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Research article

The possible application of fly ash (FA) to ameliorate acid mine water (AMD) for irrigation of potato (*Solanum tuberosum* L.)

Maropeng Vellry Raletsena [*], Nkoana Ishmael Mongalo

College of Agriculture and Environmental Sciences, Department of Agriculture and Animal Health, CAES Laboratories, Private Bag X6, Florida, 1710, South Africa

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ABSTRACT

Some areas in Johannesburg abounds with mine wastes namely, acid mine drainage (AMD) as well as fly ash (FA), which are by-products of gold mining and coal burning, respectively. Studies show that a solution formed through mixing these wastes neutralises the acidity of AMD and is an alternative source of irrigation. While studies show improved growth and yield of plants irrigated with fly ash-amended AMD, there are rarely sufficient studies conducted in South Africa showing evidence of altered pH of AMD and that food crops irrigated with fly ash-amended AMD exhibit improved concentration of essential nutrient elements. In this study, AMD was sourced from a gold mine in Johannesburg and fly ash collected from a coal-burning power station in the Mpumalanga Province, mixed at 1:0, 1:1, and 3:1 (w/v) of fly ash to AMD and used to irrigate potatoes. The objective was to assess whether the solutions of FA-amended AMD alter the pH of the AMD and to evaluate if irrigating potatoes with the aforementioned improve the concentration of essential nutrient elements and heavy metals in the tubers. Results show that the pH of AMD was increased in the 1:0 and 1:1 solutions but decreased in the 3:1 solution. The concentrations of Pb and Co were decreased in tubers irrigated with the 50 % AMD and 75 % AMD while that of Ni and Cd were markedly increased in tubers irrigated with solutions of fly ash-amended AMD. In the main, the potato tubers exhibited significantly higher concentrations of Al, Mo, Cu, Ca, Mg, and Zn when irrigated with fly-ash-amended AMD. The pH range levels from FA-AMD treated samples were within the acceptable pH range (5.5–6.5) which is acceptable for water that could be used for irrigation of crops. Also, the decreased Co and Pb and improved concentration of essential nutrient elements indicate that the constituents absorbed large quantities of the heavy metals while releasing the nutrients. In conclusion, the selected fly ash has proven as an alternative low-cost readily-available, affordable, and accessible adsorbent that neutralize the acidity of AMD, decrease the concentration of heavy metals, and increase the concentration of essential nutrient elements. Importantly, the liming potential among other traits of the fly ash improved the quality of the AMD such that the wastes were proven in this study suitable to irrigate potatoes.

1. Introduction

Across the world, freshwater is sourced from rainfall, groundwater, and rivers. In South Africa, the aforementioned sources of

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[*] Corresponding author.
E-mail addresses: Raletmv@unisa.ac.za (M.V. Raletsena), Mongani@unisa.ac.za (N.I. Mongalo).

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freshwater contribute less than that required, making it a water-scarce country and as a result, the country is projected to experience critical shortage of freshwater soon [1]. The largest volume of South Africa's scarce freshwater is used by households and for irrigation; however, its safety is challenged largely by contamination [2], followed by other factors including high populace advancement rates, industrialization, and urbanization [3–5].

Pollutants that contribute to the largest contamination of freshwater, especially in areas around the Johannesburg area of South Africa are from mining activities [6,7]. In particular, after exhaustion of mineral resources in a mine, the mined area should be rehabilitated properly. Should it not, rocks composed of hazardous minerals including pyrite disintegrate to form acid mine drainage (AMD) [8–11]. AMD lead to the solubility, mobility, and release of toxic metals into surrounding areas and contaminate water bodies and soils [12]. In the case of neglected mines, the burden of rehabilitation of mines often falls to the state [13], which has failed to address the challenge effectively. As a result, scholarly studies reveal that topsoil near defunct mines exhibit high concentration of toxic elements, high acidity, and salinity [14–17].

Some studies show that a solution formed through mixing FA with AMD exhibit relatively lower pH and concentrations of heavy metals but increased availability of essential nutrient elements [14]. However, the aforementioned benefits are associated with the weight of the FA and temperature, among other factors [15]. Results of research studies conducted in the Gauteng Province of South Africa, particularly that which assessed whether fly ash-amended AMD is suitable for irrigating food crops and increasing the quality of food crops is promising [16,17]. However, currently, there is rarely sufficient studies that assessed whether fly ash-amended AMD alter the pH of the solution as well as the concentration of heavy metals and essential nutrient elements in tubers of potatoes. This study is intend to contribute knowledge to this gap through evaluating the effect of different ratios of flay ash to AMD on the pH as well as the concentration of selected heavy metals and essential nutrient elements in tubers of potato cultivars.

1.1. *The rationale of the study*

Freshwater generated in South Africa is largely partitioned for agricultural activities, game and cattle grazing, industrial, mining, power generation, and domestic use, however, the largest volume is diverted to sustain electricity generation. Irrigation is allocated the least volume, which is restricted by water cuts and tight regulation by the Water and Sanitation Department. The scarcity of freshwater meant for use in irrigation has motivated researchers and farmers to search for alternative water sources. Of alternatives is reclaimed sewage water as well as treat acid mine drainage. Of these, literature has largely focussed on the effect of acid mine water given that it is a common occurrence and make a significant negative effect on water bodies in the Gauteng Province of South Africa [18]. When assessed for irrigation, AMD is amended with various products including fly ash. This study seeks to establish whether AMD mixed with fly ash, is suitable for use to irrigate potatoes and to establish whether it has effects on the biochemical composition and physiological aspects of potatoes.

When plants are irrigated with water that is contaminated by toxic elements, the mechanisms they adopt to tolerate them differ between species or genotypes of the same plant species. So far, no scholarly study has assessed whether selected cultivars of potato, among that sold in South Africa, grown under irrigation with fly-ash-amended AMD have ability to tolerate the toxic elements. Therefore, this study aimed to evaluate the response of two cultivars of potato (Fianna and Lady rosetta), established under irrigation with acid mine drainage water mixed with fly ash (loaded with HMs). The objective of the study was to determine concentration of essential and heavy metals in the cultivars of potato grown in FA-amended growth media.

Since wastewater is a rich source of nutrients for crop growth and extra water for crop production, it is widely used in agriculture in most developing counties. Additionally, wastewater is more dependable than surface water because it is continuously available from treatment facilities and local sources, allowing farmers to cultivate more crops all year long and increasing cropping intensity and output. To maintain crop productivity and lessen water scarcity and shortages, wastewater irrigation is essential. The main objective of this research was to determine if the toxicity of AMD can be decreased to use it for irrigation purposes.

2. Materials and methods

2.1. *Preparation of samples*

The AMD used in the experiments was collected from one of South Africa's gold-producing mines, located in the Randfontein area, in the Gauteng Province of South Africa while the FA was sourced from one of ESKOM's power generation plants in the Mpumalanga Province of South Africa. The AMD was mixed with FA (FA-treated AMD) in different irrigation ratios (w/v) of 1:1 (80 g FA and 800 mL AMD), 3:1 (quote in g and mL) while the untreated AMD and the control was prepared in ratios of 1:0 (800 mL) and 0:0 (0 g FA and 0 mL tap water), respectively. Therefore, this study involved these treatments: control, 1:0, 1:1, and 3:1. Each FA:AMD irrigation solution (FA-treated AMD) was mixed in a 220 L barrel [19,20], and mixed thoroughly for 30 min, using a stirrer. A benchtop pH meter (model: ADWA AD 1020, Hungary) was used to measure pH, as described by Takahashi et al. [21], at various predetermined time intervals and temperatures [22].

2.2. *Determination of concentration of metals in potato tuber, soil and water*

Soil samples were digested using the reference method by the EPA 3050B (acid digestion of sediments, sludges, and soils). About 1 g of dried potato tuber and soil samples was weighed and milled into a medium wall digestion tube (4IS 0 mm id × 276 mmm length). About 15 mL of concentrated Nitric Acid (65 %) (Merck, South Africa) was added into the vessels with the samples. Water samples

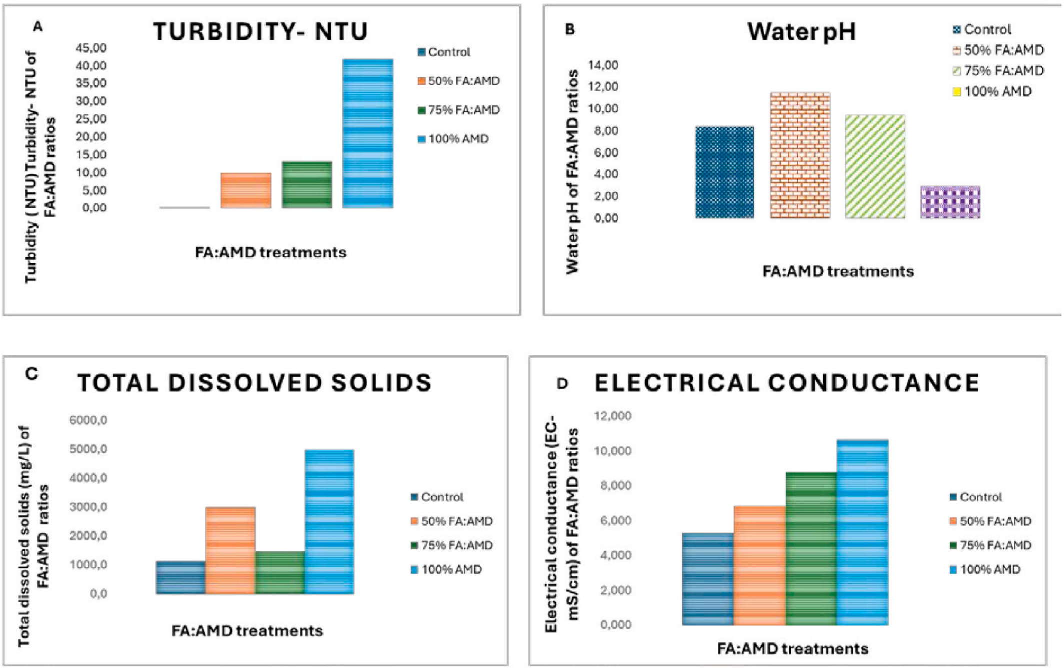

Fig. 1(A–D). The pH of FA: AMD ratios (A). The turbidity of FA: AMD ratios (B). Total dissolved solids (mg/L) of FA: AMD ratios (C). Electrical conductivity (EC) of FA: AMD ratios (D).

were digested using the reference method by the EPA 3015B (Microwave assisted acid digestion of aqueous samples and extracts). A 40 mL aliquot of a homogenized and well-shaken material was measured using a suitable volumetric measuring. Three replicates' samples were taken for each sample. About 15 mL of concentrated nitric acid (65 %) (Merck, South Africa) was added to the vessels with the water samples. The vessels contained a quantified vertical blast/safety bolt design that ensures samples to be closed completely which ensure the digestion vessel be sealed completely under normal working conditions.

Concentration of toxic metals was measured in potato tubers, soil and water samples through using the microwave digestion system (MDS-6G, Sineo Microwave Chemistry Technology China), as reported by Ref. [23]. Digestion vessels were soaked in hot hydrochloric acid (1:1) for 2 h, rinsed with deionized water, and weighed. For the water samples, 45 mL of each was transferred to a vessel and 5 mL of concentrated HNO_3 added. Prior to allowing cooling, for 30 min at 200 °C. Jars were allowed to cool for 5 min before removing from the microwave. After removal from the microwave, samples were allowed to cool in a water bath at 25 °C in vessels. Thereafter, digested material was filtered, using Whatman #4 filter paper into volumetric flasks, and contents filled to the 30 mL mark. The concentration of Cd, Pb, Zn, and Ni were determined using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (Agilent 5800 ICP-OES, USA). The ICP-OES principle relies on those excited atoms releasing light at specific wavelengths as they transition to a lower energy level [23].

2.3. Analysis of fly ash and fly ash sludge

Fresh fly ash, 50 % FA:AMD and 75 % FA:AMD FA samples were collected into zipper sample plastic bags. The concentration of macronutrients and major constituents of the FA were determined using plasma atomic emission spectrometer (ICPE-9820) (Shimadzu, Japan). From each sample, 1 g was put into, followed by digestion in 9 mL of concentrated nitric acid and 2 mL of hydrogen peroxide. Hydrofluoric and hydrochloric acids were among other acid and reagent combinations used in the procedure. Thereafter, the vessels were placed and heated in microwave vessels, at 180 °C, for 30 min, followed by cooling, for 60 min [24].

2.4. Experimental set-up

The plants were grown in a greenhouse located at the Florida Science campus of the University of South Africa (26° 10′ 30″S, 27° 55′ 22.8″ E) where only temperature was controlled, kept at15-30 °C. Nutrient elements in the soil samples were determined at the Agricultural Research Council, Institute for Soil, Climate and Water (ARC-ISWC) in Pretoria (25° 44′ 19.4 S ″ 28° 12′ 26.4″ E). The growth media comprised topsoil, river sand, and vermiculite in the ratio 3:1:1 (v/v/v). Certified seeds of two cultivars, *Lady rosetta* (determinate) and *Fianna* (indeterminate), were obtained from First Potato Dynamics in Western Cape Province and stored at the National Potato Co-op (Nationale Aartappelkantoor (NAK)), Bethal, in the Mpumalanga Province. Seed tubers were first stored at a temperature of 3 °C and later transferred to 15 °C at 14-day intervals. The design of the pot experiment was completely randomized, with each treatment replicated five (5) times. One seedling was grown in each experimental pot and treatments constituted of: a control, 1:0, 1:1, and 3:1. Plants were well irrigated before the imposition of the treatments. Irrigation treatments were executed two weeks after seedling establishment. Plants were harvested during the maturity stage, at 90 days after planting.

2.5. Data analysis

A T-test was conducted to determine differences between two potato cultivars (Fianna and Lady rosetta) to AMD treatments. The F-test for homogeneity of variances showed significant differences for the parameters, thus separate analysis was done for the seasons. All parameters (PIXI) and elementary analysis were compared using a two-way ANOVA. All parameters (potato tubers, soil, sludge, and water samples) and measurements were tested at a $p < 0.05$ significance level using the Duncan's Multiple Test Range to separate means. Statistica v. 10, StatSoft (USA) software was used for all statistical analysis.

3. Results and discussion

3.1. FA impact on pH of AMD

Results shown in Fig. 1 (B) reveal that adding the fly ash to the AMD significantly increased the pH of control, 50 % FA:AMD, and 75 % FA:AMD compared to the untreated AMD (100 % AMD). Overall, irrespective of an increase in temperature, the change in pH of the FA-treated, observed over the period 5–240 min, was minimal (Fig. 1 (A)). At 18 °C, 100 % AMD water exhibited pH 2.88 and temperature rose to 27 °C, the pH showed no significant differences were recorded on the AMD over 240 min and an average temperature of 22 °C (Fig. 1 (A)). While an increase in temperature did not alter the pH of 100 % AMD treatment, that for FA-treated AMD (1:1 and 3:1) was significantly increased, which has implications on ion solubility and mobility [25].

The changes in pH observed in the FA:AMD treatments were relative to the weight of FA added to the AMD solution and the period over which the pH was measured. As shown in Fig. 1 (A), the pH of the FA:AMD ratios were 8.42, 11.45, 9.38, and 2.88 respectively. Of the selected temperatures, the 1:1 treatment showed the highest increase in pH compared to the 1:0, and the 0:0 revealed no change in pH (Fig. 1 (A)). The study showed significant increase in pH of the 1:1 (9.35) and 3:1 (7.68). A strong buffering capacity, as shown by an increase of pH from 2.88 to 9.35, was revealed for 50 % AMD and according to Ref. [26], could be associated with oxidation and hydrolysis of Fe^{2+} which released H^+ and delayed rise in pH.

Of the treatments, that made of AMD plus 50 % FA recorded the highest pH (9.35) while the 3:1 had pH 7.68. Clearly, the weight of FA mixed with the AMD played a major role in increasing the pH of the solutions. Matsi and Keramidas [27] confirmed that indeed, the pH of a solution formed through adding FA to AMD is increased.

Hafez et al. [28] explained that the changes in pH of media used for irrigation affect the availability of mineral nutrients, improving or supressing their absorption, which has a direct effect on the growth and development of the irrigated crops. While certain plant species that grow under certain conditions absorb most essential nutrients at lower or higher pH range, in the main, the pH range of 4.0–6.5 is the most suitable for uptake of mineral nutrients [29]. Indeed, the pH of a growth media has a direct effect on the solubility and therefore availability of essential and non-essential, and harmful nutrient elements, and as shown by Ref. [30], the uptake of Ca and Mg were reduced as soil pH declined, while that of Zn, Mn, and Fe increased as soil pH decreased. In particular, when a solution used to irrigate crops is acidic, it can improve the mobility and phyto-availability of potentially harmful elements, as shown by a study where pH ranged between 2.0 and 3.5 and promoted the mobilization of Al, Fe, and Mn [31]. Studies show that in general, the mobility of the aforementioned metals tend to increase as pH of a growth media decreases. Therefore, it can be concluded that in a growth media made of fly ash and AMD, the fly ash absorbs the HMs contained in the acid mine drainage.

3.2. The impacts of turbidity, total dissolved solids, and electric conductivity on the irrigation water

According to Ref. [32], turbidity is used widely across the world as an indicator of the quality of water. Sludge that forms at outlets of water treatment plants can reach high levels and such can be acceptable, as stipulated in current legislation on drinking water [33, 34] - Edition 2 for drinking water, the microbiological determinants of drinking water quality include *Escherichia coli, Faecal coliforms, Cryptosporidium species, Giardia species, Total coliforms,* and *Heterotrophic plate count*. Fig. 1(A) could be explained in that, as the weight of fly ash was increased, more organic compounds could have been adsorbed on the fly ash sludge. Turbidity scores were recorded for all FA:AMD treatments as 0.01, 9.81, 13.18, and 42.00, respectively. This study demonstrates that an increase in fly ash significantly affected the turbidity of the AMD water, and these results are supported by that of [35–40].

Specifically, as more FA was added, the turbidity of the FA:AMD solution decreased. Fig. 1 (A) showed that the turbidity decreased from 42.00 to 13.18, then 9.81 and 0.01 NTU respectively for FA:AMD treatments. The turbidity standard limit for operational use is less or equal to 1 and 5 for aesthetic and operational use respectively were reported to be compliant with set limits [33]. Doyle and Smart [41] proved that high turbidity of a growth media affects the leaves of plants. Fig. 1 (C) shows the Total Dissolved Solids (TDS) of the FA-treated growth media and clearly, the untreated acid mine drainage had the most significant effect on the TDS. Total dissolved solids comprise of inorganic minerals and organic matter, along a variety of salts [42].

Water that exhibits elevated TDS indicate that it contains aesthetics associated with stains, taste, or precipitation [1]. In the broadest sense, TDS values reflect the extent to which water systems are polluted [43]. In this study, the TDS was markedly higher in treatment two (2) and the untreated acid mine drainage, compared to control and treatment three (3). Therefore, the solution labelled as treatment three (3) in this study, can be considered suitable for irrigation of crops.

It is important to assess the quality of especially drinking water in order to ensure improved and sustained safety [43]. As seen in

Table 1
The concentration of essential and heavy metals in the tuber of potatoes grown under irrigation with AMD mixed with fly ash water.

Treatment	Al	Pb	Co	Ni	Mo	Cd	Cu
Control	0.20 ± 0.0^{c}	0.02 ± 0.0^{a}	0.03 ± 0.0^{b}	0.02 ± 0.0^{b}	0.01 ± 0.00^{c}	0.01 ± 0.0^{d}	0.06 ± 0.00^{c}
50 % AMD	0.04 ± 0.0^{d}	0.01 ± 0.0^{d}	0.01 ± 0.0^{c}	2.26 ± 0.0^{c}	0.37 ± 0.00^{a}	0.04 ± 0.1^{b}	0.11 ± 0.00^{d}
75 % AMD	2.83 ± 0.0^{b}	0.00 ± 0.0^{c}	0.00 ± 0.0^{d}	0.76 ± 0.0^{d}	0.27 ± 0.00^{b}	0.02 ± 0.0^{c}	0.08 ± 0.00^{b}
100 % AMD	14.73 ± 0.1^{a}	0.33 ± 0.0^{b}	0.64 ± 0.0^{a}	6.48 ± 0.0^{a}	0.00 ± 0.00^{d}	0.16 ± 0.1^{a}	1.01 ± 0.00^{a}
F-Statistics							
Treatment	78714.67***	1825513***	1176442***	649297.32***	1265328***	1253.26***	652220.22***

Treatment	Fe	Ca	Mg	Zn
Control	4.50 ± 0.00^{b}	50.00 ± 0.00^{d}	28.33 ± 0.33^{c}	0.73 ± 0.00^{b}
50 % AMD	0.00 ± 0.00^{b}	462.47 ± 0.03^{c}	20.37 ± 0.23^{d}	7.02 ± 0.00^{d}
75 % AMD	0.00 ± 0.00^{b}	730.67 ± 0.33^{a}	120.33 ± 1.23^{b}	1.33 ± 0.00^{c}
100 % AMD	50.67 ± 2.96^{a}	496.67 ± 0.33^{b}	294.00 ± 26.58^{a}	50.56 ± 0.00^{a}
F-Statistics				
Treatment	1408361***	1434036***	116248.41***	649337.33***

Values (Mean ± S.E.) followed by dissimilar letters in a column are significantly different at $^{*}p \leq 0.05$, $^{**}p \leq 0.01$, $^{***}p \leq 0.001$.

Fig. 1 (D), the non-FA-treated acid mine drainage recorded 10.66 mS/ms electrical conductivity. Such high EC may be attributed to the high concentration of HMs in the water, as was also described by Ref. [44]. In this study, the result prove that FA can decrease the EC, in fact, the FA:AMD ratios both recorded 6.83 and 8.79 mS/cm, respectively, for 1:1 and 3:1. As expected, the control (0 % AMD) recorded the least electrical conductivity 5.31 mS/cm (Fig. 1 (D)). A study by Ref. [45] also showed similar results that, EC affects the solubility, availability of plant nutrients, and therefore the plant growth and yield.

3.3. Cadmium (Cd) in AMD and FA-treated AMD treatments

In this study, the control treatment (0 % AMD) showed 0.010 mg/L Cd, which was significantly ($P < 0.001$) lower compared to both FA-treated AMD (Table 1). This was markedly lower relative to that of the 1:1 and 3:1 treatment, with concentrations of 0.043 mg/L and 0.020 mg/L, respectively (Table 1). Most likely, the fly ash absorbed the cadmium ions in the acid mine drainage water. These results are supported by that shown in Refs. [35,36,46–49] who found fly ash neutralize AMD and adsorb Cd.

A growth media that contain a high concentration of cadmium is associated with low concentrations of essential nutrients such as Fe, Mn, Ca, Mg, K, and P especially in organs of plants [50–52]. On the other hand, the concentration of Cd determined in the FA-AMD solution used to irrigate the potatoes in this study was slightly below that recommended by the South African Water Quality Guidelines (DWAF) [53,54]. When available in croplands, gardens or other growth media in especially the range 0.5–10 mg/kg, Cd reduce the yields of plant yields. The concentration of that used in this study was within acceptable levels, as reported in Ref. [33]. It can be said therefore that the weight of the FA that was weight added to the AMD treatments decreased the availability of Cd in all FA-treated AMD treatments to levels that were lower than that of the untreated AMD solution (Table 1).

There exist standards that guide limits on the concentration of Cd allowable in irrigation water [54], including maximum allowable limits of other HMs in water meant for irrigation [33], however, the concentration of Cd in irrigation water should be below 3 μg/L. For this study, all the four acid mine drainage treatments had Cd concentrations that were below that stipulated in Ref. [33] standards for irrigation water. As shown in Table 1, the concentration of Cd was lower in the irrigation treatments and if used to irrigate plants, they would not cause toxicity nor pose a health risk if such plants were to be consumed by humans or animals.

It has been confirmed that long-term exposure to cadmium leads to renal dysfunction in humans [55–58]. Other researchers also confirmed that cadmium also triggers hypertension and osteoporosis and there are few cases of abnormal albuminuria, glycosuria, and blood sugar [59,60]. Cadmium is a highly toxic heavy metal that can easily accumulate in crops, leading to chronic toxicity diseases in livestock and humans [61].

Intriguingly, Cd is readily taken up by plants despite not being an essential nutrient element [62,63]. Das [59,64] note that while the exposure and uptake of Cd by plants affect their growth and physiology, however, the effects vary in trait sensitivity to Cd. Whatever the case, Cd is not essential for plants and is toxic to plants, when absorbed in high concentrations [65–67]. The Cd determined in this study suggest that the solutions can be used for irrigation.

3.4. Copper (Cu) and aluminum (Al) in AMD and FA-treated AMD treatments

Table 1 show that adding the fly ash markedly improved the Cu of the FA:AMD treatments, 50 % AMD and 75 % AMD. According to the findings by many researchers including [68–70], Cu is needed to support the growth, development, and yield of plants. Their research revealed that among other functions, Cu significantly increased the yield (tuber number per plant and mean weight of tuber increased) in potatoes. The absorption of Cu by plants, similar to that of other nutrient elements, is affected by many factors including soil pH and its concentration present in the soil thereof. It is proven that once inside the plant, Cu is sparingly immobile [71]. In this study, the results show that untreated AMD exhibited a substantially higher ($P \leq 0.001$) concentration of Cu of 1.01 mg/L compared to that of the two FA-treated AMD treatments, 1:1 and 1:3 (Table 1). The findings of [72] are similar to that shown in this study in that the results showed that adding limestone to AMD improved the adsorption of metals including Cd, Cu^{2+}, Ni, and Pb^{2+}. Furthermore,

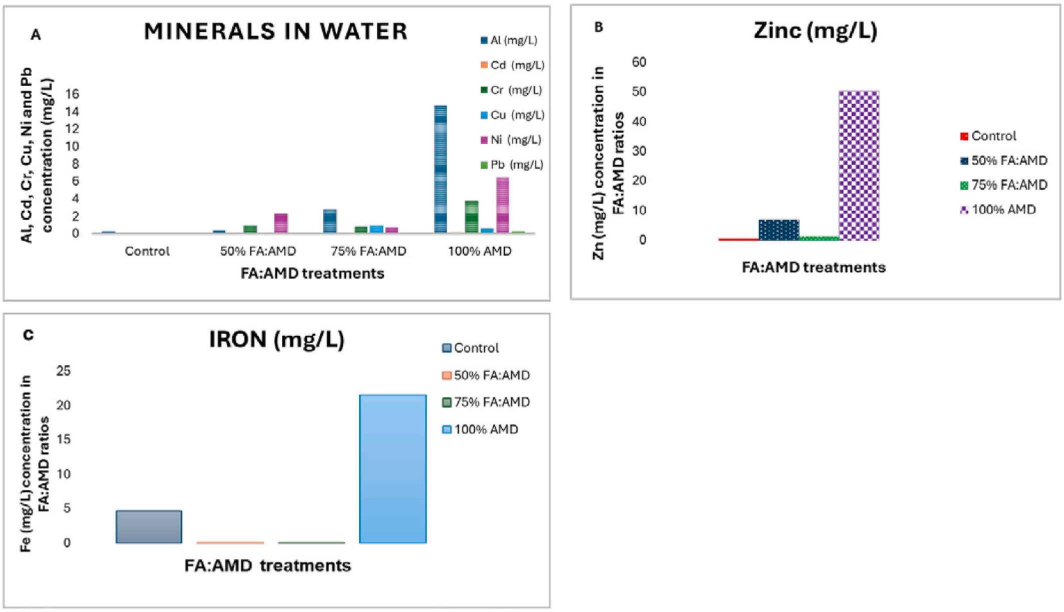

Fig. 2(A–C). The heavy metal concentration in FA: AMD ratios and untreated AMD. Figure A (Al, Cd, Cu, Ni, and Pb concentration in mg/L), B illustrates the Zn concentration in samples, and C demonstrates the Fe concentration (mg/L) in all FA: AMD treatments.

compared to untreated AMD and FA-treated AMD treatments, the control revealed the lowest concentration of Cu^{2+}. Guidelines recommend that the availability of copper ions in irrigation water should not exceed 5 mg/L and not exceed 0.2 mg/L, according to ANZECC and ARMCANZ [73] irrigation water guidelines.

All FA-treated AMD treatments used in this study had Cu^{2+} levels that were lower than that recommended in the standards, as shown by ANZECC and ARMCANZ [73], implying that this irrigation water had appropriate levels of Cu^{2+} that would not hinder plant growth or produce Cu^{2+} a build-up to unacceptable levels in the plants and substrates. Furthermore, the standard limit for copper in drinking water, according to SANS 241:2015 Edition 2, is roughly 2 mg/L. Nonetheless, it is proposed in this study that the fly ash absorbed the ions of Cu, and the treated AMD is, therefore, could be considered safe for irrigation, as shown in Table 1.

The results shown in Fig. 2 (A) show that there was a significant difference of ($P \leq 0.001$) in the concentration of Aluminium (Al) in the ameliorated and untreated acid mine drainage water. For example, treatment four showed significantly ($P \leq 0.001$) higher Al (14.73 mg/L) compared to treatments that were ameliorated with FA and control (Table 1). On the other hand, treatment 1 (0 % AMD) displayed significant ($P \leq 0.001$) lower Al (0.04 mg/L) compared to treatments. All FA-treated AMD treatments, including 1:0, had Al significantly ($P \leq 0.001$) higher Al compared to the control. According to DWS minimum [54], the standard limit for Al is approximately 300 μg/L for operational usage. In conclusion, all the FA: AMD ratios meet the minimum standard limits, which proves that the FA was able to adsorb the Al ions in the AMD sample. Lastly [74,75], note that Al ions can be adsorbed using fly ash.

3.5. Nickel (Ni) and cobalt (Co) in AMD and FA-treated AMD treatments

Irrigation with untreated AMD enhanced the Ni (6.48 mg/L) significantly ($P \leq 0.001$) compared to in potato tubers of plants irrigated with the FA-amended treatments as well as the control (Table 1). By contrast, the flesh of tubers from plants irrigated using 75 % AMD had a significantly ($P \leq 0.001$) lower Ni (0.76 mg/L) compared to that (2.26 mg/L) supplied with 50 % AMD. The flesh of tubers of the potato plants grown under irrigation with all the FA-treated AMD treatments, exhibited markedly ($P \leq 0.001$) greater Ni compared to that of plants supplied with the control. Irrigating with all the FA-treated AMD treatments significantly decreased Ni. This finding suggests that the FA adsorbed Ni ions hence its concentration was significantly lower in treatments ameliorated with FA but significantly high in the AMD not treated with FA. When present in growth media in lower concentrations, Ni can improve the growth of some plants, including oats and mustard, however, when present in high concentrations, it decreases the growth of plants [53,54]. Studies have shown that Ni is toxic to several plants, when available at concentrations ranging from 0.5 to 1.0 mg/kg [76]. Table 1 illustrates that the availability of Ni in the FA-treated AMD treatments increased with the weight of FA used to treat AMD, that is, the availability of Ni in the treatments increased as the amount of FA added to AMD was increased.

This was demonstrated by an increase in Ni in the 75 % AMD treatment due to the 75 % FA added to AMD compared to the second treatment (50 % AMD), which was mixed with 50 % FA. Irrigating potatoes with the non-FA-treated AMD solution resulted in significantly high ($P \leq 0.001$) Ni (6.49 mg/L) in tuber flesh compared with the other two FA-treated AMD treatments (50 % and 75 % AMD). It could be concluded that at low quantities of FA mixed with AMD, the Ni adsorption ability of FA was significantly ($P \leq 0.001$) lower compared to the Ni adsorption ability demonstrated by irrigation treatments not mixed with significantly large amounts of FA. This finding agrees with the conclusion of [25,77–79] who evaluated effects that FA had on the availability of HMs in AMD treated with FA and results revealed decreases in Co, Ni, Cu, and Pb in all FA:AMD treatments. Results of this study demonstrated that there was a significant difference of ($P \leq 0.001$) observed on the concentration of Co in the flesh of potato tubers grown with irrigation using ameliorated and untreated acid mine drainage water. For example, irrigating with 100 % AMD significantly ($P \leq 0.001$) enhanced Co (0.64 mg/L) in the flesh of tubers compared to that established under irrigating with FA as well as the control (Table 1). In contrast, irrigating with treatment 3 (75 % AMD) markedly decreased ($P \leq 0.001$) Co (0.002 mg/L) in tubers compared to that of plants raised under irrigation with treatment two (50 % AMD) (0.004 mg/L).

Tubers of potatoes grown under irrigation using all FA-treated AMD treatments recorded significantly greater Co compared with the control. This could be due to the mass of FA mixed with AMD. However, in South Africa, there exist no standard limits recommended for Co in water used for long-term irrigation ANZECC [17,33,34,73,80]. Khan and Khan [69,70] concluded that the concentration of Co in irrigation water can affect plants negatively, particularly, it can inhibit the germination of seeds. Also, Co present in growth media at higher concentrations adversely hinder the growth of plants. It is therefore evident that higher Co concentration of Co in growth media and/or irrigation water affects the shoot biomass, resulting in a smaller number of branches. The findings on Ni and Co are affirmed by Refs. [81–87] who found that these metals are reduced especially in irrigation solutions through the application of a neutralizing agent such as fly ash. They carried out these experiments on crops such as cabbage and barley.

It has been confirmed by Ref. [25] that higher levels of Ni, either in growth media or irrigation water, affect the uptake and translocation of macro-and micronutrients. Specifically, higher concentration of Ni tends to decrease the uptake of iron, copper, zinc, and manganese by some plant species, as stated by Refs. [53,54,78,79,88,89]. The above was the agreement with the results in the present study. According to DWAF [53], the concentration of Ni in irrigation water should be less or equal to 70 μg/L according to DWAF [53,54]. The results shown in Table 1 show high Ni levels, above the standard limits, and therefore may pose a danger in plant development due to interference with metabolism and growth.

3.6. Lead (Pb) and zinc (Zn) in AMD and FA-treated AMD treatments

Irrigating the potatoes with untreated AMD resulted in significantly ($P \leq 0.001$) higher Pb (2.37 mg/L) in the flesh of the tubers compared to that of plants irrigated with FA and control (Table 1). Tubers of plants irrigated using 75 % AMD displayed significantly ($P \leq 0.001$) lower Pb (0.001 mg/L) compared to that of plants supplied with 50 % AMD (0.004 mg/L). When all FA-treated AMD solutions were used to irrigate the potatoes, their tubers exhibited Pb that was significantly ($P \leq 0.001$) higher compared with that of plants grown under irrigation with tap water (Table 1). On the contrary, tubers of plants irrigated with all FA-treated AMD treatments displayed significantly lower Pb. This finding suggested that FA could have adsorbed Pb ions hence its concentration was significantly lower in treatments ameliorated with FA but significantly high in the AMD not treated with FA. Lead has been proven to cause negative effects on the growth of plants, retard seed germination, limit root growth as well as the development of biomass [84,85,90–92]. Most plant species including potatoes, hay, and lettuce, according to Ref. [93], can accumulate large concentration of Pb^{2+} however, such does not affect their biomass and/or or yield. The results showing the concentration of Pb in the irrigation water reveal that they were lower than that recommended, as shown in Refs. [53,54,73] regulations. Therefore, it can be said that the growth of plants irrigated using these solutions would not be hindered by the presence of this element in the soil treatment. The results shown in Fig. 2 (B) reveal significantly ($P \leq 0.01$) higher (50.56 mg/L) Zn in the untreated AMD treatment. However, there was a substantial ($P = 0.001$) difference in Zn concentration (50 % AMD). When compared to previous AMD combined with FA therapies, the 1:3 treatment, which contained 75 % FA, had a decrease in Zn. The concentration of Zn decreased as the amount of FA mixed with AMD was increased. Zinc is an essential plant nutrient that is required in small amounts [94–99]. The concentration of Zn in water is ought to be low, typically around 5 mg/L [54]. When in higher concentrations, it causes toxic responses by inducing iron deficiency [46,47]. The toxicity of Zn in plants appears to be induced at concentrations ranging from 0.3 to 10 mg/L and symptoms of Zn toxicity include iron chlorosis, reduced leaf size, necrosis of tips, and distortion of foliage [100–102]. Zinc availability in the treatments decreased to levels that were suitable for the irrigation of plants. The above findings are similar to the ones by Ref. [48] who showed that fly ash can adsorb the Zn ions in acid mine water. The growth and development of plants was therefore not negatively impacted due to the lowered levels of Zn as they were toxic at below 5 mg/L [54].

3.7. Iron (Fe) in AMD and FA-treated AMD treatments

Fig. 2 (C) show significantly high Fe (50.67 mg/L) in tubers of plants irrigated with the untreated AMD solution) compared to that of potatoes irrigated using the other two FA-treated AMD treatments (50 % and 75 %). Iron plays an essential role in physiological processes in plants such as photosynthesis and respiration [103]. Santos et al. [104] agreed that Fe is an essential element for plant growth. It could be deduced that at low quantities of FA mixed with AMD, the Fe adsorption ability of FA was significantly ($P \leq 0.001$) lower compared to the Fe adsorption ability demonstrated by irrigation treatments not mixed with significantly large amounts of FA. Tubers of the potato plants irrigated using treatment one (control) recorded 4.50 mg/L, 0.001 mg/L of Fe, 0.001 mg/L, and 50.67 mg/L for 50 % AMD ratio, 75 % AMD, and untreated AMD respectively.

This finding agrees with those of [19,20,22–24] where 3:1 FA:AMD ameliorated almost all the Fe ions in the acid mine drainage water. This conclusion on the other hand conflicts with the findings of [25], who reported that minor elements such as Fe, Ni, Cu, and Pb decreased significantly in all FA:AMD samples. The difference is that the concentration of Fe in treatment 4 (100 % AMD), exceeded the minimum standard limits as stated in the [54] of 300 μg/L in the present study. While for the 50 % AMD and 75 % AMD; the Fe ions were adsorbed, and they are safe for irrigation purposes. The treatments (two and three) which contained calcium from the fly ash had the lowest concentration of Fe because the iron was adsorbed compared to untreated acid mine water.

Table 2

Concentration of heavy metals determined in fallowed soil as well as that used to grow potatoes under irrigation with different levels of acid mine drainage (AMD) water mixed with fly ash (FA).

Cultivar	Al	Pb	Co	Ni	Cd	Sr
Fianna	2.2 ± 0.9^{a}	0.11 ± 0.00^{a}	0.09 ± 0.04^{a}	0.19 ± 0.07^{a}	0.69 ± 0.14^{a}	3.02 ± 0.79^{a}
Lady rosetta	2.2 ± 0.9^{a}	0.17 ± 0.17^{a}	0.09 ± 0.04^{a}	0.19 ± 0.07^{a}	0.68 ± 0.13^{a}	3.02 ± 0.79^{a}
Treatment						
Fallow soil	0.0 ± 0.0^{c}	0.00 ± 0.00^{a}	0.32 ± 0.00^{b}	31.83 ± 0.08^{d}	0.32 ± 0.00^{d}	0.45 ± 0.20^{d}
Control	0.6 ± 0.2^{c}	0.00 ± 0.00^{a}	0.50 ± 0.04^{b}	31.87 ± 0.08^{d}	0.50 ± 0.00^{d}	0.87 ± 0.39^{d}
50 % AMD	0.1 ± 0.0^{d}	0.01 ± 0.00^{a}	10.85 ± 0.04^{b}	54.55 ± 0.97^{c}	10.85 ± 0.06^{a}	3.20 ± 0.02^{c}
75 % AMD	4.2 ± 1.4^{a}	0.35 ± 0.33^{a}	1.04 ± 0.06^{a}	22.75 ± 0.31^{b}	1.04 ± 0.00^{c}	4.44 ± 1.20^{a}
100 % AMD	3.8 ± 1.6^{b}	0.01 ± 0.00^{a}	23.07 ± 0.06^{a}	79.29 ± 0.39^{a}	23.07 ± 0.22^{b}	3.57 ± 1.60^{b}
Interactions						
Fianna x 50 % AMD	0.1 ± 0.0^{c}	0.01 ± 0.0^{a}	0.02 ± 0.0^{b}	0.07 ± 0.0^{b}	0.98 ± 0.0^{b}	3.19 ± 0.0^{b}
Fianna x Control	0.1 ± 0.0^{c}	0.00 ± 0.0^{a}	0.01 ± 0.0^{c}	0.06 ± 0.0^{c}	0.29 ± 0.0^{c}	0.00 ± 0.0^{d}
Fianna x 75 % AMD	1.0 ± 0.0^{b}	0.01 ± 0.0^{a}	0.01 ± 0.0^{c}	0.03 ± 0.0^{d}	0.22 ± 0.0^{d}	1.74 ± 0.0^{c}
Fianna x 100 % AMD	7.5 ± 0.0^{a}	0.02 ± 0.0^{a}	0.30 ± 0.0^{a}	0.61 ± 0.0^{a}	1.27 ± 0.0^{a}	7.14 ± 0.0^{a}
Lady rosetta x 50 % AMD	0.1 ± 0.0^{c}	0.01 ± 0.0^{a}	0.02 ± 0.0^{b}	0.07 ± 0.0^{b}	0.98 ± 0.0^{b}	3.22 ± 0.0^{b}
Lady rosetta x Control	1.0 ± 0.0^{b}	0.01 ± 0.0^{a}	0.01 ± 0.0^{c}	0.03 ± 0.0^{d}	0.21 ± 0.0^{d}	1.75 ± 0.0^{c}
Lady rosetta x 75 % AMD	7.5 ± 0.0^{a}	0.69 ± 0.0^{a}	0.30 ± 0.0^{a}	0.61 ± 0.0^{a}	1.23 ± 0.0^{a}	7.13 ± 0.0^{a}
Lady rosetta x 100 % AMD	0.1 ± 0.0^{c}	0.00 ± 0.0^{a}	0.01 ± 0.0^{c}	0.06 ± 0.0^{c}	0.28 ± 0.0^{c}	0.00 ± 0.0^{d}
F-Statistics						
Cultivar (C)	0.0^{ns}	1.0^{ns}	0.6^{ns}	1.6^{ns}	0.8^{ns}	0.6^{ns}
Treatment (T)	831684.5***	1.035701ns	482518.2***	374241.9***	657.5433***	30308.07***
C x T	1443395***	1.057251ns	1007687***	833773.6***	1157.005***	90506.43***

Values (Mean ± S.E.) within a column followed by similar letters are significantly different at $^{*}p \leq 0.05$, $^{**}p \leq 0.01$, $^{***}p \leq 0.001$. NS = not significant.

3.8. Calcium (Ca) and magnesium (Mg) in AMD and FA-treated AMD treatments

The concentrations of calcium and Mg in the treatments had a similar pattern to the increased quantities of FA. Table 1 shows that the AMD that was mixed with 75 % FA resulted in Ca and Mg concentrations of 496.67 mg/L and 294.00 mg/L respectively and the treatment with a mixture of 50 % FA:AMD quantity yielded amounts of 462.47 mg/L of Ca and 20.37 mg/L of Mg. Furthermore, Table 1 illustrates that an increase in the weight of FA used to ameliorate AMD resulted in increases in Ca and Mg availability in the treatments.

This phenomenon demonstrated that FA released these elements into the irrigation treated water, however, Ca is beneficial for plant growth and development. While higher concentration of Ca improves the growth of plants, lower concentrations decrease biomass and/or yield [105,106]. Nonetheless, this finding suggested that the FA adsorbed Mg ions hence its concentration was significantly lower in treatments ameliorated with FA but significantly high in the AMD not treated with FA. The Mg concentration for all FA:AMD ratios showed a significant difference, and the concentration met the [54–73] UNFAO ANZECC, standard limits for irrigation.

The concentrations for Mg in the test irrigation media are relatively lower compared to that in DWS guidelines, for the irrigation of crops. However, long-term irrigation of plants with these treatments cannot only lead to the build-up of metals in soils but also their absorption, translocation, and accumulation in plant organs [107]. Results by Zhou et al. [49,50] confirm the current findings in that, the FA absorbed the Mg ions which resulted in acceptable levels for irrigation, this is based on the chemical analyses of water chemical constituents before post-experimentation. A study by Burstrom [108] showed that the relatively greater calcium in plants is partly as a result of uneven distribution in different soils. Hao and Papadopoulos [109] proved that a lack of biological processes adds to the difficulty of characterizing calcium activities.

It should be noted that in environmental conditions, the implicit implications of calcium content changes may be more noticeable than the direct ones [110]. In the present research, see Table 1, the concentration of Ca in FA:AMD and untreated AMD treatments was significantly higher. Tubers of plants raised with application of untreated AMD recorded 496.67 mg/L, followed by that of plants irrigated with 50.00 mg/L. The tubers of potato plants irrigated with FA:AMD ratios recorded significantly higher calcium. It should be noted that the Ca in flesh of potato tubers grown with irrigation using solutions of both ratios was increased. These results prove that FA constitutes calcium and magnesium content hence the higher concentration of calcium, as also suggested by Refs. [111–113]. Other researchers [114,115] also confirmed that calcium is essential for elongation of cells, in shoots and roots; the prevalent perception that it hinders shoot elongation is almost definitely owing to calcium inputs considerably over what is needed.

The results in Table 2 reveal that the soils, as collected after cultivating the two potato cultivars, revealed no significant differences in concentration of Al, Pb, Co, Ni, Cd, and Sr. The concentration of some elements (Si, V, Be, and Ba) was below detection limits. Of the treatments, the concentration of Al, Co, and Sr were markedly higher in soil that had been used to grow potatoes under irrigation with the 75 % AMD while Co and Ni were increased in soil that had been used to grow potatoes under irrigation with 100 % AMD. This finding proved that, as the quantity of FA to ameliorate AMD was increased large amounts of Co and Ni were adsorbed in the 75 % AMD irrigated soil, thus Co concentration in the 75 % AMD soil sample displayed the highest Co concentration compared with soils 0 % AMD (control) and untreated AMD treatment.

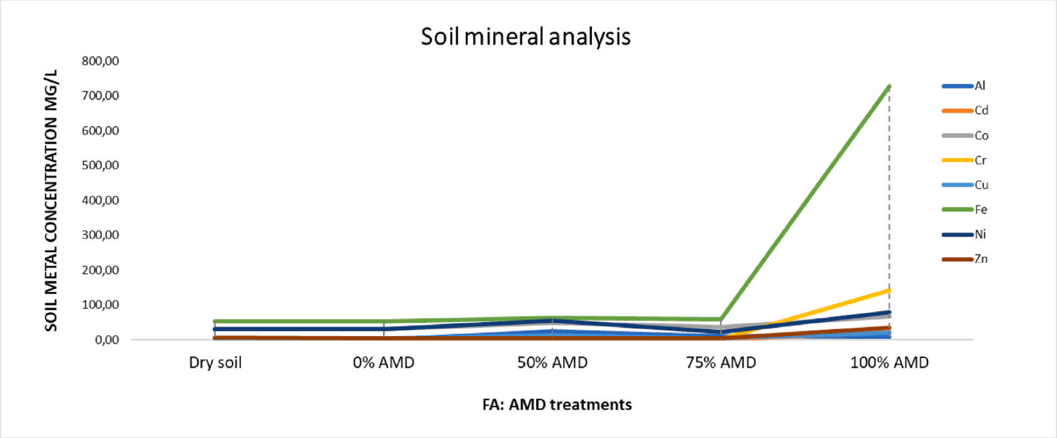

Fig. 3. Heavy metal concentration for soil samples irrigated with FA: AMD ratios and untreated AMD.

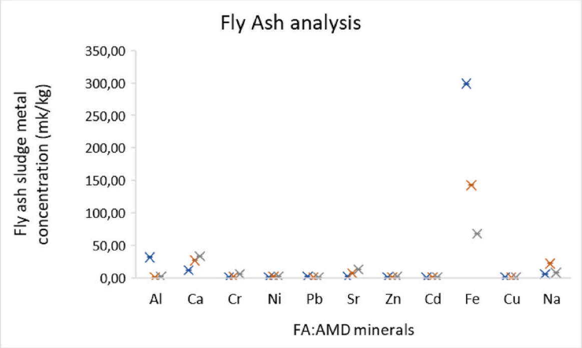

Fig. 4. Mineral analysis of fly ash and fly ash sludge.

The results shown in Table 2 can be described as meaning that, the FA successfully adsorbed Pb and Cd contained in the soil, which explain why the sample had significantly higher concentration of Pb and Cd ions compared to other soil. Cultivar × treatment interaction was significantly different. The minerals Al, Co, Ni, Cd, and Sr showed the highest difference for interactions of *Fianna* cultivar x 100 % and *Lady rosetta* x 75 % AMD (Fig. 3). There was no significant difference in all soil samples for Pb, which was below the minimum required in irrigation water, as set by UNFAO, ANZECC, and DWS, which is 5.0, 2.0, and 0.20 mg/kg respectively. However, Al, Ni, Cd, and Cr were above the minimum limits thereof.

According to research by Gad [116], cobalt increases stem and coleoptile elongation, hypocotyl hook opening, leaf disc growth, and root development in plants. In contrast to all irrigation treatments studied, soil used to establish potation under irrigation using treatment three (75 % AMD) had a slightly (P 0.001) lower Co. When comparing the availability of cobalt concentrations in all irrigation treatments to the Department of Environment and Conservation of Australias (2010), it can be noted that the content of Co in all the ratios of FA:AMD was below the standard.

The levels for Soil, Sediment, and Water were substantially ($P \leq 0.001$) higher than the recommended 0.1 mg/kg. The concentration of the test metals was in the order: Fe < Cr < Ni < Co < Zn < Cd < Cu < Al. A similar conclusion was made by Refs. [27, 117–119], who showed that application of sludge increased total metal concentration and Iron was found to be the most abundant metal in the soil.

According to Fig. 4, Zn was significantly higher in the 75 % FA:AMD sludge sample compared with the dry FA sample and 50 % AMD FA-treated AMD samples (Table 3). The behavioural pattern on the concentration of Zn in the sludge demonstrated that it decreased as the quantity of FA in the mixture was increased [120]. The presence of strontium in the sludge samples showed a positive correlation with the amount of FA mixed with AMD, which contrast the trend shown by Sr in the irrigation treatments [121]. This result indicates that as the amount of FA in the treatment was increased to ameliorate AMD, the amount of Sr and Zn adsorbed by FA increased significantly, as was also discovered by Refs. [122–124].

Table 3 show greater Co in the 75 % AMD sludge compared with other sludge samples (Table 3) and this finding concurred with the previous finding in Table 3 of this study in that the quantity of FA was increased in the solution, Co also increased. The 3:1 sludge had the highest Co compared with 50 % FA:AMD sludge sample which revealed reduced Co in the irrigation solution, which could have been due to adsorption of this element by the FA thus its high availability in the sludge.

Table 3
Heavy metal concentration on the untreated fly ash and sludge.

Treatment	Al	As	Ca	Co	Cr	Ni	Pb	Sr	Zn
Untreated FA	31.19 ± 0.12^{a}	33.64 ± 0.75^{c}	11.17 ± 0.07^{c}	0.03 ± 0.00^{c}	0.81 ± 0.00^{c}	0.76 ± 0.01^{b}	2.03 ± 0.01^{a}	1.36 ± 0.01^{c}	0.94 ± 0.00^{b}
50 % Sludge	0.63 ± 0.02^{c}	643.20 ± 37.76^{a}	26.48 ± 0.35^{b}	0.08 ± 0.00^{b}	1.25 ± 0.03^{b}	1.63 ± 0.03^{a}	0.09 ± 0.00^{c}	6.50 ± 0.00^{b}	0.80 ± 0.01^{c}
75 % Sludge	1.48 ± 0.06^{b}	409.66 ± 26.62^{b}	32.91 ± 0.80^{a}	0.11 ± 0.01^{a}	5.61 ± 0.07^{a}	1.70 ± 0.06^{a}	0.12 ± 0.00^{b}	12.83 ± 0.06^{a}	1.22 ± 0.0^{a}
F-Statistics									
Treatment	47432.63***	132.92***	484.61***	130.46***	3563.16***	183.29***	35060.84***	27766.45***	1899.53***

Essential elements

Treatment	Cd	Fe	Mg	Mn	Cu	Mo	Na
Untreated FA	0.00 ± 0.00^{c}	359.76 ± 5.61^{b}	23.96 ± 0.25^{b}	8.23 ± 0.02^{a}	0.74 ± 0.00^{a}	14.57 ± 0.46^{c}	5.71 ± 0.06^{c}
50 % Sludge	0.46 ± 0.00^{b}	410.71 ± 1.39^{a}	39.43 ± 0.32^{a}	1.08 ± 0.00^{c}	0.02 ± 0.00^{c}	52.17 ± 0.36^{b}	21.74 ± 0.19^{b}
75 % Sludge	0.69 ± 0.01^{a}	365.04 ± 0.53^{b}	42.51 ± 2.09^{a}	2.60 ± 0.02^{b}	0.05 ± 0.00^{b}	70.62 ± 0.12^{a}	7.41 ± 0.03^{b}
F-Statistics							
Treatment	9724.83***	69.89***	65.11***	66668.94***	60932.69***	6921.71***	5700.82***

Values (Mean ± S.E.) followed by dissimilar letters in a column are significantly different at $^{*}p \leq 0.05$,$^{**}p \leq 0.01$, $^{***}p \leq 0.001$, NS = not significant.

Table 4
Comparison of heavy metal concentrations means in treated and untreated irrigation treatments with UNFAO, ANZECC, and DWS maximum allowable limits of HMs for long-term irrigation.

HMs	Suggested soil limits (kg/ha)	Maximum permissible levels (mg/L)			Irrigation treatments (mg/L)			
	ANZECC[d]	**UNFAO**[a]	**ANZECC**[b]	**DWS**[c]	T1	T2	T3	T4
Parameter					**0:0**	**1:1**	**3:1**	**1:0**
Cobalt (Co)	ND	0.05	0.05	0.05	0.03	0.01	0.00	0.64
Zinc (Zn)	300	2.00	2.00	1.00	0.73	7.02	1.33	50.56
Strontium (Sr)	ND	NA	NA	NA	ND	ND	ND	ND
Nickel (Ni)	85	0.20	0.20	0.20	0.02	2.26	0.76	6.48
Molybdenum (Mo)	ND	NA	0.01	0.01	0.01	0.37	0.27	0.00
Chromium (Cr)	ND	0.10	0.10	0.10	0.04	1.01	0.86	3.78
Vanadium (V)	ND	NA	0.10	0.01	ND	ND	ND	ND
Copper (Cu)	140	0.20	0.20	0.20	0.06	0.11	0.98	0.64
Lead (Pb)	260	5.00	2.00	0.20	0.02	0.00	0.00	0.33
Cadmium (Cd)	2	0.01	0.01	0.01	0.01	0.04	0.02	0.16
Aluminum (Al)	ND	20	20		0.29	0.40	2.80	14.70
Iron (Fe)	ND	0.2	0.2		4.59	0.00	0.00	50.29

ND = Not Detected.

[a] Values for UNFAO irrigation water guidelines adopted from Strosnider et al., (2008).

[b] ANZECC irrigation water guidelines obtained from Australian Department of Environment and Conservation, Assessment levels for Soil, Sediment and Water, Version 4, Revision, (2010).

[c] DWS irrigation water guidelines obtained from the Department of Water and Sanitation, (1996) [54].

[d] ANZECC soil heavy metal guidelines obtained from Australian Department of Environment and Conservation, Assessment levels for Soil, Sediment and Water, Version 4, Revision, (2010).

The concentration of Co and Ni in the ameliorated irrigation treatments were beyond the threshold in irrigation water set by Refs. [33–35] UNFAO (2009), ANZECC (2000), and SANS 241:2015 Edition 2. The control (tap water) fly ash also showed a low concentration of HMs compared with that recommended in guidelines on irrigation water (Table 4). All other HMs for example Si, V, Be, and Ba that were available in the irrigation treatment were below detection limits, thus meeting the standards for irrigation water and could be used for short and long-term irrigation purposes. The concentration of heavy metals in tap water and irrigation treatments treated with FA about irrigation water quality guideline standards for UNFAO, ANZECC, and DWS are presented in Table 4.

4. Conclusions

In conclusion, this research has shown that adding fly ash to AMD decrease and increased the pH of the solution. In particular, when fly ash was added at lower quantities, the pH of the fly ash-AMD solution was decreased, however, when a higher quantity of fly ash was added to the AMD, it increased the pH of the solution. Irrigating potatoes with a solution made through mixing coal-generated fly ash with AMD from a gold mine markedly increased the uptake of Pb and Co while that of Ni and Cd was decreased. Lastly, the tubers of the test potato cultivars irrigated with fly ash-amended AMD exhibited significantly higher concentrations of Al, Mo, Cu, Ca, Mg, and Zn.

CRediT authorship contribution statement

Maropeng Vellry Raletsena: Writing – review & editing, Writing – original draft, Software, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Nkoana Ishmael Mongalo:** Writing – review & editing, Methodology, Investigation.

Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

[1] V. Masindi, A novel technology for neutralizing acidity and attenuating toxic chemical species from acid mine drainage using cryptocrystalline magnesite tailings, J. Water Process Eng. 10 (2016) 67–77.

[2] N. Masood, K. Hudsone-Edwards, A. Farooqi, The true cost of coal: coal mining industry and its associated environmental impacts on water resource development, Journal of Sustainable. Mining. 19 (2022) 35–149.

[3] T. Genty, B. Bussière, R. Potvin, M. Benzaazoua, G.J. Zagury, Dissolution of calcitic marble and dolomitic rock in high iron concentrated acid mine drainage: application to anoxic limestone drains, Environ. Earth Sci. 66 (2012) 2387–2401.

[4] B. Rezaie, A. Anderson, Sustainable resolutions for the environmental threat of the acid mine drainage, Sci. Total Environ. 717 (2020) 1–9.

[5] B.S. Acharya, G. Kharel, Acid mine drainage from coal mining in the United States–An overview, J. Hydrol. 588 (2020) 1–14.

[6] A. Akcil, S. Koldas, Acid Mine Drainage (AMD): causes, treatment, and case studies, J. Clean. Prod. 14 (12–13) (2006) 1139–1145.

[7] P.K. Sahoo, K. Kim, S.M. Equeenuddin, M.A. Powell, Current approaches for mitigating acid mine drainage, Rev. Environ. Contam. Toxicol. 226 (2013) 1–32. *Volume*.

[8] B.C. Egboka, G.I. Nwankwor, I.P. Orajaka, A.O. Ejiofor, Principles and problems of environmental pollution of groundwater resources with case examples from developing countries, Environ. Health Perspect. 83 (1989) 39–68.

[9] D.B. Johnson, K.B. Hallberg, Acid mine drainage remediation options: a review, Sci. Total Environ. 338 (1–2) (2005) 3–14.

[10] A. Luptakova, M. Kusnierova, Bioremediation of acid mine drainage contaminated by SRB, Hydrometallurgy 77 (1–2) (2005) 97–102.

[11] S. Kumari, G. Udayabhanu, B. Prasad, Studies on the environmental impact of acid mine drainage generation and its treatment: an appraisal, Indian J. Environ. Protect. 30 (11) (2010) 953–967.

[12] G.S. Simate, S. Ndlovu, Acid mine drainage: challenges and opportunities, J. Environ. Chem. Eng. 2 (3) (2014) 1785–1803.

[13] A. Jaiswal, A. Verma, P. Jaiswal, Detrimental effects of HMs in soil, plants, and aquatic ecosystems, and humans, J. Environ. Pathol. Toxicol. Oncol. 37 (3) (2018) 183–197.

[14] F. Maya, C.P. Cabello, R.M. Frizzarin, J.M. Estela, G.T. Palomino, V. Cerda, Magnetic solid-phase extraction using metal-organic frameworks (MOFs) and their derived carbons, TrAC, Trends Anal. Chem. 90 (2017) 142–152.

[15] M. Jopony, F. Tongkul, Acid mine drainage at mamut copper mine, Sabah, Malaysia, Borneo Science 24 (2009) 83–94.

[16] K. Naicker, E. Cukrowska, T.S. McCarthy, Acid mine drainage arising from gold mining activity in Johannesburg, South Africa Journal of Environmental Pollution 122 (2003) 29–40.

[17] S. Hendriks, Food security in South Africa: status quo and policy imperatives, Agrekon 53 (2) (2014) 1–24.

[18] WHO, WHO Multicountry Study on Improving Household Food and Nutrition Security for the Vulnerable: South Africa: a Qualitative Study on Food Security and Caring Patterns of Vulnerable Young Children in South Africa (No. WHO/NHD/00.4), World Health Organization, 2000.

[19] S. Drimie, S. Ruysenaar, The integrated food security strategy of South Africa: an institutional analysis, Agrekon 49 (3) (2010) 316–337.

[20] M.V. Nemutanzhela, D.M. Modise, K.J. Siyoko, S.A. Kanu, Assessment of growth, tuber elemental composition, stomatal conductance, and chlorophyll content of two potato cultivars under irrigation with fly ash-treated acid mine drainage, Am. J. Potato Res. 94 (2017) 367–378.

[21] R. Munyai, M.V. Raletsena, D.M. Modise, LC-MS based metabolomics analysis of potato (*Solanum tuberosum* L.) cultivars irrigated with quicklime treated acid mine drainage water, Metabolites 12 (3) (2022) 221.

[22] S. Takahashi, Y. Kagami, K. Hanaoka, T. Terai, T. Komatsu, T. Ueno, M. Uchiyama, I. Koyama-Honda, N. Mizushima, T. Taguchi, H. Arai, Development of a series of practical fluorescent chemical tools to measure pH values in living samples, J. Am. Chem. Soc. 140 (18) (2018) 5925–5933.

[23] M.V. Raletsena, S. Mdlalose, O.S. Bodede, H.A. Assress, A.A. Woldesemayat, D.M. Modise, 1H-NMR and LC-MS based metabolomics analysis of potato (*Solanum tuberosum* L.) cultivars irrigated with fly ash treated acid mine drainage, Molecules 27 (4) (2022) 1187.

[24] M.V. Raletsena, R. Munyai, N.I. Mongalo, Accumulation of heavy metals, yield, and nutritional composition of potato (*Solanum tuberosum* L.) cultivars irrigated with fly-ash-treated acid mine drainage, Sustainability 15 (2) (2023) 1327.

[25] M.V. Raletsena, N.I. Mongalo, R. Munyai, Heavy metal analysis and health risk assessment of potato (*Solanum tuberosum* L.) cultivars irrigated with fly ash-treated acid mine drainage, Horticulturae 9 (2) (2023) 192.

[26] M. Basu, M. Pande, P.B.S. Bhadoria, S.C. Mahapatra, Potential fly-ash utilization in agriculture: a global review, Prog. Nat. Sci. 19 (2008) 1173–1186.

[27] W. Stumm, G.F. Lee, Oxygenation of ferrous iron, Ind. Eng. Chem. 53 (2) (1961) 143–146.

[28] T. Matsi, V.Z. Keramidas, Fly ash application on two acid soils and its effect on soil salinity, pH, B, P, and on ryegrass growth and composition, J. Environ. Pollut. 104 (1999) 107–112.

[29] E.M. Hafez, H.S. Osman, S.M. Gowayed, S.A. Okasha, A.E.D. Omara, R. Sami, A. El-Monem, M. Ahmed, A. El-Razek, A. Usama, Minimizing the adverse impacts of water deficit and soil salinity on maize growth and productivity in response to the application of plant growth-promoting rhizobacteria and silica nanoparticles, Agronomy 11 (4) (2021) 676–699.

[30] L. Sivachandiran, A. Khacef, Enhanced seed germination and plant growth by atmospheric pressure cold air plasma: combined effect of seed and water treatment, RSC Adv. 7 (4) (2017) 1822–1832.

[31] N. Fageria, F. Zimmermann, Influence of pH on growth and nutrient uptake by crop species in an Oxisol, Commun. Soil Sci. Plant Anal. 29 (1998) 2675–2682.

[32] R. Nawaz, P. Parkpian, M. Arshad, F. Ahmad, H. Garivait, A.S. Ali, Mobilization and leaching of trace elements (Fe, Al, and Mn) in agricultural soils as affected by simulated acid rain, Asian J. Chem. 25 (2013) 9891–9897.

[33] V. Gauthier, B. Barbeau, G. Tremblay, R. Millette, A.M. Bernier, Impact of raw water turbidity fluctuations on drinking water quality in a distribution system, J. Environ. Eng. Sci. 2 (4) (2003) 281–291.

[34] SANS 241-1:2015; Edition 2 Drinking Water, SABS Standards Division, Pretoria, South Africa, 2015, p. 2.

[35] SANS 241-2:2015; Edition 2 Drinking Water Part 2: Application of SANS, SABS Standards Division, Pretoria, South Africa, 2015, p. 241, 1.

[36] R.K. Sharma, M. Agrawal, Biological effects of HMs: an overview, J. Environ. Biol. 26 (2) (2005) 301–313.

[37] R.K. Sharma, A. Puri, Y. Monga, A. Adholeya, Newly modified silica-based magnetically driven nano: a sustainable and versatile platform for efficient and selective recovery of cadmium from water and fly-ash ameliorated soil, Separ. Purif. Technol. 127 (2014) 121–130.

[38] M. Spadoni, M. Voltaggio, E. Sacchi, R. Sanam, P.R. Pujari, C. Padmakar, P.K. Labhasetwar, S.R. Wate, Impact of the disposal and re-use of fly ash on water quality: the case of the Koradi and Khaperkheda thermal power plants (Maharashtra, India), Sci. Total Environ. 479 (2014) 159–170.

[39] S.F.A. Shah, A. Aftab, N. Soomro, M.S. Nawaz, K. Vafai, Wastewater treatment bed of coal fly ash for dyes and pigments industry, Pakistan Journal of Analytical & Environmental Chemistry 16 (2) (2015) 48–56.

[40] T. Shah, F. Munsif, R. D'amato, L. Nie, Lead toxicity-induced phytotoxic impacts on rapeseed and clover can be lowered by biofilm-forming tolerant lead-tolerant bacteria, Chemosphere 246 (2020) 125766–125777.

[41] Y. Sun, Z. Liu, P. Fatehi, Treating thermomechanical pulping wastewater with biomass-based fly ash: modeling and experimental studies, Separ. Purif. Technol. 183 (2017) 6–116.

[42] R.D. Doyle, R.M. Smart, Impacts of water column turbidity on the survival and growth of Vallisneria Americana winter buds and seedlings, Lake Reservoir Manag. 17 (1) (2001) 17–28.

[43] J. Miranda, G. Krishnakumar, Microalgal diversity about the physicochemical parameters of some Industrial sites in Mangalore, South India, Environ. Monit. Assess. 187 (11) (2015) 1–25.

[44] S.B. Jonnalagadda, G. Mhere, Water quality of the Odzi River in the eastern highlands of Zimbabwe, Water Res. 35 (10) (2001) 2371–2376.

[45] A. Christou, E. Eliadou, C. Michael, E. Hapeshi, D. Fatta-Kassinos, Assessment of long-term wastewater irrigation impacts on the soil geochemical properties and the bioaccumulation of HMs to the agricultural products, Environ. Monit. Assess. 186 (8) (2014) 4857–4870.

[46] U.C. Samarakoon, P.A. Weerasinghe, W.A.P. Weerakkody, Effect of electrical conductivity [EC] of the nutrient solution on nutrient uptake, growth, and yield of leaf lettuce (*Lactuca sativa* L.) in stationary culture, Tropical Agricultural Research 18 (2006) 1–30.

[47] M. Rizwan, S. Ali, M. Adrees, H. Rizvi, M. Zia-ur-Rehman, F. Hannan, M.F. Qayyum, F. Hafeez, Y.S. Ok, Cadmium stress in rice: toxic effects, tolerance mechanisms, and management: a critical review, Environ. Sci. Pollut. Control Ser. 23 (18) (2016) 17859–17879.

[48] M. Rizwan, S. Ali, B. Ali, M. Adrees, M. Arshad, A. Hussain, M.Z. ur Rehman, A.A. Waris, Zinc and iron oxide nanoparticles improved plant growth and reduced oxidative stress and cadmium concentration in wheat, Chemosphere 214 (2019) 269–277.

[49] F. Zhou, Y. Liu, H. Guo, Application of multivariate statistical methods to water quality assessment of the watercourses in Northwestern New Territories, Hong Kong, Environ. Monit. Assess. 132 (1–3) (2007) 1–13.

[50] W. Zhou, X. Lu, C. Qi, M. Yang, The utilization of ultrasonic treatment to improve the soil amelioration property of coal fly ash, J. Environ. Manag. 276 (2020) 111311–111322.

[51] H. Obata, M. Umebayashi, Effects of cadmium on mineral nutrient concentrations in plants differing intolerance for cadmium, J. Plant Nutr. 20 (1) (1997) 97–105.

[52] N.A. Maier, M.J. McLaughlin, M. Heap, M. Butt, M.K. Smart, Effect of nitrogen source and calcitic lime on soil pH and potato yield, leaf chemical composition, and tuber cadmium concentrations, J. Plant Nutr. 25 (3) (2002) 523–544.

[53] N. Elloumi, F. Ben, A. Rhouma, B. Ben, I. Mezghani, M. Boukhris, Cadmium-induced growth inhibition and alteration of biochemical parameters in almond seedlings grown in solution culture, Acta Physiol. Plant. 29 (2007) 57–62.

[54] Department of Water Affairs and Forestry (DWAF), Waste generation in South Africa, Water Quality Management Series 432 (2001). Regulation Gazette No. 7079,Pretoria.

[55] Department of Water Affairs and Forestry, South African Water Quality Guideline, in: Agricultural Use: Irrigation, vol. 4, Government Press, Pretoria, South Africa, 1996.

[56] C. Shiwen, Y. Lin, H. Zhineng, Z. Xianzu, Y. Zhaolu, X. Huidong, L. Yuanrong, J. Rongdi, Z. Wenhua, Z. Fangyuan, Cadmium exposure and health effects among residents in an irrigation area with ore dressing wastewater, Sci. Total Environ. 90 (1990) 67–73.

[57] M. Greger, E. Brammer, S. Lindberg, G. Larsson, J. Idestam-Almquist, Uptake and physiological effects of cadmium in sugar beet (*Beta vulgaris*) related to mineral provision, J. Exp. Bot. 42 (6) (1991) 729–737.

[58] S. Cai, L. Yue, Q. Shang, G. Nordberg, Cadmium exposure among residents in an area contaminated by irrigation water in China, Bull. World Health Organ. 73 (3) (1995) 359–367.

[59] D. Mani, B. Sharma, C. Kumar, S. Balak, Cadmium and lead bioaccumulation during growth stages alter sugar and vitamin C content in dietary vegetables. Proceedings of the National Academy of Sciences, India Section B, Biol. Sci. 82 (4) (2012) 477–488.

[60] P. Hu, Z. Li, C. Yuan, Y. Ouyang, L. Zhou, J. Huang, Y. Huang, Y. Luo, P. Christie, L. Wu, Effect of water management on cadmium and arsenic accumulation by rice (Oryza sativa L.) with different metal accumulation capacities, J. Soils Sediments 13 (5) (2013) 916–924.

[61] S. Satarug, J.R. Baker, S. Urbenjapol, M. Haswell-Elkins, P.E.B. Reilly, D.J. Williams, M.R. Moore, A global perspective on cadmium pollution and toxicity in the non-occupationally exposed population, Journal of Toxicology Letters 137 (2003) 65–83.

[62] T. Arao, S. Ishikawa, M. Murakami, K. Abe, Y. Maejima, T. Makino, Heavy metal contamination of agricultural soil and countermeasures in Japan, Paddy and Water Environment Journal 8 (2010) 247–257.

[63] K. Ahmad, A. Ejaz, M. Azam, Z.I. Khan, M. Ashraf, F. Al-Qurainy, A. Fardous, S. Gondal, A.R. Bayat, E.E. Valeem, Lead, cadmium, and chromium contents of canola irrigated with sewage water, Pakistan J. Bot. 43 (2) (2011) 1403–1410.

[64] N. Sarwar, S.S. Malhi, M.H. Zia, A. Naeem, S. Bibi, G. Farid, Role of mineral nutrition in minimizing cadmium accumulation by plants, J. Sci. Food Agric. 90 (6) (2010) 925–937.

[65] P. Das, S. Samantaray, G.R. Rout, Studies on cadmium toxicity in plants: a review, Environ. Pollut. 98 (1) (1997) 29–36.

[66] M.I. Rubio, I. Escrig, C. Martinez-Cortina, F.J. Lopez-Benet, A. Sanz, Cadmium and nickel accumulation in rice plants. Effects on mineral nutrition and possible interactions of abscisic and gibberellic acids, Plant Growth Regul. 14 (2) (1994) 151–157.

[67] M.D. Mingorance, B. Valdés, S.R. Olivioa, Strategies of heavy metal uptake by plants growing under industrial emissions, Environ. Int. 33 (2007) 514–520.

[68] F.U. Haider, C. Liqun, J.A. Coulter, S.A. Cheema, J. Wu, R. Zhang, M. Wenjun, M. Farooq, Cadmium toxicity in plants: impacts and remediation strategies, Ecotoxicol. Environ. Saf. 211 (2021) 111887–111909.

[69] K.M. Al-Jobori, S.A. Al-Hadithy, Response of potato (*Solanum tuberosum* L.) to foliar application of iron, manganese, copper, and zinc, Intl. J. Agric. Crop Sci. 7 (7) (2014) 358–363.

[70] M.R. Khan, M.M. Khan, Effect of varying concentrations of nickel and cobalt on the plant growth and yield of chickpea, Australian Journal of Basic and Applied Sciences 4 (6) (2010) 1036–1046.

[71] Z.I. Khan, K. Ahmad, S. Yasmeen, N.A. Akram, M. Ashraf, N. Mehmood, Potential health risk assessment of potato (*Solanum tuberosum* L.) grown on metal-contaminated soils in the central zone of Punjab, Pakistan, Chemosphere 166 (2017) 157–162.

[72] A.H. AbdelGadir, M.A. Errebhi, H.M. Al-Sarhan, M. Ibrahim, The effect of different levels of additional potassium on yield and industrial qualities of potato (*Solanum tuberosum* L.) in an irrigated arid region, Am. J. Potato Res. 80 (3) (2003) 219–222.

[73] J. Xu, L. Yang, Z. Wang, G. Dong, J. Huang, Y. Wang, Toxicity of copper on rice growth and accumulation of copper in rice grain in copper contaminated soil, Chemosphere 62 (4) (2006) 602–607.

[74] ANZECC, Australian and New Zealand guidelines for irrigation water guidelines obtained from the Australian Department of Environment and Conservation, assessment levels for soil, Sediment and Water, Version 4, Revision (2000) 2010.

[75] G.F. Liebig, A.P. Vanselow, H.D. Chapman, Effects of aluminum on copper toxicity, as revealed by solution-culture and spectrographic studies of citrus, Soil Sci. 53 (5) (1942) 341–352.

[76] S. Silambarasan, P. Logeswari, P. Cornejo, J. Abraham, A. Valentine, Simultaneous mitigation of aluminum, salinity, and drought stress in Lactuca sativa growth via formulated plant growth-promoting Rhodotorula mucilaginosa CAM4, Ecotoxicol. Environ. Saf. 180 (2019) 63–72.

[77] M. Cempel, G. Nikel, Nickel: a review of its sources and environmental toxicology, Polish Journal of Environmental Science 15 (2005) 375–382.

[78] J. Moya, R. Ros, I. Picazo, Influence of cadmium and nickel on growth, net photosynthesis, and carbohydrate distribution in rice plants, Photosynth. Res. 36 (2) (1993) 75–80.

[79] W.M. Gitari, V.S. Somerset, L.F. Petrik, D. Key, E. Iwuoha, C. Okujeni, Treatment of acid mine drainage with fly ash: removal of major, minor elements, SO_4, and utilization of the solid residues for wastewater treatment, in: International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, 2003, pp. 1–23.

[80] W.M. Gitari, L.F. Petrik, D.L. Key, C. Okujeni, Partitioning of major and trace inorganic contaminants in fly ash acid mine drainage derived solid residues, Int. J. Environ. Sci. Technol. 7 (2010) 519–534.

[81] WHO, Trace Elements in Human Nutrition and Health, World Health Organization, Geneva, 1996.

[82] A.J. Aller, J.L. Bernal, M.J.D. Nozal, L. Deban, Effects of selected trace elements on plant growth, J. Sci. Food Agric. 51 (4) (1990) 447–479.

[83] S. Palit, A. Sharma, G. Talukder, Effects of cobalt on plants, Bot. Rev. 60 (2) (1994) 149–181.

[84] I.M. Zeid, Responses of Phaseolus vulgaris chromium and cobalt treatments, Biol. Plantarum 44 (1) (2001) 111–115.

[85] N. Pandey, C.P. Sharma, Effect of HMs Co^{2+}, $Ni^{2+,}$ and Cd^{2+} on growth and metabolism of cabbage, Plant Sci. 163 (4) (2002) 753–758.

[86] S. Pandey, K. Gupta, A.K. Mukherjee, Impact of cadmium and lead on Catharanthus roseus-A phytoremediation study, J. Environ. Biol. 28 (3) (2007) 655–663.

[87] S.D. Polishchuk, A.A. Nazarova, M.V. Kutskir, D.G. Churilov, Y.N. Ivanycheva, V.A. Kiryshin, G.I. Churilov, Ecologic-biological effects of cobalt, cuprum, copper oxide nano-powders, and humic acids on wheat seeds, Mod. Appl. Sci. 9 (6) (2015) 354–366.

[88] J.L. Lwalaba, G. Zvogbo, M. Mulembo, M. Mundende, G. Zhang, The effect of cobalt stress on growth and physiological traits and its association with cobalt accumulation in barley genotypes differing in cobalt tolerance, J. Plant Nutr. 40 (15) (2017) 2192–2199.

[89] R. Shukla, Nickel level and toxicity and metabolism of potato, Int. J. Veg. Sci. 16 (2) (2010) 160–166.

[90] R. Shukla, R. Gopal, Excess nickel alters the growth, metabolism, and translocation of certain nutrients in potatoes, J. Plant Nutr. 32 (6) (2009) 1005–1014.

[91] X. Zhang, L. Yang, Y. Li, H. Li, W. Wang, B. Ye, Impacts of lead/zinc mining and smelting on the environment and human health in China, Environ. Monit. Assess. 184 (4) (2012) 2261–2273.

[92] F. Aref, Concentration and uptake of zinc and boron in corn leaf as affected by zinc sulfate and boric acid fertilizers in deficient soil, Life Sci. J. 8 (2011) 26–32.

[93] M. Shabaan, H.N. Asghar, M.J. Akhtar, Q. Ali, M. Ejaz, Role of plant growth-promoting rhizobacteria in the alleviation of lead toxicity to *Pisum sativum* L, Int. J. Phytoremediation 11 (2020) 1–9.

[94] M. Saleem, H.N. Asghar, Z.A. Zahir, M. Shahid, Evaluation of lead tolerant plant growth-promoting rhizobacteria for plant growth and phytoremediation in lead contamination, Rev. Int. Contam. Ambient. 35 (4) (2019) 999–1009.

[95] B.J. Eghball, J.E. Wienhold, J.E. Gilley, R.A. Eigenberg, Mineralization of manure nutrients, J. Soil Water Conserv. 53 (2002) 470–473.

[96] P.A. Wani, M.S. Khan, A. Zaidi, Impact of heavy metal toxicity on plant growth, symbiosis, seed yield, and nitrogen and metal uptake in chickpea, Aust. J. Exp. Agric. 47 (6) (2007) 712–720.

[97] P.A. Wani, M.S. Khan, A. Zaidi, Impact of zinc-tolerant plant growth-promoting rhizobacteria on lentils grown in zinc-amended soil, Agron. Sustain. Dev. 28 (3) (2008) 449–455.
[98] N. Garg, H. Kaur, Impact of cadmium-zinc interactions on metal uptake, translocation, and yield in pigeon pea genotypes colonized by arbuscular mycorrhizal fungi, J. Plant Nutr. 36 (2013) 67–90.
[99] K. Rudani, V. Patel, P. Kalavati, The importance of zinc in plant growth—a review, International Research Journal of Natural and Applied Sciences 5 (2) (2018) 38–48.
[100] D. Jain, R. Kour, A.A. Bhojiya, R.H. Meena, A. Singh, S.R. Mohanty, D. Rajpurohit, K.D. Ameta, Zinc-tolerant plant growth-promoting bacteria alleviate phytotoxic effects of zinc on maize through zinc immobilization, Sci. Rep. 10 (1) (2020) 1–13.
[101] M. Gawęda, Changes in the contents of some carbohydrates in vegetables cumulating lead, Journal of Pollution and Environmental Studies 16 (1) (2007) 57–65.
[102] R. John, P. Ahmad, K. Gadgil, S. Sharma, Heavy metal toxicity: effect on plant growth, biochemical parameters and metal accumulation by *Brassica juncea* L, Int. J. Plant Prod. 3 (3) (2009) 65–76.
[103] I. Naz, H. Ahmad, S.N. Khokhar, K. Khan, A.H. Shah, Impact of zinc solubilizing bacteria on zinc contents of wheat, Am. Euras. Journal of Agriculture and Environmental Sciences 16 (2016) 449–454.
[104] Q. Liu, Q. Guo, S. Akbar, Y. Zhi, A. El Tahchy, M. Mitchell, Z. Li, P. Shrestha, T. Vanhercke, J.P. Ral, G. Liang, Genetic enhancement of oil content in potato tuber (*Solanum tuberosum* L.) through an integrated metabolic engineering strategy, Plant Biotechnol. J. 15 (1) (2017) 56–67.
[105] C.S. Santos, M. Roriz, S.M. Carvalho, M.W. Vasconcelos, Iron partitioning at an early growth stage impacts iron deficiency response in soybean plants (*Glycine max* L.), Front. Plant Sci. 6 (2015) 325–337.
[106] K.R. Dunbar, M.J. Mclaughlin, R.J. Reid, The uptake and partitioning of cadmium in two cultivars of potato (*Solanum tuberosum* L.), J. Exp. Bot. 54 (381) (2003) 349–354.
[107] D.M. Wheeler, D.C. Edmeades, Effect of varying solution calcium or magnesium concentrations in the presence or absence of aluminum on yield and plant calcium or magnesium concentrations in wheat, J. Plant Nutr. 18 (10) (1995) 2229–2245.
[108] A. Gransee, H. Führs, Magnesium mobility in soils is a challenge for soil and plant analysis, magnesium fertilization, and root uptake under adverse growth conditions, Plant Soil 368 (1) (2013) 5–21.
[109] H.G. Burstrom, Calcium and plant growth, Biol. Rev. 43 (3) (1968) 287–316.
[110] X. Hao, A.P. Papadopoulos, Effects of calcium and magnesium on plant growth, biomass partitioning, and fruit yield of winter greenhouse tomato, Hortic. Sci. (HORTSCI) 39 (3) (2004) 512–515.
[111] R.J. Reid, F.A. Smith, The limits of sodium/calcium interactions in plant growth, Funct. Plant Biol. 27 (7) (2000) 709–715.
[112] J.L. Brewbaker, B.H. Kwack, The essential role of calcium ion in pollen germination and pollen tube growth, Am. J. Bot. 50 (9) (1963) 859–865.
[113] J.J. Bornman, L. Bornman, R.O. Barnard, The effects of calcium carbonate and calcium hydroxide on plant growth during overcoming, Soil Sci. 163 (6) (1998) 498–507.
[114] A.L. Tuna, C. Kaya, M. Ashraf, H. Altunlu, I. Yokas, B. Yagmur, The effects of calcium sulfate on growth, membrane stability, and nutrient uptake of tomato plants grown under salt stress, Environ. Exp. Bot. 59 (2) (2007) 173–178.
[115] H.A. Aziz, N.M. Adlan, K. Ariffin, HMs (Cd, Pb, Ni, Cu and Cr (III) removal from water in Malaysia: post-treatment by high-quality limestone, Bioresour. Technol. 99 (2007) 1578–1583.
[116] D. Huang, X. Gong, Y. Liu, G. Zeng, C. Lai, H. Bashir, L. Zhou, D. Wang, P. Xu, M. Cheng, J. Wan, Effects of calcium at toxic concentrations of cadmium in plants, Planta 245 (5) (2017) 863–873.
[117] N. Gad, Role and importance of Co nutrition on groundnut (*Arachis hypogaea*) production, World Appl. Sci. J. 20 (2012) 359–367.
[118] Z. Mian, T. Ahmed, Cd, Cu, Ni, and Pb accumulation in soils and plants of river Soan near an industrial area, Model town, Humak, Islamabad, in: J. Hanif, M. I. Hanif (Eds.), Proc. Nat. Symp, vols. 24–26, Modern Trends in Contemporary Chemistry on Environmental Pollution, 1997, pp. 313–317.
[119] A. Mireles, C. Solıs, E. Andrade, M. Lagunas-Solar, C. Pina, R.G. Flocchini, Heavy metal accumulation in plants and soil irrigated with wastewater from Mexico City, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 219 (2004) 187–190.
[120] S. Manzoor, M.H. Shah, N. Shaheen, S.R. Tariq, A. Khaliq, M. Jaffar, Distribution of heavy toxic metals in industrial effluents and relevant soils from selected oil and ghee industries in Hattar, J. Chem. Soc. Pakistan 26 (4) (2004) 429–435.
[121] B.S. Connel, M. Cox, I. Singer, Nickel and chromium in brunner, in: F, J.W. Coburn (Eds.), Disorders of Minerals Metabolism, vol. 15, Academic Press, 1984, pp. 472–532.
[122] M.S. Butt, K. Sharif, B.E. Bajwa, A. Aziz, Hazardous effects of sewage water on the environment; focus on HMs and chemical composition of soil and vegetables, Manag. Environ. Qual. Int. J. 16 (2005) 338–346.
[123] L.Y. Bai, X.B. Zeng, L.F. Li, P.E.N. Chang, S.H. Li, Effects of land use on heavy metal accumulation in soils and sources analysis, Agric. Sci. China 9 (11) (2010) 1650–1658.
[124] M. Wang, R. Liu, W. Chen, C. Peng, B. Markert, Effects of urbanization on heavy metal accumulation in surface soils, Beijing, J. Environ. Sci. 64 (2018) 328–334.