

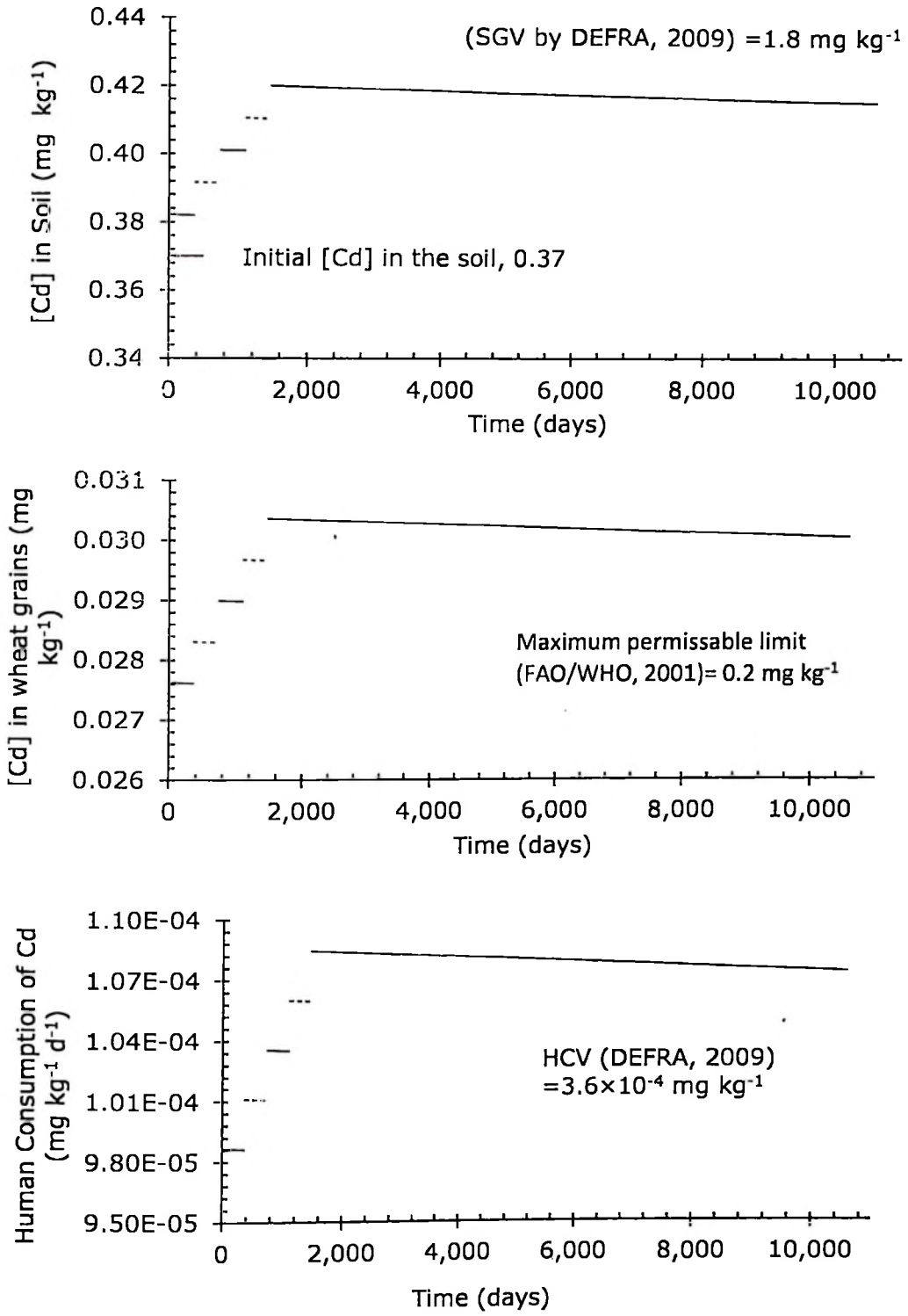

Figure 7-3: *Cd concentrations in the soil and wheat grain, and human consumption of Cd after amendment of arable soil with 2% of the Tanzanian (TZ1) ash for 5 consecutive years (1825 days) and then calculating the residual effects of ash on Cd concentrations up to 30 years (10950 days). SGV=Soil Guideline Value, HCV= Health Criteria Value.*

Table 7-3: *PTE concentrations in soil and wheat grain and human consumption of PTEs at the end of each year, following the amendment of arable soil with 2% of the Tanzanian (TZ1) ash for 5 consecutive years and then calculating the residual effects of ash up to 30 years.*

	Soil contamination with time						**Maximum permissible limit**
PTEs (mg kg^{-1})	Year 1	Year 2	Year 3	Year 4	Year 5	**Year 30**	
As	7.54	7.65	7.76	7.87	7.93	**7.68**	43[a]
Cd	0.382	0.391	0.401	0.410	0.419	**0.416**	1.8[a]
Cr	12.0	12.2	12.4	12.7	12.9	**12.7**	100[b]
Pb	68.1	68.4	68.7	69.1	69.3	**68.8**	60[b]
Zn	44.7	46.2	47.8	49.2	50.5	**49.5**	200[b]
	Wheat grain contamination with time						
PTEs (mg kg^{-1})	Year 1	Year 2	Year 3	Year 4	Year 5	**Year 30**	**FAO/WHO 2001 amended 2017**
As	0.0351	0.0356	0.0361	0.0366	0.0369	**0.0357**	0.2(rice)
Cd	0.0276	0.0283	0.0290	0.0297	0.0303	**0.0301**	0.2
Cr	0.500	0.509	0.519	0.528	0.537	**0.532**	2.3
Pb	0.0166	0.0167	0.0168	0.0169	0.0170	**0.0168**	0.2
Zn	34.0	35.1	36.2	37.4	38.3	**37.6**	99.4
	Human consumption of PTEs (mg kg^{-1} bw day^{-1}) with time						
PTEs	Year 1	Year 2	Year 3	Year 4	Year 5	**Year 30**	
As	1.25×10^{-4}	1.27×10^{-4}	1.29×10^{-4}	1.31×10^{-4}	1.32×10^{-4}	$\mathbf{1.28\times10^{-4}}$	3×10^{-4}[d]
Cd	9.9×10^{-5}	1.01×10^{-4}	1.04×10^{-4}	1.06×10^{-4}	1.08×10^{-4}	$\mathbf{1.07\times10^{-4}}$	3.6×10^{-4}[d]
Cr	1.79×10^{-3}	1.82×10^{-3}	1.85×10^{-3}	1.89×10^{-3}	1.92×10^{-3}	$\mathbf{1.90\times10^{-3}}$	2.1[e]
Pb	5.94×10^{-5}	5.97×10^{-5}	6.0×10^{-5}	6.03×10^{-5}	6.06×10^{-5}	$\mathbf{6.01\times10^{-5}}$	2.0×10^{-5} – 3.0×10^{-3}[c]
Zn	0.121	0.125	0.129	0.133	0.137	**0.134**	0.3-1[f]

a= *Soil Guideline Value (SGV, 2009) for allotments by Department of Environment, Food and Rural Affairs (DEFRA 2009, amended 2013) UK.*

b= Threshold values by Ministry of Environment Finland (MEF, 2007) representing the mean values of most EU countries and India, also as international applicable values for agricultural soils according to UNEP, 2013 (In: Toth et al., 2016).

c= Joint evaluation of FAO/WHO Expert Committee for food additives (JECFA, 2011)-estimated exposure of Lead for an adult. http://apps.who.int/food-additives-contaminants-jecfa-database/chemical.aspx?chemID=3511# accessed 10/7/2018.

d= Health criteria value (HCV) or Low Levels of Toxicological Concern (LLTC) for allotments by Department of Environment, Food and Rural Affairs (DEFRA 2009, amended 2013) UK.

e= Generic Assessment Criteria (GAC) for chromium (VI) for allotments by Nathanail et al. (2009) in Department of Environment, Food and Rural Affairs (DEFRA 2009, amended 2013) UK.

F= Provisional Maximum Tolerable Daily Intake (PMTDI) recommended by FAO/WHO 1982, amended 2017.

7.4 DISCUSSION

Due to the presence of PTEs in coal ash, application of this ash to arable soil will result in soil and plant contamination and, ultimately, to an increased risk of human consumption of contaminated plant material. In this study a model evaluation of soil and wheat grain contamination and consequent human ingestion of PTEs was undertaken based on five consecutive annual applications of Tanzanian coal ash to an arable soil. The PTE concentrations and human ingestion rates were modelled during the five years of coal ash application and for a further 25 years after the fifth and final application.

The concentrations of As and Cd in the soil increased with time up to the 5th year of ash application and then decreased slowly over the following 25 years; however, their unit values were 6 and 4 times lower (for As and Cd, respectively) than the soil guideline values recommended by DEFRA (2009). The concentrations of Cr and Zn in the soil followed similar trends to As and Cd and their unit values were 8 and 4 times lower (for Cr and Zn, respectively) than the threshold values recommended internationally by UNEP, (2013). The concentration of Pb in the arable soil (67.7 mg kg^{-1}) was higher than the threshold value recommended by UNEP (2013) (60 mg kg^{-1}) even before ash was applied. This may be linked to its limited solubility and strong interaction with soil particles (Clemens, 2006; Marwa et al., 2012) which strongly retains Pb in the soil. Amendment of the soil with 2% of the Tanzanian ash for five consecutive years increased the concentration of Pb in soil by 1.62 mg kg^{-1}.

Despite the apparently high initial Pb concentration in the soil, the concentration of Pb in wheat grain was 12 times lower than the maximum permissible limit recommended by FAO (FAO, 2001- amended 2017). This can be attributed to its low solubility and its limited absorption by plants reported in previous studies (Kabala and Singh, 2001). The concentrations of all other studied PTEs in wheat grain over the 30-year modelling period were 6, 7, 4 and 3 times lower (for As, Cd, Cr and Zn, respectively) than the maximum permissible limits recommended by FAO (FAO, 2001-amended 2017). This implies very low risks of human dietary exposure to these potentially toxic elements following soil amendment with the Tanzanian ash.

The daily intake of potentially toxic elements by ingestion depends on the dietary habits of individuals, the concentrations of PTEs in their food and the amount of food consumed (Singh et al., 2016). Wheat is a staple food in both temperate and tropical countries and the presence of high concentrations of PTEs in wheat grain is of significant concern with respect to long-term human health. In this study, the risk associated with the consumption of contaminated wheat grain was evaluated by comparing the calculated daily intake of PTEs of an adult (assumed 70 kg body weight consuming 0.25 kg of wheat grain daily) with the provisional maximum tolerable daily intake (PMTDI) values based on FAO guidelines for Zn, the Joint Evaluation of FAO/WHO Expert Committee for Food Additives (JECFA, 2011) for Pb and health criteria values (HCV) and generic values recommended by DEFRA (2009) for As, Cd and Cr. The daily intakes in wheat grain of all PTEs studied (As, Cd, Cr, Pb and Zn) were 2, 3, 1094, 0.33-50, and 2-7 times lower (for As, Cd, Cr, Pb and Zn, respectively) than the suggested maximum permissible limits. These results reveal that, even after 5 consecutive annual ash applications, wheat grain grown in arable soil amended with 2% of the Tanzanian ash was safe for human consumption with regard to all the PTEs studied.

The residual contamination of PTEs in soil and grain showed a slight decrease over the 25 years following the final application in year 5. This can be attributed to a generally low rate of leaching from the plough layer of the soil, resulting from the generally high K_d values of these PTEs in arable soils after fly ash application (which is within the range of K_d values for the same elements in agricultural soils suggested by IAEA, 2009). Despite this general persistence of the coal ash-derived PTEs in soil over at least three decades, 'permissible' concentrations in soil and grain were never breached and human dietary intake rates were never exceeded in the scenario considered.

7.5 CONCLUSIONS

Based on this study using Tanzanian coal ash (TZ1), it is safe to apply 2% w/w (dry) of fly ash repeatedly to an agricultural soil for 5 years consecutively without exceeding the maximum permissible limits of PTEs in soil and wheat grain or human dietary intake. The concentrations of the studied PTEs (As, Cd, Cr, Pb and Zn) in the soil and wheat grain and the calculated dietary intake of humans were far below 'permissible' limits, thus suggesting the possibility of applying ash with similar properties either more frequently or over more cropping cycles than the 5 annual applications considered here. It is interesting that the concentration of Pb even in soil not amended with fly ash was above the guideline value suggested by UNEP (2013) for agricultural soils. This underlines the importance of baseline measurements of soil contaminants prior to addition of soil amendments which may potentially introduce further contamination. However, further research to assess the risks of multiple applications of fly ash to agricultural soils on soil and plant contamination with PTEs, and associated human health risks, is highly recommended.

8 GENERAL DISCUSSION

8.1 GENERAL FINDINGS

The key findings from each experimental chapter are summarized in the table below.

Table 8-1: *Key findings from Chapters 3, 4, 5, 6 and 7*

Chapter	Key Findings
Chapter 3: Spatial and temporal variation of ash from the UK, Czech Republic and Tanzania	• Coal ash collected from the UK, Czech Republic and Tanzania each contains essential nutrients and PTEs; however, the amounts of nutrients and PTEs vary from one ash to another. • The chemistry of coal ashes (pH, C and N, nutrients and PTEs) collected from the UK, Czech Republic and Tanzania are highly variable; the variation is brought about by differences in coal ranks and the combustion conditions of power plants/industries in these countries. • The pH of coal ashes varies from very acidic to very alkaline (UK1, UK2, TZ2, CR and TZ1 have pH of 12.3, 10.6, 7.7, 5.1 and 4.2, respectively). • Sampling time has a great influence on the characteristics of ash besides the similarity of the feed coal in the same power plant.
Chapter 4: Effects of ash on chemical and biological soil properties (short and long-term)	• Application of alkaline fly ashes (the UK ashes in this study) to a very acidic soil (woodland soil) increases the soil pH and this increase may persist over the long-term. • Application of an alkaline fly ash (UK1) at 0-16% to acidic soil increases soil respiration and nutritional status over the long-term (2 years). • Application of higher concentrations (8-16%) of fly ash to the soil tends to contaminate the soil with PTEs and this risk may be over the long-term.

	• The effect of coal ashes (alkaline/acidic) on general soil characteristics depends on the characteristics of each individual ash and the amount of the ash applied to the soil (incubation experiment 2).
Chapter 5: Effects of ash on soil enzyme activities	• Soil amendment with coal ash may result in either a beneficial effect akin to 'liming' acidic soils or a detrimental effect in which acidic soils are further acidified. However, these effects will depend on the pH and the concentration of the applied ash. • Application of low concentrations (0-4%) of an alkaline ash (UK1) to acidic soils (woodland and arable soils) increases the microbial activity (dehydrogenase and urease activities) and vegetative wheat growth. • Amendment of acidic soils with an acidic ash like TZ1 tends to inhibit microbial activities (enzyme activities) due to further acidification of soils.
Chapter 6: Effects of ash on wheat growth and yield and PTEs accumulation in soils and wheat plants.	• Application of an alkaline ash at concentrations of 0-32% to acidic soils (woodland and arable) increases the soil pH while application of an acidic ash to the same soils and over the same concentration range decreases the soil pH. • Soil amendment with low concentrations (0-4%) of either an alkaline or acidic ash increases the total concentration and extractability of nutrients and wheat growth and yield. • Soil amendment with high concentrations (16-32%) of either an alkaline or acidic ash tends to contaminate the soil and wheat plants with PTEs, particularly Zn, Cd and As. • Application of either alkaline or acidic ash from 2-32% in the arable soil reduces the extractability of P in the soil thus lowering the wheat yield.

	• Application of an alkaline ash (UK1) from 2-32% to woodland soil reduced the Mn extractability in the soil thus causing Mn deficiency symptoms to wheat plants. • Application of an alkaline ash (UK1) to the woodland and arable soils decreases the concentration of Zn in wheat grains thus lowering the grain quality.
Chapter 7: Risk assessment	• It is safe to apply 2% w/w (dry) of fly ash annually to an agricultural soil for 5 years consecutively without exceeding the maximum 'permissible' limits of PTEs in soil and wheat grain or human dietary intake. • It is possible to apply ash with similar characteristics to TZ1 ash more frequently or over more cropping cycles than 5 annual applications because the concentrations of the studied PTEs (As, Cd, Cr, Pb and Zn) in the soil and wheat grain and the calculated dietary intake of humans were far below the 'permissible' limits. • The residual contamination of PTEs in soils and grains decreased slightly over the 25 years following the final application of ash in year 5 but, despite the persistence of the PTEs in soil over at least three decades, 'permissible' concentrations in soil and grain were never breached and human dietary intake limits were never exceeded. • Baseline measurements of soil contaminants prior to addition of soil amendments which may potentially introduce further contamination are important. In this study, the concentration of Pb in soil prior to the application of fly ash was above the guideline value suggested by UNEP (2013) for agricultural soils.

8.1.1 Variation between coal ash from the UK, Czech Republic and Tanzania

Coal ash, a by-product of coal combustion in power plants/industries from many countries, has a variable elemental composition primarily because of differences in feedstock origin (i.e. coal rank and geology) (Seshadri et al., 2010). Coal ash variability has also been linked to other factors such as combustion conditions of power plants/industries within or between countries, the pulverization process, sulphur content and storage and handling (Jala and Goyal, 2006; Tharaniyil, 2013). In the current study, differences in pH, C, N and other elemental concentrations including PTEs for the ashes collected in the UK, Czech Republic and Tanzania were observed which might reflect the differences in coal ranks of these countries and the geological variation between these countries (or the country(ies) of origin of the coal in the case of the UK ash). Variation in the C and N content of the UK, CR and TZ ashes may be attributed to the differences in combustion conditions between the power plants/industries because N always tends to be oxidized during the combustion process (Shaheen et al., 2014) and C in ash is the unburnt C from the parent coal (Tharaniyil, 2013). Moreover, different coal ash characteristics for the samples collected from the same power plant/industry at different times were observed in two ash sample batches collected in the UK and two ash sample batches collected from Tanzania. The variation in the UK ashes, collected from the Ratcliffe on Soar power plant (Nottingham) at different times, could be attributed to differences in the parent coal combusted, because the coal which is burnt at this power plant is imported from various parts of the world. Variation between the Tanzanian ash samples collected from the 21st Century Textile industry at different times could be linked to the variability of coal characteristics within the coal field because this power plants burns coal from the same source (Ngaka coal field, Ruvuma, Tanzania).

8.1.2 Effects of coal ash on soil characteristics, wheat growth and yields and uptake of PTEs by plants

The application of fly ash to soils induces some changes to soil characteristics (Adriano and Weber, 2001; Yeledhalli et al., 2007) but the magnitude of change depends on the characteristics of the ash, the amount of the ash applied to the soil and the characteristics of the recipient soils. In the current study, the direct and short-term effect of fly ash on the chemical and biological soil

characteristics of the woodland and arable soils, studied by applying different ashes collected from the UK, Czech Republic and Tanzania, varied depending on the specific characteristic of an individual ash, the concentration of the ash applied (% w/w) and the characteristics of each recipient soil. Soil amendment with alkaline ashes (two batches collected from UK) increased the pH of the woodland and arable soil (incubation experiments 1 & 2) while the acidic ashes (TZ1 and CR ashes) and the slightly alkaline ash (TZ2) either did not have any effect, or reduced the soil pH of the woodland soil (incubation experiment 2). The increase in soil pH following application of a very alkaline ash (UK1) to a very acidic woodland soil (with pH 3.8) persisted over 2 years in incubation experiment 1, which suggests that coal ash is a useful soil 'liming' material. Besides the beneficial effects of soil liming from the applied alkaline ash, soil respiration (measured by the rate of CO_2 evolution), soil nutritional status (total concentration) and the extractability of most nutrients were also improved by this amendment; this improvement persisted for 2 years in incubation experiment 1). Despite the positive effects of alkaline ash when applied to a very acidic soil on pH, soil respiration and nutrient concentrations, this ash also contaminated the soil with the PTEs particularly when the highest concentration (16%) was applied; this risk persisted for 2 years during incubation experiment 1. These findings highlight the importance of matching the ash characteristics to the characteristics of the recipient soil and the application of low concentrations of ash to the soil. The responses of various soil characteristics like pH, C and N, nutrients and PTEs (total and extractable) following the amendment of very acidic woodland soil with different ashes (UK2, CR, TZ1 and TZ2) (incubation experiment 2) varied depending on the characteristics of each individual ash and the concentration of the ash applied. This highlights the importance of considering variation in ash characteristics before its application to the soil as an agricultural amendment.

Soil amendment with <10% fly ash concentration either influenced positively or did not have any significant influence on soil enzymatic activities; however, ash concentrations above 10% tend to inhibit soil enzyme activities (Lai et al., 1999; Pati and Sahu, 2004; Sanchez et al., 2015). In the current study, soil amendment of acidic soils (woodland and arable soils) with an alkaline ash (UK1), particularly at lower concentration (0-4%), increased soil dehydrogenase and urease activities and vegetative wheat growth (number of

leaves, number of tillers, shoot biomass and root biomass). However, soil amendment with an acidic ash (TZ1) to the same soils and at the same concentration range either did not show any significant effect or inhibited the soil enzyme activities. Moreover, application of high concentrations (8-16%) of either an alkaline (UK1) or an acidic (TZ1) ash also inhibited the soil enzyme activities. The positive and negative effects of these ashes noted on soil enzyme activities were, respectively, linked to the beneficial 'liming' effect of the UK1 ash and the detrimental acidification effects of the TZ1 ash when applied to acidic soils, because the activities of all enzymes are strongly pH-dependent (Siddaramappa et al., 1994; Pati and Sahu, 2004). The positive influence of ash (particularly at low ash concentrations 0-4%) on soil enzymatic activities could also be linked to the ability of fly ashes to supply nutrients, increase root biomass and associated rhizospheric microbes and increase soil C content. However, besides the detrimental acidification effect of the TZ1 ash, the inhibitory effects of either alkaline or acidic fly ash (particularly at high ash concentrations 8-16%) on soil enzymatic activities might be attributed to the high pH induced by alkaline ash, low extractability of some nutrients like P and C in fly ash amended soil, and the toxicity of PTEs within the fly ash (Pan and Yu, 2011; Sanchez et al., 2015). Although the enzyme assays in the current study were performed in soils which were stored in a freezer (-20°C), the effects of sample storage by freezing were noted to be minor in previous studies (ISO, 2009; Kendeler and Gebger, 1988; Wallenius et al., 2010).

Soil amendment with fly ash significantly affected the growth and yield of wheat; however, the magnitude of response varied depending on the soil type (woodland/arable), ash type (UK1/TZ1) and the concentration of ash applied (0%, 2%, 4%, 8%, 16% and 32%). Application of an alkaline ash (UK1), particularly at low concentrations (0-4%), had a positive influence on wheat growth and yield but this influence was more evident in plants grown in the woodland soil than in the arable soil. However, application of the high ash concentration (8-32%) to woodland soil did not show any further significant increase in growth and yield while, in the arable soil, growth and yield decreased significantly. The positive effects of the UK1 ash on wheat growth and yield might be linked to its 'liming' effects in both soils, enhanced supply of P, Mg, Ca, Mn and Fe, and improved extractability of most nutrients (particularly P and B in the woodland soil) which was noted after harvesting.

However, lack of further positive effects in the woodland soil and the negative response in the arable soil might be linked to a decrease in Mn and P extractability in the woodland and arable soils, respectively, which was noted after harvesting. Moreover, poor response in both soils after being amended with high ash concentrations might be attributed to the accumulation of PTEs in both soils and plant parts which tends to impair the biochemical and physiological activities of plants, thus reducing plant growth and yields (Singh et al., 2008).

Soil amendment with an acidic ash (TZ1), particularly at low concentrations (0-2%), had a positive influence on wheat growth and dry matter yield in woodland soil but had no significant effect on plant growth in the arable soil. Positive responses in growth parameters in woodland soil were linked to the increased extractability of Ca, S, Mg, Mn and B, noted after harvesting. Application of high concentrations of the TZ1 ash (4-32%) did not show any positive effect on plant growth in the woodland soil while, in the arable soil, retarded growth and poor yield were observed. Generally poor response of wheat yield in both soils after amendment with the TZ1 ash might be linked to further acidification of soils induced by this ash, low concentrations and decreased extractability of P and K in the woodland soil, decreased concentrations and extractability of P, Mg and Mn in the arable soil and the accumulation of PTEs in both soils and in plant parts. Whilst water and ammonium nitrate extractability of elemental nutrients and PTEs were quantified throughout the thesis, these measurements only give a 'snapshot' of their bioavailability at the time of measurement. Ideally, the elemental concentration in soil solution, plant uptake and the re-supply to soil solution would be measured over time, using for example, the diffusive gradient in thin film technique (Dočekalova et al., 2012), or isotopic dilution methods and sequential extractions to measure solubility, lability and bioavailability (Mao et al., 2014). Understanding the lability of the PTEs in particular within the experimental soil-ash combinations would be beneficial in providing accurate data to any risk analysis. However, these techniques were not used within this study.

Soil amendment with either an alkaline ash (UK1) or an acidic ash (TZ1), particularly at high ash concentration (8-32%), contaminated the soils and plants with PTEs, but most PTEs in the soils were below the maximum

permissible limits suggested by DEFRA (2009), UNEP (2013) and Tanzanian standards (2007) except Cd and Zn when both soils were amended with 32% of the UK1 ash. Following the uptake of PTEs by plants, the concentrations of As and Cd in wheat grains were above the maximum permissible limits suggested by FAO (FAO, 2001-amended 2017) for wheat grown in UK1 ash and TZ1 ash amended soils, respectively.

Differences in ash characteristics between the UK1 and TZ1 ashes explain their different effects on soil chemistry, enzymatic activities and wheat growth and yields. Generally, the growth and yield response of wheat grown in both soils amended with an alkaline ash (UK1 ash) correspond to the data for soil respiration and enzyme activities (Chapters 4 and 5), where low ash concentrations stimulated microbial activities while high ash concentrations inhibited microbial activities. Growth and yield response of wheat grown in the arable and woodland soils amended with an acidic ash (TZ1 ash) also correspond to the response in the soil enzyme activities noted in Chapter 5 where enzyme activities decreased significantly with increasing ash concentration. It is difficult to separate the effects of altered pH and increased nutrient availability resulting from low ash amendments from any beneficial effects of enhanced microbial activity, although both are likely to have been influential. What is unknown here is the effect of ash on microbial diversity, although ash-enhanced enzyme activity (Chapter 5) and CO_2 production (Chapter 4) signify a more functional microbial community following ash amendment at low concentrations. Aside from increased nutrient availability resulting from enhanced microbial activity, the rhizosphere microbiome may have had other positive effects since it is known that many species have plant growth promoting properties (e.g. Compant et al., 2010). Furthermore, microbial enhancement of PTE uptake (phytoremediation) has been demonstrated (e.g. Tiwary et al., 2011), although in the current investigation, microbial activity and CO_2 production were significantly reduced by ash concentrations above 4%. It is therefore unlikely that rhizosphere microbes played a significant role in uptake of PTEs by wheat when in the presence of higher ash concentrations, despite the greater concentration of As and Cd in wheat grains at concentrations above those recommended by FAO/WHO (Chapter 6). When plants were grown with 16% and 32% of the UK1 ash (in arable and woodland soil) and TZ1 ash (in woodland soil) respectively, grain

yield was only lower in plants grown in the arable soil with 32% ash, therefore higher PTE concentrations were not due to a concentration effect. The interactions between the rhizosphere microbiome, elemental availability, plant uptake and yield are likely to be complex and elucidation is outside the scope of this project.

Based on these findings, the characteristics of an individual ash, the concentration of the applied ash and the characteristics of the recipient soil will determine the applicability of coal ash as a soil amendment. Following the accumulation of PTEs in soils and plants, particularly in wheat grains for the plants grown in coal ash amended soils, assessment of potential health impacts due to human consumption of plant produce grown in coal ash amended soils is important.

8.1.3 Risk analysis following the long-term/multiple application of coal ash to arable soils

Model calculations were carried out to assess soil and plant concentrations and human consumption of selected PTEs (As, Cd, Cr, Pb and Zn) following annual application of TZ1 ash to the arable soil for 5 years, consecutively. This assessment showed that, even when residual contamination over a 25-year period was taken into account, applications of 2 % ash to the soil are unlikely to result in breaches of permissible standards for soil and wheat grain contamination and human dietary intake of PTEs. Based on this analysis, it is possible to apply ash with similar characteristics to TZ1 ash more frequently or over more cropping cycles than 5 annual applications because the concentrations of the studied PTEs (As, Cd, Cr, Pb and Zn) in the soil and wheat grain and the calculated dietary intake of humans were far below the 'permissible' limits. The concentrations of As and Cd in the soil were 6 and 4 times lower, respectively, than the soil guideline values recommended by DEFRA (2009). The concentrations of Cr and Zn were 8 and 4 times lower, respectively, than the threshold values recommended internationally by UNEP (2013). The initial concentration of Pb in the arable soil (67.7 mg kg^{-1}) was higher than the threshold value recommended by UNEP (2013) (60 mg kg^{-1}) even before ash was applied, but soil amendment with 2 % of the Tanzanian ash for 5 consecutive years only increased the concentration of Pb in soil by 1.62 mg kg^{-1}. In wheat grains, the concentrations of all the PTEs considered,

over the 30-year modelling period, were 6, 7, 4, 12 and 3 times lower for As, Cd, Cr, Pb and Zn respectively, than the maximum permissible limits recommended by FAO (FAO, 2001-amended 2017). This implies very low risks of human dietary exposure to these PTEs following soil amendment with the Tanzanian ash. The daily intake in wheat grain of all PTEs studied (As, Cd, Cr, Pb and Zn) was 2, 3, 1094, 0.33-50, and 2-7 times lower, respectively, than the suggested maximum permissible limits. These results show that, even after five consecutive annual ash applications, wheat grain grown in arable soil amended with 2 % of the Tanzanian ash will be safe for human consumption with regard to all the PTEs studied.

However, due to the variations in ash chemistry observed in the five samples analysed in this study (UK1, UK2, TZ1, TZ2, CR), the risk analysis results may not be applicable to other ashes apart from the TZ1 ash, or if more than 2 % (50 tonnes ha^{-1}) of ash were applied to the soil. The variation in the composition of ash underlines the importance of analysing the specific ash characteristics prior to its use as an agricultural soil amendment.

8.1.4 General conclusions and recommendations

Based on the findings from this study, coal ash can be used as an agricultural soil conditioner because of its positive influence on soil chemistry, soil respiration, enzyme activities and growth and yield of wheat. However, due to variations in coal ash characteristics, strategic agronomical use of coal ash is highly recommended. Application of low ash concentrations (0-4%) is recommended in order to avoid short-term and long-term accumulation of PTEs in soils and plants, inhibition of soil microbial activities and reduction in extractability of nutrient such as P and Mn. In the case of acidic ashes similar to TZ1 ash, the long term/multiple application of 2% (w/w, equivalent to 50 tonnes ha^{-1}) may be recommended to avoid accumulation of PTEs in soils, plants and for the safe use of wheat grains for human consumption. Moreover, studying the specific characteristics of an individual coal ash and matching these with the specific soil characteristics is highly recommended before ash amendments are made. Specifically, problematic soils such as very acidic or very alkaline soils, soils with poor nutritional status or soils with low S content could benefit from carefully targeted coal ash applications.

Supplementing coal ash with other sources of Zn, such as organic materials or inorganic fertilizers, to improve uptake of Zn by plants and its concentration in wheat grains is also recommended.

8.1.5 Suggestions for future studies

- Applications of coal ash to problematic soils tailoring applications of different ashes to specific soils is recommended.
- Since the current study was conducted in controlled environmental conditions and in small pot sizes (for wheat growth experiments), similar study in field conditions is recommended.
- Since some plants exclude (uptake of) heavy metals (e.g. some cereals), a similar study including several crop types to compare their growth and yield response to ash and their PTE uptake is recommended.
- Risk assessment following long-term/multiple applications of several coal ashes to arable soils is recommended.
- Co-application of coal ash with other sources of Zn and readily available P and Mn is recommended.

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APPENDIX

Appendix 7-1

1. Initial soil contamination immediately after ash application (mg kg^{-1}):

$$[S]_i = \left(\frac{(AR_{tot} \times C_s) \times (1 - F)}{\rho \times d}\right) + C_i$$

2. Initial crop contamination immediately after ash application (mg kg^{-1}):

$$[P]_i = \left(\frac{(AR_{tot} \times C_s) \times F}{W}\right)$$

3. Soil contamination at time t after initial contamination (mg kg^{-1}):

$$[S]_t = \left([S]_i \times exp^{-\lambda_S \times t}\right) + \left(\frac{P_i \times \left(1 - exp^{-\lambda_P \times t}\right)}{\rho \times d}\right)$$

λ_S in equation 3 is given by Baes and Sharpe's (1983) equation (y^{-1}):

$$\lambda_S = \frac{V_W}{d \times \left(1 + \frac{\rho \times K_D}{\theta}\right)}$$

4. Crop contamination at time t after initial contamination ((mg kg^{-1}):

$$[P]_t = [P]_i \times \left(1 - exp^{-\lambda_P \times t}\right) + (TF \times [S]_t)$$

5. The human consumption/ingestion rates of PTEs from wheat grains

$$IR_P = \frac{[P]_t \times CR_P}{BW}$$

(Model developed by Shaw, unpublished).