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# Liming Characteristics of a High-Calcium, Dry Flue Gas Desulfurization By-product and its Effects on Runoff Water Quality

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# Liming Characteristics of a High-Calcium, Dry Flue Gas Desulfurization By-product and its Effects on Runoff Water Quality

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Crop, Soil, and Environmental Science

by

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University of Arkansas
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This thesis is approved for recommendation to the Graduate Council.

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# Abstract

In 2013, only 37% of the 32 million Mg of flue gas desulfurization (FGD) by-products generated in the United States were reused beneficially. If FGD by-products could be used as a beneficial soil amendment, millions of megagrams may be diverted away from surface impoundments and landfills. The purpose of this research was to identify the liming characteristics of a high-Ca dry FGD (DFGD) by-product in comparison to a Class-C fly ash (FA) and reagent-grade $CaCO_3$, and to evaluate the effects of land application to a managed grassland on runoff, plant, and soil quality. Liming characteristics were determined by measuring the calcium carbonate equivalence (CCE), degree of fineness (DOF) and calculating the effective neutralizing value (ENV). The DFGD by-product was land-applied to a managed grassland in May 2015 and runoff, plant, and soil samples were collected over a 12-mo period. The ENV of 79.4% for the DFGD by-product was lower ($P < 0.05$) than that of reagent-grade $CaCO_3$, but similar to the ENV of commercially available liming materials. The DFGD by-product was as effective as reagent-grade $CaCO_3$ at raising soil pH when incubated at a rate equivalent to the soil's lime requirement and more effective than reagent-grade $CaCO_3$ when incubated at 2x the soil's lime requirement. Seasonal flow-weighted mean Ni concentrations and seasonal V loads were 44.5 and 86.9%, respectively, greater ($P < 0.05$) when amended compared to the unamended control during at least one season. One month after application, aboveground dry matter and tissue As, Se, Cr, Co, Hg, V, and U concentrations were between 53 and 471% greater in the amended treatment than in the unamended control. Trace element concentrations decreased to pre-application levels within six months. Results demonstrated that the high-Ca DFGD by-product used in this study is a viable liming material and has minimal effects on runoff and plant quality when applied at a rate of 9 Mg $ha^{-1}$. Consequently, land application of high-Ca DFGD by-products may be a viable alternative to current disposal methods.

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I would like to express my gratitude for the support my parents, Deborah Burgess and Richard Conforti, have provided throughout my life. Words cannot express how appreciative I am for the love, support, and sacrifices of my parents.

# Dedication

This thesis is dedicated to the friends and family who have supported me through this endeavor

In memory of

Richard E. and Richard L. Conforti

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Burgess-Conforti, J.R., D.M Miller, K.R. Brye, L.S Wood, and E.D. Pollock. 2016. Liming characteristics of a high-Calcium dry flue gas desulfurization by-product and a Class-C fly ash. J. Environ. Prot. 7:1592-1604.

# Introduction

Over 3,936 billion kilowatt-hours of electricity were produced in the United States in 2014, with approximately 3,724 billion kilowatt-hours being consumed by residential, commercial, industrial, and transportation industries (USEIA, 2015a). As a result of population growth, electricity generation is estimated to increase at a rate 0.8% year$^{-1}$ from 3,936 billion kilowatt-hours in 2014 to 4,797 billion kilowatt-hours in 2040 (USEIA, 2015b). Of the 3,936 billion kilowatt-hours of electricity generated by the United States in 2014, 39% were generated by coal-fired power plants. Although natural gas is expected to eventually surpass coal as the primary fossil fuel source of electrical power generation in the United States, the broad availability and low material cost of coal will cause coal to continue to be a major source of energy for the next 35 years.

In 2008, it was estimated that more than 123 million Mg of coal combustion by-products (CCBs) were produced, which made coal combustion the second largest producer of waste behind municipal solid waste (Luther, 2010). In 2007, only 40% of the CCBs generated in the United States were used beneficially, which left 68 million Mg to be disposed of in landfills or settling ponds (ACAA, 2008). The need for alternative storage and disposal of CCBs came to the public’s attention in 2007 when approximately 0.9 billion Mg of coal-ash slurry were released from the Kingston Fossil Plant in Roane County, Tennessee after a surface impoundment pond was breached. The large quantity of ash released resulted in fish kills and soil and water contamination that will take decades and millions of dollars to remediate. However, the chemical and physical properties of some CCBs provide potential for use in agronomic applications.

The primary beneficial use of CCBs in agriculture is utilization as a liming material to mitigate soil acidity. Acidic soils can increase solubility of Al and Mn, which can severely impair root function and growth, decrease solubility of essential plant nutrients, and increase solubility of potentially phytotoxic trace elements. Fly ashes originating from lignite and subbituminous coal are rich in calcium oxide (CaO) and may also contain other alkalizing agents capable of raising soil pH. Flue-gas-desulfurization (FGD) by-products are enriched with calcium sorbents like calcium hydroxide [$Ca(OH)_2$] that are used in the desulfurization process as well as the other alkalizing agents originally present in fly ash. Coal combustion by-products have been extensively reviewed for their use as an agricultural liming agent, and CCBs behave similarly to calcium carbonate ($CaCO_3$) as a liming agent depending on their $CaCO_3$ equivalence (CCE) (Phung et al., 1978; Page et al., 1979; Korcak, 1985; McCarty et al., 1994). The large concentrations of $CaSO_4$ present in FGD by-products are also considerably more soluble compared to $CaCO_3$ and can provide essential nutrients to help mitigate subsoil acidity symptoms (Sumner et al., 1986).

Coal combustion by-products are also rich in nutrients vital to plant and animal growth. Fly ashes have large concentrations of essential nutrients such as P, Ca, S, B, Cu, Fe, Na Mg, K, and Zn, which may limit plant growth and agricultural yields when present in suboptimal amounts. The desulfurization process also enriches the coal by-products with Ca and S, which may be limited in certain geographic regions and can increase crop yields. Coal combustion by-products have been used as a soil amendment and successfully increased yields of several crops including alfalfa (*Medicago sativa*), soybean (*Glycine max*), corn (*Zea mays*), barley (*Hordeum vulgare*), rice (*Oryza sativa*), wheat (*Triticum aestivum*) and white clover (*Trifolium repens*) (Chen et al., 2005; Adriano et al., 1978; Sale et al., 1996; Sikka and Kansal, 1995; Hill and

Lamp, 1980). Although the agronomic benefits of land applying CCBs are well-documented, environmental concerns regarding bioaccumulation, runoff, plant uptake, and leaching of potentially toxic trace elements have prevented large-scale use of CCBs in agriculture. This is further complicated by the fact that actual CCBs characteristics vary greatly depending on coal type and origin as well as the power plant operating conditions and technology. Leaching characteristics and plant uptake of trace elements in soils amended with CCBs have been documented (Crews and Dick, 1998; Izquierdo and Querol, 2012; Grisafe et al., 1988; Stehouwer et al., 1996), but field experiments monitoring runoff quality under natural precipitation are nonexistent.

If large volumes of CCBs were to be land applied as a soil amendment on agricultural land, runoff water could contribute to degradation of nearby terrestrial, aquatic, and agricultural ecosystems. More information is needed on the effects of land application of CCBs on runoff water from agricultural land. Land application onto managed grasslands with dense vegetative cover provides the potential for increased rainfall interception, which can decrease the volume of runoff water leaving the grassland, but long-term analysis is needed.

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# Chapter One

# Literature Review

## Coal Combustion By-product Generation and Characteristics

### Electrical Generation and Consumption

Over 3,936 billion kilowatt-hours of electricity were produced in the United States in 2014, with approximately 3,724 billion kilowatt-hours being consumed by residential, commercial, industrial and transportation industries (USEIA, 2015a). As a result of population growth, electricity generation is estimated to increase at a rate 0.8% year$^{-1}$ from 3,936 billion kilowatt-hours in 2014 to 4,797 billion kilowatt-hours in 2040 (USEIA, 2015b). Globally, it is predicted that energy consumption will grow 56%, from 524 quadrillion British thermal units (BTU) in 2010 to 820 quadrillion BTU in 2040 (USEIA, 2013).

In the United States, electricity is primarily generated by the combustion of fossil fuels. In 2014, fossil fuels were responsible for 67% of electricity generation (USEIA, 2015a). Of the 3,936 billion kilowatt-hours of electricity generated, 39% were generated by coal-fired power plants. The remaining major energy sources were natural gas (27%), nuclear (19%), hydropower (6%) and other renewable resources (7%). Use of coal for electrical generation peaked in 2007 at 2,016 billion kilowatt-hours, but has been decreasing steadily as consumption of natural gas increases. The switch away from coal-fired power plants may be attributed to several factors including an increase in government regulations, fuel prices and a lower overall efficiency compared to alternative fuel sources (USEIA, 2013). Coal-fired power plants operate with an efficiency of 25-45%, while natural gas power plants operate with an efficiency of 30-50% (IEA, 2008). At the current growth rate, it is estimated that natural gas will produce more than 60% of electricity between 2025 and 2040 (USEIA, 2015b). Although natural gas consumption is expected to surpass coal, due to the broad availability and low material cost, coal is expected to be a major source of energy for the next 35 years.

## Origin and Classification of Coal Products

In 2008, it was estimated that more than 122 million Mg of coal combustion by-products (CCBs) were produced, which made coal combustion the second largest producer of waste behind municipal solid waste (Luther, 2010). The physical and chemical properties of CCBs are directly related to the properties of the coal being used in the production of energy. Currently, coal is being mined from the surface and subsurface of coal reserves in the Colorado Plateau, Western Interior Illinois Basin, Gulf Coast, Northern Rocky Mountains and Great Plains, and Appalachian basin areas of the United States (USGS, 2013a).

There are four categories of coal that are based on the geologic age and degree of metamorphism. The four ranks of coal are lignite, subbituminous, bituminous, and anthracite (USGS, 2009). America Society for Testing and Materials standard D388 is the most common system for ranking coal and is based on the fixed-carbon content (%), volatile matter limits (%), and the caloric value (BTU/lb). Coals that contain 69% or greater fixed C are classified solely by their fixed carbon content (ASTM, 2015a). Coals that contain below 69% fixed carbon are classified solely by their caloric value. Subbituminous and bituminous coal are the primary sources of coal-fired energy in the United States, accounting for 92% of coal production by weight and 95% by total energy production (USEIA, 2010). Lignite, which has the lowest energy content, comprises 7% of U.S coal production by weight and 5% by energy production. Although anthracitic coal has the largest carbon content (86 to 97%), it is extremely rare in the United States and only comprises 0.2% of total coal production. This thesis focuses primarily on subbituminous coal mined from the Gillette coal field of the Powder River Basin in Wyoming and Montana.

The Powder River Basin (PRB) is a coal basin that covers approximately 50,500 km$^2$ in northeastern Wyoming and southeastern Montana (USGS, 2013a). The PRB contains the largest reservoir of low-sulfur subbituminous coal in the world. In 2011, 42% of total coal production in the United States originated from the PRB, of which 92% of coal produced came from the Gillette coal field. Coal mined from the Gillette coal field in the PRB is described as “clean coal” due to its low S content and low concentration of contaminants and trace elements (USGS, 1999). Total S content of coal mined from the Gillette coal field ranges from 0.2 to 1.2% (Table 1). Potentially environmentally damaging elements such as As, Co, Cr, Pb, Se and U all have mean concentrations less than 10 mg kg$^{-1}$.

## Coal-combustion By-products

Use of coal in coal-fired power plants results in the generation of large volumes of coal-combustion by-products (CCBs). Coal combustion by-products are solid phase particles originating from chemical compounds in coal that are not combusted during electric generation. These by-products are then collected through emissions control processes. Coal combustion by-products which include fly ash, bottom ash, boiler slag, and flue gas desulfurization by-products (FGD) (Luther, 2010). This thesis will focus primarily on fly ash and FGD, although bottom ash and boiler slag will be briefly discussed.

Bottom ash is formed when ash particles that are too large to be carried in flue gases soften and adhere to boiler tubes or furnace walls (WE, 2013). Bottom ash particles are coarse and range in size from fine sand (0.125 to 0.250mm) to gravel (2 to 10mm). Due to the large particle size, bottom ash particles are typically inert and less pozzolanic than other ashes. Boiler slag is formed when a wet-bottom furnace is used during the coal combustion process. Molten non-combustible minerals in the furnace are combined with quenching water causing the minerals to crystallize and subsequently fracture into coarse, black, angular, and glassy particles. As of 2007, the largest use for boiler slag was as blasting grit and roofing granules (ACAA, 2008).

Fly ash is responsible for 57% of CCBs generated in the United States and is captured in the chimney or stack of a power plant by electrostatic precipitators, fabric filters, or baghouses (Luther, 2010). Fly ash consists of particles that have been fused into spherical, glassy, amorphous aluminosilicates that typically range in size from 2 to 10 µm (Ismail et al., 2007). Fly ash is further classified into two categories dependent on the coal being burned. Class C fly ash (high calcium) is derived from the burning of lignite and subbituminous coal, whereas Class F (low calcium) fly ash originates from anthracitic and bituminous coal (WE, 2013). The primary difference between Class C and Class F fly ash is the greater silicon dioxide ($SiO_2$) content in the Class F fly ash (50-65% vs 20-40% in Class C fly ash) and the greater calcium oxide (CaO) content of Class C fly ash (25-35% vs 0-10% in Class F fly ash) (Table 2). Aluminum oxides and ferrous oxides are the other main constituents of both Class C and Class F fly ashes.

Due to the pozzolanic nature of CaO, fly ash particles in Class C become cementitious when exposed to water (Sajwan et al, 2006). Class C fly ash is often used in conjunction with portland cement or as a replacement due to large CaO content (i.e., portlandite). Class C fly ash is also used as a soil stabilizer for reducing subgrade support capacity for pavements, acting as a drying agent in moist soils and reducing the shrink-swell potential of soils with vertic properties (WE, 2013). In 2007, 71.7 million tons of fly ash were produced with approximately 44% being used beneficially, which was as a component in concrete and/or blended cement (ACAA, 2008).

There are 76 potential elements present in coal which are subsequently potentially present in the ash of CCBs (USGS, 2013b). Major elements present in coal ash include Al, Ca, Fe, K, Mg, S, and Si, which range in concentration from 1.9 to 34 g $kg^{-1}$ for S to 160 to 270 g $kg^{-1}$ for Si (Table 3). Trace elements present in fly ash have been an environmental concern for decades and are the primary factor hindering the beneficial use of fly ash. Potentially toxic trace elements, such as As, Cd, Cr, Pb, Hg, Se, Sr, and U, may be present in large concentrations. Boron is also present in large concentrations, ranging from 120 to 1000 mg $kg^{-1}$, and can cause environmental degradation when present in large quantities. Although some trace elements may be toxic to plants and animals in large quantities, elements such as copper, vanadium, selenium, strontium, molybdenum, and zinc may be beneficial in small amounts (Banfalvi, 2011).

Flue gas desulfurization by-products result from chemical processes used at coal-fired power plants to remove sulfur dioxide ($SO_2$) from flue gasses in order to comply with the 1990 Clean Air Act Amendment (CAAA) (U.S. Congress, 1990). Sulfur dioxide is removed from flue gasses by combining the flue gasses with a calcium sorbent, such as limestone ($CaCO_3$), burnt lime (CaO), or hydrated lime [$Ca(OH)_2$] (Luther, 2010). The use of a calcium sorbent yields a by-product with a large calcium content when compared to other CCBs. Depending on the technology being used at the coal-fired power plant, FGD may be a dry powder (DFGD) or a wet sludge (WFGD). Due to the reaction of lime or limestone with the $SO_2$ in flue gasses, FGD contains large levels of calcium sulfite hemihydrate ($CaSO_3 \cdot ½H_2O$) and calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$; gypsum). Dry FGD by-products containing high levels of $CaSO4 \cdot 2H_2O$ may be identified as FGD gypsum. In 2010, FGD comprised 24% of total CCB generation in the United States, although the percentage tends to increase every year (Luther, 2010). According to ACAA (2008), 67% of FGD gypsum was used in the production of gypsum panel products such as panels and drywalls. The primary beneficial use for WFGD and DFGD is in mining applications as a mine spoil amendment (ACAA, 2008).

Flue gas desulfurization by-products from coal-fired power plants typically contain spherical or irregularly shaped fly ash particles that range in size from 5 to 50 µm (WE, 2013). Chemically, FGD contains the same 76 potential elements as fly ash, although the concentrations differ. The largest difference in the major elemental composition is with Al (70-140 compared to 13-74 g $kg^{-1}$ for fly ash and FGD, respectively), Ca (7.4-150 compared to 122-312 g $kg^{-1}$ for fly ash and FGD, respectively), S (1.9-34 compared to 41-126 g $kg^{-1}$ for fly ash and FGD, respectively), and Si (160-270 compared to 25-139 g $kg^{-1}$ for fly ash and FGD, respectively) (Table 3). The large Ca and S contents present in FGD originated from the calcium sorbents and $SO_2$ removed from the flue gasses. Trace element concentrations of B, Cr, Mn, Ni, Pb, and Sr in FGD are generally lower than those present in fly ash (Table 3).

## Storage and Disposal of CCBs and Associated Issues

When not being used beneficially, CCBs are disposed of in two ways, in landfills or in settling ponds (Carlson and Adriano, 1993). In settling ponds, CCBs are mixed with water to form a slurry, which is then transported to surface impoundments for storage. As ash settles in the settling ponds, effluent water may be pumped back to the power plant or pumped to nearby streams. Landfills are areas that receive CCBs directly from the coal-fired power plant, which are then disposed of into an excavated area and buried. As of 2012, 310 active on-site landfills and 735 on-site settling ponds were being used to handle CCBs not being used beneficially (USEPA, 2015). Storage of CCBs in landfills and surface impoundments has raised concerns regarding potential environmental damage to terrestrial and aquatic ecosystems.

The potential for groundwater contamination from CCB leachate is a concern regarding long-term disposal and storage (EPA, 1998). The elevated levels of potentially toxic trace elements, such as As, B, Cd, Cr, Hg, Mo, Pb, and Se, as well as soluble salts present in CCBs, increase the chance of groundwater contamination over time as landfills and storage lagoons degrade (Carlson and Adriano, 1993). The fine particle size of CCBs makes them particularly susceptible to wind erosion. Unmanaged and abandoned landfills and storage lagoons are a noteworthy source of ash resuspension into the atmosphere (Dellantonio et al., 2010). Suspended ash particles in the air can cause health problems, including irritation to the eyes, throat, and respiratory tracks of animals and humans near ash disposal sites. Respiration of air-borne ash particles can also lead to the ingestion of potentially toxic trace elements, such as As, Pb, Hg, Cr, Cd, and Se (Smith et al., 2006). The most environmentally conscious method of alleviating environmental contamination from ash disposal is the use of a vegetative cover. Although vegetative covers can minimize erosion of ash, as well as leaching of toxic metals and soluble salts, bioaccumulation of toxic elements in the food chain has been an observed problem in ecosystems adjacent to ash disposal sites (Dellantonio et al., 2010). Plants growing in ash-incorporated soils frequently accumulate substantial levels of Se, which may be toxic for animals. In China, approximately 500 cases of selenosis in humans resulted from consumption of water originating from Se-rich soils being amended with Se-rich CCBs (Finkelman et al., 2002). Plant uptake of Mo from CCB-amended soil and subsequent consumption by ruminants has been reported to lead to a Cu:Mo ratio imbalance, increasing the risk for hypocuprosis in ruminants (Dellantonio et al., 2010).

The potential for toxic elements and pH-altering cations to enter aquatic ecosystems is also a major concern for long-term storage of CCBs. Elements such as B, Mo, Se, Cr, and V have been reported to be the most soluble and water-extractable elements present in CCBs and can enter aquatic ecosystems as effluent discharge from ash disposal sites (Dellantonio et al., 2010; Moreno et al., 2005). Effluent discharge from ash disposal sites to aquatic ecosystems can affect water quality by increasing turbidity, alkalinity, electrical conductivity, and siltation and may lead to a decrease in photosynthetic activity, animal metabolism, and animal reproduction leading to an increase in mortality rates and a decrease in species diversity (Carlson and Adriano, 1993). Accidental releases from ash disposal sites have occurred in the past and have caused significant environmental damage, property damage, and health issues.

On October 11, 2000, an ash storage lagoon located in Martin County, Kentucky released an estimated 946.4 million liters of ash sludge into the Coldwater Fork and Wolf Creek (Counter Spill, 2011). Ash sludge from the coal-fired power plant affected areas over 160 kilometers downstream from the location of the spill contaminating surface and groundwater and affecting aquatic and terrestrial ecosystems. Sludge from the spill eventually reached the Ohio River, which may have caused substantial damage to aquatic and riparian ecosystems along the Ohio River. Shortly after the spill, a state of emergency was declared due to unsafe drinking water as a result of the sludge spill.

In 2006, the Anne Arundel County Department of Health received notification from the Maryland Department of the Environment that a well within 305 meters of an ash disposal site was shown to have an elevated level of metals in the water (AA Health, 2013). Well water for 83 homes and in the surrounding area was tested over a 6-month period by the Department of Health for compliance with EPA’s maximum contaminant levels (MCLs). Samples collected from well water in the sampling area showed levels of Al, As, Be, Cd, Mg, Ti, and sulfates that exceeded EPA’s MCLs.

The largest incident regarding CCB disposal and storage occurred on December 22, 2008 at the Tennessee Valley Authority's (TVA) Kingston Tennessee coal-fired plant. An estimated 4.16 billion liters of ash sludge were released as a result of a breach of an impoundment pond located at the coal-fired plant (Luther, 2010). The sludge released from the impoundment pond covered over 121.4 hectares resulting in large-spread environmental contamination, property damage, and eventual contamination of the Emory and Clinch Rivers. Ruhl et al. (2010) examined the environmental impact of the TVA ash spill and reported that ash buried from the spill was highly reactive and will continue to release large levels of As, B, Sr, and Ba into pore waters. Large fish kills were reported at both Emory and Clinch Rivers as a result of the contamination. Dredging efforts undertaken by TVA have also resulted in a minimal impact of contamination remediation due to the low ash/water ratios and large amounts of dilution. The scale of the TVA spill resulted in national attention being drawn to the issue of CCB management and disposal. As a result of the TVA spill, EPA began proceedings to address regulatory issues associated with CCB management and storage (Luther, 2010).

## CCB Regulations

Regulations for the combustion of coal products in power plants originated from the Clean Air Act (CAA) passed by the United States Congress in 1970. The CAA delegated authority to EPA to develop regulations for mitigating air pollution (U.S. Congress, 1970). The 1970 CAA established National Ambient Air Quality Standards (NAAQS) for states to regulate six widespread pollutants: ozone, particulate matter, carbon monoxide (CO), nitrogen oxides ($NO_x$), $SO_2$, and Pb. States were also to develop and force State Implementation Plans (SIPs) to maintain air quality. The CAA required stationary sources of air pollution, such as coal-fired power plants, to adopt best-available technologies available for mitigating air pollution.

The 1977 Clean Air Act Amendment (CAAA) was passed by Congress to address concern with the preventing significant deterioration of air quality attained by NAAQS (U.S. Congress, 1977). The 1977 CAAA outlined requirements for non-attainment areas of NAAQS. Non-attainment areas are geographic regions whose air quality falls below NAAQS established by the EPA, or below SIPs passed by the state.

The 1990 CAAA introduced new regulations aimed at further reducing air pollution from point and non-point sources (CAAA, 1990). A primary focus of the 1990 CAAA was to address acid rain problems resulting from $NO_x$ and $SO_2$ emissions. The 1990 CAAA mandated $SO_2$ emission of coal-fired power plants be reduced below 0.91 kg of $SO_2$/mBTU by 1995 and below 0.54 kg of $SO_2$/mBTU by 2000. The 1990 CAAA $SO_2$ regulations resulted in a dramatic increase in FGD technologies, and a subsequent increase in FGD by-products. In addition to reduction of acid rain, the 1990 CAAA put forth regulations to control 189 toxic pollutants, phase out ozone-depleting chemicals such as chlorofluorocarbons (CFCs), and provided a framework for alternative clean fuels to be used in business or government owned vehicles.

The Resource Conservation and Recovery Act (RCRA) of 1976 is the primary regulation governing the disposal of solid waste such as CCBs (USEPA, 2014). Section C of RCRA established regulations for handling hazardous waste with the intent of managing hazardous wastes from creation to disposal, or “cradle to grave”. Hazardous wastes under RCRA were defined as being toxic, reactive, ignitable, or corrosive, and are determined by using the toxicity characteristic leaching procedure (TCLP) established by the EPA. Section C also established a permitting process for facilities handling, storing, or disposing hazardous wastes.

The Solid Waste Disposal Act (SWDA) of 1980, otherwise known as the Bevill Amendment, was an amendment to RCRA that exempted CCBs from regulation under Subtitle C until further assessment of risk was conducted (Luther, 2013). The CCBs exempted under the Bevill Amendment were fly ash waste, bottom ash waste, slag waste, and wastes produced by flue gas emission controls produced from the combustion of coals or other fossil fuels. The 1988 Report to Congress (RTC) reported the four CCBs studied were not a major concern and did not exhibit hazardous waste characteristics in the TCLP and therefore should not be classified and regulated as a hazardous waste. In response to the 1988 RTC, EPA made a regulatory determination that CCBs did not warrant regulation as a hazardous waste under Subtitle C (58 FR 42466, 1993). In 2000, a second RTC was issued that reaffirmed that hazardous waste regulations under Subtitle C were not necessary for CCBs when disposed of in landfills or surface impoundments. The EPA also stated that no further regulations were necessary, and that further regulations may inhibit beneficial use of CCBs. In 2014, in response the TVA disaster, EPA issued a final rule to regulate the disposal of CCBs under Subtitle D of RCRA (U.S. Congress, 1976; USEPA, 2015). The final rule created minimum criteria for existing and future CCB disposal sites and required any existing unlined CCB surface impoundment that was contributing to groundwater contamination to immediately stop receiving CCBs and retrofit or close the surface impoundment. Landfills or surface impoundments that cannot meet performance criteria must be closed.

## Agricultural Benefits

### Effects of Acid Soils on Plant Growth

Soil acidity is a major factor limiting the growth of plants and is a major agricultural and environmental concern worldwide. Soil acidy is due to acidic parent materials low in basic cations, application of ammonium-based fertilizers, or because basic cations have been removed by plant uptake or leaching (Foy et al., 1978; DeSutter and Cihacek, 2009). Soils with pH below 7.0 are considered acidic, but soil acidity can be further classified as extremely acidic (< 4.5), very strongly acidic (4.5 to 5.0), strongly acidic (5.1 to 5.5) or moderately acidic (5.6 to 6.0) (DeSutter and Cihacek, 2009). Acid soil toxicity is a series of complex factors that may affect plant growth and is dependent on several factors including plant genotype, clay mineralogy, organic matter types and concentrations, and soil salinity (Foy, 1992). The three primary ways that soil acidity can disrupt plant growth are through H, Mn and Al toxicity.

Hydrogen ion toxicity is a direct result of the increase in the H ion concentration as the soil pH decreases. Symptoms associated with H ion toxicities are often hard to diagnose due to the prevalence of Al and Mn toxicities at soil pH above 4.0 (Kamprath and Foy, 1985). Excess H ions can cause leaky root membranes and interfere with ion transport by competing with other cations for root absorption sites (Foy, 1992). Leaky root membranes can cause a loss in root cations and important organic substrates. Hydrogen ion toxicity has been shown to reduce growth of cotton (*Gossypium hirsutum* L.) and wheat (*Triticum aestivum* L.) roots in acidic soils (Howard and Adams, 1965). Hydrogen ion toxicity has also been reported to restrict survival and inhibit reproduction of rhizobia and other soil microorganisms (Moore, 1974; Kamprath and Foy, 1985). Excess $H^+$ ions can also cause root infection, nodule initiation, and nodulation of the host plant, which will limit legume growth (Andrew, 1978).

Manganese toxicity has a larger effect on plant shoots than Mn toxicity does on plant roots, although root damage may occur when toxicity is severe (Foy, 1974). Manganese availability and potential toxicity depends on soil characteristics, such as Mn content of the parent material, soil pH, microbial activity, soil Eh, soil aeration and porosity, and organic matter type and concentration. Certain soils, such as those of the Atlantic coastal plain, do not have sufficient Mn to produce toxicity (Adams and Pearson, 1967). Manganese toxicity typically occurs below pH 5.5, but Mn toxicity has been reported in poorly drained or aerated soils where reducing conditions cause microbial respiration of $MnO_2$ and the subsequent production of soluble divalent Mn. Manganese toxicity can occur in calcareous soils where plants, such as flax (*Linum usitatissimum* L.), can create reducing or low pH conditions in their root zones (Moraghan and Ralowicz, 1979). Excess manganese can cause leaf puckering, chlorosis (i.e., pale or yellowing of leaves), and necrotic spots to appear on older leaves. Severe Mn toxicity may cause impaired root function and stunting and may be associated with Fe deficiencies.

Aluminum toxicity is one of the largest inhibitors of plant growth in acidic soils and is most prevalent at $pH < 5.0$. The pH that Al becomes available in toxic concentrations is dependent on several soil factors, including clay mineralogy, organic matter concentrations, salts, plant species, cation and anion concentrations (Foy, 1974; Kamprath and Foy, 1972). Symptoms such as drought stress or poor root development in acidic soils are most likely the result of Al toxicity. Aluminum toxicity cause symptoms similar to plants deficient in P (e.g., stunted growth, late maturity, and purpling of stems), Ca (e.g., curling of young leaves and collapse of plant growing points), Fe (e.g., interveinal chlorosis and yellow or white leaves), and Mg (e.g., interveinal chlorosis and reduction in photosynthetic and enzymatic activities) (Foy, 1992). Reduced root growth from Al toxicity in acidic soils results from Al interference with root tip cell division, decrease in root respiration, reduction of water uptake and the fixation of P in less-available forms in the soil and on the surface of plant roots. Aluminum toxicity in plants can increase the rigidity of the deoxyribonucleic acid (DNA) double helix causing a reduction in DNA replication, interfere with enzymes responsible for sugar phosphorylation, decrease production of cytokins, and hinder uptake, transport, and metabolism of essential nutrients (Ulmer, 1979).

### CCBs as a Soil Ameliorant of Soil Acidity and Soil Acidity Symptoms

Historically, liming agents, such as limestone ($CaCO_3$), burnt lime (CaO), hydrated lime [$Ca(OH)_2$], and dolomitic limestone [$CaMg(CO_3)_2$], have been used to alleviate soil acidity and subsequently improve plant growth and crop production. Soil acidity is neutralized by the oxide anions produced from dissolution of the liming materials, which then react with $H^+$ ions to form water or carbonic acid. However, the relative insolubility of limestone and dolomitic limestone (0.013 g $L^{-1}$ at 25°C) means that limestone is only effective at the site of application or incorporation and will be unable to leach and neutralize subsoil acidity (Aylward, 2008; Oates, 1998). In order to make limestone available to the subsoil, the soil must be cultivated or disturbed to incorporate the liming material deeper into the soil profile. Liming materials such as burnt lime and hydrated lime are significantly more soluble in water (~1.2 and 1.9 g $L^{-1}$ at 25°C for burnt lime and hydrated lime, respectively) and are much more effect at neutralizing soil surface and subsoil acidity (Aylward, 2008; Oates, 1998). Although gypsum ($CaSO_4{\cdot}2H_2O$) does not act as a liming material, gypsum is able to mitigate subsoil acidity by decreasing the exchangeable $Al^{3+}$ concentration (Sumner et al., 1986). Gypsum mitigates subsoil acidity through the precipitation or sorption of $Al^{3+}$, which reduces the influence of Al on plants. The large availability and presence of alkalizing agents [$CaCO_3$, CaO, MgO, $Ca(OH)_2$ and $CaMg(CO_3)_2$] present make certain CCBs good candidates for use as a liming agent (McCarty et al., 1994; Jala and Goyal, 2006). Additionally, due to the nature of the desulfurization process, DFGD by-products contain large amounts of gypsum which can be used to mitigate subsoil acidity (Chen et al., 2001).

Phung et al. (1978) measured the impact of liming an acidic Reyes silty clay (Sulfic Haplaquept) (pH 4.1) with Class F fly ash at rates of 0, 0.4, 1, 2, 5, and 10% by weight for a 4-month period. After 4 months, application of 5% (w/w) fly ash increased the soil pH from 4.1 to 6.3 and exchangeable soil Ca increased from 5 to 20.1 $cmol_c$ $kg^{-1}$. Exchangeable soil Al in the soil decreased from 8.8 $cmol_c$ $kg^{-1}$ in the control soil to 0.2 and 0 $cmol_c$ $kg^{-1}$ for the 5 and 10% (w/w), respectively. The increase in exchangeable soil Ca and soil pH and decrease in exchangeable soil Al created soil conditions that were more favorable for plant growth (Phung et al., 1978).

Chapman (1984) surface applied fly ash to silt-loam fields in Pulaski County, Arkansas at application rates equivalent to 4.5, 9, and 13.5 Mg $ha^{-1}$ to monitor effectiveness of fly ash as a lime source in comparison to agricultural lime applied at a rate equivalent to 4.5 Mg $ha^{-1}$. After 12 months, the pH of the soil within the top 10-cm had increased from 5.2 to 5.8 for the limestone treatment and from 5.2 to 5.5, 5.7, and 5.9 for the 4.5, 9, and 13.5 Mg $ha^{-1}$ treatments, respectively. Fly ash applied at the 9 and 13.5 Mg $ha^{-1}$ application rates was as effective as limestone applied at a 4.5 Mg $ha^{-1}$ application rate. Electrical conductivity (EC) was greatest in soil that received limestone and was 10 µS $cm^{-1}$ greater than that for the fly ash treatment with the largest EC. Extractable soil P, K, and Na were similar between the limestone and fly ash treatments. Soil treated with limestone had greater extractable soil Ca, whereas soil treated with fly ash had greater levels of extractable soil Mg compared to an unamended control.

Crews and Dick (1998) incorporated an FGD by-product into the A horizon (0-17 cm depth interval) of an acid (pH ~ 4.4) forest Hapludult (Rayne silt loam) at rates equivalent to 0.25, 0.5, 1, 1.5, 2, and 2.5 times the soil's lime requirement. Soil pH in the 0-17 cm depth interval increased from DFGD by-product application from 4.4 to 6.0, 7.0, and 7.0 for the 0.5, 1, and 2 times application rates, respectively.

McCarty et al. (1994) investigated the liming potential of fly ash, bed ash, residue from a limestone-injection multistage burner (LIMB), and spray dryer baghouse residue (SDBR) by incorporating the liming materials into bulk samples of an acidic (pH 4.2) Psammentic Hapludult at rates equivalent to 0, 2.8, 5.6, 11.2, and 22.5 Mg ha$^{-1}$. At the 5.6 Mg ha$^{-1}$ application rate, soil pH was 5.7, 5.5, 5.1, and 5.0 for the bed ash, LIMB residue, SDBR residue, and fly ash, respectively. At the 22.4 Mg ha$^{-1}$ application rate, soil pH was 8.0, 7.7, 7.1, and 6.1 bed ash, LIMB residue, SDBR residue, and fly ash, respectively. As a comparison, the pH of soil incubated with calcium carbonate at a rate equivalent to 9.0 Mg ha$^{-1}$ was 7.7. When the application rates of liming materials were adjusted from a weight basis to a $CaCO_3$ equivalence basis, the differences between the liming materials were greatly reduced. When adjusted to a $CaCO_3$ equivalence, there was no difference in pH between soils treated with fly ash and $CaCO_3$ and there was no difference between bed ash, LIMB residue, and SDBR residue.

## Crop Response to CCB Land Application

In addition to use as a liming material, the presence of several plant essential nutrients provides potential for CCBs, such as fly ash and DFGD by-products, to be used as a fertilizer or soil amendment to improve plant growth. Fly ash and DFGD by-products contain elevated concentrations of P, K, Ca, Mg, S, Fe, B, Mo, Ni, and Zn, all of which are considered essential plant nutrients.

Chen et al. (2005) examined the use of DFGD by-products as a S source and the effect of land application on growth of alfalfa (*Medicago sativa*) and soybean (*Glycine max*) by applying DFGD by-products at rates equivalent to 0, 16 and 67 kg S $ha^{-1}$. Aboveground alfalfa biomass increased up to 40% by the treatments of DFGD by-products compared to untreated controls. There was no difference in yield between plots that received DFGD by-products and conventional agricultural gypsum. Plots receiving application of the DFGD by-product had a yield increase over the untreated control by 3.3 to 11.6%.

Chen et al. (2001) surface applied several FGD by-products to an acidic soil at rates equivalent to 0, 0.5, 1 and 2 times the soil's lime requirement to monitor alfalfa growth. Alfalfa productivity at the 1x application rate was 7-8 times greater than that for the unamended control and 30% greater than that for the conventional agricultural lime. Alfalfa yield was similar from the 2x compared to the 1x application rate. A yield increase compared to conventional ag lime can be attributed to the elevated concentrations of essential plant nutrients added in DFGD by-products.

Chen et al. (2008) examined the use of a DFGD by-product as a S source for growing corn. A DFGD by-product was applied to a silt-loam soil with neutral pH at rates equivalent to 0 (control) and 33 kg S $ha^{-1}$ annually over a 4-yr period from 2002 to 2005. Corn yield significantly increased during the first two years, but did not differ from the control in the final two years.

Sharma et al. (2001) investigated the effect of incorporating fly ash into the 0-30 cm depth of soil and the effect that incorporation would have on maize and rice yields. Fly ash was added to soil at rates equivalent to 0 (control) and 22.4 Mg ha$^{-1}$ at two locations for both maize and rice. Corn yield significantly increased at both locations from 5.8 to 6.3 Mg ha$^{-1}$ and from 13.2 to 13.9 Mg ha$^{-1}$. Rice yield response to fly ash was less than that for corn, but rice yield increased by 1.3% and 4.4% compared to an unamended control. The results from this experiment were similar to an experiment performed by Sikka and Kansal (1995) who noted an increase in rice yield in plots that received 2 and 4% (w/w) application of fly ash.

Wang and Shi (2015) used a modified FGD by-product (MFGD) as a soil amendment for the growth of sweet potatoes *(Ipomoea batatas)*. Modified FGD by-product was applied to soil at rates equivalent to 0 (control), 750 (T1), and 1500 kg ha$^{-1}$ (T2). Addition of the MFGD increased the average potato weight from 0.11 kg to 0.17 and 0.19 kg for T1 and T2, respectively. Total sweet potato yield increased from 18.8 Mg ha$^{-1}$ for the control to 26.5 and 28.9 Mg ha$^{-1}$ for T1 and T2, respectively. Addition of MFGD by-products to sweet potato also resulted in a change in size distribution of harvested potatoes. Treatments receiving MFGD had a significant decrease in the amount of small potatoes and a significant increase in medium- and large-sized potatoes. In addition to an increase in overall yield, total concentrations of sugars, protein, starch, β-carotene, and vitamin C were significantly greater than those in potatoes that did not receive treatment.

Sale et al. (1996) added unweathered fly ash to a clay-loam topsoil in soil mixtures ranging from 0 to 100% fly ash (v/v) to monitor barley (*Hordeum vulgare L.* var. Leduc) growth response. Barley emergence was delayed in soil mixtures greater than 6.25% fly ash, but overall growth was not reduced until > 25% application rates. Barley height and grain yields were significantly greater from the 6.25 and 12.5% application rates compared to an unamended control. Barley height and grain yield did not differ between the control and the 25% application rate. Barley height and yield were significantly reduced when soil received > 50% fly ash compared to an unamended control. The decrease in yield were attributed to an increase in pH, EC, and excess concentrations of B due to the presence of alkalizing agents and soluble salts in the fly ash.

Khan and Khan (1996) added Class F fly ash to a loamy soil at rates ranging from 0 to 100% (v/v) at 10% increments to monitor growth response of tomatoes *(Solanum lyopersicum)*. Tomato shoot length increased 40-90% and root length increased 20-80% compared to the unamended control across all fly ash application rates. Tomato shoot and root length, yield, and plant height were all significantly greater than that from the unamended control at all application rates, although increases were most pronounced at application rates ranging from 40-70%. Increases in tomato characteristics and yield followed a parabolic trend with 10% and 90% application rates being most similar to the unamended control. The decreases were attributed to trace element toxicity, boron toxicity, an increase in salinity, or a combination of all three.

## Environmental Impacts

### Arsenic, Selenium, and Mercury

The presence of potentially toxic and phytotoxic elements in CCBs has inhibited the large-scale use of CCBs as a soil amendment. Arsenic, Se, and Hg are the three major trace elements that pose a significant risk form the land application of CCBs (USEPA, 2008, Korcak, 1995, Wright et al., 1998). The fate and transport of As from the combustion of coal is a concern due to the high concentration present in CCBs and the acute toxicity of As. Eary et al. (1990) reported the concentration of As in fly ashes can range from 2 to 400 mg $kg^{-1}$ compared to the typical soil ranges of 1 to 50 mg $kg^{-1}$. Arsenic may be present in several chemical compounds in fly ashes depending on the type of coal, operating conditions and ash pH. In Class C fly ashes with high concentrations of CaO, volatile arsenic trioxide ($As_2O_3$) may react with CaO to form calcium arsenate ($Ca_3As_2O_8$). Arsenic compounds primarily exist in two oxidation states, As (III) and As (V), and are commonly present in the environment as the oxyanions arsenite ($AsO_3^{3-}$) and arsenate ($AsO_4^{3-}$). The speciation of As in CCBs is important because speciation will dictate the fate and transport of As in the environment.

Jackson and Miller (1998) analyzed 23 fly ashes from coal-fired power plants in the southeastern United States using ion chromatography-inductively coupled plasma mass spectrometry to determine the speciation of As. Twenty-one of the 23 fly ashes analyzed had As (V) as the predominant As species. The two fly ashes that had As (III) as the predominant As species were acidic fly ashes.

In the desulfurization process, calcium sorbents react with $SO_2$ in the flue gas forming calcium sulfate and facilitates the capture of As as calcium arsenate (Al-Abed et al., 2008). Al-abed et al. (2008) analyzed several FGD samples from coal-fired power plants in Pennsylvania for speciation and environmental availability of As. Arsenic in the FGD light fraction (i.e., less than 0.01% total weight) was 10 times greater than that in the heavy fraction. The labile fraction of As was 18.1% and the oxide (i.e., amorphous and crystalline) was 56.7%. The As leaching profile was observed to be amphoteric with concentrations being greatest at low and high pH. Spectroscopy indicated that As existed primarily as As (V). The alkalinity of FGD by-products and presence of insoluble Ca-As compounds resulted in low environmental availability. However, in acidic conditions, arsenic may be released due to the acidic dissolution of Ca-As compounds (Al-Abed et al., 2008).

In the environment, As behaves similarly to orthophosphate, but the existence of two oxidation states makes As more susceptible to soil pH and redox chemistry (Walsh et al., 1977). In aerated soil conditions, arsenate [As (V)] predominates; however, in reducing conditions, arsenite is the most prevalent form. The change of As (V) to As (III) can be driven solely by a change in redox potential (Eh)/pH, but the reduction may be assisted by anaerobic microorganisms. When soil Eh drops below 300 mV in acidic conditions or -100 mV in alkaline conditions, arsenous acid ($H_3AsO_3$) becomes the stable arsenic species. In aerated soils, arsenate comprised 90% of dissolved As, but only 15-40% in anaerobic conditions. Although As exists in the soil primarily as an oxyanion, leaching of arsenic from soils is inhibited by Fe and Al oxides, clays and SOM. In general, sorption of As (V) is greater than As (III), but less than orthophosphate. Based on a study of lake sediment suspensions indicated that As solubility increased 25 times when soil Eh decreased from 500 to -200 mV and up to 50% of soil As was solubilized (Alloway, 1995). The solubility of As was directly related to the concentration of iron in solution indicating that the dissolution of oxyhydroxides released sorbed arsenic. The release of As from the dissolution of oxyhydroxides may also occur when soils become acidic, especially below pH 5.0.

Plants vary considerably in their tolerance to elevated concentrations of As in the soil. Certain crops, such as potatoes (*Solanum tuberosum*), tomatoes, and tobacco (*Nicotiana tabacum*), are highly tolerant to As toxicity, whereas crops such as cucumbers (*Cucumis sativus*), onions (*Allium cepa*), and alfalfa are highly susceptible (Walsh et al., 1977). Arsenic is taken up from the soil solution as arsenate by phosphate transporters in plants (Zhao et al., 2009). However, certain crops, such as rice, are able to take up arsenite through the silicon pathway in root cells and efflux towards the xylem. Bioaccumulation of As in the environment is a concern, but arsenic rarely accumulates in the edible portions of plants because phytotoxicity typically occurs before plants reach maturity. The greatest concentration of As in plants is usually present in plant roots and intermediate levels in vegetative tissue. Animal or human As toxicity is typically attributed to the ingestion of surface residues rather than consumption of edible portions of plants (Walsh et al., 1977).

Transport of arsenic in the environment is determined by speciation of As. Arsenic (V) compounds are typically bound to soil and organic matter and less susceptible to runoff than As (III). Similar to sorbed orthophosphate, As (V) can be lost from the soil profile via erosion. The more soluble As (III) can be lost from the soil profile in runoff water or by leaching through the profile.

Selenium occurs naturally in the environment, but the combustion of coal releases Se into the environment at a rate 1.5 to 2.5 times greater than natural weathering (Klein et al., 1975). Unlike other trace elements in CCBs, Se is an essential nutrient for humans and animals in small quantities. However, Se has a very narrow range between what is considered a deficiency (< 40 µg day$^{-1}$) and what is considered to be toxic (> 400 µg day$^{-1}$), making accumulation of Se in the environment problematic (Fordyce, 2007). Although Se is essential for animal and human health, Se is not considered an essential plant nutrient. Eary et al. (1990) reported that the concentration of Se in fly ashes can range from 0.2 to 130 mg kg$^{-1}$ compared to the typical soil ranges of 0.1 to 2 mg kg$^{-1}$. Selenium compounds can exist in four oxidation states, but Se (IV) and Se (VI) are the most prominent and exist in the environment as selenite ($SeO_3^{2-}$) and selenate ($SeO_4^{2-}$), respectively. The speciation of Se in CCBs is important because selenite and selenite behave differently in the environment.

Jackson and Miller (1998) analyzed 23 fly ashes from coal-fired power plants in the southeastern United States using ion chromatography-inductively coupled-plasma mass spectrometry (IC-ICP-MS) to determine the predominant speciation of Se . Similar to As, 21 of the 23 fly ashes analyzed had Se (IV) as the predominant Se species. The two fly ashes that had Se (VI) as the predominant Se species were acidic fly ashes.

During the desulfurization process, calcium sorbents used to trap $SO_2$ emissions react with semi-volatile Se to produce calcium selenite ($CaSeO_3$) (Al-Abed et al., 2008). Al-Abed et al. (2008) analyzed several FGD samples from Pennsylvania coal-fired power plants for speciation and environmental availability of Se using x-ray absorption spectroscopy (XAS), x-ray fluorescence spectroscopy (XRF), and sequential chemical extraction (SCE) techniques. The concentration of Se in the light fraction of the FGD by-products was 10 times greater than those in the heavier fraction. The concentrations of labile Se were 34% compared to 18.1% for As. Due to the increase in the labile fraction, the oxide fraction contained only 38.5% selenium. X-ray absorption spectroscopy results indicated that the predominant presence of Se (IV) as the major selenium species. Although Se (IV) was the dominant species present in the FGD samples, Se (VI) was measured in only small amounts. Selenium leachate concentrations were lowest at acidic pHs (pH 4 to 5) and increased steadily with maximum concentrations of Se being identified at pH 11.

Plant availability and movement of Se within the soil profile are influenced by soil pH, Eh, oxidation state, and soil characteristics. Selenate is most prevalent in aerated, alkaline soils, whereas selenite and biselenite ($HSeO_3^-$) are typically present in neutral and acidic soils. Selenite adsorption is due to a mechanism known as ligand exchange and selenite behaves similar to phosphate and arsenate (Alloway, 1995). Selenate behaves similar to nitrate and sulfate by forming outer-sphere, surface complexes and is adsorbed much weaker than selenite. Although selenite adsorbs tightly to soil colloids, selenite can be displaced by addition of phosphate to the soil. Increasing soil pH results in increased mobility of both selenite and selenate (Alloway, 1995). Soil pH is the primary factor affecting selenium sorption, but clay mineralogy is also a factor.

Plants are able to absorb Se from both the soil and atmosphere, but plants vary greatly in their ability to accumulate selenium. Some plants, such as rapeseed (*Brassica napus*), are able to absorb large concentrations of Se (i.e., > 1000 mg kg$^{-1}$) without negative effects, whereas plants such as alfalfa can only tolerate Se concentrations of less than ~ 250 µg L$^{-1}$ without suffering from selenium toxicosis (Alloway, 1995). Selenite is the more toxic form of selenium, but, due to immobilization by adsorption to soil colloids, selenate is typically the cause of selenium toxicity in plants. Asher et al. (1977) concluded that selenate was transported within the plant followed the same pathway as $SO_4^{2-}$-S and absorbed selenium is immediately transported to new growth. Once in the plant, inorganic Se is converted to organoselenium compounds by plant metabolic processes. Organoselenium compounds act as analogues for S, effectively interfering with cellular biochemical reactions. Sulfate effectively competes with Se for plant uptake and excess sulfate can drastically reduce the amount of Se absorbed by plants. Mikkelson et al. (1988) reported that Se uptake by alfalfa was reduced from 948 to 6 mg kg$^{-1}$ in the presence of sulfate. Therefore, excess concentrations of sulfate in DFGD by-products may inhibit accumulation of Se in plant biomass.

Due to the acute toxicity of Hg, there is concern regarding the release of Hg from CCBs. Mercury salts produce highly acute toxicity, whereas organomercurials such as alkyl-mercury compounds cause chronic and irreversible nervous system damage. The amount of Hg in FGD materials is below the limit set by CWA-503 and ranges from 0.14 to 1.17 mg $kg^{-1}$ compared to background soil concentrations of 100 µg $kg^{-1}$ (Baligar et al., 2011; Watts and Dick, 2014). Mercury exists in the environment in three oxidation states, Hg (0), Hg (I), and Hg (II), with Hg (0) and Hg (II) being the most prevalent.

Al-Abed et al. (2008) analyzed several FGD residues from Pennslyvania power plants for the speciation, distribution, and leaching characteristics of Hg. Mercury concentrations located in the light fraction of FGD residues were 100 times greater than in the heavy fraction (i.e., 115.4 compared to 1.1 mg $kg^{-1}$ for the light and heavy fractions, respectively) indicating the importance of the size distribution of FGD particles. Only 0.3% of FGD-Hg was water soluble compared to 72.3% of FGD-Hg being strongly complexed. Residual Hg in the form of mercuric sulfide accounted for 27.3% of extracted Hg. Leachate concentrations were greatest at a pH around 1.2, but was only 0.1 mg $kg^{-1}$ in the range of pH 5 to 11, which is more representative of natural soil conditions.

Soil Eh, pH, and $Cl^-$ concentrations are the parameters that determine the speciation of Hg in the environment, which will affect Hg retention and mobility (Alloway, 1995). Although oxidation of Hg can occur solely by soil chemical characteristics, transformations of Hg may also be facilitated by soil microbes. Mercury (II) is the most common oxidation state present in nature and normally occurs as $HgCl_2$ at pH < 7 and with a redox potential above 400 mV (Alloway, 1995). In alkaline soils, $Hg(OH)_2$ is the more stable form of Hg (II). In reducing soil conditions, Hg (0) is stable in the form of $Hg_2S$ or $HS^-$. As soil Eh increases, HgS can form and precipitate out of soil solution. Mercury (II) rarely exists in soil solution and is typically adsorbed on the surfaces of inorganic and organic soil material. Retention of Hg (II) is due to hydroxoligands in the presence of sesquioxides and various ligands in the presence of humic materials. Mercury (II) may also be fixed in low-solubility sulphide and selenide precipitates. Mercury adsorption is greatest at pH 7 where HgOHCl is the prominent species. At acidic pH < 5.5 SOM is responsible for Hg sorption. Due to the strong adsorption of Hg in soil, plant uptake is minimal and leaching is insignificant. Lindberg et al. (1979) reported excess concentrations of Hg located adjacent to plant roots, indicating that the roots act as a barrier to plant uptake.

Plant uptake of Hg can also be inhibited by interactions with other trace elements present in CCBs. Shanker et al. (1996) investigated the interaction between Se and Hg in soil and their impact on uptake of Hg by radish (*Raphanus sativus*) plants. The Hg-Se interaction was examined by adding selenite and selenate at concentrations ranging from 0 to 6 µg $mL^{-1}$ to sandy and loamy soils with 2 and 5 µg $mL^{-1}$ mercury and subsequently analyzing plant concentrations of mercury. As concentrations of selenite and selenate increased, there was a significant decrease in Hg uptake in both soils as evidenced by plant tissue concentrations of Hg. Shanker et al. (1996) proposed that the formation of insoluble Hg-Se complexes made Hg unavailable for plant uptake. The presence of excess Se in CCBs may further inhibit uptake of Hg by plants grown on CCB-amended soil.

## Leaching and Runoff of Trace Elements

The addition of excess CCBs to agricultural land can result in the off-site movement of toxic trace elements through runoff and leaching. Movement of effluent and leachate to nearby aquatic ecosystems can cause changes in turbidity, pH, EC, alkalinity, and hardness (Dellantonio et al., 2010). The physiochemical characteristics of CCB effluent and leachate determines the environmental availability of trace elements. Effluent and leachate redox potential determine the speciation of trace elements, whereas effluent and leachate pH determines availability. The redox potential of CCB leachate and effluent is strongly correlated to the disposal method, whereas effluent and leachate originating from wet disposal sites tend to have the lowest redox potentials (Ladwig et al., 2005). These solutions are still considered oxidizing with Eh values ranging between -50 and +400 mV. Coal combustion by-product mineralogy determines the mode of occurrence which, along with pH, plays an essential role in the environmental availability of trace elements. Elements located within the glassy crystalline structure of CCBs are typically considered environmentally unavailable, whereas surface-associated elements are more susceptible to leaching and runoff. As flue gases cool, volatile elements, such as As, B, Hg, Cl, Cr, Mo, Se, and S, adsorb to the surface of fly ash particles, whereas elements such as Ba, Co, Cr, Mn, Ni, and Pb tend to be evenly distributed between the ash matrix and surface (Izquierdo and Querol, 2012). The alkaline nature of Class C fly ashes and high-Ca DFGD by-products effectively inhibits the environmental availability of several trace elements.

Beryllium, Cd, Co, Ni, Pb, and Zn are minimally soluble at pH 7 to 10 and can be considered a low concern under environmental conditions (i.e., mildly acidic to alkaline soil pH) (Izquierdo and Querol, 2012). Although these elements may not be available under normal environmental conditions, solubility may be increased significantly if applied or incorporated into acidic soils. Because their availability is directly correlated to pH, addition of excess CCBs will not result in a substantial release of these elements as long as effluent and leachate pH are not acidic.

Mobility of trace elements such as Be, Cd, Co, Ni, Pb, and Zn vary between CCB samples and is dependent on solution pH and concentration within the CCB. EPRI (2006) analyzed 84 US fly ashes and identified only five samples that had detectable Be concentrations. The five samples that had detectable Be had concentrations of 0.8 to 0.9 µg kg$^{-1}$ Be and were below pH 6. Although Cd can be highly soluble and toxic, fly ashes tend to have very low concentrations of Cd (<1.5 ppm) (Izquierdo and Querol, 2012). Cadmium in fly ash is insoluble at near neutral and alkaline pHs and only 3 to 9% of fly-ash cadmium was extractable at pH 4. Cobalt in CCBs is primarily associated with crystalline-Fe species making Co insoluble and environmentally unavailable at acidic, neutral, and alkaline pHs (Izuierdo and Querol, 2012). Ward et al. (2003) reported only 1.5 to 2.5% Co was available under TCLP leaching. Nickel has been reported to be distributed between the silicate and magnetic fractions, where the extractable Ni is solubilized from the non-magnetic fraction (Kim and Kazonich, 2004). The largest leachate concentrations of Ni occurred using a pH 1 extractant, but sharply decreased to < 1% in mildly acidic conditions (Kim et al., 2003; Ward et al., 2003). The majority of fly ash-Pb exists in the internal glassy matrix and therefore is environmentally unavailable (Warren and Dudas, 1988). Several authors (Kim et al., 2003; Moreno et al., 2005; Nathan et al., 1999; Praharaj et al., 2002; Ward et al., 2003) reported < 1% and < 0.1% leachable Pb for acidic and alkaline ash samples, respectively, demonstrating the unlikeliness for Pb to leach to groundwater or reach surface water in runoff. Zinc is usually present at greater concentrations than other trace elements, but the amphoteric nature of Zn makes Zn highly insoluble at near neutral to near alkaline pH. Zinc may be present in leachate and runoff at 1.0 and 0.1 mg $kg^{-1}$ for acidic and alkaline solutions, respectively (Izquierdo and Querol, 2012).

Unlike the previously mentioned elements, oxyanionic-forming species such as As, Cr, and Se display maximum solubility at pH 7 to 10. Boron and Mo solubility do not vary with pH, making solubility at acidic pHs an issue (Izquierdo and Querol, 2012). Arsenic, Cr, and Se are of a greater concern due to their potentially acute toxicity and increased mobility in the environment. The mobility of these elements may be further enhanced by changes in redox potential.

As mentioned previously, As has a tendency to form oxyanionic species in the form of arsenite and arsenate. Arsenate behaves similarly to orthophosphate by sorbing to soil particles and will not leach or runoff. However, similar to orthophosphate, arsenate can be eroded from a soil profile in runoff. Arsenic is most soluble at low pH, which decreases with increasing pH (Grisafe et al., 1988). Although As is amphoteric in nature, the formation of insoluble Ca-arsenate compounds at alkaline pHs makes loss of arsenic through leaching or runoff at alkaline pH unlikely. Grisafe et al. (1988) reported toxic concentrations of arsenic in acidic (pH 4.0) leachates, but As concentrations at pH 6 were below EPA toxicity levels. Leachate redox potential plays an equally important role as pH in determining the mobility of As. Dusing et al. (1992) leached three coal fly ashes with solutions ranging in Eh from -300 to + 600 mV. In oxidizing conditions, arsenic concentrations ranged from 0.2 to 0.7 mg $kg^{-1}$ and increased to 3.6 to 7.4 mg $kg^{-1}$ in reducing conditions. The large increase in leachate arsenic concentrations can be attributed to the reduction of insoluble arsenate to highly soluble arsenite.

The solubility and mobility of Cr in the environment are dependent on oxidation state. Hexavalent Cr compounds, such as chromates ($CrO_4^{2-}$) and dichromates ($Cr_2O_7^{2-}$), are widely recognized for their high solubility and for being carcinogenic (Huggins and Hoffman, 2004). Trivalent Cr is significantly less soluble than Cr (VI) and is of less of an environmental and health concern. Huggins et al. (1999) analyzed several coal fly ash samples using x-ray absorption, fine-structure spectroscopy to determine chromium speciation. Of the fly ash samples analyzed, Cr (VI) only comprised 3 to 5% of the total chromium present in the fly ash with the remaining being Cr (III). Under normal environmental conditions, Cr (III) behaves similarly to other trace metal cations. Adsorption and solubility of Cr (III) are influenced by soil CEC and soil pH and movement throughout the soil profile is lowest at near neutral pH and greatest in alkaline conditions (Izquierdo and Querol, 2012). Under alkaline and oxidizing conditions, Cr is likely to exist in the highly mobile Cr (VI) form. In conjunction with alkaline pHs, adsorption of Cr (VI) to soil colloids is further inhibited by excess sulfate in CCBs (Fruchter et al., 1990). Unlike As, Cr (VI) mobility is not inhibited by the formation of insoluble Ca compounds in alkaline conditions.

Of all the trace elements present in fly ash and DFGD by-products, selenium poses the greatest risk for groundwater and surface water contamination. Selinite and selenate compounds display greater mobility in the environment compared to other metalates (Cornelis et al., 2008). Grisafe et al. (1988) leached several fly ash samples in solutions of varying pH. When using a pH 4 leachate, concentrations of As, Cd, Cr, Pb, and Se were all above the EPA maximum contamination levels of 10 µg $L^{-1}$ and the safe levels for aquatic life of 5 µg $L^{-1}$. However, at pH 6, Se was the only trace element that was above EPA toxicity levels. Concentrations of Se at pH 8 ranged from 70 to 170 µg $L^{-1}$, which exceeded EPA toxicity limits and did not drop below accepted levels until pH 11.6. Rainwater that has been exposed to atmospheric conditions has a pH of ~ 5.7 (Grisafe et al., 1988), which is sufficient to solubilize CCB-Se and cause leaching and runoff of Se at concentrations that exceed EPA's maximum contaminant level. Ecological data suggests that Se concentrations of 8 to 14 µg $L^{-1}$ can cause reproductive failure and dietary toxicity in aquatic organisms (Grisafe et al., 1988). The elevated concentrations of Se present at pH > 6 can be attributed to the presence of the highly soluble selenate ion. Cantrell et al. (2014) leached a weathered and a fresh Class-C FA with deionized water, rainwater, and groundwater and reported concentrations of Se, As, and Cr at or near EPA maximum daily loads (MDL) regardless of water type and extraction time. Extraction of As and Se were unaffected by extraction time whereas Cr concentrations increased with extraction time.

Due to potential acute toxicity of Hg, environmental contamination from Hg through runoff or leaching has been a primary focus of the EPA. Sorption of Hg to fly ash is controlled by $Cl^-$ due to the formation of mobile $HgCL_2$, which is mobile in the environment. Although Hg is of concern when land applying CCBs, low concentrations of Hg have been reported in fly ash leachate. Several authors (Nathan et al., 1999; Pflughoeft-Hassett, 2004; Sanchez et al., 2006) have reported that concentrations of Hg in leachate across pH ranges of 4.5 to 13 were below < 0.2 μg $L^{-1}$.

Unlike As, Cr, and Se, B and Mo are considered plant essential nutrients. Up to 80% of Mo in fly ash is associated with the surface of coal combustion by-products, which is three times more soluble than Mo associated with the magnetic fraction of fly ash (Kukier et al., 2003). The solubility of molybdate ($MoO_4^{2-}$) is fairly consistent in the pH range 5 to 11.5. Decreased solubility of molybdate has been observed below pH 5 when it is believed to be associated with Al oxyhydroxides and above pH 11.5 when it is believed to incorporate into ettringite structures (Kumarathasan et al., 1990; Jones, 1995).

Similar to Mo, B has a dominant surface association in fly ash and is therefore extremely mobile. Cox et al. (1978) analyzed several fly ash samples from southern Illinois and western low-sulfur coal for B and reported a concentration range of 1320 to 1900 mg B $kg^{-1}$. Leachate pH did not affect leachate B concentrations with 50% B being leached at pHs between 6 and 8 and 38% at pH 10. In the pH range 6 to 8, a 15-min contact with water resulted in leaching of all soluble B from the fly ash. Although pH did not affect leachate concentrations, pH affected dissolution rate. There was no difference between leachate B concentrations between acidic and alkaline fly ashes, indicating a lack of pH dependency on solubility. Several authors (James et al., 1982; Sear et al., 2003; Ward et al., 2003) reported leachate B concentrations ranging from 17 to 65%. The high solubility and lack of pH dependence makes B contamination of surface and groundwater a concern. This is further complicated by the rate of B dissolution limiting the effectiveness of settling ponds at mitigating B runoff.

## Plant Uptake

There is concern that application of CCBs in large volumes may lead to phytotoxicity and plant uptake of trace elements that may be toxic to humans and/or animals. Similar to leaching and runoff, soil conditions such as pH, redox potential, and CEC affect the phytoavailability of trace elements and heavy metals. Under reducing conditions, elements such as selenium and chromium are adsorbed to the soil and will be less available than when under oxidizing conditions. In contrast, under reducing conditions, elements such as arsenic are more soluble and mobile in the environment. The elements that are of the most concern with regards to plant uptake are B, As, Cr, Se, and Mo due to the high mobility of oxyanionic compounds (Clark et al., 2001).

Stehouwer et al. (1996) planted alfalfa and tall fescue (*Festuca arundinacea*) in soil mixed with FGD by-products at rates equivalent to 0, 3.5, 7, 14 and 29 g $kg^{-1}$ to monitor plant uptake of macro-, micro-, and trace elements. Application of FGD by-products to alfalfa resulted in an increase in N and a decrease in P and K, whereas application to fescue had no effect on the uptake of N, P, and K. Tissue concentrations of Ca, S, Mo, and B increased for both alfalfa and fescue. Boron tissue concentrations increased from 65.1 to 76.8 mg $kg^{-1}$ in alfalfa and from 21.8 to 39.9 mg $kg^{-1}$ in fescue. Molybdenum concentrations increased from $< 0.1$ to 4.9 mg $kg^{-1}$ in alfalfa and from 0.2 to 4.3 mg $kg^{-1}$. Tissue concentrations of As, Ba, Cd, Cr, Pb, and Se did not change due to addition of the FGD products.

Chen et al. (2001) applied FGD by-products and ag lime to an acidic Typic Fragiudalf at rates equivalent to 0, 0.5, 1, and 2 times the soil's lime requirement to monitor uptake of trace elements by alfalfa. Similar to Stehouwer (1996), tissue concentrations of Mo increased significantly with application of FGD by-products. There was no difference in tissue concentrations of Mo between FGD by-product and ag-lime treatments. The increase in Mo uptake can be attributed to the increase in Mo solubility and mobility at alkaline pH. Tissue B concentrations increased significantly compared to the unamended control. Essential plant micronutrient tissue concentrations were in the range normally present in alfalfa. Tissue concentrations of As, Cr, Pb, Hg, and Se were unaffected by the application of FGD by-products.

Adriano et al. (2001) conducted a 3-yr field study to assess the effects of land applying large quantities of coal fly ash, at rates equivalent to 0, 280, 560 and 1120 Mg $ha^{-1}$, to centipedegrass (*Eremochloa ophioroides*). Fly ash applied was rototilled 15 cm into the soil and allowed to weather for 8 months prior to the seeding of the centipedegrass. There was no effect of fly ash application on N, K, Ca, Na, Al, Cu, Fe, Ag, Cd, Cr, Hg, Ni, Pb, Sb, and Tl on grass tissue concentrations at all application rates. However, grass tissue concentrations of As, B, Mo, and Se increased as application rate increased (Adriano et al., 2001).

Sale et al. (1996) incorporated unweathered fly ash from a Canadian power plant at concentrations ranging from 0 to 100% (v/v) fly ash to monitor growth response of barley on fly-ash-incorporated soils. Although the incorporated fly ash increased plant growth, barley tissue concentrations of B, Mo, and Se in certain treatments resulted in toxicity or excess uptake that could prove to be harmful to animal and/or human consumption. Boron toxicity symptoms became evident in soil treated with ≥ 6.25% fly ash and silage and straw B concentrations exceeded concentrations considered necessary for plant growth. Grain, straw, and silage tissue Se concentrations increased consistently as the amount of fly ash increased. Selenium concentrations increased from < 0.1 to 2, < 0.1 to 3.4, and from < 0.1 to 1.2 mg kg$^{-1}$ in the silage, grain, and straw, respectively. Molybdenum concentrations increased from < 0.1 to 12.3, < 0.1 to 4, and from < 0.1 to 21.3 mg kg$^{-1}$ in the silage, grain, and straw, respectively. The increase in tissue-Mo altered the Cu/Mo ratio from 216 to 0.6, 186 to 1.6, and from 133 to 0.5 in the silage, gain, and straw, respectively. The decrease in the tissue Cu/Mo concentration ratio can cause molybdenosis in ruminant animals and must be accounted for when using CCBs as a soil amendment for forage crops (Miller et al., 1991).

## Justification

Coal production in the United States is responsible for generating more than 123 million Mg of CCBs, of which only 40% are being used beneficially (ACAA, 2008). This leaves approximately 68 million Mg of CCBc to be disposed of in landfills and surface impoundment ponds. Coal by-products, such as fly ash by-products, have physical and chemical characteristics that are beneficial for use in agriculture as a soil amendment. Coal by-products contain vital essential plant mineral nutrients, such as B, Ca, Cu, Fe, Na, Mg, K, S, and Zn. Dry flue gas desulfurization by-products originating from lignitic and subbituminous coal have large concentrations of calcium and gypsum, providing potential for use as a liming material and as an amelioration option for treating subsoil acidity. However, emissions control technologies installed by coal burning power plants in response to environmental regulations have resulted in the generation of new and unstudied by-products, particularly DFGD products. In response to environmental regulations, coal-fired power plants have combined conventional desulfurization processes with the injection of activated carbon to remove Hg (Personal communication with Mark Cantrell, 2016). This new emission control process has resulted in the generation of new DFGD by-products that may be chemically dissimilar from DFGD by-products produced previously.

Although the liming characteristics of fly ash and DFGD by-products have been studied previously, the incorporation of new desulfurization technologies at the John W. Turk Coal Plant in Fulton, Arkansas and the generation of high-calcium-containing DFGD by-products warrants further research into the liming characteristics and environmental impacts of land application. Plant uptake and bioaccumulation of potentially toxic trace elements, especially in agroecosystems, is a concern with sustained land application. Furthermore, if large volumes of DFGD by-products were to be utilized as a soil amendment, runoff water could lead to the degradation of nearby adjacent aquatic and terrestrial ecosystems. Research is needed to understand the long-term impacts of land applying DFGD by-products on soil, plant, and runoff water quality.

## Objectives and Hypotheses

The first objective of this study was to quantify the liming characteristics of a DFGD by-product in comparison to a high-Ca fly ash and reagent-grade $CaCO_3$ and to monitor the ability of the DFGD by-product to increase soil pH when incubated with an acidic clay soil. The second and primary objective of this study was to determine the effects of land applying a high-Ca DFGD by-product to a silt-loam pasture soil on 1) runoff and runoff chemistry; 2) plant uptake of trace elements from DFGD application; 3) the potential accumulation of trace elements in the soil over a 1-yr time period. It was hypothesized that due to the high Ca concentrations of Class-C FAs, the coal by-products would be as effective as $CaCO_3$ at increasing soil pH at the 1x application rate, and more effective at the 2x application rate. Additionally, It was hypothesized that land application of a high-Ca DFGD by-product to a silt-loam pasture soil would 1) increase runoff FWM concentrations and loads of Cr, Se, V, and U in the first 3 mo following application relative to an unamended control; 2) increase runoff pH and EC in the first 3 mo following application relative to an unamended control; 3) increase plant biomass relative to an unamended control over a 12 month period; 4) increase plant tissue concentrations of As, Cr, Se, V, and U in the first 3 mo relative to an amended control; 5) increase soil concentrations of As, Ca, S, and V for 6 months following application relative to an unamended control.

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**Table 1.** Physical and chemical characteristics of coal mined from the Gillette coal field in the Powder River Basin, Wyoming (USGS, 1999).

| Variable | # of Samples | Range | | Mean |
|---|---|---|---|---|
| | | Minimum | Maximum | |
| Moisture[1] | 108 | 14.5 | 42.3 | 27.47 |
| Ash[1] | 87 | 3.5 | 25.06 | 7.45 |
| Total Sulfur[1] | 87 | 0.2 | 1.16 | 0.48 |
| Calorific Value[2] | 85 | 3740 | 9950 | 8220 |
| lb SO2[3] | 85 | 0.44 | 3.27 | 1.25 |
| MMMFBTU[4] | 85 | 4580 | 10560 | 8910 |
| Antimony[5] | 49 | <0.01 | 17 | 0.72 |
| Arsenic[5] | 62 | <0.20 | 19 | 2.3 |
| Beryllium[5] | 64 | <0.078 | 3.3 | 0.35 |
| Cadmium[5] | 56 | <0.007 | 3 | 0.39 |
| Chromium[5] | 65 | <0.59 | 50 | 7 |
| Cobalt[5] | 65 | <0.38 | 27 | 2.3 |
| Lead[5] | 65 | <0.50 | 17 | 2.9 |
| Manganese[5] | 66 | 0.18 | 210 | 22 |
| Mercury[5] | 66 | <0.006 | 27 | 0.17 |
| Nickel[5] | 66 | <0.71 | 35 | 5 |
| Selenium[5] | 56 | <0.08 | 16 | 1.4 |
| Uranium[5] | 61 | <0.11 | 12 | 1.5 |

[1] Values are in percent and on as-received basis

[2] Value is in British thermal units (Btu)

[3] Value is in pounds per million Btu and on an as-received basis

[4] Value is in Btu and on a moist, mineral-matter-free basis

[5] Values are in parts per million (ppm) on a whole-coal and remnant moisture basis

**Table 2.** Typical chemical characteristics of Class-C and F fly ashes (U.S. Patent WO2012091915 A1).

| | Proportion (wt. %) | |
|---|---|---|
| Component | Class C | Class F |
| $SiO_2$ | 20-40 | 50-65 |
| $Al_2O_2$ | 10-30 | 10-30 |
| $Fe_2O_3$ | 3-10 | 3-10 |
| MgO | 0.5-8 | 0.5-3 |
| $SO_3$ | 1-8 | 0.3-8 |
| C | 0.5-2 | 0.25-3 |
| $H_2O$ | 0.33-3 | 0.33-3 |
| CaO | 25-35 | 0-10 |
| $K_2O$ | 0.5-4 | 0.5-4 |
| $Na_2O$ | 0.5-6 | 1-6 |

**Table 3.** Major and trace elements in fly ash, flue gas desulfurization (FGD) by-products, and bottom ash.

| Major Elements (g $kg^{-1}$) | Fly Ash[1] | FGD[2] | Bottom Ash[1] |
|---|---|---|---|
| Al | 70-140 | 13-74 | 59-130 |
| Ca | 7.4-150 | 122-312 | 5.7-150 |
| Fe | 34-130 | 29-110 | 40-160 |
| K | 6.2-21 | 1.2-8.8 | 4.6-18 |
| Mg | 3.9-23 | 5.9-69 | 1.6-11 |
| S | 1.9-34 | 41-126 | BDL-15 |
| Si | 160-270 | 25-139 | 160-280 |
| Trace Elements (mg $kg^{-1}$) | | | |
| As | 22-260 | 44.1-186 | 2.6-21 |
| B | 120-1000 | 145-418 | BDL-3600 |
| Be | 2.2-26 | 1.6-15.1 | 0.21-14 |
| Cd | BDL-3.7 | 1.7-4.9 | BDL |
| Cr | 27-300 | 16.9-76.6 | 51-1100 |
| Cu | 62-220 | 30.8-251 | 39-120 |
| Hg | 0.01-0.51 | BDL | BDL-0.07 |
| Mn | 91-700 | 127-207 | 85-890 |
| Mo | 9.0-60 | 8.6-25.5 | 3.8-27 |
| Ni | 47-230 | 29.0-80.6 | 39-440 |
| Pb | 21-230 | 11.3-59.2 | 8.1-53 |
| Se | 1.8-18 | 3.6-15.2 | BDL-4.2 |
| Sr | 270-3100 | 308-565 | 270-2000 |
| V | BDL-360 | 20.1-122 | BDL-250 |
| Zn | 63-680 | 108-208 | 16-370 |

BDL: Below detection limit

[1] EPRI (2009)

[2] Kost et al. (2005)

# Chapter Two

# Liming Characteristics of a High-calcium Dry Flue Gas Desulfurization By-product and a Class-C Fly Ash

## Abstract

Due to coal's availability and low cost, coal combustion continues to be the United States' primary energy source. However, coal combustion produces large quantities of waste material. Some coal combustion by-products (CCBs) have chemical and physical characteristics that make them potentially useful as soil amendments. The objectives of this study were to characterize a relatively new, high-calcium dry flue gas desulfurization (DFGD) by-product and compare its agronomic liming potential to a Class-C fly ash (FA) and reagent-grade calcium carbonate ($CaCO_3$). Calcium carbonate equivalence (CCE), degree of fineness (DOF), and effective neutralizing value (ENV) for each CCB were determined using standard methods. The CCBs and $CaCO_3$ were also incubated with an acidic (~ 4.5) clay sub-soil at application rates equivalent to 0, 0.5, 1, and 2 times the soil's lime requirement and compared to an unamended control. Soil pH was then measured periodically during a 40-day incubation. The ENV of 79.4% for the DFGD by-product and 57.3% for the FA were comparable to those of commercially available liming materials, but were significantly lower ($P < 0.05$) than that of reagent-grade $CaCO_3$. After 40 days of incubation at the 0.5x application rate, both CCBs raised the pH of the clay soil to only 5.0, while the $CaCO_3$ raised the pH to 6.5. After 40 days at the 1x rate, all three materials had raised the soil pH to between 6.5 and 7.0, although the FA increased the soil pH more slowly than did the other two materials. At the 2x rate, both CCBs increased the soil pH to between 7.5 and 8.0, while the $CaCO_3$ increased the soil pH to only 7.0. Both CCBs appear to be useful as soil liming materials, although care should be taken to avoid over-application, as this may make the soil too alkaline for optimum plant growth.

## Introduction

Coal combustion for energy production accounted for 39% of the 3.9 billion kilowatt-hours of electricity generated in the United States in 2014 [1]. Although natural gas is expected to eventually surpass coal as the primary fossil fuel source for electrical power generation in the United States, the availability and low cost of coal will likely allow coal to continue to be a major source of energy for approximately the next 35 years [1]. However, in addition to electricity, the coal-combustion process also produces large quantities of waste materials. In 2008, it was estimated that more than 123 million Mg of coal combustion by-products (CCBs) were produced, making CCBs the second largest waste stream in the United States behind municipal solid waste [2]. In 2007, only 44% of the CCBs generated in the United States were beneficially reused, which left 68 million Mg to be disposed of in landfills or surface impoundments [3]. The primary beneficial reuse fly ash is in concrete and concrete products, which represents 43% of beneficially reused fly ash. As of 2012 in the United States, 310 active on-site landfills and 735 on-site surface impoundments were used to dispose of CCBs that were not beneficially reused [4].

Several types of waste products are produced from the combustion of coal for power generation. Fly ash (FA) is a CCB that is removed from flue gases by various types of particle-filtration equipment at coal-fired power plants. Fly ash consists of particles that have been fused into spherical, glassy, amorphous aluminosilicates and is classified into one of two categories depending on the composition of the coal being burned. Class-C FA has a high calcium (Ca) concentration (25 to 35%) and is derived from the burning of lignite and subbituminous coals, whereas Class-F FA has a low Ca concentration (0 to 10%) and originates from the burning of anthracite and bituminous coals [5]. Class-C FA is often referred to as “high-lime ash” and is a common by-product of coal-fired power plants burning low sulfur coals from Wyoming and Montana [6].

A more recently produced waste material is flue gas desulfurization (FGD) by-products, which result from emissions-control processes that inject a calcium sorbent into the flue gases to trap and remove sulfur dioxide ($SO_2$) from the emissions streams. Dry FGD (DFGD) systems often remove $SO_2$ and FAs simultaneously, resulting in a by-product that is a mixture of FA, unreacted sorbent, calcium sulfite ($CaSO_3 \cdot \frac{1}{2} H_2O$), and calcium sulfate ($CaSO_4 \cdot 2H_2O$) [7]. In response to recent environmental regulations, coal-fired power plants have combined conventional desulfurization processes with the injection of activated carbon to remove mercury (Hg) (personal communication, Mark Cantrell, Arkansas Electric Power2016). This new emissions-control process has resulted in the generation of new DFGD by-products that may be chemically dissimilar from DFGD by-products produced previously.

Because they contain unspent sorbent, DFGD by-products are typically alkaline and have the potential to be used as substitutes for agricultural lime. Dry FGD by-products containing Class-C FA can have particularly high concentrations of Ca and are often described as high-Ca DFGD by-products. The growing concern regarding long-term storage of CCBs has led to increased interest in finding beneficial uses for these by-products. High-Ca CCBs may have potential for use in agriculture as a liming material, which can lead to a reduction in the volume of CCBs destined for disposal in landfills and surface impoundments, while helping to ameliorate soil acidification.

It is estimated that 25 to 30% of the world's soils are acidic enough to cause reductions in crop yields, decreased bioavailability of essential plant nutrients, and increased availability of potentially phytotoxic elements such as aluminum (Al) and manganese (Mn) [8]. Acidification of soils may be caused by a variety of processes including acidic precipitation and leaching of basic cations, but is most often caused by nitrification, the process whereby ammonium ($NH_4^+$) is oxidized to nitrate ($NO_3^-$), which yields protons (i.e., $H^+$ ions) [9]. Regular application of liming materials, such as lime ($CaCO_3$), burnt lime (CaO), hydrated lime [$Ca(OH)_2$], and dolomitic limestone [$CaMg(CO_3)_2$], have been used historically to raise soil pH back to desired levels after years of acidification has lowered the soil pH beyond the minimum desired pH range for optimal plant growth. The presence of highly soluble CaO and $Ca(OH)_2$ in Class-C FA and DFGD by-products provides greater risk for increasing soil pH above 7 and neutralizing soil acidity beyond the site of incorporation [10].

Considering that DFGD by-products are a relatively new CCB that has been minimally studied, the objectives of this study were to characterize a high-Ca DFGD by-product and compare its agronomic liming potential to a Class-C FA and reagent-grade $CaCO_3$. It was hypothesized that due to the high Ca concentrations of Class-C FAs, the coal by-products would be as effective as $CaCO_3$ at increasing soil pH at the 1x application rate, and more effective at the 2x application rate.

## Materials and Methods

### Initial Soil Collection and Characterization

A grab sample of soil was collected from the 122 to 155-cm depth interval of a Pickwick silt loam (fine-silty, mixed, semiactive, thermic Typic Paleudults) [11] located under a Loblolly pine (*Pinus taeda*) plantation at the University of Arkansas Agricultural Research and Extension Center in Fayetteville, Arkansas (36°09’91.54”N 94°16’58.39”W). This soil was chosen for its acidic pH (~ 4.5) and high clay content. The soil was air-dried at 21°C for 7 d and ground to pass a 2-mm sieve. Soil texture was determined to be clay (i.e., 37% sand, 20% silt, 43% clay) using a modified 12-hr hydrometer method [12]. The liming requirement of the soil (to achieve pH 7.0) was measured using the Shoemaker, Mclean and Pratt (SMP) buffer method [13] and was determined to be 34.9 Mg ha$^{-1}$. Initial soil pH was determined potentiometrically using a 1:1 (v:v) soil:0.01$M$ $CaCl_2$ slurry.

### Liming Reagents

The three liming materials used in this experiment were reagent-grade $CaCO_3$, a Class-C FA, and a high-Ca, DFGD by-product. The Class-C FA was collected by an electrostatic precipitator and a silo baghouse from the Flint Creek Power Plant in Benton County, Arkansas [14]. The DFGD by-product was generated by a dry scrubber using an Alstom Novel Integrated Desulfurization design at the John W. Turk Power Plant in Hempstead County, Arkansas (personal communication, Mark Cantrell, 2015). Both power plants burn subbituminous coal from the Powder River Basin in Wyoming (personal communication, Mark Cantrell, 2015). The John W. Turk power plant utilizes calcium hydroxide [$Ca(OH)_2$] as the sorbent in the desulfurization process (personal communication, Mark Cantrell, 2015). Trace element concentrations of the Class-C FA and DFGD by-product were determined by inductively coupled plasma mass spectrometry (ICP-MS) following a microwave digestion in concentrated $HNO_3$.

### Effective Neutralizing Value

The effective neutralizing value (ENV) of the liming materials was calculated using the degree of fineness (DOF) and the $CaCO_3$ equivalence (CCE). The DOF was determined in triplicate by passing each of the three liming materials through 20-, 60-, and 100-mesh sieves

(0.84, 0.25, and 0.15-mm mesh size, respectively) and calculating the percentage of material by weight that passed through each sieve relative to the 20 g of initial material. Sieving of the material was conducted in accordance with ASTM C110-14 by manually sieving in a lateral and vertical motion, while occasionally jarring the sieve, for a total of 10 minutes [15]. Calcium carbonate equivalence was determined potentiometrically using an Orion 710a pH meter and an Orion 9107bn pH probe (ThermoFisher Scientific, Waltham, MA) by adding 100 mL of 1N hydrochloric acid (HCl) to 2.0 g of liming material and back-titrating to pH 7.0 with 1N sodium hydroxide (NaOH) in accordance with ASTM C25-11 [16]. The ENV was calculated using the following equation:

$$ENV = \frac{(A+B+C)\times CCE}{100}, \qquad [1]$$

where A is equal to 0.4 times the percentage of particle passing a 20-mesh sieve minus the percentage of particle passing a 60-mesh sieve, B is equal to 0.8 times the percentage of particle passing a 60-mesh sieve minus the percentage of particle passing a 100-mesh sieve, and C is equal to 1.0 times the percentage particle passing a 100-mesh sieve.

## Incubation Study

Samples were prepared in triplicate for each of the three liming materials (i.e., reagent-grade $CaCO_3$, FA, and DFGD) and an unamended control that were destructively sampled at nine sampling times (i.e., 0, 5, 10, 15, 20, 25, 30, 35, and 40 d of incubation). Therefore, there were a total of 270 samples prepared initially for incubation (3 liming materials x 9 time points x 3 rates x 3 replicates + 1 control x 9 time points x 3 replicates). Liming materials were added to

20 g of air-dry soil in 50-mL centrifuge tubes at application rates equivalent to 0x (control), 0.5x, 1x, and 2x (0, 0.175, 0.35, and 0.7 g, respectively) the soil's SMP buffer liming requirement. The tubes were thoroughly mixed by shaking for 5 min in a side-to-side shaker. Following mixing, samples were adjusted to a gravimetric moisture content of 22%, based on the estimated field moisture capacity using deionized water [17]. Soil pH was measured by adding 20 mL of 0.01*M* $CaCl_2$ to 20 g of soil and mixing for 5 min in a side-to-side shaker. The pH of the resulting slurry was measured within 1 min of shaking the mixture. Soil pH measurements were made on triplicate samples every 5 days for the duration of the 40-d incubation period.

## Statistical Analyses

A one-factor analysis of variance (ANOVA) was conducted using the PROC MIXED procedure in SAS (version 9.3; SAS Institute Inc., Cary, NC) to evaluate the effect of liming material on their liming characteristics (i.e., DOF, CCE, and ENV). In addition, a three-factor ANOVA was conducted using the PROC MIXED procedure in SAS to evaluate the effects of liming material, rate, time, and their interactions on soil pH response. When appropriate, means were separated by least significant difference (LSD) at the $\alpha = 0.05$ level.

## Results and Discussion

### Initial CCB Characterization

The mean pH of the three liming reagents used was 10.6, 12.3, and 8.4 for the DFGD by-product, FA, and reagent-grade $CaCO_3$, respectively (Table 1). Both the DFGD by-product and Class-C FA had elevated concentrations of trace elements which may warrant concern when being evaluated as a soil amendment. As a result of the high concentration of trace elements and soluble salts, the EC was 2.41 and 2.73 mS $cm^{-1}$ for the DFGD by-product and Class-C FA, respectively (Table 1). The EC of the reagent-grade $CaCO_3$ was 0.042 mS $cm^{-1}$. Continuous application of either the DFGD by-product or Class-C FA may cause an increase in soil EC and limit growth for plants that are sensitive to saline soils [10].

## Liming Characteristics

All three liming characteristics evaluated in this study (i.e., CCE, DOF, and ENV) differed somewhat among liming materials. The CCE of the DFGD by-product (84.4%) was lower ($P < 0.05$) than that for reagent-grade $CaCO_3$ (100%), while CCE for Class-C FA (60.3%) was also lower ($P < 0.05$) than that for the DFGD by-product (Figure 1). In contrast to CCE, DOF for the DFGD by-product and Class-C FA were similar to one another ($P > 0.05$), averaging 94.1 and 95.1 %, but both were lower ($P < 0.05$) than that for reagent-grade $CaCO_3$ (Figure 1). Similar to CCE, but in contrast to DOF, ENV of the DFGD by-product (79.4%) was lower ($P < 0.05$) than that for reagent-grade $CaCO_3$ (100%), while CCE for Class-C FA (57.3%) was also lower ($P < 0.05$) than that for the DFGD by-product (Figure 1). The low ENV for the Class-C FA can be attributed to the low CCE of 60.3%. The DFGD CCE of 84.4% was similar to the values reported by Kost et al. [7] who reported a CCE range of 41.6 to 97.7% for spray-dryer DFGD by-products. Schlossberg et al. [18] stated that CCEs of Class-C FAs can be as high as 60%, which is similar to the CCE of the Class-C FA examined in this experiment. Although CCE and ENV of the DFGD by-product were lower than that for reagent-grade $CaCO_3$, most commercially available liming materials have ENVs ranging between 70 and 90, which is a range that includes the mean measured ENV for the DFGD by-product evaluated in this study [19].

## Incubation Study

As expected, soil pH differed ($P < 0.001$) among liming material-application rate treatment combinations over time throughout the 40-d incubation period (Table 2). For all material-rate combinations, with the exception of the unamended control, soil pH generally sharply increased from day 0 to day 20, followed by a period of either a more gradual soil pH increase or no further increase from day 20 to day 40. The greatest differences among treatment combinations occurred among liming materials over time within an application rate.

Within 1 min after shaking the soil of the unamended control treatment, initial soil pH averaged 4.3 (Figure 2; Table 3). Soil pH in the unamended control remained virtually unchanged throughout the entire duration of the 40-d incubation period (Figure 2; Table 3). Within 5 d of incubation, the pH of soil receiving $CaCO_3$ at the 0.5x application rate was significantly greater (5.8) than the pH of soil that was incubated with the Class-C FA or DFGD by-product (4.6) (Figure 2; Table 3). After 10 d of incubation, the pH of soil receiving the 0.5x rate of $CaCO_3$ was significantly greater (6.3) than the pH of the DFGD- (5.0) and the FA-treated soil (4.7). From day 20 to day 40, soil pH did not differ between the DFGD and FA-treated soils. After 40 d of incubation, the pH of soil receiving the three liming materials had increased ($P < 0.05$) from a pH of 4.3 in the unamended control to 6.7, 5.0 and 4.8 for the reagent-grade $CaCO_3$, DFGD by-product, and FA treatments, respectively.

At the 1x application rate, the DFGD by-product and FA were more effective at raising soil pH than at the 0.5x application rate. After 5 d of incubation, the pH of the soils incubated with the DFGD by-product and FA at the 1x application rate were greater ($P < 0.05$) than those in the soils receiving the same amendments at the 0.5x application rate (Figure 2; Table 3). After 10 d of incubation, and for the remainder of the 40-d incubation period, there was no difference in soil pH between reagent-grade $CaCO_3$-amended soil and DFGD by-product-amended soil at the 1x application rate. Between 10 and 30 d of incubation at the 1 x rate, soil pH was lower ($P < 0.05$) in the FA treatment than in the reagent-grade $CaCO_3$ and DFGD by-product treatments, which did not differ. Soil pH did not differ among the three treatments at the 1x rate after 30 d of incubation. After 40 d of incubation at the 1x application rate, soil pH had increased ($P < 0 .05$) from 4.3 in the unamended control to 7.0, 7.0, and 6.7 in the reagent-grade $CaCO_3$, DFGD by-product, and FA treatments, respectively, which did not differ from one another.

Compared to the 0.5 and 1x rates, soil pH responses were even more pronounced for the 2x application rate. After 10 d of incubation at the 2x rate, the pH of the soil that was amended with either the DFGD by-product or FA was greater ($P < 0.05$) than that for the soil amended with the reagent-grade $CaCO_3$ (Figure 2; Table 3). From day 10 to day 40, the pH of soil incubated with either the Class-C FA or DFGD by-product at the 2x application rate was greater ($P < 0.05$) than the pH of soil incubated with reagent-grade $CaCO_{3.}$ After 40 d of incubation, the pH of the soils receiving the three liming materials at the 2x application rate had increased from 4.3 in the unamended control to 7.3, 8.0, and 8.0 for the reagent-grade $CaCO_3$, DFGD by-product, and FA treatments, respectively. The pH of soils incubated with either the Class-C FA or DFGD by-product was greater ($P < 0.05$) than the pH of soil incubated with reagent-grade $CaCO_{3,}$ but did not differ from each other.

Both CCBs evaluated in this study have potential for use as soil liming materials. Calcium carbonate is relatively insoluble in water and the solubility of $CaCO_3$ decreases rapidly above pH 6.0 [20]. Once the soil pH exceeds 7.0, $CaCO_3$ effectively becomes insoluble. This explains why the pH of soil amended with $CaCO_3$ at the 2x application rate was not greater ($P > 0.05$) than that of the soil amended with $CaCO_3$ at the 1x application rate. Calcium oxide (CaO) and $Ca(OH)_2$ have greater CCEs and continue to be soluble at greater pHs than $CaCO_3$, resulting in greater equilibrium soil pHs. The large concentrations of CaO and $Ca(OH)_2$ typically present in the Class-C FA and DFGD by-product may explain why both liming materials were able to raise soil pH to 8.0 when amended at the 2x application rate.

The ability of the FA and DFGD by-product to raise soil pH to 7 over approximately the same time period as $CaCO_3$ suggests that these by-products may be viable alternatives to traditional liming materials. The results of this experiment are similar to those reported in previous experiments where different CCBs were used. Punshon et al. [21] mixed a weathered FGD by-product with an acidic Paleudult (pH 5.4) at several application rates and reported an increase in soil pH from 5.5 to 8.1 in soil amended with by-product at application rates of 168 and 224 Mg $ha^{-1}$. Adriano et al. [6] mixed a Class-F (i.e., low calcium) FA with an acidic Udifluvent (pH 4.9) at an application rate of 1120 Mg $ha^{-1}$ and reported an increase in soil pH to 6.45. McCarty et al. [22] incubated soil with bed ash, FA, limestone-injection multistage burner (LIMB) residue, spray dryer residue (SDR), and $CaCO_3$ with an acidic Hapludult (pH 4.2) at application rates ranging up to 22.4, 22.4, 22.5, 89.6 and 18.0 Mg $ha^{-1}$ for the bed ash, LIMB, SDR residue, FA and $CaCO_3$, respectively. The pH of the soils at the largest application rates were 8.0, 7.7, 7.1, 7.7 and 7.8 for the bed ash, LIMB residue, SDR residue, FA, and $CaCO_3$, respectively. The ability for the CCBs tested to increase soil pH in that experiment was in directly related to their respective CCEs [22]. When the means of soil pH were adjusted for covariance of CCE, there was no difference between the FA and $CaCO_3$.

In this study, both the Class-C FA and DFGD by-product were able to raise the soil pH to 8.0 when applied at the 2x application rate. Most crops grow best in soils with a slightly acidic pH and can become stressed (i.e., due to a nutrient limitation or toxicity) if the soil pH is too alkaline. Therefore, caution must be exercised when using CCBs to avoid over-application and raising the soil pH so high that plant growth and productivity are negatively affected.

In addition to the ability to neutralize soil acidity at the surface, DFGD by-products contain large concentrations of $CaSO_4•2H_2O$ (i.e., gypsum), which has been shown to ameliorate subsoil acidity. Sumner et al. [23] reported a 20% decrease in exchangeable Al at a depth of 105 cm following surface application of gypsum at a rate of 10 Mg $ha^{-1}$. Gypsum-amended soil had a greater Ca saturation in the subsoil (i.e., the 5- to 105-cm depth interval) than the unamended control. Wendell and Ritchey [24] observed a similar trend in acidic soil columns amended with a high-Ca DFGD by-product. Leachate-Al concentrations were greater than that in the unamended control as a result of DFGD by-product addition, resulting in a decrease in the soil's exchangeable Al percentage [24].

Another possible use for these CCBs is in the reclamation of soils that have been disturbed by surface mining. Surface mining is a process can that cause severe soil acidification resulting from the exposure of Fe-sulfides in overburden materials [25]. Because acid mine lands are often very acidic (pH < 4.50), there is potential for large-scale use of alkaline CCBs to neutralize overburden acidity without creating alkaline soils. By increasing soil pH, the solubility and mobility of potentially toxic elements, such as arsenic, can be reduced [26]. Stehouwer et al. [25] and Stehouwer et al. [27] examined the effects on element solubility and mobility, as well as plant growth by amending minespoil material with DFGD by-products in a series of greenhouse studies. When applied at rates ranging from 30 to 120 g $kg^{-1}$, fescue (*Festuca arundinacea* Shreber) growth improved likely due to the increase in tissue concentrations of Ca, Mg, and S. At rates exceeding 120 g $kg^{-1}$, the soil became too alkaline and cementation of the soil occurred as a result of the formation of ettringite $[(Ca_6Al_2(SO_4)_3(OH)_{12}•26\ H_2O)]$. With increasing application rate of the DFGD by-products, there was an increase in leachate pH, EC, dissolved organic C, Ca, Mg, and S. The concentrations of leachate As, B, Cu, Ni, and Se varied depending on the concentration of DFGD by-product and spoil type. Utilizing CCBs as a minespoil amendment may be more desirable than as an agronomic soil amendment because of the potential for plant uptake of trace elements by agronomic crops.

## Summary and Conclusions

Each year, millions of megagrams of CCBs are disposed of in landfills and surface impoundments, which increases the likelihood of accidental releases to the environment. Certain CCBs, such as Class-C FAs and DFGD by-products, possess physical and chemical properties that make them potentially useful as soil liming materials. Use of CCBs in lieu of conventional agriculture liming materials may be a viable alternative to mitigating soil acidity in an economical and environmentally friendly manner, provided a local source of CCBs is available. The presence of gypsum in DFGD by-products provides the additional benefit of reducing subsoil acidity by acting as a source of $Ca^{2+}$ ions and lowering levels of exchangeable $Al^{3+}$. However, the presence of trace elements and heavy metals warrants caution if CCBs are used as a soil amendment.

The results of this experiment support the hypothesis that when CCBs, specifically Class-C FA and DFGD by-product, are added to an acidic subsoil at a rate equivalent to the SMP buffer lime requirement, the soil pH after 40 d would be similar to the pH in reagent-grade $CaCO_3$-amended soil. Results also supported the hypothesis that the pH of soil incubated with the DFGD by-product and Class-C FA at 2x the SMP buffer lime requirement would be greater than soil incubated with reagent-grade $CaCO_3$. This experiment demonstrated that the relatively new DFGD by-product has similar liming characteristics to reagent-grade $CaCO_3$ and a Class-C FA, which may provide a viable alternative use of DFGD by-product as a soil amendment and liming material and would diminish the need to dispose of these materials in landfills and surface impoundments.

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**Table 1.** Mean chemical characteristics of a high-Ca dry flue gas desulfurization (DFGD) by-product from the John W. Turk Power Plant in Hempstead County, Arkansas and a Class-C fly ash (FA) from the Flint Creek Power Plant in Benton County, Arkansas. The $CaCO_3$ used in this experiment was reagent grade.

| Parameter | DFGD | FA |
|---|---|---|
| pH† | 10.64 | 12.28 |
| EC‡ (mS $cm^{-1}$) | 2.41 | 2.73 |
| | | |
| Trace element (mg $kg^{-1}$) | | |
| Be | 21.47 | 3.98 |
| V | 137.68 | 57.71 |
| Cr | 81.14 | 72.07 |
| Co | 16.92 | 54.32 |
| Ni | 43.08 | 29.19 |
| Cu | 73.16 | 49.60 |
| Zn | 140.83 | 50.50 |
| As | 13.33 | 14.56 |
| Se | 12.86 | 5.28 |
| Rb | 1.38 | 48.39 |
| Cd | 0.44 | 0.71 |
| Cs | 1.27 | 2.60 |
| Hg | 0.81 | 0.00 |
| Pb | 0.20 | 108.24 |
| Th | 3.43 | 28.40 |
| U | 5.34 | 1.57 |

† pH was measured in a 1:1 0.01 *M* $CaCl_2$: solid slurry

‡ EC was measured in a 2:1 DI water: Reagent slurry

° $CaCO_3$ pH= 8.44; EC= 0.042 mS $cm^{-1}$

**Table 2.** Analysis of variance summary of the effects of liming material (i.e., product), rate, and time (i.e., days into incubation), and their interactions on soil pH after 40 days of incubation in a clay soil.

| **Source of Variation** | **Soil pH** |
|---|---|
| | — P — |
| Liming material | < 0.001 |
| Rate | < 0.001 |
| Liming material*rate | < 0.001 |
| Time | < 0.001 |
| Liming material*time | 0.002 |
| Rate*time | < 0.001 |
| Liming material*rate*time | < 0.001 |

**Table 3.** Mean pH of soil incubated with reagent-grade $CaCO_3$, Class-C fly ash (FA), and a high-Ca dry flue gas desulfurization (DFGD) by-product at rates equivalent to 0.5x, 1x, and 2x the Shoemaker-Mclean-Pratt (SMP) lime requirement over a 40-day period.

| | | Application Rate | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.5x | | | 1x | | | 2x | | |
| Day | Control | FA | DFGD | $CaCO_3$ | FA | DFGD | $CaCO_3$ | FA | DFGD | $CaCO_3$ |
| 0 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 |
| 5 | 4.0e[†] | 4.6d | 4.6d | 5.8bc | 5.0d | 5.7c | 6.2b | 6.7a | 6.8a | 6.7a |
| 10 | 4.1e | 4.7d | 5.0cd | 6.3b | 5.3c | 6.2b | 6.4b | 7.5a | 7.4a | 6.3b |
| 15 | 4.3e | 4.7e | 4.7e | 6.6bc | 5.4d | 6.4c | 6.6bc | 7.9a | 7.6a | 6.8b |
| 20 | 4.3f | 4.6f | 4.7f | 6.7cd | 6.0e | 6.4de | 6.4de | 8.2a | 7.7b | 7.0c |
| 25 | 4.2f | 5.1e | 4.9e | 6.6bc | 6.0d | 6.5c | 6.8bc | 7.7a | 7.9a | 6.9b |
| 30 | 4.2f | 4.8e | 4.7e | 6.9d | 6.9d | 6.9d | 7.0cd | 8.1a | 7.6b | 7.1c |
| 35 | 4.2d | 4.8d | 4.8d | 6.8bc | 6.8bc | 6.5c | 7.0b | 7.9a | 7.7a | 7.1b |
| 40 | 4.2e | 4.8d | 5.0d | 6.7c | 6.7c | 7.0bc | 7.0bc | 8.0a | 8.0a | 7.3b |

[†] Means followed by a different letter within a row are significantly different ($P < 0.05$)

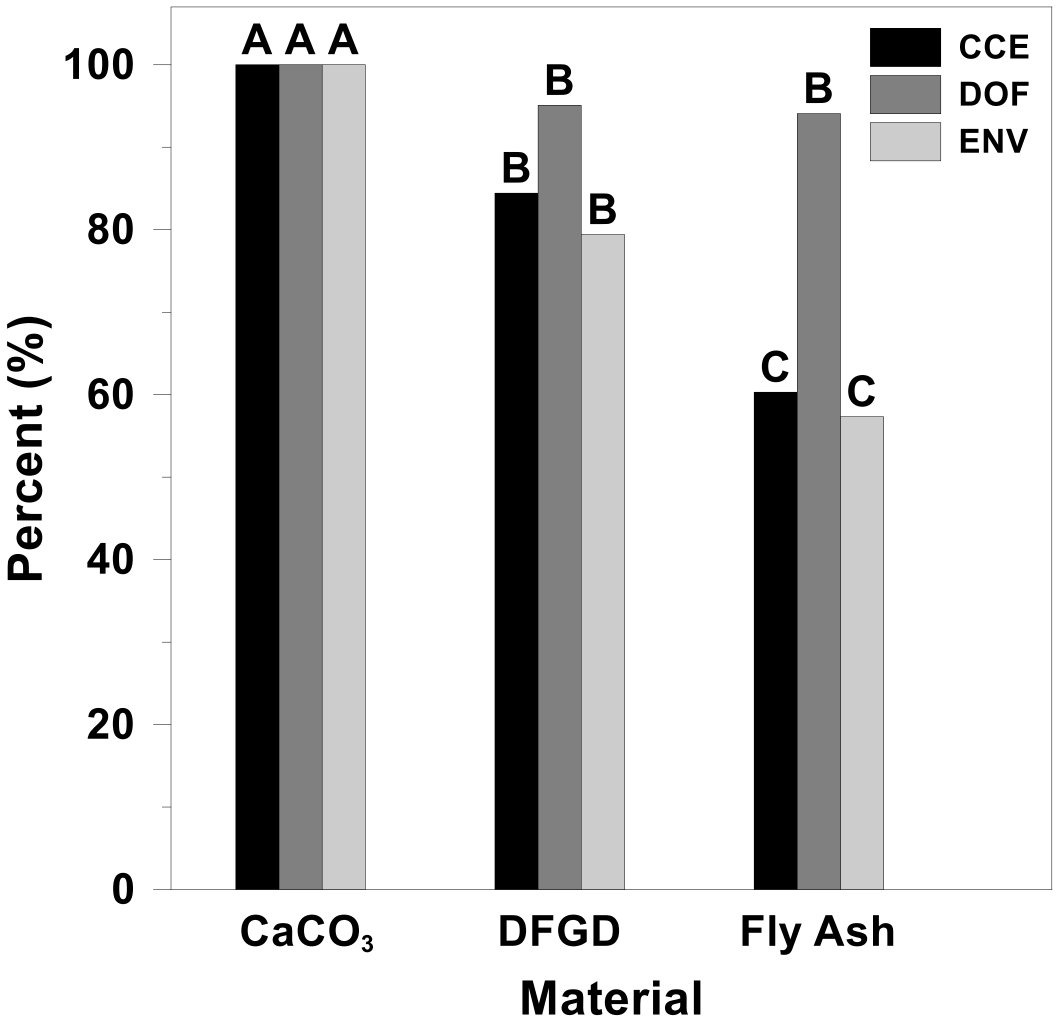

**Figure 1.** Calcium carbonate equivalence (CCE), degree of fineness (DOF), and effective neutralizing value (ENV) of reagent-grade $CaCO_3$, a high-Ca dry flue gas desulfurization (DFGD) by-product, and a Class-C fly ash. Bars of the same color with different letters are significantly different ($P < 0.05$).

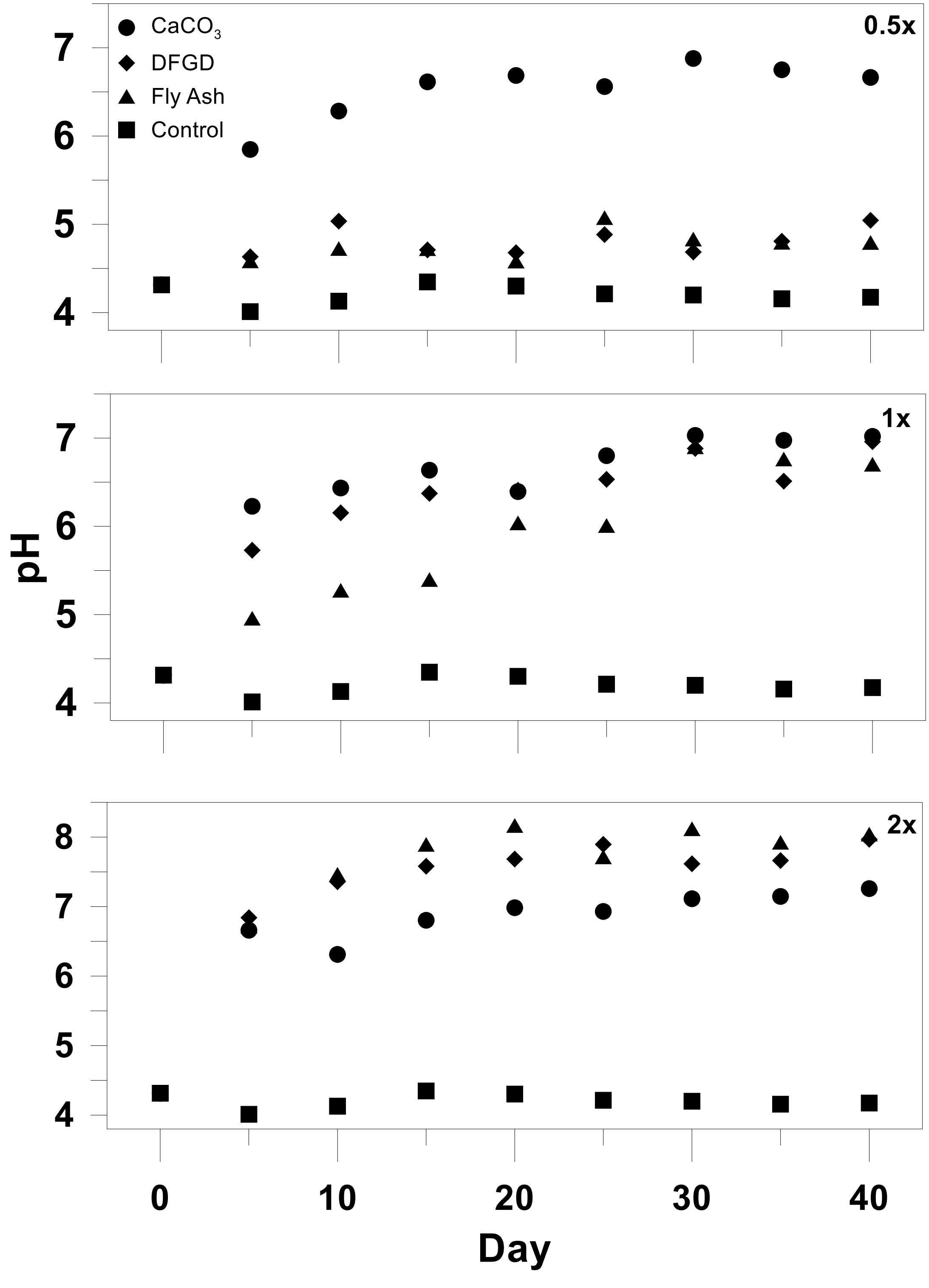

**Figure 2.** Soil pH response after incubation at 0.5x, 1x, and 2x the Shoemaker-Mclean-Pratt (SMP) liming requirement with reagent-grade $CaCO_3$, Class-C fly ash, and a high-Ca dry flue gas desulfurization (DFGD) by-product over a 40-day period.

# Chapter Three

## Land Application Effects of a High-Calcium, Dry Flue Gas Desulfurization By-product on Trace Elements in Runoff

## Abstract

Due to its low cost and large abundance, coal continues to be the primary energy source for electricity generation in the United States. The desulfurization of flue gases during coal combustion produces dry flue gas desulfurization (DFGD) by-products that have properties that make them potentially useful as a soil amendment. However, DFGD by-product behavior once land-applied and exposed in the environment has not been well investigated, particularly trace element levels in runoff from DFGD-treated fields. The objective of this study was to evaluate the effects of land application of a high-Ca, DFGD by-product compared to an unamended control on trace elements in runoff, plant tissue, and the top 30 cm of the soil profile throughout one year following application. A high-Ca, DFGD by-product was applied once on May 18, 2015 at 9 Mg DFGD ha$^{-1}$ to small plots of a highly weathered Ultisol under managed-grassland land use in northwest Arkansas. Runoff was collected following each runoff-producing precipitation event. Plant and soil samples were collected prior to application and several times following application. Seasonal [i.e., Summer (May to August), Fall (August to November), Winter (November to February), and Spring (February to May)] and annual runoff and runoff pH and electrical conductivity did not differ ($P > 0.05$) between DFGD treatments. Seasonal flow-weighted mean Ni concentrations and seasonal V loads were greater ($P < 0.05$) when amended compared to the unamended control during at least one season by 44.5 and 86.9% for Ni and V, respectively. Aboveground dry matter and tissue concentrations of As, Se, Cr, Co, Hg, V, and U were greater ($P < 0.05$) when amended compared to the unamended control. In June 2015, aboveground DM and tissue concentrations of As, Se, Cr, Co, Hg, V, and U were greater in the amended treatment than in the unamended control by 83.3, 175, 235, 119, 134, 52.9, 471, and 254%, respectively. Trace element concentrations in plant tissue decreased from the greatest

concentration to pre-application concentrations within 6 mo following application. The soil pH in the amended treatment 6 mo after application (pH = 6.44) was greater ($P < 0.05$) than in the unamended control, which did not change ($P > 0.05$) over time throughout the experiment. Soil concentrations and contents of Ca, S, and Na increased ($P < 0.05$) compared to the unamended control over time from DFGD amendment. Six months after application, Mehlich-3 extractable S and Na concentrations were 170 and 52.1%, respectively, greater in the amended than in the unamended control, and Mehlich-3 extractable S and Na contents were 166 and 50.9% greater, respectively, than in the unamended control. Mehlich-3 extractable Ca concentration and content in the top 10 cm were 26.6 and 30.4% greater, respectively, in the amended than in the unamended control. Based on the results of this study, it appears that land application of a high-Ca DFGD by-product at rates ≤ 9 Mg $ha^{-1}$ can increase soil pH and extractable soil Ca and S with only temporary effect on trace element concentrations in plant tissue, while having minimal effects on trace elements in runoff and soil. Thus, this material may be suitable for land application as a liming material.

## Introduction

The Clean Air Act Amendment (CAAA) of 1990 required coal-fired power plants to reduce emissions of sulfur dioxide ($SO_2$) resulting in the installation of desulfurization systems, which create flue gas desulfurization (FGD) by-products. Sulfur dioxide is removed from emission streams by injecting a calcium based sorbent [i.e., calcium carbonate ($CaCO_3$), calcium hydroxide [$Ca(OH)_2$], or calcium oxide (CaO)] into the flue gases to react with and remove $SO_2$ from the emissions stream (Punshon et al., 2001). The desulfurization process results in the generation of FGD by-products that are primarily hydrous and anhydrous calcium sulfite ($CaSO_3$) and calcium sulfate ($CaSO_4$). Dry FGD (DFGD) emissions control systems often stabilize FGD by-products with fly ash, resulting in a by-product that is a mixture of unreacted calcium sorbent, fly ash, calcium sulfite hemihydrate ($CaSO_3$•0.5 $H_2O$), anhydrite ($CaSO_4$) and gypsum ($CaSO_4$•$2H_2O$) (Kost et al., 2005). Dry FGD systems that stabilize FGD by-products with Class-C (high lime; Adriano et al., 2001) fly ash result in the generation of high-Ca DFGD by-products.

Considering DFGD by-products contain unreacted sorbent and Ca-oxides, which are present in fly ash, DFGD by-products are typically alkaline and have been successfully used as a substitute for agricultural lime for increasing soil pH (Stehouwer et al., 1996; Crews and Dick, 1998; Chen et al., 2001). Although $CaCO_3$ is the most commonly used agricultural liming material, the relative insolubility of $CaCO_3$ inhibits the ability of $CaCO_3$ to raise the soil pH much beyond the site of incorporation (Baligar et al., 2011). The presence of highly soluble Ca-oxides such as $Ca(OH)_2$ and CaO in DFGD by-products, provide greater potential for increasing soil pH beyond the site of application (Clark et al., 2001). The ability of $CaCO_3$ to raise soil pH decreases as soil pH nears 7, whereas CaO and $Ca(OH)_2$ can continue to increase soil pH above

7. The ability to raise soil pH can mitigate Al and Mn toxicity, which can become prevalent in acidic soils. Manganese toxicity can cause necrosis and chlorosis in some plant leaves and Al toxicity can cause a reduction in root growth and symptoms similar to drought stress (Foy, 1984; Kamprath and Foy, 1985). Alleviating Al and Mn toxicity by soil liming can increase plant growth and crop yields (Foy, 1984). Application of gypsum ($CaSO_4 \bullet 2H_2O$) to soil has been reported to alleviate subsoil acidity symptoms by forming soluble, but non-phytotoxic, cationic aluminum sulfate ($AlSO_4^+$) complexes, which reduces Al phytotoxicity (Sumner et al., 1986). Wendell and Ritchey (1996) reported a 25-fold increase in leachate-Al in soil columns that received FGD by-products as a soil amendment, resulting in a reduction in the soils exchangeable Al percentage.

Flue gas desulfurization by-products can also be used as a nutrient source due to elevated concentrations of plant-essential nutrients. Kost et al. (2005) performed an extensive assessment of 59 DFGD by-products from 13 coal-fired power plants and reported that appreciable quantities of plant-essential Ca, Mg, Fe, S, B, Cu, Mn, Ni, P, and Zn were present among the various DFGD by-products. Sloan et al. (1999) applied FGD residue to alfalfa (*Medicago sativa L.*) grown on B-deficient soils at rates of 0, 0.46, and 3.75 Mg $ha^{-1}$ prior to seeding. Alfalfa root concentrations of B, S, and Mo significantly increased in the FGD-amended treatment compared to an unamended control. Similar to Sloan et al. (1999), Chen et al. (2001) reported increased B and Mo concentrations in alfalfa tissue grown on an acidic (pH 4.8) Fragiudalf amended with a FGD by-product compared to an unamended control. However, unlike Sloan et al. (1999), Chen et al. (2001) reported a 7-8-fold yield increase of alfalfa compared to an unamended control when the FGD by-product was applied at a rate equivalent to the liming requirement of the soil. When three different FGD by-products were mixed with an acidic (pH 4.0) Dystrochept in pots, there was a significant increase in plant dry matter, soil pH, and maize (*Zea mays L.*) shoot concentrations of Ca, P, and Mg compared to an unamended control (Clark et al., 2006). There was also a decrease in P- and Mg-deficiency symptoms and Al toxicity compared to an unamended control (Clark et al., 2006). Punshon et al. (2001) conducted a mesocosm experiment to monitor the effects of FGD by-product incorporation on establishment of maize, soybean (*Glycine max L.*), radish (*Raphanus sativus L*), and cotton (*Gossypius hirsutus*), as well as the effects of incorporation on nutrient concentrations in the plant and soil. Application of the FGD by-product resulted in significantly greater soil pH and $HNO_3$-extractable B, Ca, and Mg and a numerical increase in extractable K in the soil below the incorporation layer (Punshon et al., 2001). In addition, leaf B and Mo concentrations increased in maize, cotton, soybean, and radish compared to the unamended control (Punshon et al., 2001). Leaf and root Ca concentrations in maize and cotton were also significantly increased compared to an unamended control (Punshon et al., 2001).

Although DFGD by-products have potential for use as a soil amendment, the presence of soluble salts and potentially toxic trace elements warrant concern when these by-products are used as a soil amendment. Punshon et al. (2001) reported an increase in leaf and root As and Se concentrations in maize, cotton, soybean, and radish compared to an unamended control. Application of the FGD residue also resulted in a significant increase in $HNO_3$-extractable soil As, Se, and Sr as well as an increase in total elemental soil As, Be, Co, and Se concentrations below the incorporation layer (Punshon et al., 2001). There was also a significant increase in leachate salinity in all mesocosms receiving FGD by-products compared to an unamended control. Similar to Punshon et al. (2001), Chen et al. (2001) reported an increase in alfalfa tissue As and Hg concentrations compared to an unamended control. Crews and Dick (1998) reported

B toxicity in the plant tissue of Northern red oak (*Quercus rubra* L.) when a FGD by-product was applied at a rate that was twice the soil's lime requirement. Leachate Pb concentrations in treatments receiving the FGD by-products were significantly increased compared to those from an unamended control (Crews and Dick, 1998).

In 2013, 32 million megagrams of FGD by-products were generated in the United States, but only 37% were reused beneficially, leaving a plethora of FGD by-products destined for landfills or surface impoundments (ACAA, 2014). One of the primary beneficial reuses of DFGD by-products is in wallboard or concrete. Although large-scale land application in row-crop agriculture is unlikely, if it were to be shown that DFGD by-products could be utilized as a soil amendment without adverse environmental effects, millions of megagrams of DFGD by-product could be diverted from landfills and surface impoundments. If DFGD by-products were to be used as a soil amendment, the effects of land application on the various potential environmental fates of the material, including runoff, plant uptake, and soil storage changes, needs to be studied under field conditions.

Currently, there is a lack of knowledge from field studies regarding the effects of land-applying DFGD by-products, particularly regarding trace element concentrations and loads in runoff. Consequently, more information is needed before DFGD by-products can be considered environmentally safe to use as a soil amendment on agricultural lands. The objective of this field study was to evaluate seasonal and annual effects of land application of a high-Ca, DFGD by-product to a highly weathered Ultisol under managed-grassland land use on trace elements in runoff water, plant tissue, and the top 30 cm of the soil profile over a 12-mo period following a single application. It was hypothesized that, due to elevated concentrations of trace elements in coal combustion by-products, there would be a significant increase in runoff concentrations of trace elements in the first 3-month season following application. It was also hypothesized that land application would result in a significant increase in plant tissue concentrations of As, Cr, Hg, and Se for in the first 3-mo season following application. Additionally, it was hypothesized that land application would result in a significant increase in soil pH and extractable soil Ca and S.

## Materials and Methods

### Site Description

As previously described in Pirani (2005) and McMullen (2014), six plots, 6-m long by 1.5-m wide, were located at the University of Arkansas System Division of Agriculture's Arkansas Agricultural Research and Extension Center in Fayetteville, AR on a 5% west-to-east slope. The research plots were located in an area mapped as a Captina silt loam (fine-silty, siliceous, active, mesic Typic Fragiudult; USDA-NRCS, 2015) with ground cover predominately tall fescue (*Festuca arundinacea*), clover (*Trifolium spp.*), Johnson grass (*Sorghum halepense L.*) and Bermuda grass (*Cynodon dactylon L.*) (Pirani, 2005; McMullen, 2014). Pirani (2005) measured soil particle-size distribution and determined that each 10-cm interval to a depth of 30 cm was silt loam, with sand, silt, and clay ranging from 27.6 to 31.4%, 56.9 to 63.1%, and 55.5 to 15.6 %, respectively. Aluminum gutters were positioned on the down-slope edge of each plot to direct runoff into subsurface collection bottles and were covered with acrylic sheets to prevent direct precipitation from contaminating and/or diluting collected runoff. Steel borders were located around the perimeter of each plot to prevent runon and channel runoff towards the aluminum gutters.

## Study Area History

From 2003 to 2012 prior to this study, the same field plots used in this study received broiler litter as an annual soil amendment (Pirani, 2005; McMullen, 2014). Broiler litter was applied at three application rates [0 (control), 5.6 (low), and 11.2 Mg dry litter $ha^{-1}$ (high)] in a randomized complete block design with two replications for each application rate. No litter was applied in the two years immediately preceding the initiation of this study.

## Experimental Design and Application Rates

For this study, the six original experimental plots were re-arranged with three replications of two field treatments (i.e., amended and unamended) to evaluate the effects of DFGD land application on runoff, plant, and soil properties. To compensate for the three application rates of broiler litter previously used, each treatment (amended and unamended) contained a randomly assigned replicate plot of the control, low, and high broiler-litter treatments from the previous broiler litter experiment. Dry FGD by-product treatments in this study included two application rates imposed once as a single application. The DFGD by-product was applied at a rate of 0 (unamended) and 9 (amended) Mg DFGD $ha^{-1}$. The DFGD by-product was applied manually evenly over the plots using a flour sifter on May 18, 2015.

## Dry Flue Gas Desulfurization Byproduct Analyses

The DFGD by-product was collected from the John W. Turk Power Plant in Hempstead County, AR and was produced by a dry scrubber using an Alstom Novel Integrated Desulfurization design (Personal communication with Mark Cantrell, Arkansas Electric Power, 2015). The pH of the DFGD byproduct was determined potentiometrically using a 2:1 (v/m)

0.01*M* $CaCl_2$:DFGD mixture using an Orion 710a pH meter with an Orion 9107bn pH probe (Thermofisher Scientific, Waltham, MA). The electrical conductivity (EC) of the DFGD by-product was also determined potentiometrically using a 2:1 (v/m) distilled water: DFGD mixture using an Orion Star A215 conductivity meter with an Orion 01305MD conductivity cell (Thermofisher Scientific, Waltham, MA). Acid-extractable plant nutrients (i.e., P, K, Ca, Mg, S, Na, Fe, Mn, Zn, Cu, and B) and trace elements (i.e., Be, V, Cr, Co, Ni, As, Se, Rb, Cd, Cs, Hg, Pb, Th, and U) were determined by inductively coupled, argon-plasma mass spectrometry (ICP-MS) (iCAP™ Q ICP-MS, Thermo Scientific, Waltham, MA) following microwave acid digestion using 12 mL of 70% (w/w) $HNO_3$ and 3 mL of 37% (w/w) HCl per 0.5 g DFGD by-product. Dry FGD-Hg concentrations were determined by ALS Environmental, Inc. (Tucson, AZ) by thermal decomposition amalgamation in accordance with EPA method 7473 (USEPA, 2007).

### Soil Collection and Analyses

Prior to application of the DFGD by-product to field plots in May 2015, four soil samples were collected in 10-cm intervals from the top 30 cm in each plot and combined to form a single composite soil sample per depth per plot. Soil samples were also collected six and 12 months following application in November 2015 and May 2016 in 10-cm intervals from the top 30 cm in each plot and combined to form a single composite soil sample per depth per plot. Soil samples were oven dried at 70°C for at least 48 hours and ground to pass a 2-mm mesh sieve for chemical analyses. Mehlich-3 extractable soil nutrients (i.e., P, K, Ca, Mg, S, Na, Fe, Mn, Zn, Cu, and B) were determined using a 1:10 (m/v) soil-to-extractant ratio (Zhang, 2014) and analyzed by ICP. Acid-extractable trace elements (i.e., As, Cd, Co, Cr, Ni, Pb, Rb, Se, V, Th, and U) were determined by ICP-MS (iCAP™ Q ICP-MS, Thermo Scientific, Waltham, MA) following microwave acid digestion using 12 mL of 70% (w/w) $HNO_3$ and 3 mL of 37% (w/w) HCl per 0.5 g of soil using a CEM MARS 5 microwave reaction system (CEM Corporation, Matthews, NC). Soil-Hg concentrations were determined for the 0- and 6-mo time periods by thermal decomposition amalgamation (ALS Environmental, Inc., Tucson, AZ) in accordance with EPA method 7473 (USEPA, 2007).

In May 2016, soil bulk density samples were collected in 10-cm intervals from the top 30 cm in each plot. A 4.8-cm-diameter, stainless steel core chamber was manually driven into the ground with a slidehammer. Samples were oven-dried at 70°C for at least 48 hours and weighed for bulk density determinations. Measured soil concentrations for each of the three soil sampling times were converted to soil contents, on a plot-by-plot basis, using a 10-cm sampling interval and the measured bulk densities from the May 2016 sampling. Therefore, it was assumed that soil bulk density in each 10-cm interval in the top 30 cm did not change over the 1-yr period following by-product application.

## Plant Sampling and Analyses

Plant biomass samples were hand-collected to a height of 10 cm using two randomly located 0.25-$m^2$ quadrats from each plot that were combined to form one composite sample per plot. Biomass samples were collected in November 2014, May, June, July, August, September, and November 2015, and May 2016. Collected biomass samples were dried for 1 week at 55°C in a forced-air drier and weighed for dry matter (DM) determination. Dried biomass was ground, sieved through a 2-mm mesh screen, and then digested using 12 mL of 70% (w/w) $HNO_3$ and 3 mL of 37% (w/w) HCl per 0.5 g DM using a CEM MARS 5 microwave reaction system (CEM Corporation, Matthews, NC). Digested tissue samples were used to determine trace element concentrations (As, Cd, Co, Cr, Cu, Ni, Pb, Rb, Se, V, Th, U, and Zn) by inductively coupled, argon-plasma mass spectrometry (iCAP™ Q ICP-MS, Thermo Scientific, Waltham, MA). Dry-matter-Hg concentrations were determined for November 2014 and May, June, July, August, September, and November 2015 tissue samples by thermal decomposition amalgamation (ALS Environmental, Inc., Tucson, AZ) in accordance with EPA method 7473 (USEPA, 2007).

### Runoff Collection and Analyses

Following DFGD application, runoff water was collected from each plot after every runoff-producing precipitation event from May 18, 2015 to May 18, 2016. The first 15 mL of runoff from each plot was used to determine pH and EC in the laboratory immediately following runoff collection and then discarded. Runoff pH was measured using a pH electrode (Orion Triode, No. 91-79) and EC was measured using a conductivity cell (VWR symphony, No. 11388-382). Any remaining runoff sub-sample, up to 250 mL, was filtered through a 1.6-µm glass microfiber filter (Whatman GFA- 1820-110; Whatman International Ltd., Maidston, England) and then vacuum-filtered through a 0.45-µm Metricel membrane filter (GN-6; Pall Life Sciences Corporation, Ann Arbor, MI). Runoff volumes varied between runoff-producing precipitation events, thus the first 15 mL used for pH and EC measurements were prioritized. Following filtration, up to three, 20-mL aliquots were acidified using one drop of 36% (w/w) HCl per 10 mL of filtrate. Acidified samples were stored at 4°C until further analyses. Excess runoff samples were then discarded. Acidified aliquots were used to determine trace element concentrations (As, Be, Cd, Co, Cr, Cu, Ni, Pb, Rb, Se, V, Th, U, and Zn) by ICP-MS (iCAP™ Q ICP-MS, Thermo Scientific, Waltham, MA). Runoff-Hg was determined using a manual cold-vapor technique (ALS Environmental, Inc., Tucson, AZ) in accordance with EPA method 7470a

(USEPA, 1994) for the first 7 mo following application only (i.e., May to December 2015) due to the cost of Hg analyses.

## Plot Management and Weather Data Collection

After each biomass sampling, all remaining above-ground biomass in the plots was removed using a push mower to a height of approximately 10 cm. Runoff collection gutters and bottles were cleaned prior to most precipitation events.

An on-site weather station monitored wind speed, air temperature, relative humidity, and solar radiation every 30 min. Precipitation was measured using an on-site tipping bucket rain gauge.

## Calculations

Flow-weighted mean (FWM) runoff concentrations (mg $L^{-1}$) and cumulative runoff loads (g $ha^{-1}$) were determined seasonally (i.e., Summer, Autumn, Winter, and Spring) and annually for the 12-mo period following application of the DFGD by-product. For the purpose of this experiment, Summer was defined as the third week of May to the third week of August, Autumn was defined as the third week of August to the third week of November, Winter was defined as the third week of November to the third week of February, and Spring was defined as the third week of February to the third week of May. Flow-weighted mean concentrations were calculated by dividing the total elemental mass collected in runoff for each plot during the time period of interest by the total volume of runoff for the respective time period. Loads were calculated by dividing the total elemental mass in runoff for each plot during the time period of interest by the plot area (9 $m^2$). Mean runoff pH and EC were calculated for each plot seasonally and annually.

Cumulative plant uptake was calculated by multiplying measured elemental concentrations in the aboveground DM by the mass of harvested DM, and then summing the mass of elements for the 12-mo experimental duration.

### Statistical Analyses

Based on a completely random design, a two-factor analysis of variance (ANOVA) was used to evaluate seasonal effects of DFGD by-product application on runoff volume, runoff pH and EC, and runoff FWM trace element concentrations and loads using the PROC MIXED procedure in SAS (version 9.4; SAS Institute Inc., Cary, NC). Similarly, a two-factor ANOVA was used to evaluate the effects of DFGD by-product application and time on plant tissue concentrations of trace elements using the PROC MIXED procedure in SAS. A one-factor ANOVA was used to evaluate the effects of by-product application on annual FWM runoff concentrations and loads and cumulative 1-yr plant uptake of trace elements using the PROC MIXED procedure in SAS. A three-factor ANOVA was used to evaluate the effects of DFGD by-product application, time, and depth on Mehlich-3 extractable soil nutrient and trace element concentrations and contents using the PROC MIXED procedure in SAS. When appropriate, means were separated by least significant difference (LSD) at the 0.05 level.

## Results and Discussion

### DFGD By-product Characterization

The DFGD by-product used in this study contained appreciable concentrations of both essential plant nutrients and trace elements. Plant nutrient concentrations in the DFGD by-product ranged from 0.3 to 410 g kg$^{-1}$ for Zn and Ca, respectively (Table 1). Trace element concentrations ranged from 0.4 to 138 mg kg$^{-1}$ for Cd and V, respectively (Table 1). The major and trace element concentrations contained in the DFGD by-product used in this experiment were similar to the concentration ranges reported by Kost et al. (2005) for 59 different DFGD by-products from IL, KY, MI, MN, NY, OH, TN, and WV. Considering the elemental composition of the DFGD by-product used in this field study, runoff water quality concerns could potentially arise from land application of this material.

## Pre-treatment Uniformity

Due to the varied history of the plots used in this field study, it was necessary to evaluate pre-treatment uniformity of DM and near-surface soil characteristics prior to initial DFGD by-product application. Based on two aboveground DM harvests (i.e., November 2014 and May 2015) and one soil sampling (i.e., May 2015) prior to DFGD by-product application, there was no difference in aboveground DM between the amended treatment and the unamended control on either sample date (Table 2). Only one plant property differed between treatments, where plant-tissue Hg concentration was 42.2% greater ($P < 0.05$) in the amended treatment than in the unamended control in November 2014 (Table 2). In May 2015, there was no difference in tissue-Hg concentration between the amended treatment and unamended control (Table 2). However, tissue-Cu concentrations in the May 2015 sampling were 54% greater ($P < 0.05$) in the amended treatment than in the unamended control.

Soil pH and EC and Mehlich-3 extractable soil nutrient concentrations did not differ between the amended treatment and unamended control in all depth intervals prior to application (Table 3). Soil Ni concentrations (Table 3) and contents (Table 4) were greater ($P < 0.05$) in the 10- to 20-cm depth interval of the unamended control and soil U concentrations (Table 3) were greater ($P < 0.05$) in the unamended control in the 20- to 30-cm depth interval than in the amended treatment. Although the plots used in this field experiment received annual broiler litter application for an extended period of time prior to DFGD by-product application, the plots had not been amended with broiler litter for at least two years prior to the initiation of this experiment. Consequently, since plant tissue and soil trace element concentrations between pre-assigned treatments differed only slightly, any differences observed after DFGD application in this study were assumed to be the result of the actual DFGD by-product application rather than due to inherent differences among plots prior to land application of the DFGD by-product.

### DFGD-Application Effects on Runoff and Runoff Water Quality

No noticeable temporal patterns in runoff (Figure 1) and runoff pH and EC (Figure 2) existed over the 12-mo study period. There were also no discernable patterns in mean runoff concentrations of As, Se, Cu, Be, and Cs (Figures 1, 3, and 4). However, in contrast to runoff and runoff pH and EC, runoff V concentrations in both the amended treatment and unamended control were greatest immediately following application, and then slowly decreased over 75 days following application (Figure 5). In contrast to V, runoff Zn concentrations started low immediately after application, but continued to increase for the remainder of the field experiment in both the amended treatment and unamended control (Figure 5). Mean runoff concentrations of U in the unamended control and amended treatment were near 0.5 $\mu g \ L^{-1}$ immediately following application, but concentrations decreased to ~ 0.1 $\mu g$ U $L^{-1}$ 25 days following application (Figure 6). Although runoff V and U were initially high concentrations, the temporal trends for both treatments were similar. Mean runoff concentrations of Co, Ni, and Pb spiked midway through the experiment. Runoff Co concentrations from the amended treatment noticeably increased starting 92 days after application and ending 187 days after application, while the unamended control remained relatively unchanged (Figure 6). Runoff Ni concentrations from the amended treatment increased 78 days after application and decreased 209 days after application (Figure 7). Mean runoff Ni concentration in the unamended control increased periodically between day 78 and 209 after application. Runoff Pb concentrations from the amended treatment began to increase 78 days after application and decreased 187 days after application (Figure 7). In the unamended control, there was a similar increase in runoff Pb concentrations 112 days after application, but an immediate decrease occurred thereafter, which did not occur in the amended treatment. Similar to runoff Pb, runoff Rb concentrations started to increase 78 days after application, but a similar trend was also observed from the unamended control (Figure 8). Runoff Cr concentrations in the amended treatment increased to 4 $\mu g\ L^{-1}$ by 94 days after application and to 6.6 $\mu g\ L^{-1}$ by 116 days after application, but a similar trend did not occur in the unamended control (Figure 8). There was a spike in runoff Cd concentrations by 27 days after application and a similar spike in runoff Th concentrations by 43 days after application (Figure 9). However, there were also similar spikes in mean runoff concentrations of Cd and Th concentrations in the unamended control (Figure 9).

Annual FWM concentrations and loads of all trace elements examined in this study were unaffected ($P > 0.05$) by DFGD application (Table 5). Similarly, annual runoff and runoff pH and EC (Table 5) were unaffected ($P > 0.05$) by DFGD application. Of the 99 runoff samples collected that were analyzed for Hg, only 17 were above the detection limit of 0.05 $\mu g\ L^{-1}$. Consequently, neither annual FWM Hg concentrations nor cumulative loads differed between treatments.

Flow-weighted mean Ni concentration and V load differed ($P < 0.05$) between DFGD treatments among seasons (Table 6). Flow-weighted mean Ni concentration was 44.5%, greater ($P < 0.05$) from the amended treatment than the unamended control during the Fall season, while there was no effect of by-product treatment during the other three seasons (Figure 10). Vanadium load was 86.9% greater ($P < 0.05$) from the amended treatment than from the unamended control during the summer season, while there was no difference between treatments during the other three seasons (Figure 11). Flow-weighted mean As and U concentrations and Cr, Co, Ni, Cu, Se, Cd, Pb, and U loads were unaffected ($P > 0.05$) by both DFGD-by-product treatment and season (Table 6).

Despite no treatment effects on annual FWM concentrations or loads, numerous seasonal differences in runoff water quality occurred between treatments. Averaged across DFGD treatment, runoff and runoff pH and EC, 12 of the 15 measured FWM elemental concentrations and 6 of the 15 elemental loads differed ($P < 0.05$) among seasons (Table 6). Seasonal runoff was greatest ($P < 0.05$) during the winter season, which did not differ from that during the summer season (Table 7). Seasonal EC was greatest ($P < 0.05$) during the fall season and lowest in the winter season (Table 7). The increase in runoff EC during the fall season may be attributed to the large FWM concentrations of Cr, Co, Ni, Cu, and Rb, which were also greatest during the fall season (Table 7). Runoff pH was greater ($P < 0.05$) during the fall, winter, and spring seasons, which did not differ, than during the summer season (Table 7). Flow-weighted mean V and Cs concentrations were greatest during the summer season, whereas FWM Se, Pb, and Cd concentrations were greatest during the spring season (Table 7). Seasonal Cs and Th loads were greatest during the summer season, whereas seasonal Be, Zn, As, and Rb loads were greatest during the winter season (Table 7). The increase in Be, Zn, As, and Rb loads during the winter season may be attributed to increased runoff during the winter season (Table 7).

Averaged across seasons, by-product treatment had little effect on the water quality parameters examined in this study. Runoff and runoff pH and EC were unaffected ($P > 0.05$) by by-product treatment (Table 8). Flow-weighed mean Rb concentration and load were 47.2 and 69.8% greater ($P < 0.05$), respectively, in the unamended control compared to the amended treatment (Table 8).

Currently, there is a lack of literature on the land-application effects of DFGD by-products on runoff quantity and quality. The lack of impact of land application of DFGD by-product on runoff FWM trace element concentrations and loads measured in this study was similar to that reported by Haefner et al. (1997), who evaluated the effects of land application of a FGD by-product to an abandoned mine land. Haefner et al. (1997) applied DFGD by-products at a rate of 280 Mg $ha^{-1}$ and reported measured runoff As, Hg, Pb, and Se concentrations were typically below the detection limit and never exceeded the Environmental Protection Agency's (EPA) maximum contaminant levels (MCLs; USEPA, 2016). Torbert and Watts (2014) applied FGD gypsum, which differs from DFGD by-products due to the lack of fly ash, to a sandy-loam Hapludult at rates of 0 (control), 2.2, 4.4, and 8.9 Mg $ha^{-1}$ to evaluate the effect of application on runoff quality under simulated rainfall. After a 1-hr runoff event, runoff concentrations of trace elements (i.e., total As, Hg, Al, Sb, Ba, Be, Cd, Cr, Co, Cu, Pb, Ni, Ag, V, Se, Th, and $Cr^{VI}$) were all below minimum detection limits, which ranged from 0.1 to 30 µg $L^{-1}$ for Hg and Al, respectively.

## DFGD-Application Effects on Aboveground Dry Matter

Unlike the runoff water quality parameters that were examined, there were greater effects of DFGD-by-product application on aboveground DM and trace element concentrations in plant tissue. Prior to application of the DFGD by-product (i.e., May 2015), there was no difference in aboveground DM and tissue concentrations of As, Se, V, Cr, Co, Hg and U between treatments. However, after treatment, aboveground DM and tissue V, Cr, Co, As, Se, Hg, and U concentrations differed ($P < 0.05$) between DFGD-by-product treatments over time (Table 9). Following the first harvest, when aboveground DM did not differ between DFGD-by-product treatments, aboveground DM decreased and remained similar over time for the remainder of the 1-yr study period (Figure 12). The periodic disturbance from harvesting aboveground DM may have prevented growth from returning to pre-application levels. However, with the exception of the November 2015 sampling, aboveground DM was greater from the amended treatment than from the unamended control, indicating that land application of the DFGD by-product has fertilizer-nutrient value to stimulate plant growth. The composition of plant species in each plot may have also affected aboveground DM over time. Each plot had varying abundances of Johnson grass, clover, tall fescue, and Bermuda grass. Clover and tall fescue are cool-season species, whereas Johnson and Bermuda grass are warm-season species. The decrease in aboveground DM from August to November 2015 may be the result of the warm-season plants beginning to go dormant for the up-coming fall/winter seasons. Similar to the results of this study, application of a DFGD by-product to an acidic (pH ~ 4.4) Hapludult resulted in a 75% increase in growth of Northern red oak compared to the unamended control when applied at a rate equivalent to 1.5 times the soil’s lime requirement (Crews and Dick, 1998).

Tissue concentrations of Hg, As, V, Se, Cr, Co, and U increased in the amended treatment 1 mo after application (i.e., June 2015) compared to the unamended control. One mo after application, the tissue Hg concentration in the amended treatment was 52.9% greater ($P < 0.05$) than that in the unamended control (Figure 12). Tissue As concentrations in the amended treatment were 175% greater ($P < 0.05$) than those in the unamended control in June 2015, but did not differ ($P > 0.05$) from the unamended control in July and August 2015 (Figure 13). After the June 2015 sampling, tissue As concentrations in the amended treatment did not change over time ($P > 0.05$) for the remainder of the experiment, but were again greater ($P < 0.05$) than the unamended control in November 2015 and May 2016. Tissue As concentrations in the amended treatment were 104 and 70.5% greater than the unamended control for November 2015 and May 2016, respectively. Selenium and Cr tissue concentrations in the amended treatment were greater ($P < 0.05$) than those in the unamended control in June and July 2015, but did not differ ($P > 0.05$) from the unamended control in August and November 2015 and May 2016 (Figure 14). Tissue Se concentrations were 235 and 134% greater in the amended treatment than in the unamended control in June and July 2015. Tissue Cr concentrations in the amended treatment were 119 and 228% greater than those in the unamended control in June and July 2015 (Figure 14). After June 2015, there was no difference in tissue V and Co concentrations between treatments (Figures 13 and 15). In the June 2015 sampling, tissue V and Co concentrations in the amended treatment were 471 and 134% greater, respectively, than those in the unamended control. Tissue U concentrations in the amended treatment were two-fold greater than those in the unamended control (Figure 15). Tissue U concentrations in the amended treatment were 254% greater than those in the unamended control in June 2015 and 140% greater than those in the unamended control in August 2015.

The large increases in tissue Cr and Se concentrations were somewhat expected due to the increased mobility of selenate and chromate in the oxidizing environments (Alloway, 1995), which existed in this field study. Unlike Cr and Se, the significant increase in tissue concentrations of As were somewhat unexpected. Although As tends to undergo ligand exchange in soils and becomes bound to soil colloids, the somewhat low clay content (i.e., 5 to 15 % clay) in the top 30 cm of the soil profile may have limited As fixation and increased As bioavailability. Another possible explanation for the significant increase in tissue As concentrations in the amended treatment is the competitive uptake of phosphate with arsenate. Meharg and Macnair (1992) reported that phosphate and arsenate are taken up by plants through the same transport system. Similar to As, V exists in oxidizing soil environments primarily as the oxyanion vanadate ($H_2VO_4^-$) and behaves similarly to As and P in the environment (Alloway, 1995; Gabler et al., 2009). Because vanadate competes with As and P for adsorption sites on soil colloids, the significant increase in tissue V concentrations in the amended treatment may be the result of being out competed by phosphate and arsenate, which tend to have greater affinities than V for adsorption onto soil colloids (Mikkonen and Tummavuori, 1994; Jeong et al., 2007). Punshon et al. (2001) incubated a Typic Paleudult with FGD by-products at rates of 0, 55.5, 111, 167, and 222 Mg FGD ha$^{-1}$ to monitor the effects of application on plant growth and tissue composition in corn, soybean, radish, and cotton. Leaf and root tissue As and Se concentrations of all four crops were significantly affected by FGD incorporation (Punshon et al., 2001). Although tissue As and Se concentrations increased relative to the unamended control, there was no effect of FGD application on germination rates and all FGD application rates resulted in increased aboveground DM (Punshon et al., 2001).

Similar FGD treatment effects were reported by Adriano et al. (2001), where a Class-F fly ash, which has less Ca-oxides than Class-C fly ash, was incorporated into a silt-loam soil. Incorporation resulted in a significant increase in tissue As and Se concentrations in centipedegrass (*Eremochloa ophiroides*) (Adriano et al., 2001). Adriano et al. (2001) reported no increase in tissue Cr and Hg concentrations, which differed from the results of this experiment. Trace element concentrations measured in this study were dissimilar to those reported by Chen et al. (2001), who reported no effect of application of a FGD by-product on alfalfa tissue As, Cr, Pb, Hg, and Se concentrations. The soil used in the Chen et al. (2001) study was an acidic, silt-loam-textured Alfisol, which may have had differential effects on the bioavailability of trace elements compared to the slightly acidic Ultisol soil used in the present field study.

Averaged across DFGD-by-product treatment, plant tissue Cu, Rb, Cs, Pb, and Th concentrations differed ($P < 0.05$) over time (Table 9). Tissue concentrations of Cu, Cs, and Th were greatest ($P <0.05$) in June 2015, whereas tissue Rb concentrations were greatest ($P < 0.05$) in July 2015 (Table 10). In August 2015, tissue Pb concentrations were greatest, but did not differ ($P > 0.05$) from those in May and June 2015 (Table 10).

Averaged across time, tissue Cu, Zn and Cs concentrations differed ($P < 0.05$) between DFGD-by-product treatments (Table 9). Both tissue Cu and Cs concentrations were greater in the amended treatment than in the unamended control (Table 11). Tissue Be, Ni, and Cd concentrations were unaffected ($P > 0.05$) by both DFGD-by-product treatment and time (Table 9).

Application of the DFGD by-product also had a significant effect on the cumulative plant uptake of trace elements. Cumulative plant uptake of V, Cr, Co, Cu, Zn, As, Se, Cs, Hg, Pb, Th, and U was greater ($P < 0.05$) in the amended treatment than in the unamended control (Table

11). Cumulative plant uptake of V, Cr, Co, Cu, Zn, As, Se, Cs, Hg, Pb, Th, and U were 318, 144, 100, 63.4, 65.7, 157, 169, 139, 100, 83.3, 100, and 400% greater, respectively, in the amended treatment than in the unamended control. In contrast, cumulative plant uptake of Be, Ni, Rb, and Cd were unaffected ($P > 0.05$) by DFGD-by-product treatment (Table 11).

**DFGD-Application Effects on Soil Properties**

With the exception of soil EC and acid-extractable Se concentration, all other soil properties measured in this study were affected ($P < 0.05$) by time, DFGD-by-product application, soil depth, or their interactions (Table 12). Soil EC and Se concentration were unaffected ($P > 0.05$) by any experiment factor evaluated in this study and averaged 150 µS $cm^{-1}$ and 1.2 µg $kg^{-1}$, respectively, throughout the duration of the study. Application of the DFGD by-product generally had a greater impact on Mehlich-3 extractable soil nutrients than on acid-extractable trace elements.

Averaged across soil depth, soil pH and Mehlich-3 extractable soil S, Na, and Mn concentrations differed ($P < 0.05$) between DFGD-by-product treatments over time (Table 12). Prior to application of the DFGD by-product, there was no difference in soil pH and Mehlich-3 extractable soil S, Na, and Mn concentrations between treatments (Figure 16). Six mo after application, soil pH for the amended treatment (pH = 6.44) was significantly greater ($P < 0.05$) than that in the unamended control (pH = 6.15; Figure 16). Soil pH did not differ ($P > 0.05$) between treatments by 1 yr after application. Mehlich-3 extractable S concentration in the amended treatment was 170% greater than in the unamended control 6 mo after application, but did not differ ($P > 0.05$) from the unamended control by 1 yr after application (Figure 16). There was a significant decrease ($P < 0.05$) in Mehlich-3 extractable Mn concentration in the amended treatment following application of the DFGD by-product (Figure 16). Mehlich-3 extractable Mn concentrations in the amended treatment were 43% lower than that in the unamended control 6 mo after application (Figure 16). Mehlich-3 extractable Na concentrations by 6 mo and 1 yr after application in both treatments were greater ($P < 0.05$) than those prior to application of the DFGD by-product. The magnitude of increase was slightly greater in the amended treatment than in the unamended control (Figure 16). Concentrations of Mehlich-3 extractable Na were 52.1 and 50.4% greater ($P < 0.05$) in the amended treatment than in the unamended control 6 mo and 1 yr after application, respectively (Figure 16).

The ability of FGD by-products to act as liming materials has been reported by others. The DFGD by-product that was used in this experiment was used in a previous study to examine its liming characteristics. The DFGD by-product used in this experiment had a $CaCO_3$ equivalence (CCE) of 84.4% and an effective neutralizing value (ENV) of 79.4%, which are similar to commercially available liming materials (Burgess-Conforti et al., 2016). The DFGD by-product used in this experiment was as effective as reagent-grade $CaCO_3$ at increasing soil pH when incubated with an acidic (pH ~4.3) clay soil at a rate equivalent to the soil's lime requirement and more effective than reagent-grade $CaCO_3$ at raising soil pH when incubated at a rate two times the soil's lime requirement. Punshon et al. (2001) reported that the surface pH of soil used in a mesocosm study increased from 5.5 to 8.1 in mesocosms receiving the FGD by-product.

Soil pH is known to vary temporally due to changes in soil moisture, microbiological activity, and root activity. In this field study, there were varying amounts of clover in each plot. Having more legumes present could have increased $N_2$ fixation, which subsequently could have undergone nitrification. Nitrification releases $H^+$ ions into the soil, which would decrease soil pH. If one or more plots had greater nitrification rates than other plots, an additional effect on soil pH could have occurred in addition to application of the DFGD by-product.

Averaged across time, Mehlich-3 extractable soil Ca and Na concentrations differed ($P < 0.05$) between DFGD-by-product treatments across soil depths (Table 12). Mehlich-3 extractable soil Ca concentration was greatest ($P < 0.05$) in the top 10 cm in both treatments compared to that in the other two depth intervals (Figure 17). In the amended treatment, Mehlich-3 extractable Ca concentration in the top 10 cm was 26.6% greater than that in the same depth interval for the unamended control (Figure 17). There was no difference ($P > 0.05$) in Mehlich-3 extractable Ca concentration between treatments in the 10- to 20- and 20- to 30-cm depth intervals. Mehlich-3 extractable Na did not differ ($P > 0.05$) in the unamended control between depth intervals. Mehlich-3 extractable Na concentrations in the amended treatment were 60.8 and 27.8% greater than the unamended control in the 0- to 10- and 20- to 30-cm depth interval, respectively, but did not differ ($P > 0.05$) from the unamended control in the 10- to 20-cm depth interval (Figure 17).

The ability of DFGD by-products to act as a Ca and S source has also been previously reported. When a FGD by-product was incorporated into a Typic Paleudult, acid-extractable soil Ca increased from 280 mg kg$^{-1}$ in the unamended control to 1677 mg kg$^{-1}$ in the soil receiving an FGD by-product at a rate of 55 Mg FGD ha$^{-1}$ (Punshon et al., 2001). Chen et al. (2005) applied two types of FGD (FGD-containing vermiculite and FGD-containing perlite) by-products to a slightly acidic (pH ~ 6.1) Fragiudalf and reported increases in Mehlich-3 extractable S concentrations in both the 0- to 15- and 15- to 30-cm depth intervals. In the same experiment, Mehlich-3 extractable Ca concentrations increased in the top 15 cm after amendment compared to the unamended control (Chen et al., 2005).

Although DFGD by-products can act as a nutrient source, application of the DFGD by-product in this field experiment resulted in a temporary decrease in Mehlich-3 extractable Mn and Zn. Punshon et al. (2001) also reported a decrease in extractable Mn and Zn in the soil receiving FGD by-products. A possible explanation may be the displacement of Mn and Zn by cations (i.e., Ca, Cd, Cu) and oxyanions (i.e., $H_2PO_4^-$, $H_2AsO_4^-$, $H_2VO_4^-$) that have greater affinities for adsorption sites, resulting in increased bioavailability and leachability.

Averaged across time and soil depth, Mehlich-3 extractable soil Fe and acid-extractable Ni, Rb, and Cs concentrations differed ($P < 0.05$) between DFGD-by-product treatments (Table 12). Mehlich-3 extractable Fe and acid-extractable Ni, Rb, and Cs concentrations were 10.0, 22.7, 17.1, and 20% greater ($P < 0.05$), respectively, in the unamended control compared to the amended treatment (Table 13).

Averaged across time and DFGD-by-product treatment, soil pH and Mehlich-3 extractable soil K, Mg, S, Fe, Zn, Cu, and B and acid-extractable Be, V, Cr, Co, Ni, Rb, Cs, Pb, and Th concentrations differed ($P < 0.05$) among soil depths (Table 12). The soil pH of 6.3 in the top 10 cm was greater ($P < 0.05$) than the pH of 6.2 and 6.1 in the 10- to 20- and 20- to 30-cm depth intervals, respectively (Table 14). Except for Fe, Mehlich-3 extractable K, Mg, S, Zn, Cu, and B concentrations were greatest in the top 10 cm compared to the other two soil depth intervals. Mehlich-3 extractable Fe concentration was greatest in the 20- to 30-cm depth interval, but did not differ ($P > 0.05$) from that in the 10- to 20-cm depth interval. Acid-extractable Be, V, Cr, Co, Ni, Pb, and Th concentrations were greatest in the 20- to 30-cm depth interval, but did not differ ($P > 0.05$) from those in the 10- to 20-cm depth interval (Table 14). Acid-extractable Rb concentration was also greater ($P < 0.05$) in the 20- to 30- than that in the 10- to 20-cm depth interval.

Averaged across soil depths and DFGD-by-product treatments, Mehlich-3 extractable soil P, Fe, and Zn and acid-extractable Be, V, Cr, Co, As, Cd, Cs, Pb, Th, and U concentrations differed ($P < 0.05$) over the 1-yr time period of this field study (Table 12). Mehlich-3 extractable P, Fe, and Zn concentrations were greatest prior to application of the DFGD by-product, but did not differ ($P > 0.05$) from those by 1 yr after application (Table 15). Prior to application, concentrations of Mehlich-3 extractable P, Fe, and Zn were greater than those 6 mo after application by 60.5, 22.8, and 60%, respectively. Acid-extractable V, Cr, As, Cs, and Pb concentrations were also greatest prior to application of the DFGD by-product. The concentrations of acid-extractable V, Cr, As, Cs, and Pb were greater than those 6-mo after application by 23.2, 59.0, 25.0, 20, and 27.5%, respectively (Table 15). Acid-extractable U concentration was greatest prior to application, but did not differ from concentrations by 6 mo after application. Concentrations of acid-extractable U were 116.7% greater than those 1 yr after application. By 1 yr after application, acid-extractable Be, Co, Cd, and Th concentrations were greater compared to prior to or by 6 mo after application. One yr after application, concentrations of acid-extractable Be, Co, Cd, and Th were 40.0, 61.5, 100, and 126% greater than those 6 mo after application (Table 15).

Using the measured soil bulk density at the end of the field study and assuming there was no change in bulk density in any of the three, 10-cm depth intervals over the course of the 1-yr study, elemental soil concentrations were converted to contents to better assess effects of DFGD application on elemental soil storage changes by soil depth and over time. With the exception of Mehlich-3 extractable soil K content, all other elemental soil contents measured in this study were affected ($P < 0.05$) by time, DFGD-by-product application, soil depth, or their interactions (Table 16). Mehlich-3 extractable soil K content was unaffected ($P > 0.05$) by any experiment factor evaluated in this study and averaged 149 kg $ha^{-1}$ in the top 30 cm throughout the duration of the study.

Similar to soil S and Na concentrations, averaged across soil depth, Mehlich-3 extractable soil S and Na contents differed ($P < 0.05$) between DFGD-by-product treatments over time (Table 16). Prior to application of the DFGD by-product, there was no difference ($P > 0.05$) in Mehlich-3 extractable S and Na contents between treatments (Figure 18). By 6 mo after application, Mehlich-3 extractable S content was 166% greater ($P < 0.05$) in the amended treatment than in the unamended control (Figure 18). Mehlich-3 extractable Na content increased ($P < 0.05$) in in both treatments by 6 mo and 1 yr after application compared to pre-application levels (Figure 18).

Similar to soil Ca concentration, averaged across time, Mehlich-3 extractable soil Ca content differed ($P < 0.05$) between DFGD-by-product treatments across soil depths (Table 16). In the top 10 cm, Mehlich-3 extractable Ca content in the amended treatment was 30.4% greater ($P < 0.05$) than in the unamended control (Figure 19). Mehlich-3 extractable Ca content did not differ among soil depth intervals in the unamended control. There was no difference ($P > 0.05$) in Mehlich-3 extractable Ca content between treatments in the 10- to 20- and 20- to 30-cm depth intervals (Figure 19).

Averaged across time and soil depth, Mehlich-3 extractable soil Fe and Mn and acid-extractable Ni, Cd, Hg, and Pb contents differed ($P < 0.05$) between DFGD-by-product treatments (Table 16). Mehlich-3 Extractable Fe and Mn and acid-extractable Ni, Cd, and Pb contents were 9.3, 25.7, 21.4, 15.7, and 16.7% greater ($P < 0.05$), respectively, in the unamended control compared to the amended treatment (Table 17). Acid-extractable Hg content in the amended treatment was 289% greater ($P < 0.05$) than in the unamended control.

Averaged across time and DFGD-by-product treatment, Mehlich-3 extractable soil Mg, S, Fe, Mn, Zn, Cu, and B and acid-extractable Be, V, Cr, Co, Ni, Se, Rb, Cd, Cs, Pb, Th, and U contents differed ($P < 0.05$) among soil depths (Table 16). Mehlich-3 extractable Mg, S, Zn, Cu, and B contents were greatest ($P < 0.05$) in the top 10 cm, whereas Mehlich-3 extractable Fe and Mn contents were greatest ($P < 0.05$) in the 20- to 30-cm depth interval (Table 18). The contents of Mehlich-3 extractable Mg, S, Zn, Cu, and B in the 0- to 10-cm depth interval were 28.9, 42.2, 62.0, 52.2, and 200%, respectively, greater than the 10- to 20-cm depth interval, (Table 18). Mehlich-3 extractable Fe and Mn in the 20- to 30-cm depth interval were 48.5 and 42.3%, respectively, greater than the 0- to 10-cm depth interval. Acid-extractable Ni, Cd, and Pb contents were greatest ($P < 0.05$) in the 20- to 30-cm depth interval. Acid-extractable Be, V, Cr, Co, Se, Rb, Th, and U contents were also greatest ($P < 0.05$) in the 20- to 30-cm depth interval, but did not differ ($P > 0.05$) from those contents in the 10- to 20-cm depth interval (Table 18). The contents of acid-extractable Be, V, Cr, Co, Se, Rb, Th, and U in the 20- to 30-cm depth interval were 66.7, 89.1, 76.6, 81.9, 62.5, 50.0, 70.0, and 82.8%, respectively, greater than the 0- to 10-cm depth interval. Acid-extractable Cs content was greatest in the 10- to 20-, but did not differ ($P > 0.05$) from that in the 20- to 30-cm depth interval. The content of acid extractable Cs was 100% greater than that of the 0- to 10-cm depth interval.

Averaged across soil depths and DFGD-by-product treatments, Mehlich-3 extractable soil P, Fe, Mn, and Zn and acid-extractable Be, V, Cr, Co, As, Se, Cs, Pb, Th, and U contents differed ($P < 0.05$) over the 1-yr duration of this field study (Table 16). Mehlich-3 extractable P, Fe, Mn, and Zn contents were greatest ($P < 0.05$) prior to application of the DFGD by-product, but did not differ ($P > 0.05$) from those contents by 1 yr after application (Table 19). The contents of Mehlich-3 extractable P, Fe, Mn, and Zn prior to application were 61.1, 23.4, 36.7, and 56.5%, respectively, greater than those 6 mo after application. Acid-extractable Cr and Th contents were greatest by 52.7 and 28.0% ($P < 0.05$) prior to application of the DFGD by-product compared to 6 mo after application. Acid-extractable V, Se, and Pb contents were also greatest ($P < 0.05$) prior to application, but did not differ ($P > 0.05$) from those by 6 mo after application (Table 19). The contents of acid-extractable V, Se, and Pb prior to application were 158, 100, and 33.3%, respectively, greater than those 1 yr after application. Acid-extractable As content was greatest ($P < 0.05$) by 6 mo after application, but did not differ ($P > 0.05$) from pre-application levels. By 1 yr after application, acid-extractable Co, Cs, and U contents were greater ($P < 0.05$) than those at the other two time periods. The contents of acid-extractable Co, Cs, and U were 32.7, 100, and 120%, respectively, greater than those prior to application (Table 19). Acid-extractable Be content was also greatest ($P < 0.05$) by 1 yr after application, but did not differ ($P > 0.05$) from pre-application levels (Table 19).

### Environmental Impacts

When utilized as a soil amendment applied to a managed grassland, DFGD by-product application produced greater aboveground DM compared to the unamended control for the three months following application, with minimal impact on environmental quality based on the measurements conducted in this study. If DFGD by-products were to be utilized as a pasture soil amendment, plant tissue and runoff concentrations of potentially toxic trace elements cannot exceed thresholds deemed safe for grazing animals. Tissue concentrations of Se were greatest one month after application and reached 2.6 mg kg$^{-1}$. According to the National Research Council (NRC, 1983), livestock do not suffer from Se toxicity until feed has reached concentrations of 4 to 5 mg Se kg$^{-1}$. The maximum mean concentration of As in the plant tissue was 0.15 mg $kg^{-1}$, which is much lower than the 2 mg As $kg^{-1}$ feed restriction set by the European Union (EU) (Bampidis et al., 2013). The NRC reported that 50 and 100 mg As $kg^{-1}$ feed are the maximum tolerable doses of inorganic and organic As, respectively, in the diet of cattle (NRC, 2001). Although there was a significant increase in tissue Co concentrations from DFGD-by-product application, tissue Co concentrations were within the recommended range of 100 to 500 µg Co $kg^{-1}$ DM for cattle feedstuffs (NRC, 2001). The maximum tolerable Cr concentration for cattle feedstuffs ranges from 1000 to 3000 mg Cr $kg^{-1}$ (NRC, 2001), which exceeds the plant tissue Cr concentrations reported in this study. The mean plant tissue Hg concentration in the DFGD-by-product amended treatment one month after application was 20.3 µg $kg^{-1}$, which is below the maximum tolerable concentration of 100 µg $kg^{-1}$ set by the EU (Bampidis et al., 2013). The mean plant tissue V concentration in the amended treatment was 0.76 mg $kg^{-1}$ one month after application, which is below the 50 mg V $kg^{-1}$ for cattle diets and below 7 mg V $kg^{-1}$ for lamb diets (NRC, 2001). Land application of DFGD by-products for pasturelands may result in the contamination of ponds used for drinking water by cattle. However, none of the runoff water quality parameters measured in this experiment exceeded EPA's Safe Drinking Water Act standards or recommended limits for trace element concentrations in cattle drinking water (USEPA, 2016; NRC, 2001; Table 20).

The significant increase in cumulative plant uptake of V, Cr, Co, Cu, Zn, As, Se, Cs, Hg, Pb, Th, and U from DFGD application compared to the unamended control also demonstrates the potential for accumulation of trace elements in aboveground DM. Land application of DFGD by-products may warrant caution depending on the designated use of the land and aboveground DM. Management techniques, including growth of hyperaccumulating vegetation, may be an advantageous method for mining the soil of trace elements applied in the DFGD by-product for disposal, while still providing environmental benefits. Unlike aboveground DM, there was minimal effect of application on soil concentrations and contents of Mehlich-3 extractable nutrients and acid-extractable trace elements. The DFGD by-product was a liming material and a Ca and S source for the top 30 cm of the soil profile without increasing trace element concentrations.

Considering two main loss mechanisms (i.e., plant uptake/removal and runoff) of elements applied in the DFGD-by-product treatment and the elemental composition of the DFGD by-product itself were directly measured, the percentages of plant uptake/removal and runoff losses of trace elements relative to that applied were calculated. Overall, the percentage of element accounted for by the sum of runoff, plant uptake/removal, and soil storage changes relative to that applied in the DFGD by-product ranged from -53.2% for Th to 1116% for Rb (Table 21). In general, the percentage of element accounted for by runoff, plant uptake/removal, and soil storage changes was typically low. Except for Rb and Cs, less than 1% of the trace elements added in the DFGD by-product were accounted for in runoff (Table 21). The percentage of element accounted for in runoff ranged from < 0.01 to 3.8% for Be and Cr and Rb, respectively. The percentage of element accounted for in plant uptake/removal was typically greater than that for runoff and ranged from 0.1 to 1112% for Be and Rb, respectively. Less than 10% of Be, V, Cr, Co, Ni, Cu, As, Hg, and Th applied in the DFGD by-product was accounted for in runoff, plant uptake/removal, and soil storage changes over the 1-yr study period (Table 21). The amount of Se, Cd, and U applied in the DFGD by-product accounted for in runoff, plant uptake/removal, and soil storage changes ranged from 11.4 to 21.5% for Se and Cd, respectively (Table 21). Zinc, Rb, Cs, and Pb applied in the DFGD by-product had greater than 50% accounted for in runoff, plant uptake/removal, and soil storage change (Table 21). More than

100% of Pb applied in the DFGD by-product was accounted for in plant uptake/removal, which may be related to the 44.8% decrease in soil Pb storage (Table 21). More than 1000% of Rb added in the DFGD by-product was accounted for by plant uptake/removal (Table 21). Over the 1-yr study period, 138.4 g Rb $ha^{-1}$, on average, were measured as cumulative plant uptake/removal from the amended treatment compared to 94 g Rb $ha^{-1}$, on average, from the unamended control. Land application of the DFGD by-product added approximately 12.4 g Rb $ha^{-1}$, which could explain the difference between the two treatments if spatial variability was taken into consideration.

In the environmental conditions present during this experiment, volatilization of the trace elements studied was not expected. It is also possible that some quantity of trace elements may have leached below the 30-cm depth interval measured in this experiment or leached below the root zone (i.e., ~ 1 m) and out of the soil profile altogether. Although the DFGD by-product had minimal effects on runoff quantity and quality, accumulation of trace elements in the environment through long-term application, in time, might increase the amount of trace elements exported from the point of application via runoff. Though this study did not monitor the effects of land application of a high-Ca DFGD by-product on leaching of trace elements below the 30-cm depth interval, it is known that certain heavy-metal trace elements, such as Se and Cr, are prone to leaching (Alloway, 1995; Kabata-Pendias and Pendias, 2001; Pirani et al., 2006), which could have implications on groundwater quality and movement of these elements in the soil profile and to neighboring ecosystems.

## Summary and Conclusions

Over the 1-yr duration of this field study, land application of the DFGD by-product had minimal effect on runoff, runoff water quality, and trace elements in the soil. There was no difference in runoff or runoff pH and EC between the amended treatment and unamended control. Flow-weighted mean Ni concentrations and seasonal V loads were greater for one of four 3-mo seasons in the amended treatment compared to the unamended control. Averaged across soil depth, the DFGD-by-product-amended treatment had greater soil S and Na concentrations and contents compared to the unamended control by 6 mo and 1 yr after application. Averaged across time, the DFGD-by-product amended treatment had greater extractable soil Ca concentrations and contents in the top 10 cm than in the other soil depth intervals. Averaged across soil depth, soil pH in the DFGD-by-product-amended treatment was also greater compared to the unamended control by 6 mo after application.

The greatest accumulation of trace elements was in the plant tissue. Over the 1-yr study, cumulative plant uptake of V, Cr, Co, Cu, Zn, As, Se, Cs, Hg, Pb, Th, and U were greater in the amended treatment compared to the unamended control. Plant tissue As, Co, Cr, Hg, Se, V, and U concentrations were significantly affected by time and DFGD application. Plant tissue As, Co, Cr, Hg, Se, V, and U concentrations significantly increased within 1 mo following application compared to pre-application concentrations, but either decreased to pre-application levels or did not differ from the unamended control within 3 to 6 mo after application. Vanadium appeared to be the most mobile trace element in the DFGD by-product, thus caution should be taken if V mobility and/or toxicity are concerns. Aboveground DM was greater in the amended treatment compared to the unamended control but never exceeded tolerable limits for cattle feed. High-Ca, DFGD by-products may be a beneficial soil amendment for pasturelands if accumulation of trace elements in the environment do not exceed levels deemed appropriate for animal feeds.

The results of this experiment partially supported the initial hypothesis that application of the DFGD by-product would increase runoff concentrations of trace elements within the first 3-mo. Only seasonal V loads significantly increased within the first 3-mo season following application in the amended treatment. Results also supported the hypothesis that plant tissue As, Cr, Hg, and Se concentrations would be increased compared to the unamended control within the first 3-mo season following application. This field study demonstrated that a high-Ca, DFGD by-product could be applied to a managed grassland with minimal effects on runoff water quality within 1-yr following land-application.

There is currently a lack of knowledge on the effects of land-application of CCBs on runoff water quality. Continued long-term study is needed to fully understand the effects of land application of CCBs on fate of trace elements contained in CCBs, particularly in diverse environmental conditions. The lack of data on trace element leaching from the amended soil in this experiment hinders any definitive conclusions about the fate and transport of trace elements in surface-applied DFGD by-products. Long-term application may also lead to accumulation of trace elements in the environment, which can further degrade soil, plant, groundwater, and/or runoff quality. If DFGD by-products were to be diverted from landfills and surface impounds for use as a soil amendment, research must show that the environmental impacts are minimal compared to current disposal methods.

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**Table 1.** Chemical characteristics of a high-Ca, dry flue gas desulfurization (DFGD) by-product from the John W. Turk Power Plant in Hempstead County, AR.

| Parameter | Mean (± Standard Error) |
|---|---|
| pH | 10.6 (0.29) |
| EC[a] | 2.4 (0.24) |
| Acid-extractable Nutrients (g $kg^{-1}$) | |
| P | 10.3 (0.05) |
| K | 4.7 (0.02) |
| Ca | 410 (0.60) |
| Mg | 49.8 (0.07) |
| S | 89.7 (0.44) |
| Na | 14.1 (0.14) |
| Fe | 64.2 (0.28) |
| Mn | 0.2 (0.01) |
| Zn | 0.3 (0.04) |
| Cu | 0.2 (0.01) |
| B | 1.0 (0.01) |
| Trace Elements (mg $kg^{-1}$) | |
| Be | 21.5 (0.11) |
| V | 138 (0.74) |
| Cr | 81.1 (0.21) |
| Co | 16.9 (0.21) |
| Ni | 43.1 (0.13) |
| As | 13.3 (0.06) |
| Se | 12.9 (0.10) |
| Rb | 1.4 (0.01) |
| Cd | 0.4 (0.02) |
| Cs | 1.3 (0.12) |
| Hg | 0.8 (0.01) |
| Pb | 0.2 (0.02) |
| Th | 3.4 (0.02) |
| U | 5.3 (0.01) |

[a] DFGD by-product electrical conductivity (EC) is in mS $cm^{-1}$

**Table 2.** Aboveground dry matter (DM) and trace element concentrations from November 2014 and May 2015 immediately prior to application of a high-Ca, dry flue gas desulfurization by-product.

| | November-14 | | May-15 | |
|---|---|---|---|---|
| Parameter | Treated | Control | Treated | Control |
| DM[a] | 2.7a† | 1.5a | 4.2a | 3.9a |
| Trace Elements (μg $kg^{-1}$) | | | | |
| Be | < 0.01a | < 0.01a | < 0.01a | 9.0a |
| V | 58.8a | 43.6a | 144a | 75.1a |
| Cr | 141a | 180a | 192a | 112a |
| Co | 85.1a | 48.4a | 146a | 102a |
| Ni | 666a | 384a | 674a | 580a |
| Cu | 5398a | 4643a | 6484a | 4211b |
| Zn | 35412a | 30902a | 36751a | 29000a |
| As | 43.6a | 32.5a | 84.6a | 66.0a |
| Se | 603a | 589.3a | 600a | 459a |
| Rb | 5870a | 4625a | 5640a | 6602a |
| Cd | 39.0a | 25.2a | 36.6a | 34.6a |
| Cs | 162a | 81.4a | 236a | 170a |
| Hg | 31.7a | 22.3b | 14.7a | 12.0a |
| Pb | 112a | 72.4a | 156a | 114a |
| Th | 108a | 47.4a | 32.1a | 20.0a |
| U | 3.6a | 1.9a | 5.5a | 2.8a |

[a] Dry matter data is in Mg $ha^{-1}$

† Means with the same letters within a row are not significantly different from each other at $\alpha = 0.05$.

**Table 3.** Initial Mehlich-3 extractable soil nutrient and trace element concentrations of a Captina silt loam in northwest Arkansas prior to application of a high-Ca, dry flue gas desulfurization by-product.

| | Depth (cm) | | | | | |
|---|---|---|---|---|---|---|
| | 0 to 10 | | 10 to 20 | | 20 to 30 | |
| Parameter | Treated | Control | Treated | Control | Treated | Control |
| pH | 6.3a† | 6.3a | 6.2a | 6.2a | 6.1a | 6.1a |
| EC[a] | 173a | 130a | 146a | 169a | 165a | 130a |
| Mehlich-3 Extractable (mg kg$^{-1}$) | | | | | | |
| P | 299a | 265a | 261a | 261a | 259a | 261a |
| K | 188a | 173a | 113a | 118a | 92.2a | 99.7a |
| Ca | 1769a | 1569a | 12410a | 1216a | 1112a | 1148a |
| Mg | 170a | 152a | 107a | 93.3a | 79.0a | 71.3a |
| S | 22.2a | 21.3a | 13.5a | 14.1a | 9.6a | 10.6a |
| Na | 8.4a | 8.2a | 6.8a | 7.1a | 7.3a | 7.7a |
| Fe | 220a | 232a | 242a | 263a | 268a | 289.0a |
| Mn | 276a | 300a | 254a | 288a | 273a | 307a |
| Zn | 27.8a | 23.3a | 11.8a | 13.5a | 6.5a | 8.4a |
| Cu | 13.6a | 11.7a | 5.8a | 7.1a | 2.6a | 3.0a |
| B | 0.3a | 0.3a | 0.1a | 0.1a | 0.02a | 0.03a |
| Trace Elements (μg kg$^{-1}$) | | | | | | |
| Be | 0.6a | 0.6a | 0.6a | 0.6a | 0.6a | 0.9a |
| V | 13.8a | 17.4a | 21.2a | 23.7a | 20.0a | 25.0a |
| Cr | 15.8a | 23.4a | 26.3a | 27.8a | 22.4a | 31.6a |
| Co | 5.5a | 6.6a | 7.0a | 10.4a | 9.3a | 8.4a |
| Ni | 3.5a | 4.0a | 4.3b | 6.4a | 4.6a | 6.3a |
| As | 4.0a | 4.9a | 6.0a | 6.1a | 5.4a | 6.6a |
| Se | 1.2a | 1.3a | 1.2a | 1.3a | 1.1a | 1.5a |
| Rb | 7.2a | 7.4a | 7.2a | 7.0a | 7.3a | 8.9a |
| Cd | 0.1a | 0.1a | 0.1a | 0.1a | 0.1a | 0.1a |
| Cs | 0.6a | 0.6a | 0.6a | 0.6a | 0.6a | 0.7a |
| Pb | 21.2a | 25.4a | 26.3a | 34.1a | 32.9a | 30.0a |
| Th | 1.6a | 1.9a | 2.5a | 2.4a | 2.9a | 2.7a |
| U | 1.3a | 1.4a | 1.3a | 1.3a | 1.2b | 1.4a |

† Means with the same letter within a soil depth are not significantly different from each other at α = 0.05.

[a] Electrical conductivity (EC) is in μS cm$^{-1}$

**Table 4.** Initial Mehlich-3 extractable soil nutrient and trace element contents of a Captina silt loam in northwest Arkansas prior to application of a high-Ca, dry flue gas desulfurization by-product.

| | Depth (cm) | | | | | |
|---|---|---|---|---|---|---|
| | 0 to 10 | | 10 to 20 | | 20 to 30 | |
| Parameter | Treated | Control | Treated | Control | Treated | Control |
| Mehlich-3 Extractable (kg ha$^{-1}$) | | | | | | |
| P | 326a† | 279a | 330a | 347a | 368a | 360a |
| K | 204a | 183a | 144a | 156a | 131a | 138a |
| Ca | 1903a | 1644a | 1587a | 1600a | 1575a | 1577a |
| Mg | 184a | 161a | 136a | 123a | 112.4a | 98.8a |
| S | 24.0a | 22.3a | 17.4a | 18.7a | 13.6a | 14.6a |
| Na | 9.1a | 8.6a | 8.7a | 9.4a | 10.3a | 10.6a |
| Fe | 238a | 243a | 311a | 347a | 380a | 399a |
| Mn | 297a | 313a | 326a | 378a | 388a | 421a |
| Zn | 30.1a | 24.6a | 14.9a | 17.7a | 9.3a | 11.5a |
| Cu | 14.9a | 12.0a | 7.3a | 9.5a | 3.7a | 4.2a |
| B | 0.4a | 0.4a | 0.1a | 0.1a | 0.03a | 0.05a |
| Trace Elements (g ha$^{-1}$) | | | | | | |
| Be | 0.6a | 0.6a | 0.8a | 0.8a | 0.9a | 1.2a |
| V | 14.8a | 18.3a | 27.4a | 31.3a | 28.4a | 34.5a |
| Cr | 17.0a | 24.8a | 34.3a | 36.6a | 31.9a | 43.6a |
| Co | 5.9a | 7.0a | 9.0a | 13.9a | 13.2a | 11.6a |
| Ni | 3.7a | 4.2a | 5.6b | 8.4a | 6.6a | 8.7a |
| As | 40.1a | 38.9a | 32.5a | 36.6a | 25.9a | 41.5a |
| Se | 4.3a | 5.2a | 7.8a | 8.1a | 7.6a | 9.1a |
| Rb | 1.3a | 1.4a | 1.5a | 1.8a | 1.5a | 2.1a |
| Cd | 7.8a | 7.8a | 9.3a | 9.1a | 10.4a | 12.2a |
| Cs | 0.1a | 0.1a | 0.1a | 0.2a | 0.2a | 0.2a |
| Pb | 0.6a | 0.6a | 0.8a | 0.7a | 0.9a | 1.0a |
| Th | 22.9a | 26.6a | 34.1a | 45.2a | 46.6a | 41.3a |
| U | 1.7a | 2.0a | 3.2a | 3.1a | 4.2a | 3.7a |

† Means with the same letter within a soil depth are not significantly different from each other at $\alpha = 0.05$.

**Table 5.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on annual runoff, runoff pH, runoff electrical conductivity, and annual flow-weighted mean (FWM) concentrations and cumulative loads of trace elements.

| Parameter | Treated | Control |
|---|---|---|
| Runoff (mm) | 185a | 219a |
| pH | 6.5a | 6.5a |
| Electrical Conductivity (µS $cm^{-1}$) | 246a | 246a |
| FWM (µg $L^{-1}$) | | |
| Be | 0.07a† | 0.08a |
| V | 8.5a | 6.2a |
| Cr | 1.4a | 1.4a |
| Co | 2.2a | 2.2a |
| Ni | 5.5a | 6.6a |
| Cu | 29.8a | 37.2a |
| Zn | 555a | 791a |
| As | 2.5a | 2.8a |
| Se | 2.2a | 3.2a |
| Rb | 29.9a | 50.6a |
| Cd | 0.6a | 1.0a |
| Cs | 0.3a | 0.2a |
| Hg | 1.9a | 0.9a |
| Pb | 4.3a | 5.2a |
| Th | 0.4a | 0.3a |
| U | 0.3a | 0.2a |
| Load (mg $ha^{-1}$) | | |
| Be | 1.4a† | 1.7a |
| V | 136a | 97.2a |
| Cr | 21.7a | 21.6a |
| Co | 33.7a | 33.5a |
| Ni | 86.4a | 103a |
| Cu | 465a | 580a |
| Zn | 8677a | 12364a |
| As | 38.9a | 43.2a |
| Se | 35.0a | 49.2a |
| Rb | 467a | 789a |
| Cd | 10.1a | 15.9a |
| Cs | 4.3a | 2.6a |
| Hg | 7.7a | 2.4a |
| Pb | 67.2a | 81.5a |
| Th | 5.5a | 4.1a |
| U | 5.1a | 3.6a |

† Means with the same letter within a row are not significantly different from each other at $\alpha = 0.05$.

**Table 6.** Analysis of variance summary of the effects of treatment, season and their interactions on runoff, runoff pH and electrical conductivity (EC), flow-weighted mean (FWM) concentrations, and runoff loads of trace elements from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product.

| | Source of Variation | | |
|---|---|---|---|
| Parameter | Treatment | Season | Treatment*Season |
| | *P* | | |
| Runoff Volume | 0.47 | 0.01 | 0.20 |
| pH | 0.66 | 0.01 | 0.64 |
| EC | 1.00 | < 0.01 | 0.65 |
| FWM Concentration | | | |
| Be | 0.95 | 0.04 | 0.24 |
| V | 0.05 | < 0.01 | 0.77 |
| Cr | 0.74 | 0.05 | 0.65 |
| Co | 0.21 | < 0.01 | 0.12 |
| Ni | 0.37 | < 0.01 | 0.05 |
| Cu | 0.40 | < 0.01 | 0.80 |
| Zn | 0.21 | < 0.01 | 0.07 |
| As | 0.47 | 0.21 | 0.31 |
| Se | 0.83 | < 0.01 | 0.91 |
| Rb | 0.03 | < 0.01 | 0.63 |
| Cd | 0.95 | < 0.01 | 0.38 |
| Cs | 0.15 | < 0.01 | 0.18 |
| Pb | 0.19 | < 0.01 | 0.47 |
| Th | 0.58 | < 0.01 | 0.85 |
| U | 0.19 | 0.30 | 0.52 |
| Load | | | |
| Be | 0.35 | 0.01 | 0.14 |
| V | 0.16 | < 0.01 | 0.01 |
| Cr | 0.99 | 0.36 | 0.02 |
| Co | 0.99 | 0.85 | 0.46 |
| Ni | 0.52 | 0.10 | 0.13 |
| Cu | 0.27 | 1.00 | 0.56 |
| Zn | 0.23 | < 0.01 | 0.24 |
| As | 0.60 | 0.01 | 0.06 |
| Se | 0.19 | 0.10 | 0.22 |
| Rb | 0.05 | 0.02 | 0.56 |
| Cd | 0.26 | 0.61 | 0.50 |
| Cs | 0.20 | < 0.01 | 0.07 |
| Pb | 0.67 | 0.35 | 0.71 |
| Th | 0.51 | < 0.01 | 0.37 |
| U | 0.24 | 0.39 | 0.13 |

**Table 7.** Effect of season on runoff, mean runoff electrical conductivity and pH, and flow-weighed mean (FWM) concentrations and cumulative loads of trace elements from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product.

| | Season | | | |
|---|---|---|---|---|
| Parameter | Summer | Fall | Winter | Spring |
| Runoff (mm) | 56.5ab† | 30.1b | 86.6a | 29.5b |
| Electrical conductivity (uS$^{-1}$ cm) | 201bc | 381a | 160c | 241b |
| pH | 6.3b | 6.6a | 6.6a | 6.51a |
| FWM Concentration (µg L$^{-1}$) | | | | |
| Be | 0.1a | 0.04b | 0.1ab | 0.1a |
| V | 13.2a | 2.7b | 2.6b | 3.28b |
| Cr | 1.0b | 2.1a | 0.8b | 0.92b |
| Co | 1.3b | 2.9a | 0.9b | 3.44a |
| Ni | 3.2c | 8.3a | 3.9bc | 5.59b |
| Cu | 23.6b | 44.7a | 15.1b | 52.56a |
| Zn | 267c | 445b | 644a | 692.99a |
| As | 2.1ab | 2.1ab | 1.8b | 2.83a |
| Se | 1.3b | 2.6b | 1.8b | 4.63a |
| Rb | 17.2c | 81.1a | 23.9bc | 38.09b |
| Cd | 0.6b | 0.7b | 0.4b | 1.38a |
| Cs | 0.4a | 0.1b | 0.04b | 0.09b |
| Pb | 1.7c | 5.5b | 1.9c | 8.90a |
| Th | 0.6a | 0.1b | 0.1b | 0.10a |
| U | 0.2a | 0.2a | 0.2a | 0.25a |
| Load (mg ha$^{-1}$) | | | | |
| Be | 0.5ab | 0.1c | 0.6a | 0.3bc |
| V | 75.4a | 8.0b | 22.8b | 8.2b |
| Cr | 5.2a | 7.0a | 6.8a | 2.7a |
| Co | 6.7a | 9.1a | 8.3a | 9.5a |
| Ni | 17.2b | 26.3ab | 37.0a | 14.6b |
| Cu | 129a | 126a | 133a | 134a |
| Zn | 1484b | 1301b | 5556a | 2179b |
| As | 11.7ab | 5.7b | 16.6a | 7.0b |
| Se | 7.3b | 7.1b | 15.7a | 12.0ab |
| Rb | 86.8b | 243a | 211a | 86.6b |
| Cd | 3.0a | 2.1a | 3.5a | 4.4a |
| Cs | 3.0a | 0.2b | 0.4b | 0.2b |
| Pb | 9.2a | 17.4a | 17.1a | 30.7a |
| Th | 3.5a | 0.3b | 0.7b | 0.3b |
| U | 1.2ab | 0.7b | 1.4a | 0.6b |

† Means within the same row with the same letter are not significantly different at α = 0.05.

**Table 8.** Effect of treatment on runoff, mean runoff electrical conductivity and pH, and flow-weighted mean (FWM) concentrations and cumulative loads of trace elements from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product.

| Parameter | Control | Treated |
|---|---|---|
| Runoff (mm) | 54.9a† | 46.9a |
| Electrical conductivity (µS cm$^{-1}$) | 246a | 246a |
| pH | 6.5a | 6.5a |
| FWM Concentration (µg L$^{-1}$) | | |
| Be | 0.8a | 0.8a |
| V | 4.9b | 6.2a |
| Cr | 1.1a | 1.3a |
| Co | 1.9a | 2.4a |
| Ni | 4.9a | 5.5a |
| Cu | 35.8a | 32a |
| Zn | 488a | 537a |
| As | 2.1a | 2.3a |
| Se | 2.6a | 2.5a |
| Rb | 47.7a | 32.4b |
| Cd | 0.8a | 0.7a |
| Cs | 0.1a | 0.2a |
| Pb | 3.9a | 5.1a |
| Th | 0.2a | 0.2a |
| U | 0.2a | 0.2a |
| Load (mg ha$^{-1}$) | | |
| Be | 0.4a | 0.3a |
| V | 24.3a | 32.9a |
| Cr | 5.4a | 5.4a |
| Co | 8.4a | 8.4a |
| Ni | 23.3a | 19.4a |
| Cu | 145a | 116a |
| Zn | 3091a | 2169a |
| As | 10.8a | 9.7a |
| Se | 12.3a | 8.8a |
| Rb | 197a | 116b |
| Cd | 4.0a | 2.5a |
| Cs | 0.6a | 1.1a |
| Pb | 20.4a | 16.8a |
| Th | 1.0a | 1.4a |
| U | 0.9a | 1.0a |

† Means within the same row with the same letter are not significantly different at α = 0.05.

**Table 9.** Analysis of variance summary of the effects of treatment (i.e., control or treated), time (i.e., 0, 1, 2, 3, 6 and 12 mo after application), and their interactions on aboveground dry matter (DM) and plant tissue concentrations of trace elements.

| | Source of Variation | | |
|---|---|---|---|
| Parameter | Treatment | Time | Treatment*Time |
| | —— | *P* | —— |
| DM | < 0.01 | < 0.01 | 0.04 |
| Be | 0.56 | 0.25 | 0.73 |
| V | 0.01 | < 0.01 | 0.01 |
| Cr | < 0.01 | < 0.01 | < 0.01 |
| Co | < 0.01 | 0.05 | 0.05 |
| Ni | 0.89 | 0.22 | 0.51 |
| Cu | 0.01 | < 0.01 | 0.17 |
| Zn | <0.01 | 0.81 | 0.96 |
| As | < 0.01 | < 0.01 | < 0.01 |
| Se | < 0.01 | < 0.01 | < 0.01 |
| Rb | 0.59 | 0.01 | 0.68 |
| Cd | 0.93 | 0.82 | 0.99 |
| Cs | 0.03 | 0.01 | 0.87 |
| Hg | < 0.01 | < 0.01 | 0.04 |
| Pb | 0.20 | 0.04 | 0.74 |
| Th | 0.20 | 0.01 | 0.78 |
| U | < 0.01 | < 0.01 | < 0.01 |

**Table 10.** Effect of time on aboveground dry matter (DM) and plant tissue concentrations of trace elements in a managed grassland amended with a high-Ca, dry flue as desulfurizatgion by-product.

| | Sample Date | | | | | |
|---|---|---|---|---|---|---|
| Parameter | May 2015 | June 2015 | July 2015 | August 2015 | November 2015 | May 2016 |
| DM[a] | 4.0a† | 2.6b | 2.6b | 2.6b | 2.4b | 2.8b |
| Trace Elements (µg kg$^{-1}$) | | | | | | |
| Be | 4.5a | 22.5a | 6.7a | 13.9a | 16.4a | 12.7a |
| V | 110b | 447a | 178b | 61.2b | 63.7b | 71.7b |
| Cr | 152b | 329a | 175b | 144b | 127b | 105b |
| Co | 124bc | 194a | 176ab | 120c | 140abc | 129bc |
| Ni | 627ab | 685a | 524ab | 477ab | 483ab | 469b |
| Cu | 5348c | 8213a | 7450ab | 6300bc | 6471bc | 3733d |
| Zn | 32876a | 34693a | 33666a | 31314a | 36123a | 33990a |
| As | 75.3b | 106a | 60.5bc | 55.5bc | 53.9c | 62.3bc |
| Se | 530c | 1720a | 1083b | 929bc | 679bc | 604c |
| Rb | 6121bc | 8030ab | 9187a | 6649bc | 5889bc | 4954c |
| Cd | 35.6a | 34.5a | 32.3a | 34.9a | 27.0a | 33.6a |
| Cs | 204b | 533a | 153b | 326ab | 174.1b | 222b |
| Hg | 13.3b | 16.8a | 7.2c | 7.3c | 9.0c | - |
| Pb | 126abc | 141ab | 39.9c | 153a | 48.8c | 58.4bc |
| Th | 26.1a | 30.7a | 12.5bc | 23.1ab | 10.4bc | 8.4c |
| U | 4.2c | 12.4a | 1.8c | 8.0b | 2.9c | 1.5c |

[a] Aboveground DM is in Mg ha$^{-1}$

† Means with the same letter within a row are not significantly different at α = 0.5.

**Table 11.** Effect of application of a high-Ca, dry flue gas desulfurization by-product on aboveground dry matter (DM) and plant tissue concentrations of trace elements, and on cumulative plant uptake of trace elements.

| | Treatment Effect | | Annual Plant Uptake (g $ha^{-1}$) | |
|---|---|---|---|---|
| Parameter | Control | Treated | Control | Treated |
| DM (Mg $ha^{-1}$) | 2.4b† | 3.3a | - | - |
| Trace Elements | | | | |
| Be | 16.3a‡ | 9.3a | 0.2a† | 0.2a |
| V | 78.8b | 231a | 1.1b | 4.6a |
| Cr | 126b | 218a | 1.8b | 4.4a |
| Co | 121b | 173a | 1.7b | 3.4a |
| Ni | 548a | 540a | 8.2a | 10.9a |
| Cu | 5789b | 6715a | 80.8b | 132a |
| Zn | 30496b | 37058a | 437b | 724a |
| As | 49.3b | 88.8a | 0.7b | 1.8a |
| Se | 640.3b | 1208a | 8.8b | 23.7a |
| Rb | 6630a | 6981a | 94.0a | 138a |
| Cd | 32.8a | 33.1a | 0.5a | 0.7a |
| Cs | 199b | 338a | 2.8b | 6.7a |
| Hg | 9.3b | 12.1a | 0.1b | 0.2a |
| Pb | 78.4a | 110a | 1.2b | 2.2a |
| Th | 16.1a | 20.8a | 0.2b | 0.4a |
| U | 2.8b | 7.4a | 0.04b | 0.2a |

† Means within the same row with the same letter are not significantly different at $\alpha = 0.05$.
‡Trace elements are in µg $kg^{-1}$

**Table 12.** Analysis of variance summary of the effects of time (T) (i.e., 0, 6 and 12 mo after application), treatment (TRT) (i.e., control or treated), soil depth (D) (i.e., 0-10, 10-20, and 20-30 cm depth interval), and their interactions on soil pH, electrical conductivity (EC), and concentrations of Mehlich-3 extractable soil nutrients and trace elements.

| | Source of Variation | | | | | | |
|---|---|---|---|---|---|---|---|
| Parameter | T | TRT | D | T*TRT | TRT*D | T*D | T*TRT*D |
| | *P* | | | | | | |
| pH | 0.08 | 0.03 | < 0.01 | 0.04 | 0.34 | 0.62 | 0.19 |
| EC | 0.80 | 0.82 | 0.48 | 0.40 | 0.14 | 0.91 | 0.35 |
| P | 0.01 | 0.37 | 0.67 | 0.30 | 0.82 | 0.99 | 0.85 |
| K | 0.22 | 0.57 | < 0.01 | 0.59 | 0.78 | 0.60 | 0.61 |
| Ca | 0.10 | 0.01 | < 0.01 | 0.52 | < 0.01 | 0.83 | 0.62 |
| Mg | 0.19 | 0.10 | < 0.01 | 0.57 | 0.87 | 0.82 | 0.20 |
| S | 0.03 | 0.01 | < 0.01 | 0.01 | 0.32 | 0.70 | 0.73 |
| Na | < 0.01 | < 0.01 | < 0.01 | < 0.01 | 0.04 | 0.56 | 0.44 |
| Fe | < 0.01 | 0.01 | 0.02 | 0.11 | 0.79 | 0.28 | 0.56 |
| Mn | < 0.01 | < 0.01 | 0.14 | 0.04 | 0.25 | 0.81 | 0.41 |
| Zn | 0.03 | 0.18 | < 0.01 | 0.10 | 0.68 | 0.36 | 0.11 |
| Cu | 0.28 | 0.67 | < 0.01 | 0.68 | 0.82 | 0.80 | 0.51 |
| B | 0.30 | 0.48 | < 0.01 | 0.49 | 0.46 | 0.73 | 0.36 |
| Be | 0.02 | 0.31 | 0.02 | 0.92 | 0.30 | 0.71 | 0.42 |
| V | < 0.01 | 0.39 | 0.01 | 0.23 | 0.91 | 0.52 | 0.72 |
| Cr | < 0.01 | 0.15 | 0.04 | 0.09 | 0.54 | 0.54 | 0.90 |
| Co | < 0.01 | 0.28 | 0.01 | 0.86 | 0.47 | 0.89 | 0.61 |
| Ni | 0.11 | < 0.01 | < 0.01 | 0.34 | 0.61 | 0.25 | 0.67 |
| As | < 0.01 | 0.41 | 0.15 | 0.46 | 0.79 | 0.34 | 0.77 |
| Se | 0.46 | 0.12 | 0.28 | 0.86 | 0.69 | 0.74 | 0.88 |
| Rb | 0.19 | 0.01 | < 0.01 | 0.52 | 0.55 | 0.34 | 0.28 |
| Cd | < 0.01 | 0.50 | 0.45 | 0.76 | 0.93 | 0.94 | 0.78 |
| Hg | 0.49 | 0.03 | 0.30 | 0.72 | 0.56 | 0.99 | 0.96 |
| Cs | < 0.01 | < 0.01 | < 0.01 | 0.18 | 0.60 | 0.71 | 0.33 |
| Pb | < 0.01 | 0.13 | < 0.01 | 0.79 | 0.43 | 0.85 | 0.59 |
| Th | < 0.01 | 0.42 | 0.01 | 0.21 | 0.92 | 0.90 | 0.86 |
| U | < 0.01 | 0.11 | 0.26 | 0.92 | 0.32 | 0.16 | 0.84 |

**Table 13.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a silt-loam soil on soil pH, electrical conductivity (EC), and concentrations of Mehlich-3 extractable soil nutrients and trace elements.

| | Treatment | |
|---|---|---|
| Parameter | Control | Treated |
| pH | 6.2b† | 6.3a |
| EC[a] | 149a | 151a |
| Mehlich-3 Extractable (mg $kg^{-1}$) | | |
| P | 238a | 216a |
| K | 119a | 127a |
| Ca | 1221b | 1360a |
| Mg | 92.5a | 109a |
| S | 16.7b | 26.0a |
| Na | 9.7b | 13.4a |
| Fe | 242a | 220b |
| Mn | 282a | 221b |
| Zn | 13.2a | 10.8a |
| Cu | 6.1a | 5.5a |
| B | 0.1a | 0.2a |
| Trace Elements (µg $kg^{-1}$) | | |
| Be | 0.7a | 0.6a |
| V | 15.4a | 14.2a |
| Cr | 18.4a | 16.1a |
| Co | 8.7a | 7.9a |
| Ni | 5.4a | 4.4b |
| As | 4.4a | 4.1a |
| Se | 1.3a | 1.1a |
| Rb | 8.2a | 7.0b |
| Cd | 0.1a | 0.1a |
| Hg | 276b | 811a |
| Cs | 0.6a | 0.5b |
| Pb | 25.6a | 23.5a |
| Th | 3.4a | 3.2a |
| U | 1.1a | 1.0a |

† Means within the same row with different letters are significantly different at $\alpha = 0.05$.

[a] EC is in µS $cm^{-1}$

**Table 14.** Effect of soil depth in a Captina silt-loam that a received a high-Ca, dry flue gas desulfurization by-product on soil pH, electrical conductivity (EC), and concentrations of Mehlich-3 extractable soil nutrients and trace elements.

| | Depth (cm) | | |
|---|---|---|---|
| Parameter | 0 to 10 | 10 to 20 | 20 to 30 |
| pH | 6.3a† | 6.2b | 6.1c |
| EC[a] | 153a | 155a | 143a |
| Mehlich-3 Extractable (mg kg$^{-1}$) | | | |
| P | 243a | 222a | 216a |
| K | 169a | 106b | 93.3b |
| Ca | 1671a | 1139b | 1061b |
| Mg | 144a | 92.6b | 65.0c |
| S | 31.0a | 18.0b | 15.0b |
| Na | 13.4a | 10.7b | 10.6b |
| Fe | 215b | 234ab | 244a |
| Mn | 243a | 241a | 270a |
| Zn | 19.6a | 9.9b | 6.5b |
| Cu | 9.9a | 5.3b | 2.3b |
| B | 0.3a | 0.1b | 0.04b |
| Trace Elements (µg kg$^{-1}$) | | | |
| Be | 0.5b | 0.6ab | 0.7a |
| V | 12.0b | 15.3ab | 17.3a |
| Cr | 14.4b | 17.8ab | 19.5a |
| Co | 6.8b | 8.8a | 9.3a |
| Ni | 4.2b | 4.9ab | 5.6a |
| As | 3.7a | 4.3a | 4.7a |
| Se | 1.1a | 1.1a | 1.3a |
| Rb | 6.8b | 7.2b | 8.7a |
| Cd | 0.1a | 0.1a | 0.1a |
| Hg | 706a | 627a | 296a |
| Cs | 0.5b | 0.5b | 0.6a |
| Pb | 20.9b | 25.7a | 27.1a |
| Th | 2.7b | 3.4ab | 3.8a |
| U | 1.1a | 1.0a | 1.0a |

† Means within the same row with different letters are significantly different at α = 0.05.

[a] EC is in µS cm$^{-1}$

**Table 15.** Effect of time on the soil pH, electrical conductivity (EC), and concentrations of Mehlich-3 extractable soil nutrients and trace elements in a Captina silt loam that received a high-Ca, dry flue gas desulfurization by-product.

| | Months After Application | | |
|---|---|---|---|
| Parameter | 0 | 6 | 12 |
| pH | 6.2b† | 6.3a | 6.2b |
| EC[a] | 153a | 146a | 152a |
| Mehlich-3 Extractable (mg kg$^{-1}$) | | | |
| P | 268a | 167b | 246a |
| K | 131a | 105a | 132 |
| Ca | 1343a | 1310ab | 1218b |
| Mg | 112a | 89.9a | 100a |
| S | 15.2b | 25.3a | 23.5a |
| Na | 7.6b | 13.2a | 13.8a |
| Fe | 253a | 206b | 234a |
| Mn | 283a | 205b | 266a |
| Zn | 15.2a | 9.5b | 11.2ab |
| Cu | 7.2a | 4.9a | 5.3a |
| B | 0.2a | 0.2a | 0.1a |
| Trace Elements (µg kg$^{-1}$) | | | |
| Be | 0.6ab | 0.5b | 0.7a |
| V | 20.2a | 16.4b | 7.9c |
| Cr | 25.6a | 16.1b | 11.0c |
| Co | 7.9b | 6.5b | 10.5a |
| Ni | 4.9ab | 4.5b | 5.3a |
| As | 5.5a | 4.4b | 2.8c |
| Se | 1.3a | 1.1a | 1.2a |
| Rb | 7.5a | 7.1a | 8.1a |
| Cd | 0.1b | 0.1b | 0.2a |
| Hg | 465a | 621a | - |
| Cs | 0.6a | 0.5b | 0.4c |
| Pb | 28.3a | 22.2b | 23.2b |
| Th | 2.3b | 2.3b | 5.2a |
| U | 1.3a | 1.2a | 0.6b |

† Means within the same row with different letters are significantly different at α = 0.05.

[a] EC is in µS cm$^{-1}$

**Table 16.** Analysis of variance summary of the effects of time (T) (i.e., 0, 6 and 12 mo after application), treatment (TRT) (i.e., control or treated), soil depth (D) (i.e., 0-10, 10-20, and 20-30 cm depth interval), and their interaction on soil contents of Mehlich-3 extractable soil nutrients and trace elements.

| | Source of Variation | | | | | | |
|---|---|---|---|---|---|---|---|
| Element | T | TRT | D | T*TRT | TRT*D | T*D | T*TRT*D |
| | *P* | | | | | | |
| P | 0.01 | 0.40 | 0.51 | 0.33 | 0.95 | 0.96 | 0.86 |
| K | 0.25 | 0.53 | 0.08 | 0.60 | 0.90 | 0.53 | 0.65 |
| Ca | 0.12 | 0.01 | < 0.01 | 0.58 | 0.01 | 0.85 | 0.76 |
| Mg | 0.22 | 0.10 | < 0.01 | 0.73 | 0.95 | 0.85 | 0.32 |
| S | 0.04 | 0.01 | 0.04 | 0.02 | 0.48 | 0.85 | 0.91 |
| Na | < 0.01 | < 0.01 | 0.66 | < 0.01 | 0.09 | 0.94 | 0.60 |
| Fe | < 0.01 | 0.05 | < 0.01 | 0.22 | 0.76 | 0.38 | 0.65 |
| Mn | < 0.01 | < 0.01 | < 0.01 | 0.06 | 0.63 | 0.93 | 0.57 |
| Zn | 0.03 | 0.19 | < 0.01 | 0.13 | 0.85 | 0.45 | 0.18 |
| Cu | 0.25 | 0.65 | < 0.01 | 0.72 | 0.89 | 0.79 | 0.51 |
| B | 0.25 | 0.44 | < 0.01 | 0.52 | 0.38 | 0.64 | 0.35 |
| Be | 0.04 | 0.35 | < 0.01 | 0.89 | 0.36 | 0.77 | 0.56 |
| V | < 0.01 | 0.54 | < 0.01 | 0.26 | 0.92 | 0.33 | 0.80 |
| Cr | < 0.01 | 0.27 | < 0.01 | 0.12 | 0.65 | 0.37 | 0.92 |
| Co | < 0.01 | 0.34 | < 0.01 | 0.88 | 0.32 | 0.75 | 0.64 |
| Ni | 0.25 | 0.01 | < 0.01 | 0.35 | 0.52 | 0.44 | 0.72 |
| As | < 0.01 | 0.43 | 0.34 | 0.55 | 0.28 | 0.69 | 0.56 |
| Se | < 0.01 | 0.60 | < 0.01 | 0.46 | 0.91 | 0.27 | 0.81 |
| Rb | 0.55 | 0.20 | 0.01 | 0.84 | 0.89 | 0.82 | 0.91 |
| Cd | 0.16 | 0.02 | < 0.01 | 0.51 | 0.44 | 0.42 | 0.37 |
| Hg | 0.45 | 0.02 | 0.46 | 0.71 | 0.62 | 0.96 | 0.95 |
| Cs | < 0.01 | 0.61 | < 0.01 | 0.77 | 0.82 | 0.85 | 0.80 |
| Pb | < 0.01 | < 0.01 | < 0.01 | 0.25 | 0.66 | 0.88 | 0.50 |
| Th | < 0.01 | 0.26 | < 0.01 | 0.90 | 0.27 | 0.78 | 0.67 |
| U | < 0.01 | 0.52 | < 0.01 | 0.22 | 0.83 | 0.48 | 0.79 |

**Table 17.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a Captina silt-loam soil on the content of Mehlich-3 extractable soil nutrients and trace elements.

| | Treatment | |
|---|---|---|
| Parameter | Control | Treated |
| Mehlich-3 Extractable (kg $ha^{-1}$) | | |
| P | 297a† | 270a |
| K | 143a | 155a |
| Ca | 1494b | 1664a |
| Mg | 111a | 132a |
| S | 20.1b | 31.4a |
| Na | 12.0b | 16.5a |
| Fe | 304a | 278b |
| Mn | 352a | 280b |
| Zn | 15.6a | 12.9a |
| Cu | 7.2a | 6.5a |
| B | 0.2a | 0.2a |
| Trace Elements (g $ha^{-1}$) | | |
| Be | 0.8a | 0.8a |
| V | 19.6a | 18.5a |
| Cr | 23.2a | 20.7a |
| Co | 11.0a | 10.1a |
| Ni | 6.8a | 5.6b |
| As | 32.8a | 29.4a |
| Se | 5.5a | 5.2a |
| Rb | 1.6a | 1.4a |
| Cd | 10.3a | 8.9b |
| Hg | 331b | 957a |
| Cs | 0.2a | 0.2a |
| Pb | 0.7a | 0.6b |
| Th | 32.3a | 30.1a |
| U | 4.3a | 4.1a |

† Means within the same row with the same letter are not significantly different at $\alpha = 0.05$.

**Table 18.** Effect of soil depth in a Captina silt-loam soil that received a high-Ca, dry flue gas desulfurization by-product on the content of Mehlich-3 extractable soil nutrients and trace elements.

| | Depth (cm) | | |
|---|---|---|---|
| Element | 0 to 10 | 10 to 20 | 20 to 30 |
| Mehlich-3 Extractable (kg ha$^{-1}$) | | | |
| P | 258a† | 292a | 302a |
| K | 180a | 137ab | 131b |
| Ca | 1778a | 1478b | 1481b |
| Mg | 154a | 119b | 91.3b |
| S | 33.0a | 23.2b | 21.1b |
| Na | 14.2a | 13.8a | 14.8a |
| Fe | 229c | 304b | 340a |
| Mn | 256c | 315b | 377a |
| Zn | 20.9a | 12.9b | 9.0b |
| Cu | 10.5a | 6.9b | 3.1c |
| B | 0.3a | 0.1b | 0.1b |
| Trace Elements (g ha$^{-1}$) | | | |
| Be | 0.6b | 0.8a | 1.0a |
| V | 12.8b | 19.9a | 24.2a |
| Cr | 15.4b | 23.2a | 27.2a |
| Co | 7.2b | 11.5a | 13.1a |
| Ni | 4.5c | 6.3b | 7.8a |
| As | 35.5a | 28.5a | 29.3a |
| Se | 4.0b | 5.8a | 6.5a |
| Rb | 1.2b | 1.4a | 1.8a |
| Cd | 7.2c | 9.4b | 12.1a |
| Hg | 730a | 788a | 416a |
| Cs | 0.1b | 0.2a | 0.19a |
| Pb | 0.5c | 0.6b | 0.8a |
| Th | 22.3b | 33.5a | 37.9a |
| U | 2.9b | 4.4a | 5.3a |

† Means within the same row with the same letter are not significantly different at $\alpha = 0.05$.

**Table 19.** Effect of time on the content of Mehlich-3 extractable soil nutrients and trace elements in a Captina silt loam that received a high-Ca, dry flue gas desulfurization by-product.

| | Months After Application | | |
|---|---|---|---|
| Parameter | 0 | 6 | 12 |
| Mehlich-3 Extractable (kg $ha^{-1}$) | | | |
| P | 335a† | 208b | 307a |
| K | 159a | 127a | 161a |
| Ca | 1648a | 1603ab | 1486b |
| Mg | 136a | 109a | 120a |
| S | 18.4b | 30.3a | 28.6a |
| Na | 9.5b | 16.3a | 17.1a |
| Fe | 320a | 259b | 294.4a |
| Mn | 354a | 259b | 334a |
| Zn | 18.0a | 11.5b | 13.2ab |
| Cu | 8.6a | 5.8a | 6.1a |
| B | 0.2a | 0.2a | 0.1a |
| Trace Elements (g $ha^{-1}$) | | | |
| Be | 0.8ab | 0.7b | 0.9a |
| V | 25.8a | 21.0a | 10.0b |
| Cr | 31.3a | 20.5b | 13.9c |
| Co | 10.1b | 8.3b | 13.4a |
| Ni | 6.2a | 5.8a | 6.7a |
| As | 35.9a | 37.6a | 19.8b |
| Se | 7.0a | 5.6a | 3.5b |
| Rb | 1.6a | 1.4a | 1.5a |
| Cd | 9.4a | 9.0a | 10.3a |
| Hg | 545a | 743a | - |
| Cs | 0.1b | 0.1b | 0.2a |
| Pb | 0.8a | 0.7a | 0.6b |
| Th | 36.1a | 28.2b | 29.4b |
| U | 3.0b | 2.9b | 6.6a |

† Means within the same row with the same letter are not significantly different at $\alpha = 0.05$.

**Table 20.** Drinking water limitations of cattle and maximum contaminant levels for trace elements under the Safe Drinking Water Act (SDWA) (NRC, 2001). Adapted from United States Safe Drinking Water Act of 1974 (USEPA, 2016).

| | Limit ($\mu$g $L^{-1}$) | |
|---|---|---|
| Element | Cattle | SDWA |
| As | 50 | 10 |
| Be | 4 | 4 |
| Cd | 5 | 5 |
| Cr | 100 | 100 |
| Co | 1000 | - |
| Cu | 1000 | 1300 |
| Pb | 15 | 15 |
| Hg | 10 | 2 |
| Ni | 250 | - |
| Se | 50 | 50 |
| V | 100 | - |
| Zn | 5000 | - |
| U | - | 30 |

**Table 21.** The percent of element from a land-applied high-Ca, dry flue gas desulfurization by-product accounted for in runoff, aboveground dry matter (DM), and soil storage changes over a 1-yr time period.

| | Percentage of Element Accounted For | | | |
|---|---|---|---|---|
| Element | Runoff | DM | Soil Storage Change | Total |
| Be | < 0.01 | 0.1 | 0.2 | 0.3 |
| V | 0.01 | 0.4 | -3 | -2.6 |
| Cr | < 0.01 | 0.6 | -6.5 | -5.9 |
| Co | 0.02 | 2.2 | 7.2 | 9.4 |
| Ni | 0.02 | 2.8 | 0.4 | 3.2 |
| Cu | 0.02 | 6.9 | -0.4 | 6.5 |
| Zn | 0.7 | 57.1 | -1.1 | 56.7 |
| As | 0.03 | 1.5 | -28.5 | -27.0 |
| Se | 0.03 | 20.5 | -9.1 | 11.4 |
| Rb | 3.8 | 1112 | -0.2 | 1116 |
| Cd | 0.3 | 16.5 | 4.7 | 21.5 |
| Cs | 0.04 | 58.7 | 2.2 | 60.9 |
| Hg | 0.03 | 2.7 | - | 2.7 |
| Pb | 3.7 | 122 | -44.8 | 80.9 |
| Th | 0.02 | 1.4 | -54.6 | -53.2 |
| U | 0.01 | 0.3 | 18.9 | 19.2 |

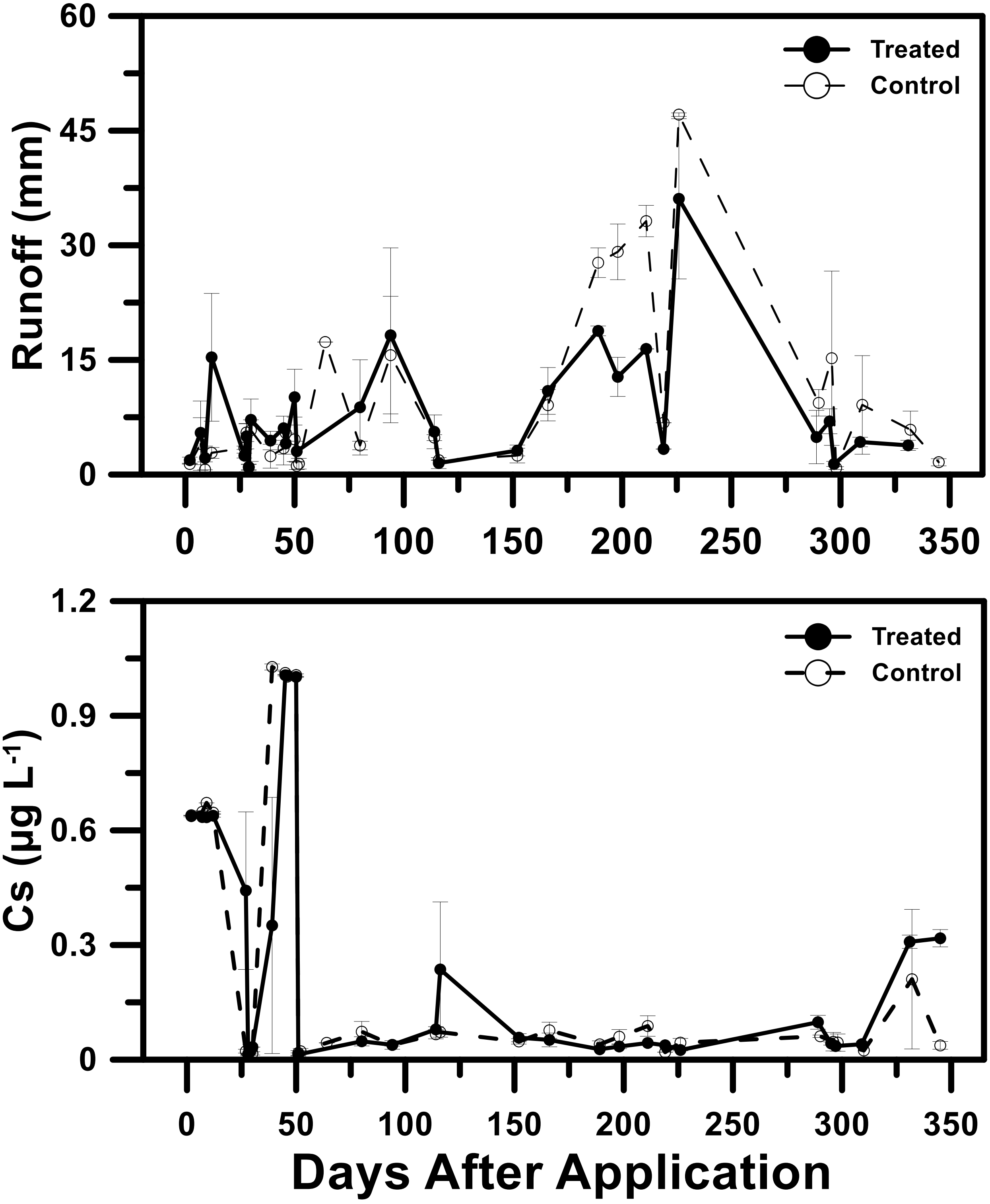

**Figure 1.** Time series trends of mean runoff and mean runoff Cs concentrations from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product. Error bars represent standard errors about the mean.

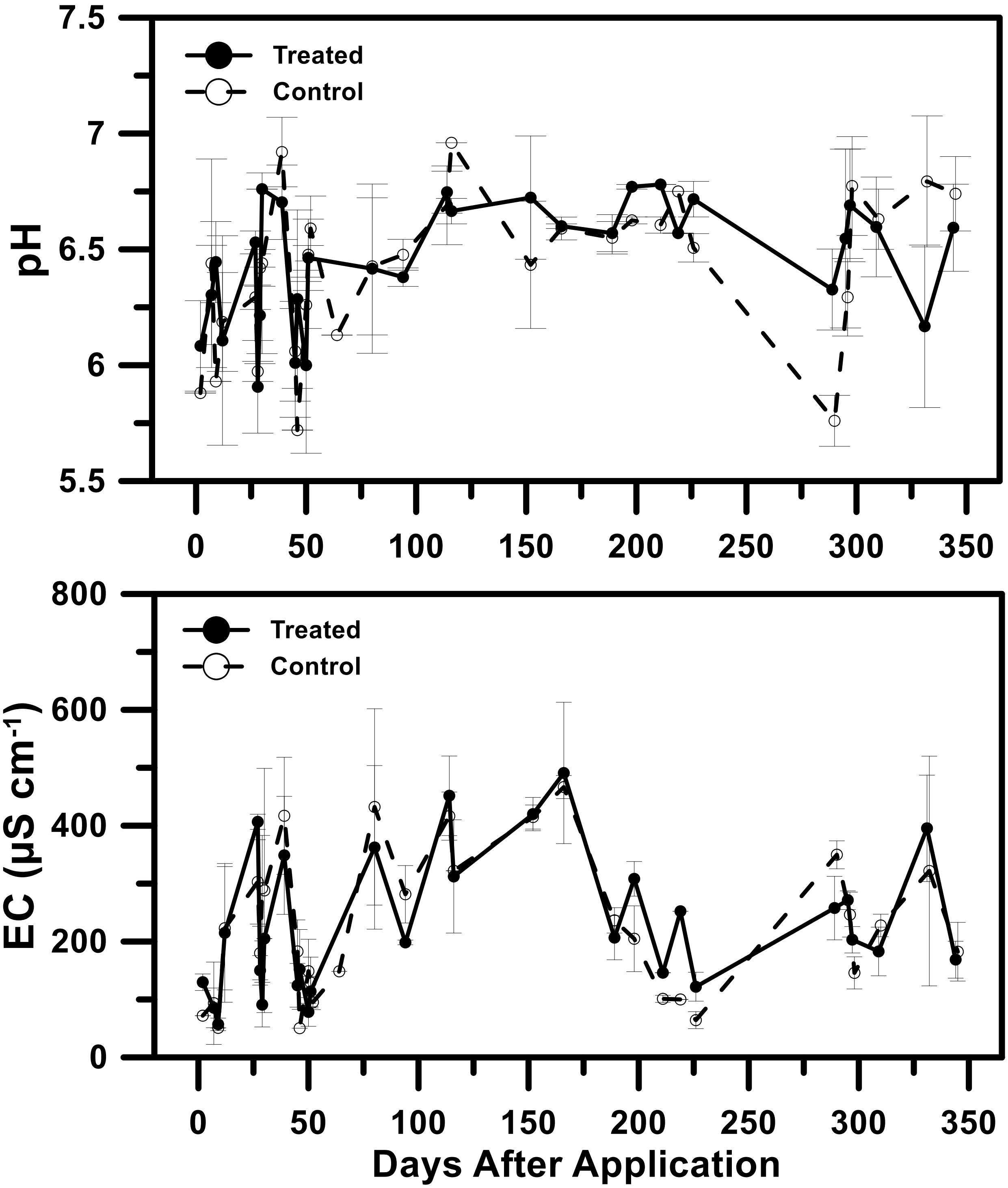

**Figure 2.** Time series trends of mean runoff pH and runoff electrical conductivity (EC) from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product. Error bars represent standard errors about the mean.

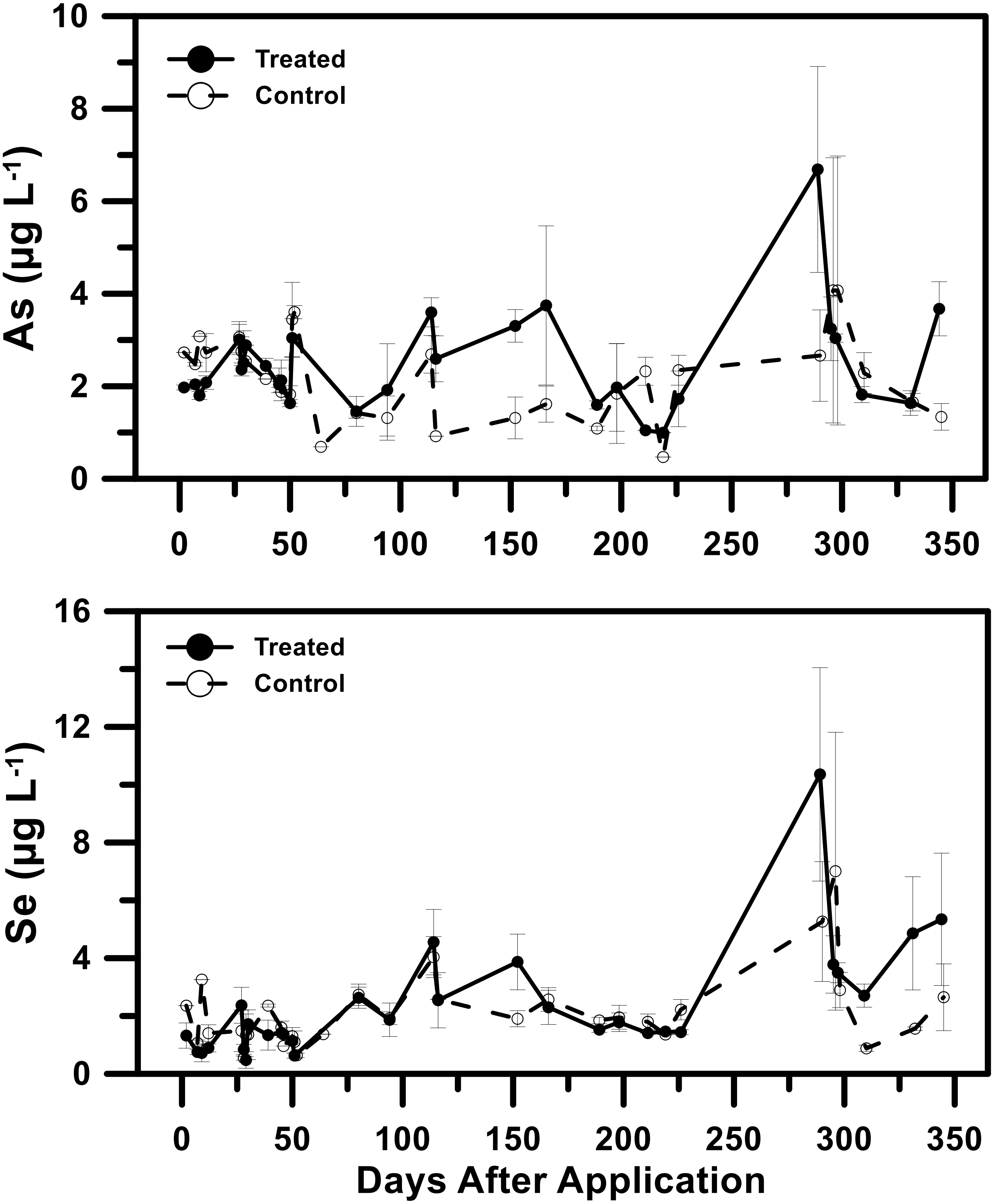

**Figure 3.** Time series trends of mean runoff As and Se concentrations from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product. Error bars represent standard errors about the mean.

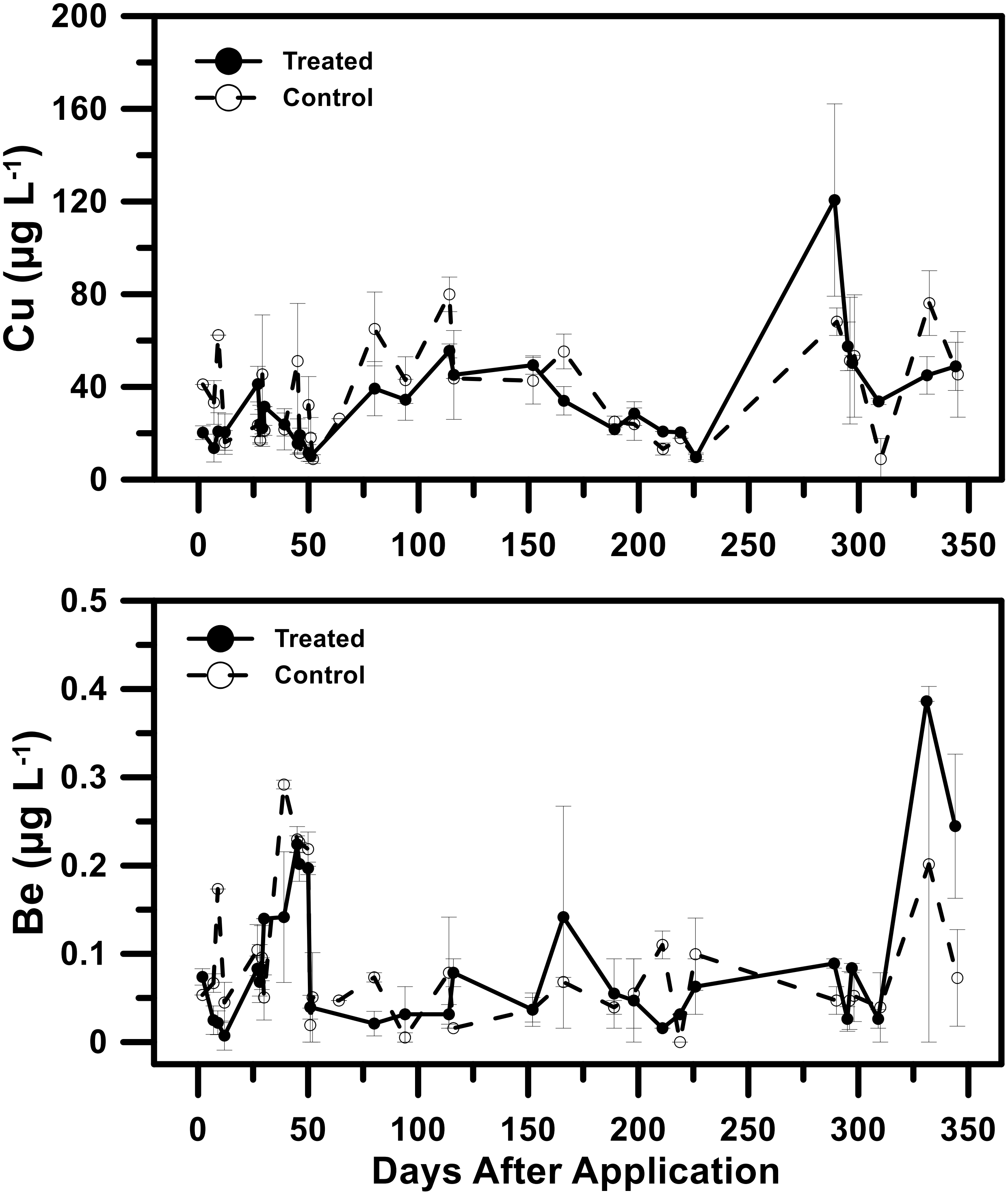

**Figure 4.** Time series trends of mean runoff Cu and Be concentrations from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product. Error bars represent standard errors about the mean.

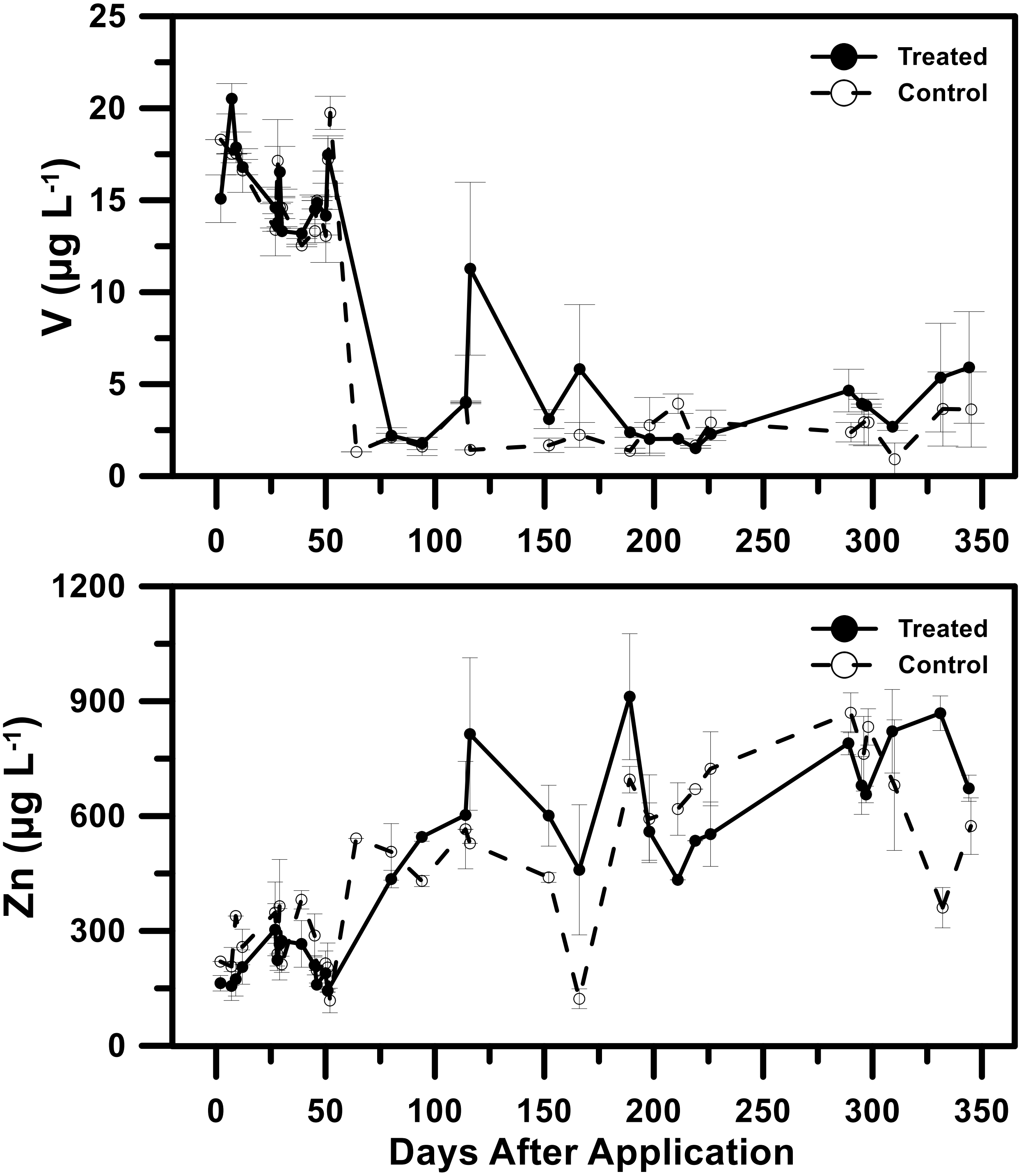

**Figure 5.** Time series trends of mean runoff V and Zn concentrations from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product. Error bars represent standard errors about the mean.

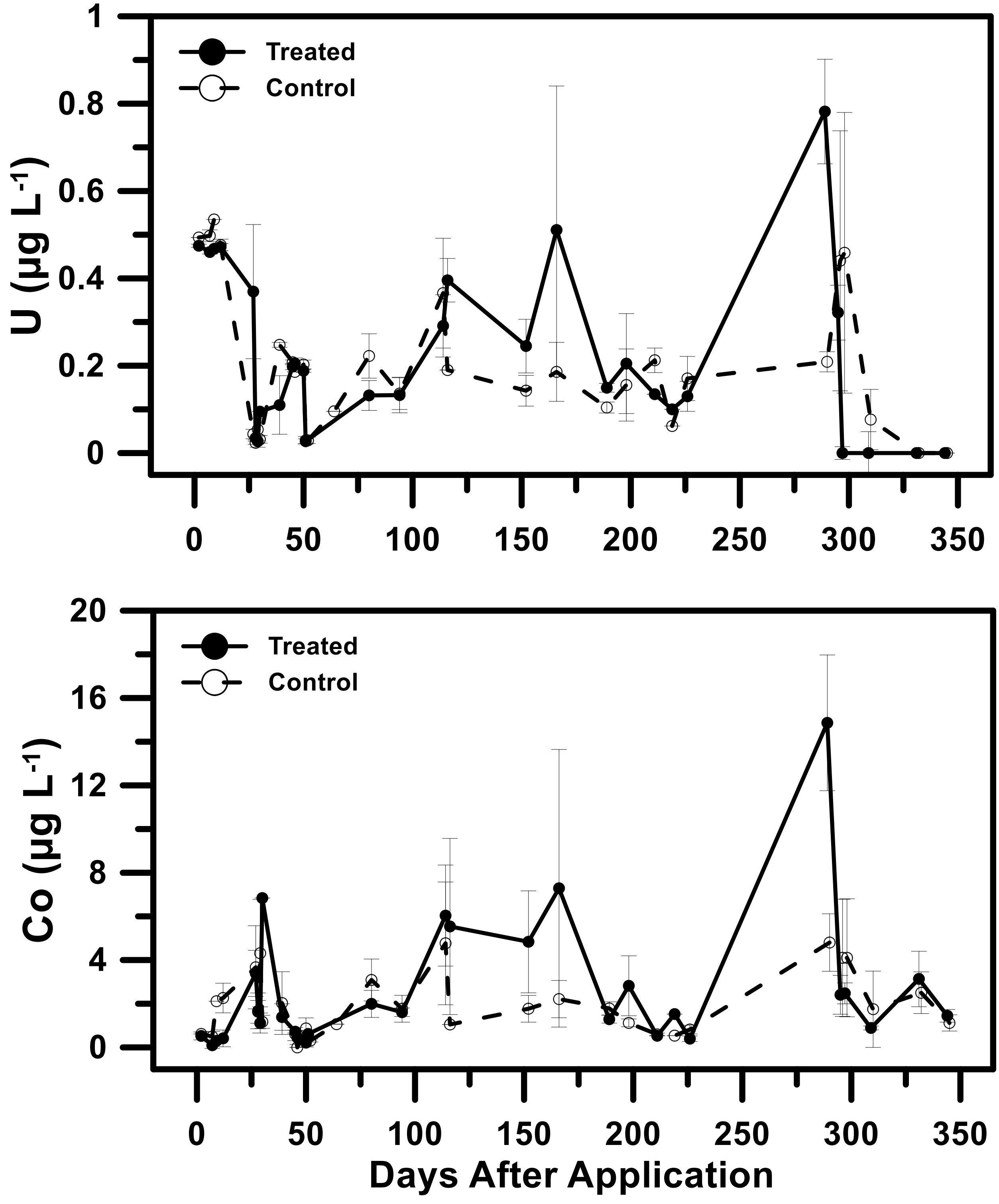

**Figure 6.** Time series trends of mean runoff U and Co concentrations from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product. Error bars represent standard errors about the mean.

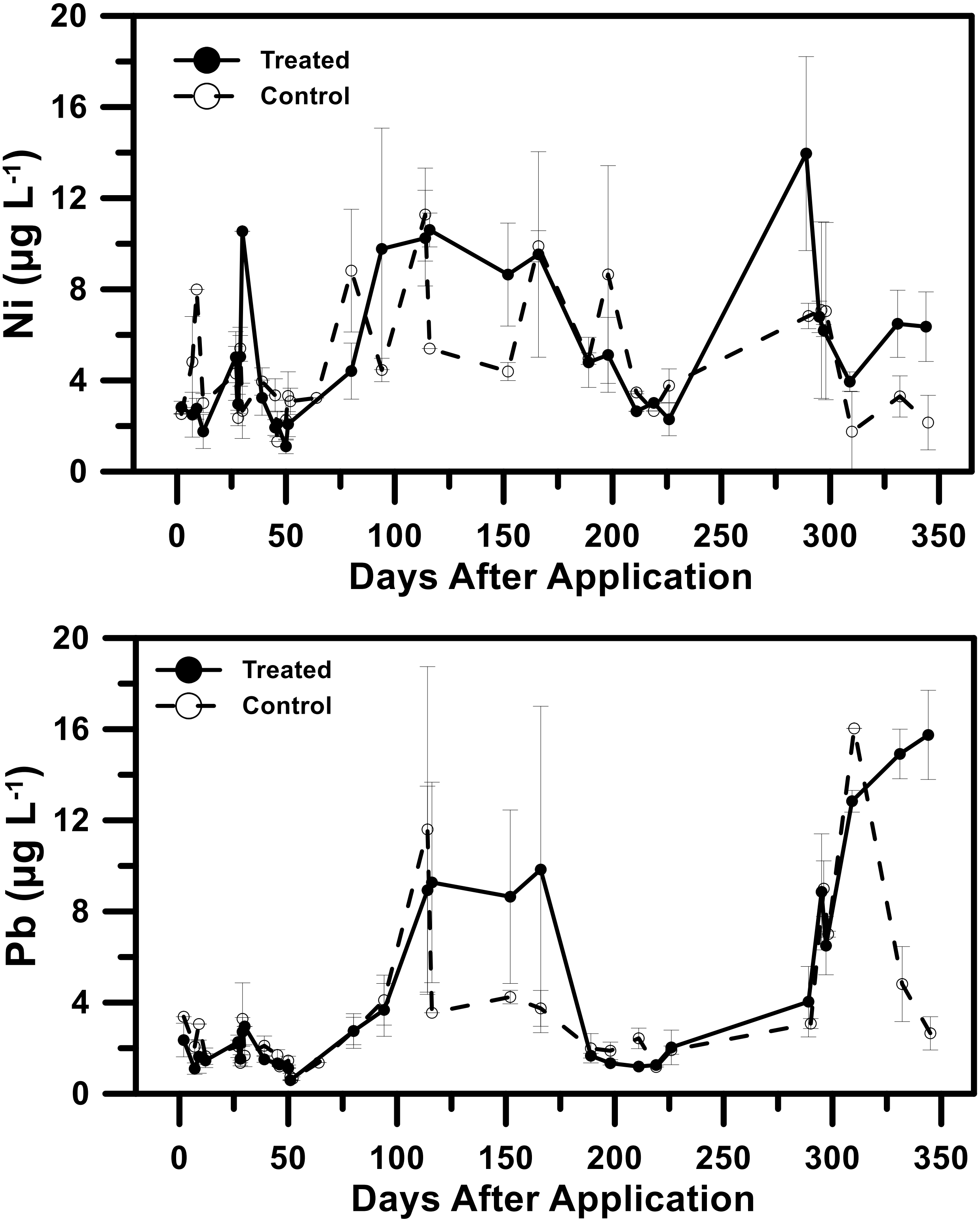

**Figure 7.** Time series trends of mean runoff Ni and Pb concentrations from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product. Error bars represent standard errors about the mean.

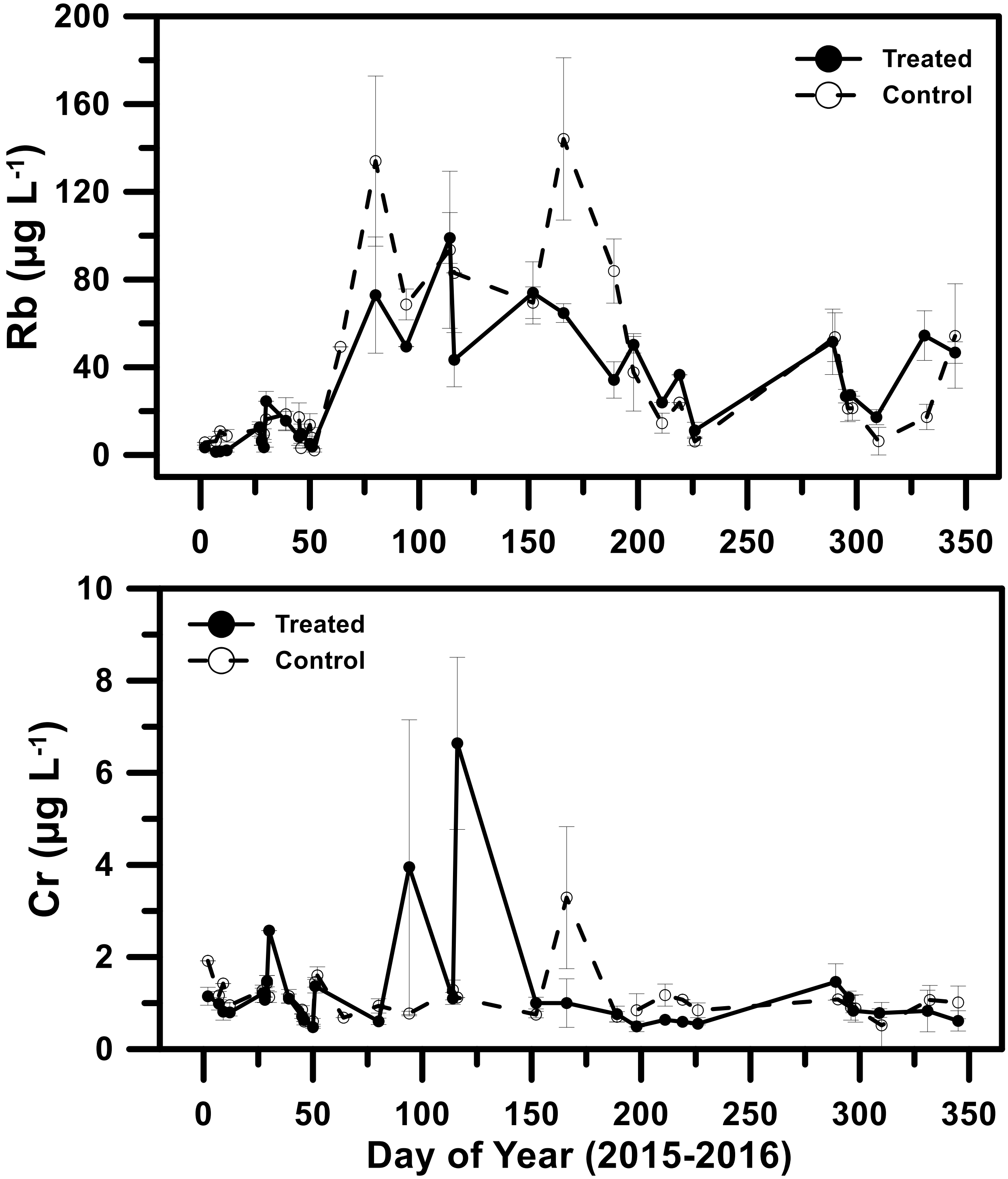

**Figure 8.** Time series trends of mean runoff Rb and Cr concentrations from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product. Error bars represent standard errors about the mean.

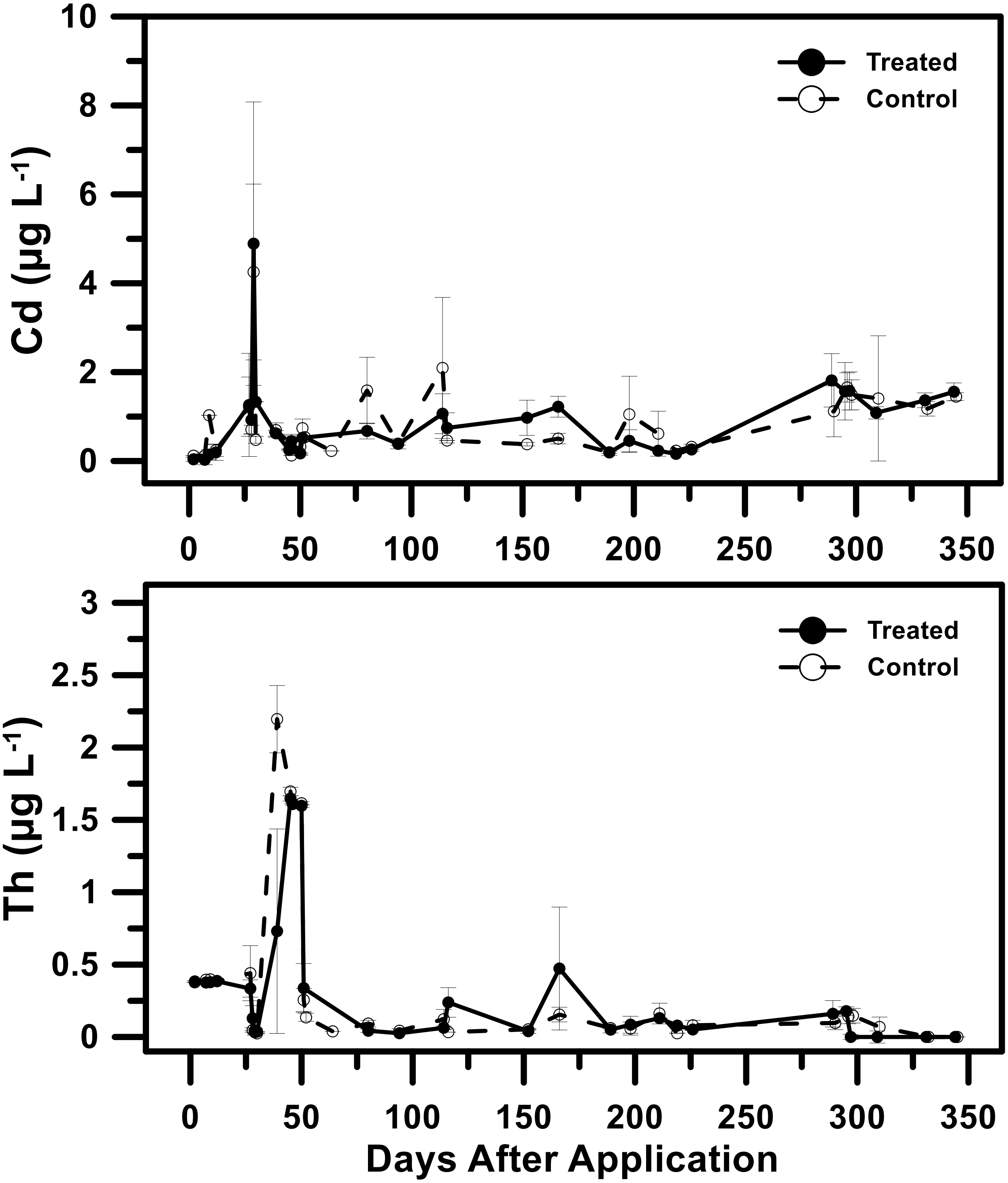

**Figure 9.** Time series trends of mean runoff Cd and Th concentrations from a managed grassland that received a high-Ca, dry flue gas desulfurization by-product. Error bars represent standard errors about the mean.

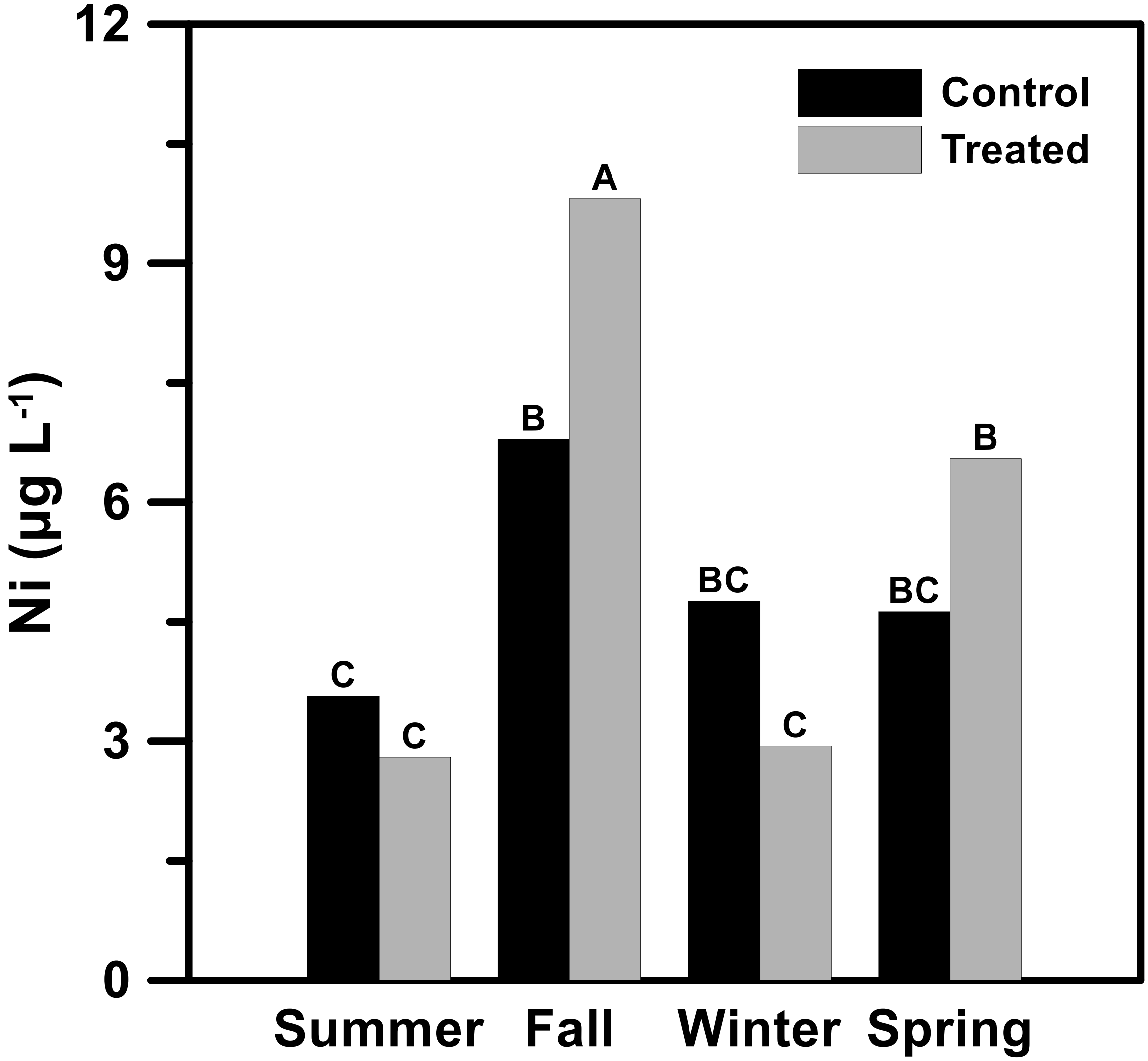

**Figure 10.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on seasonal flow-weighted mean Ni concentration. Means with the same letter are not significantly different at α = 0.05.

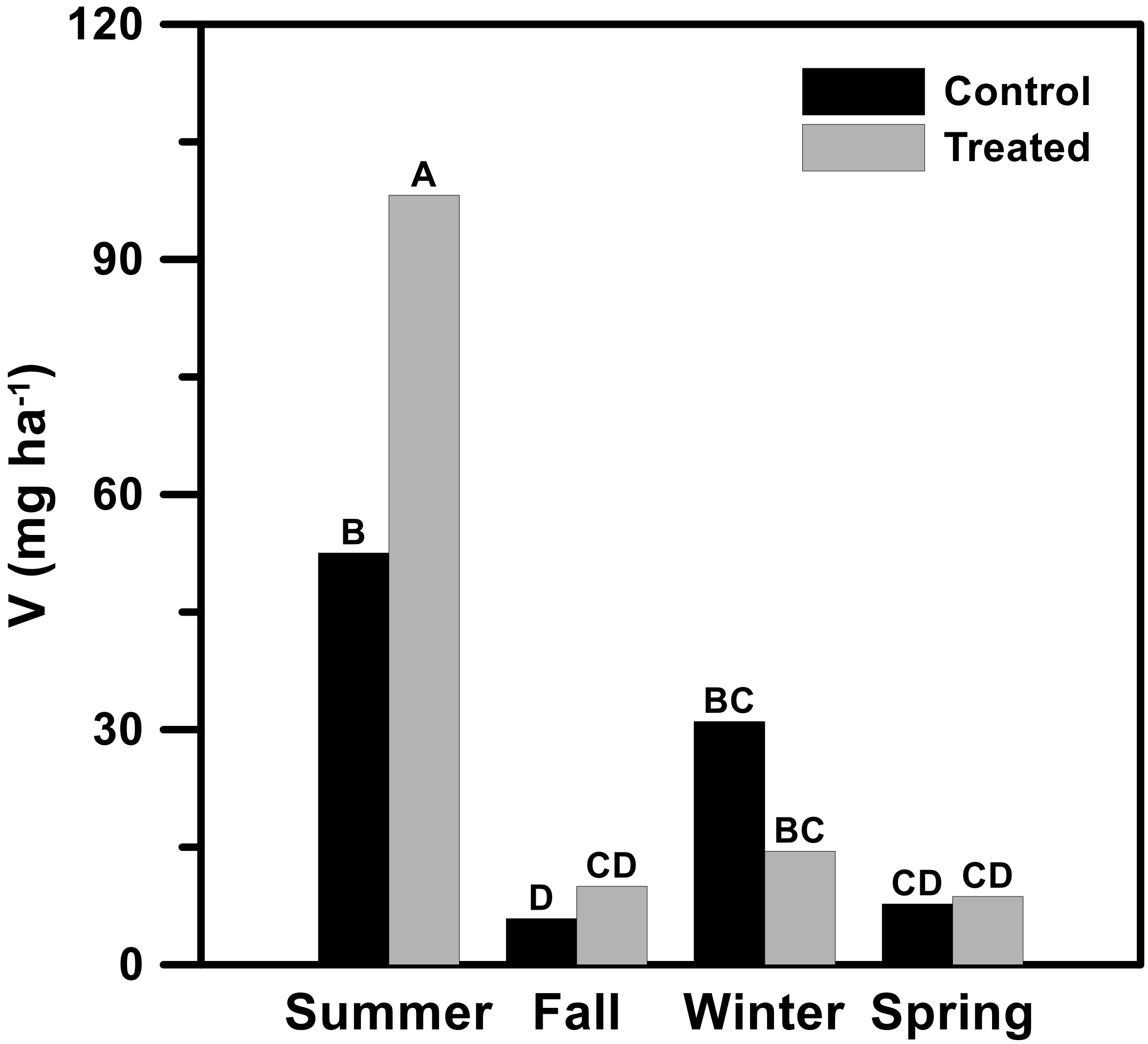

**Figure 11.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on seasonal V load. Means with the same letter are not significantly different at $\alpha = 0.05$.

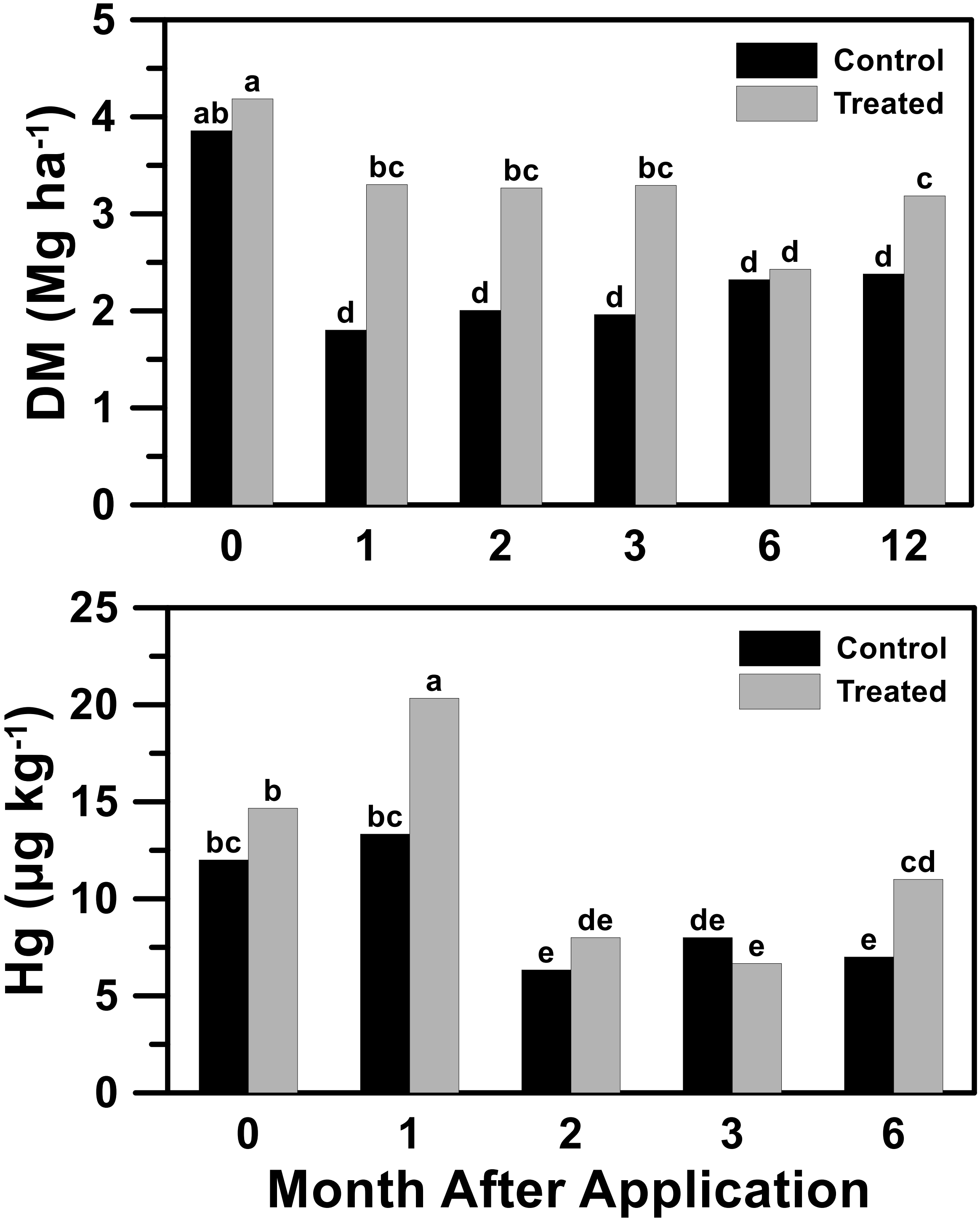

**Figure 12.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on aboveground dry matter (DM) and tissue Hg concentration. Means with the same letter are not significantly different at $\alpha = 0.05$.

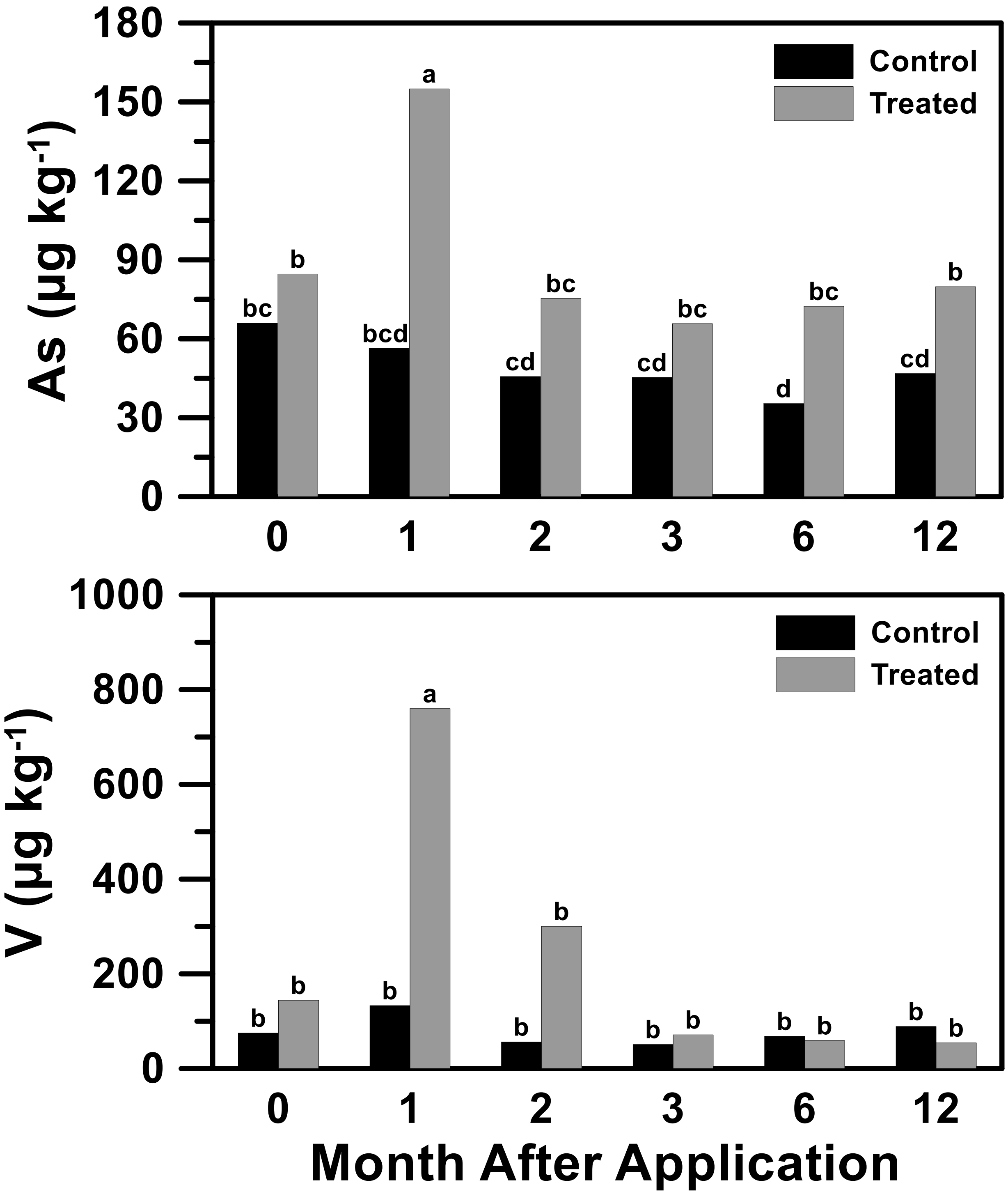

**Figure 13.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on tissue As and V concentrations. Means with the same letter are not significantly different at $\alpha = 0.05$.

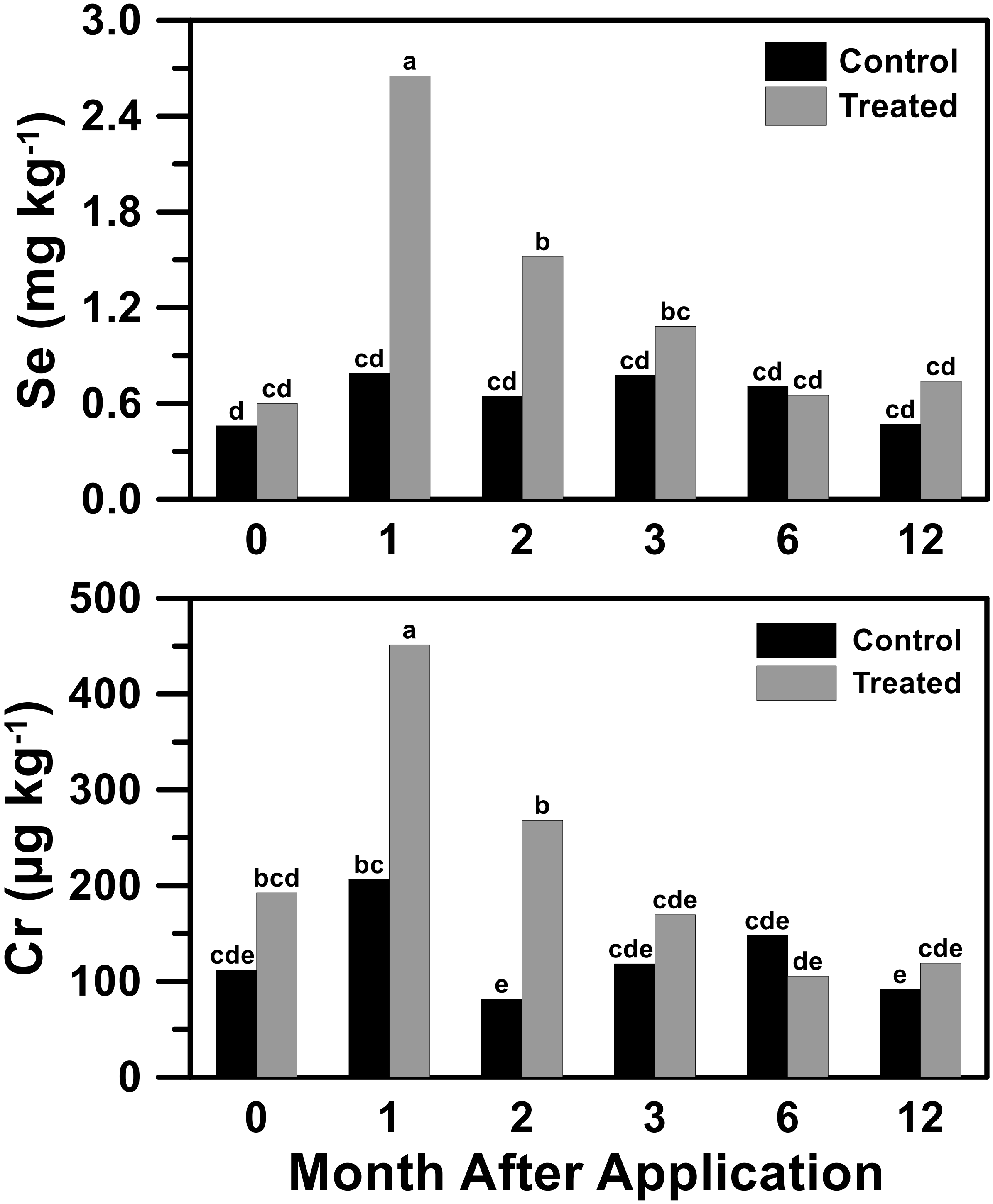

**Figure 14.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on tissue Se and Cr concentrations. Means with the same letter are not significantly different at α = 0.05.

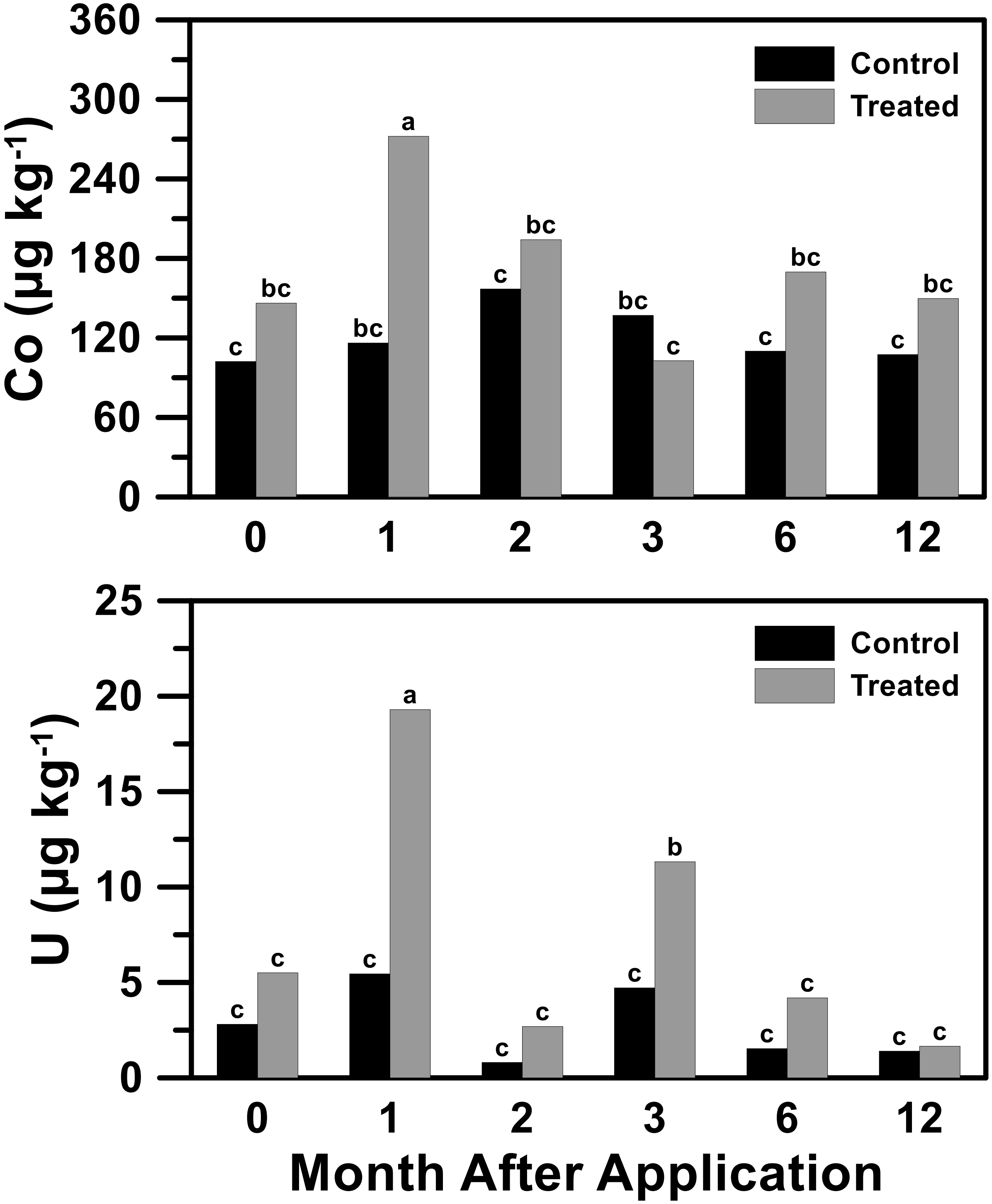

**Figure 15.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on tissue Co and U concentrations. Means with the same letter are not significantly different at $\alpha = 0.05$.

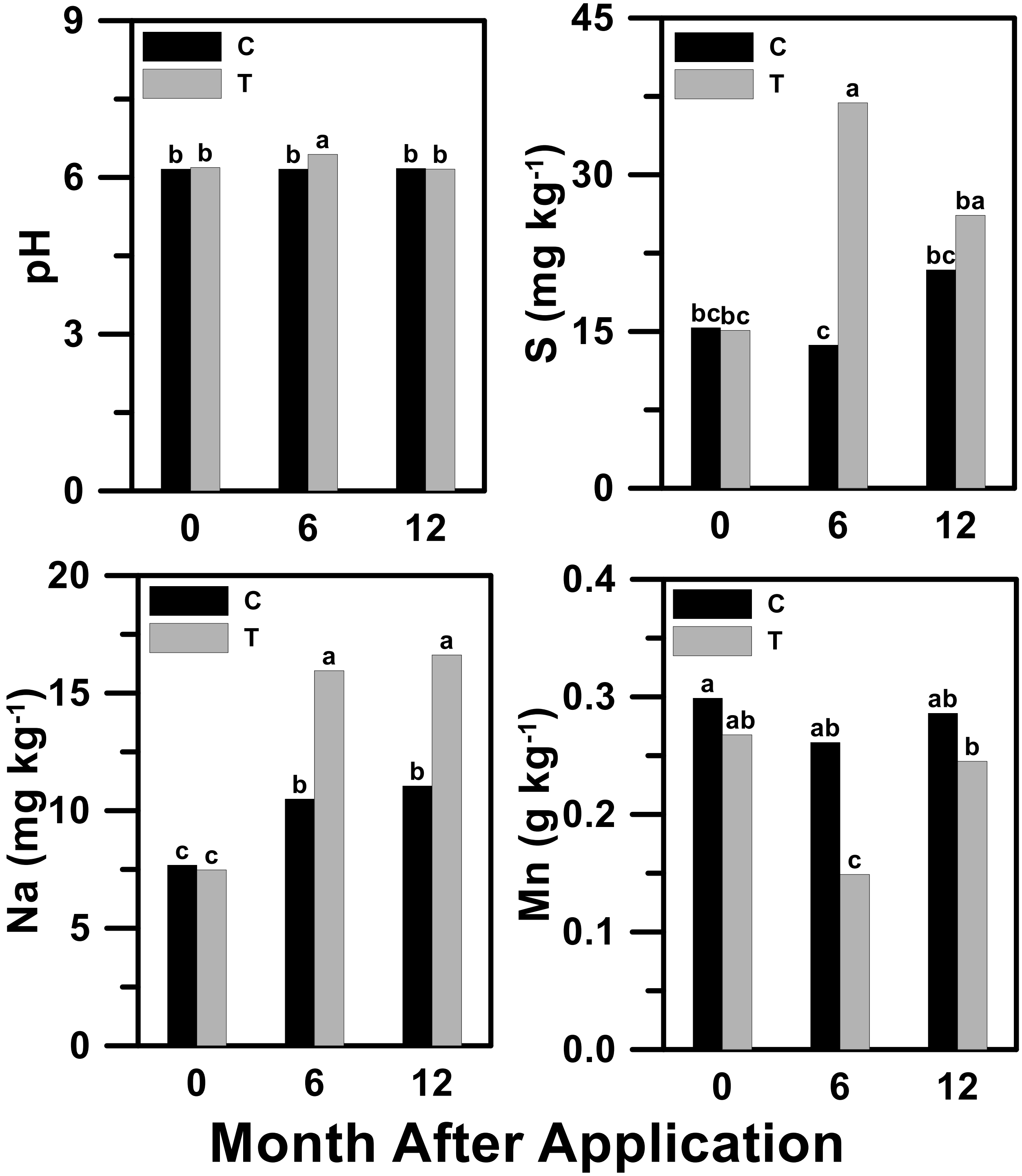

**Figure 16.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on soil pH and Mehlich-3 extractable soil S, Na, and Mn concentrations. Means with the same letter are not significantly different at $\alpha = 0.05$.

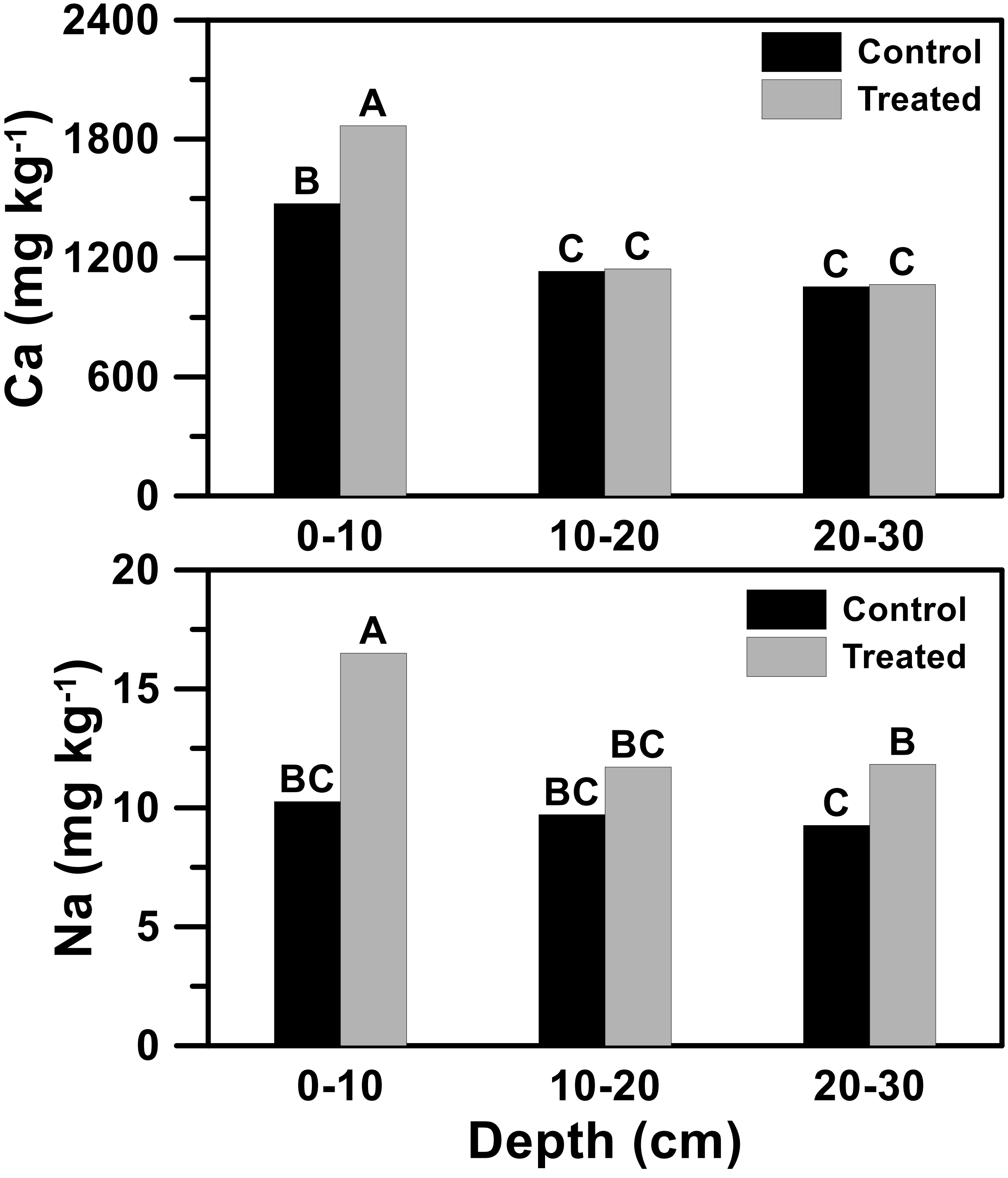

**Figure 17.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on Mehlich-3 extractable soil Ca and Na concentrations. Means with the same letter are not significantly different at $\alpha = 0.05$.

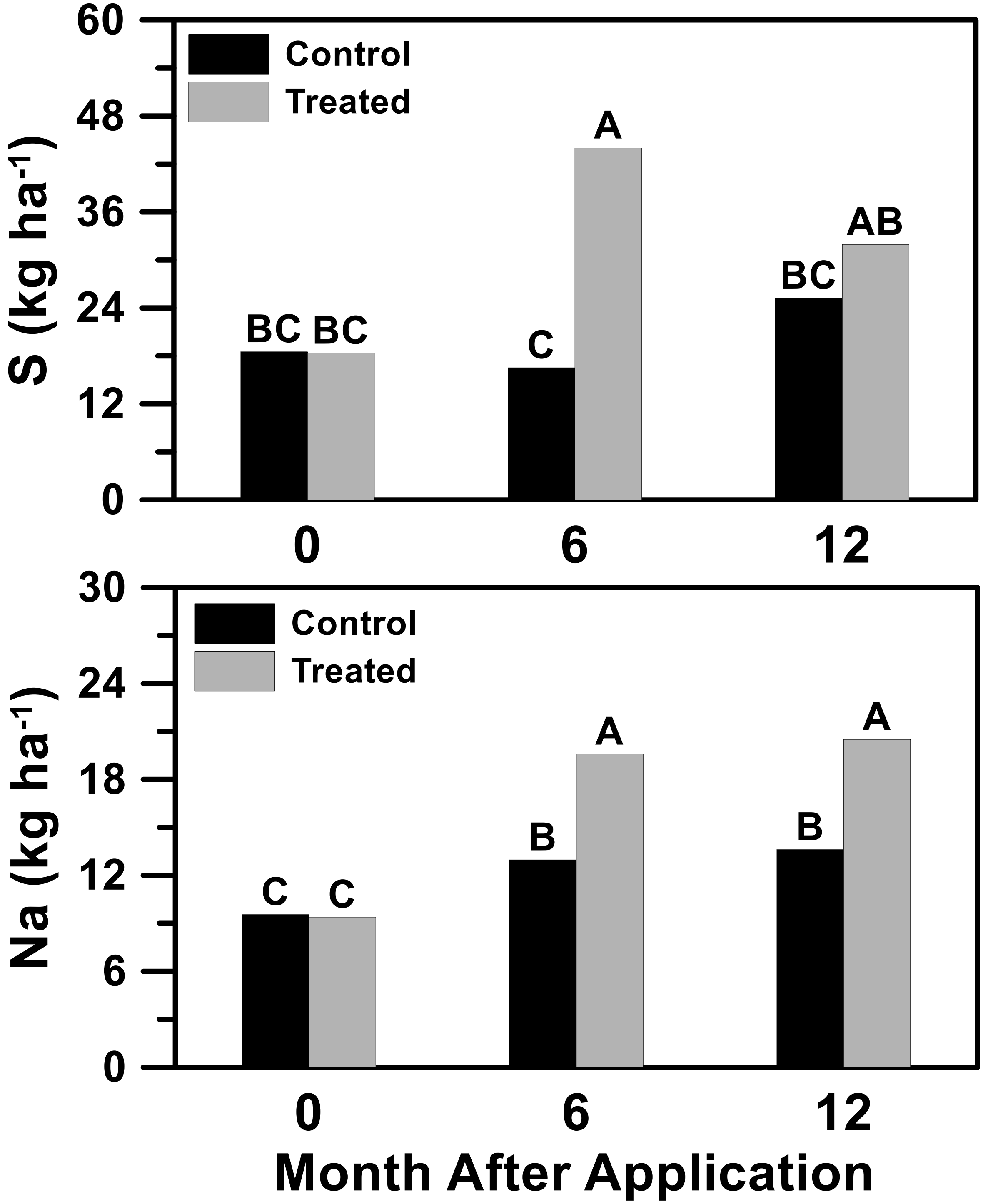

**Figure 18.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on Mehlich-3 extractable soil S and Na contents. Means with the same letter are not significantly different at $\alpha = 0.05$.

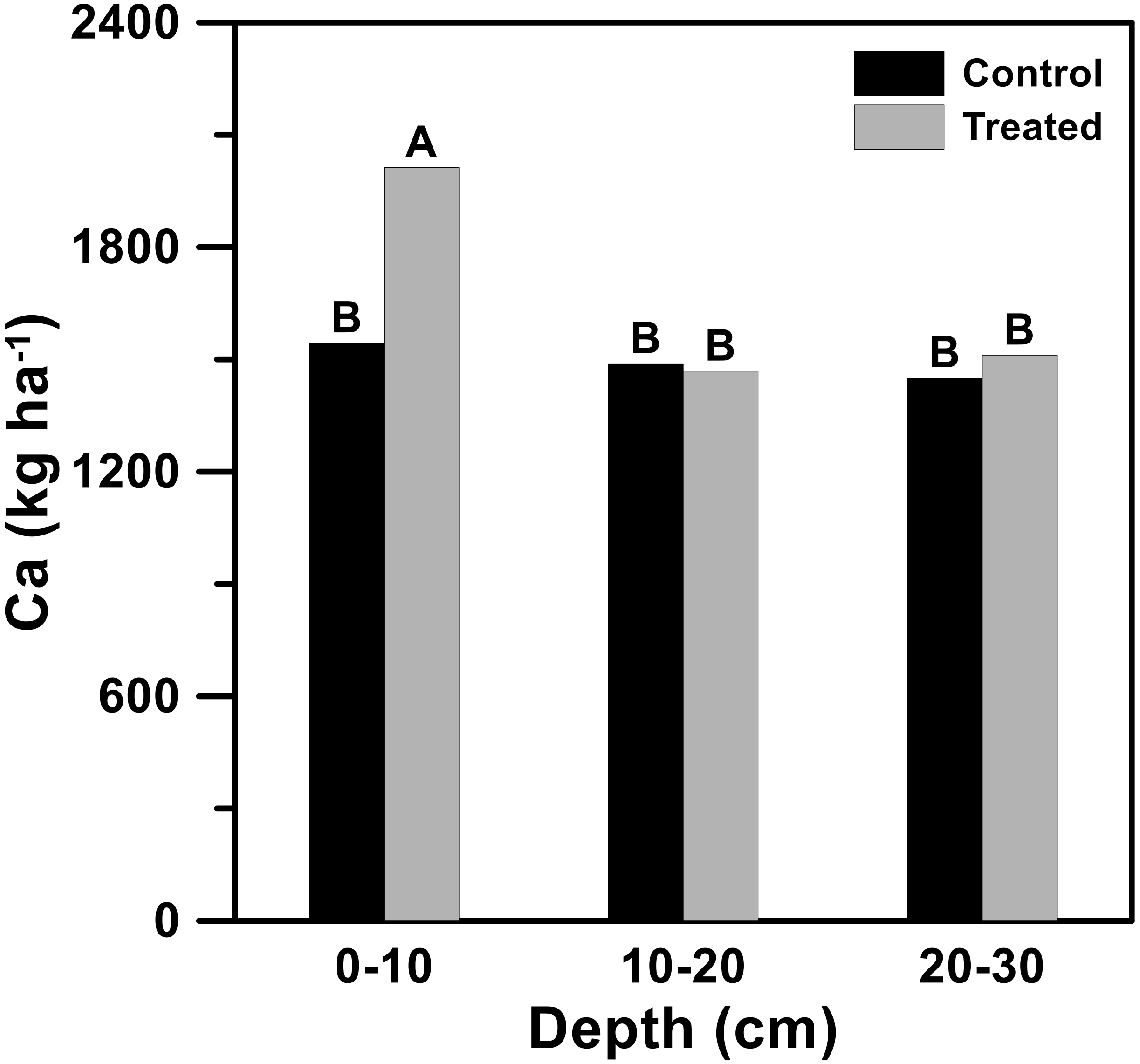

**Figure 19.** Effect of application of a high-Ca, dry flue gas desulfurization by-product to a managed grassland on Mehlich-3 extractable soil Ca content. Means with the same letter are not significantly different at $\alpha = 0.05$.

## Summary and Overall Conclusions

As predicted, the high-Ca DFGD by-product used in this experiment was as capable at raising soil pH as conventional liming materials. The ENV of the DFGD by-product was lower than that of reagent-grade $CaCO_3$, but was similar to those of most commercially available liming materials. When incubated with an acidic clay soil, the DFGD by-product was as capable as reagent-grade $CaCO_3$ at increasing soil pH, and more effective when incubated at a rate that was twice the soil's lime requirement. In the field, there was also a significant increase in soil pH in plots receiving the DFDG by-product. Although the soil pH in plots receiving the DFGD by-product 6 mo after application was only 0.3 pH units greater than the control, if soil samples were collected closer to the time of application, the soil pH would most likely be greater than 6.44. The ability for this high-Ca DFGD by-product to raise soil pH above 7.0 may be advantageous, but the possibility of increasing soil pH above 8.0 warrants caution when being applied in large amounts.

Over the 12-mo period of this experiment, seasonal FWM concentrations of Ni and seasonal loads of V were the only water quality parameters measured that significantly increased upon treatment with the DFGD by-product. There was no difference in annual or seasonal runoff volume, pH, or EC between the treated and unamended control. There was also no difference in annual FWM concentrations and 12-mo cumulative trace elements loads between the treated and unamended control.

There was a greater effect of application of the DFGD by-product on aboveground dry matter (DM) than runoff. Aboveground DM was significantly greater in the DFGD by-product amended treatment for 3 mo following application and may be attributed to the large concentrations of essential plant nutrients in the by-product. Tissue As, Co, Cr, Hg, Se, V, and U concentrations were significantly greater in the amended treatment than in the unamended control for 3 mo following application. The low clay content of the soil in the research area and the long-term application of broiler litter prior to the beginning of this study may have reduced the ability for these trace elements to adsorb to soil colloids and increased their bioavailability. However, the concentrations of these trace elements never reached or exceeded levels deemed dangerous for consumption by cattle. Except for U, tissue As, Co, Cr, Hg, Se, and V concentrations either returned to pre-application levels or did not differ from the unamended control 3 mo after application. There was no difference in tissue U concentrations between the treated and unamended control 6 mo after application. Over the 12-mo experiment, cumulative plant uptake of As, Co, Cr, Cs, Cu, Hg, Pb, Se, Th, V, U, and Zn were significantly greater in the DFGD by-product amended treatment than in the unamended control.

There was no effect of application of the DFGD by-product on trace element soil concentrations and contents. Extractable soil Ca, S, and Na concentrations and contents were significantly greater in the amended treatment than the unamended control. This demonstrates the ability of this desulfurization by-product to act as a Ca and S source and may help explain the increase in aboveground DM. There was a decrease in Mehlich-3 extractable soil Mn concentrations 6 mo after application, but concentrations returned to pre-application levels within 12 mo. Previous research has highlighted the possibility of inducing saline soils due to the large concentrations of soluble salts present in FGD by-products. Soil electrical conductivity (EC) in the amended treatment did not differ from the unamended control during the 12-mo experiment. Soil EC in both treatments did not exceed 200 µS $cm^{-1}$ during the duration of this experiment.

The results of this experiment indicate that bioaccumulation of trace elements in aboveground biomass is of greater concern than contamination of runoff waters. However, continuous long-term application of DFGD by-products may increase runoff concentrations of trace elements as accumulation in the environment occurs. Management practices could be developed to help mitigate concern regarding accumulation of DFGD-by-product-applied trace elements in the environment. Growth of hyperaccumulating plants can be used to phytoremediate soils receiving DFGD by-products by mining trace elements from the soil. Application of DFGD by-products to a soil with greater clay content may also help sequester trace elements in the soil. Further research is needed to fully understand the environmental impacts of land applying DFGD by-products. Application in diverse environmental conditions can help extend information regarding potential impacts of land application. If it were to be shown that land application of these DFGD by-products has minimal environmental impacts, millions of megagrams of DFGD by-products can be diverted from landfills and surface impoundments, which pose significant environmental risk.

**Appendix A.** This appendix contains the calcium carbonate equivalence (CCE), degree of fineness, and effective neutralizing value (ENV) data that was inserted into the SAS program in Appendix B.

| **Material** | **rep** | **CCE (%)** | **DOF** | **ENV (%)** |
|---|---|---|---|---|
| Fly Ash | 1 | 60.54 | 94.4 | 56.93473 |
| Fly Ash | 2 | 58.12 | 95.7 | 57.71243 |
| Fly Ash | 3 | 62.2 | 95.1 | 57.32056 |
| DFGD | 1 | 83.34 | 93.6 | 79.05089 |
| DFGD | 2 | 84.2 | 94.3 | 79.56585 |
| DFGD | 3 | 85.72 | 94.3 | 79.58273 |
| CaCO3 | 1 | 100 | 100 | 100 |
| CaCO3 | 2 | 100 | 100 | 100 |
| CaCO3 | 3 | 100 | 100 | 100 |

**Appendix B.** This appendix contains the SAS program used to analyze the data in Appendix A.

```
data soil;
  infile 'CCE_DOF_ENV data.csv' firstobs = 2 delimiter = "," ;
  input Material $ rep CCE DOF ENV;
run;

proc print data = soil;
run;

title3 ‘CCE’;
proc MIXED data = soil;
 class Material;
 model CCE=Material;
 lsmeans Material / diff;
 run;

title3 ‘DOF’;
proc MIXED data = soil;
 class Material;
 model DOF=Material;
 lsmeans Material / diff;
 run;

title3 ‘ENV’;
proc MIXED data = soil;
 class Material;
 model ENV=Material;
 lsmeans Material / diff;
 run;
 quit;
```

**Appendix C.** This appendix contains the spreadsheet of soil pH response data that was inserted into the SAS program contained in Appendix D.

| Day | Product | Rate | Rep | pH |
|---|---|---|---|---|
| 0 | Control | 0 | 1 | 4.398 |
| 0 | Control | 0 | 2 | 4.297 |
| 0 | Control | 0 | 3 | 4.25 |
| 5 | Control | 0 | 1 | 4.018 |
| 5 | Control | 0 | 2 | 4.073 |
| 5 | Control | 0 | 3 | 3.944 |
| 10 | Control | 0 | 1 | 4.039 |
| 10 | Control | 0 | 2 | 4.208 |
| 10 | Control | 0 | 3 | 4.129 |
| 15 | Control | 0 | 1 | 4.303 |
| 15 | Control | 0 | 2 | 4.492 |
| 15 | Control | 0 | 3 | 4.247 |
| 20 | Control | 0 | 1 | 4.262 |
| 20 | Control | 0 | 2 | 4.35 |
| 20 | Control | 0 | 3 | 4.294 |
| 25 | Control | 0 | 1 | 4.225 |
| 25 | Control | 0 | 2 | 4.18 |
| 25 | Control | 0 | 3 | 4.234 |
| 30 | Control | 0 | 1 | 4.151 |
| 30 | Control | 0 | 2 | 4.239 |
| 30 | Control | 0 | 3 | 4.207 |
| 35 | Control | 0 | 1 | 4.153 |
| 35 | Control | 0 | 2 | 4.173 |
| 35 | Control | 0 | 3 | 4.146 |
| 40 | Control | 0 | 1 | 4.256 |
| 40 | Control | 0 | 2 | 4.042 |
| 40 | Control | 0 | 3 | 4.223 |
| 0 | Lime | 0.5 | 1 | 5.268 |
| 0 | Lime | 0.5 | 2 | 5.272 |
| 0 | Lime | 0.5 | 3 | 5.539 |
| 5 | Lime | 0.5 | 1 | 5.872 |
| 5 | Lime | 0.5 | 2 | 6.105 |
| 5 | Lime | 0.5 | 3 | 5.569 |
| 10 | Lime | 0.5 | 1 | 6.235 |
| 10 | Lime | 0.5 | 2 | 6.128 |
| 10 | Lime | 0.5 | 3 | 6.487 |

**Appendix C. (continued).** This appendix contains the spreadsheet of soil pH response data that was inserted into the SAS program contained in Appendix D.

| Day | Product | Rate | Rep | pH |
|---|---|---|---|---|
| 15 | Lime | 0.5 | 1 | 6.568 |
| 15 | Lime | 0.5 | 2 | 6.627 |
| 15 | Lime | 0.5 | 3 | 6.645 |
| 20 | Lime | 0.5 | 1 | 6.696 |
| 20 | Lime | 0.5 | 2 | 6.66 |
| 20 | Lime | 0.5 | 3 | 6.701 |
| 25 | Lime | 0.5 | 1 | 6.746 |
| 25 | Lime | 0.5 | 2 | 6.689 |
| 25 | Lime | 0.5 | 3 | 6.245 |
| 30 | Lime | 0.5 | 1 | 6.875 |
| 30 | Lime | 0.5 | 2 | 6.785 |
| 30 | Lime | 0.5 | 3 | 6.973 |
| 35 | Lime | 0.5 | 1 | 6.846 |
| 35 | Lime | 0.5 | 2 | 6.748 |
| 35 | Lime | 0.5 | 3 | 6.66 |
| 40 | Lime | 0.5 | 1 | 6.933 |
| 40 | Lime | 0.5 | 2 | 5.958 |
| 40 | Lime | 0.5 | 3 | 7.103 |
| 0 | Lime | 1 | 1 | 5.509 |
| 0 | Lime | 1 | 2 | 5.988 |
| 0 | Lime | 1 | 3 | 6.089 |
| 5 | Lime | 1 | 1 | 6.401 |
| 5 | Lime | 1 | 2 | 6.711 |
| 5 | Lime | 1 | 3 | 5.569 |
| 10 | Lime | 1 | 1 | 6.477 |
| 10 | Lime | 1 | 2 | 6.53 |
| 10 | Lime | 1 | 3 | 6.295 |
| 15 | Lime | 1 | 1 | 6.49 |
| 15 | Lime | 1 | 2 | 6.773 |
| 15 | Lime | 1 | 3 | 6.644 |
| 20 | Lime | 1 | 1 | 6.471 |
| 20 | Lime | 1 | 2 | 6.45 |
| 20 | Lime | 1 | 3 | 6.262 |
| 25 | Lime | 1 | 1 | 7.044 |
| 25 | Lime | 1 | 2 | 6.62 |
| 25 | Lime | 1 | 3 | 6.736 |

**Appendix C. (continued).** This appendix contains the spreadsheet of soil pH response data that was inserted into the SAS program contained in Appendix D.

| Day | Product | Rate | Rep | pH |
|---|---|---|---|---|
| 0 | Fly Ash | 0.5 | 1 | 4.339 |
| 0 | Fly Ash | 0.5 | 2 | 4.387 |
| 0 | Fly Ash | 0.5 | 3 | 4.216 |
| 5 | Fly Ash | 0.5 | 1 | 4.55 |
| 5 | Fly Ash | 0.5 | 2 | 4.586 |
| 5 | Fly Ash | 0.5 | 3 | 4.619 |
| 10 | Fly Ash | 0.5 | 1 | 4.736 |
| 10 | Fly Ash | 0.5 | 2 | 4.667 |
| 10 | Fly Ash | 0.5 | 3 | 4.773 |
| 15 | Fly Ash | 0.5 | 1 | 4.594 |
| 15 | Fly Ash | 0.5 | 2 | 4.801 |
| 15 | Fly Ash | 0.5 | 3 | 4.776 |
| 20 | Fly Ash | 0.5 | 1 | 4.508 |
| 20 | Fly Ash | 0.5 | 2 | 4.48 |
| 20 | Fly Ash | 0.5 | 3 | 4.757 |
| 25 | Fly Ash | 0.5 | 1 | 4.98 |
| 25 | Fly Ash | 0.5 | 2 | 5.235 |
| 25 | Fly Ash | 0.5 | 3 | 5.01 |
| 30 | Fly Ash | 0.5 | 1 | 4.749 |
| 30 | Fly Ash | 0.5 | 2 | 4.909 |
| 30 | Fly Ash | 0.5 | 3 | 4.838 |
| 35 | Fly Ash | 0.5 | 1 | 4.776 |
| 35 | Fly Ash | 0.5 | 2 | 4.791 |
| 35 | Fly Ash | 0.5 | 3 | 4.821 |
| 40 | Fly Ash | 0.5 | 1 | 4.896 |
| 40 | Fly Ash | 0.5 | 2 | 4.849 |
| 40 | Fly Ash | 0.5 | 3 | 4.633 |
| 0 | Fly Ash | 1 | 1 | 4.326 |
| 0 | Fly Ash | 1 | 2 | 4.511 |
| 0 | Fly Ash | 1 | 3 | 4.524 |
| 5 | Fly Ash | 1 | 1 | 5.317 |
| 5 | Fly Ash | 1 | 2 | 4.825 |
| 5 | Fly Ash | 1 | 3 | 4.733 |
| 10 | Fly Ash | 1 | 1 | 5.261 |
| 10 | Fly Ash | 1 | 2 | 5.316 |
| 10 | Fly Ash | 1 | 3 | 5.245 |

**Appendix C. (continued).** This appendix contains the spreadsheet of soil pH response data that was inserted into the SAS program contained in Appendix D.

| **Day** | **Product** | **Rate** | **Rep** | **pH** |
|---|---|---|---|---|
| 15 | Fly Ash | 1 | 1 | 5.058 |
| 15 | Fly Ash | 1 | 2 | 5.513 |
| 15 | Fly Ash | 1 | 3 | 5.621 |
| 20 | Fly Ash | 1 | 1 | 6.442 |
| 20 | Fly Ash | 1 | 2 | 6.235 |
| 20 | Fly Ash | 1 | 3 | 5.44 |
| 25 | Fly Ash | 1 | 1 | 6.133 |
| 25 | Fly Ash | 1 | 2 | 5.913 |
| 25 | Fly Ash | 1 | 3 | 5.982 |
| 30 | Fly Ash | 1 | 1 | 6.987 |
| 30 | Fly Ash | 1 | 2 | 7.392 |
| 30 | Fly Ash | 1 | 3 | 6.322 |
| 35 | Fly Ash | 1 | 1 | 6.333 |
| 35 | Fly Ash | 1 | 2 | 6.936 |
| 35 | Fly Ash | 1 | 3 | 7.016 |
| 40 | Fly Ash | 1 | 1 | 6.166 |
| 40 | Fly Ash | 1 | 2 | 6.891 |
| 40 | Fly Ash | 1 | 3 | 7.053 |
| 0 | Fly Ash | 2 | 1 | 5.174 |
| 0 | Fly Ash | 2 | 2 | 6.028 |
| 0 | Fly Ash | 2 | 3 | 5.534 |
| 5 | Fly Ash | 2 | 1 | 6.866 |
| 5 | Fly Ash | 2 | 2 | 6.501 |
| 5 | Fly Ash | 2 | 3 | 6.781 |
| 10 | Fly Ash | 2 | 1 | 6.694 |
| 10 | Fly Ash | 2 | 2 | 7.651 |
| 10 | Fly Ash | 2 | 3 | 8.048 |
| 15 | Fly Ash | 2 | 1 | 7.945 |
| 15 | Fly Ash | 2 | 2 | 7.836 |
| 15 | Fly Ash | 2 | 3 | 7.897 |
| 20 | Fly Ash | 2 | 1 | 7.783 |
| 20 | Fly Ash | 2 | 2 | 8.21 |
| 20 | Fly Ash | 2 | 3 | 8.509 |
| 25 | Fly Ash | 2 | 1 | 7.007 |
| 25 | Fly Ash | 2 | 2 | 8.316 |
| 25 | Fly Ash | 2 | 3 | 7.821 |

**Appendix C. (continued).** This appendix contains the spreadsheet of soil pH response data that was inserted into the SAS program contained in Appendix D.

| Day | Product | Rate | Rep | pH |
|---|---|---|---|---|
| 30 | Fly Ash | 2 | 1 | 8.003 |
| 30 | Fly Ash | 2 | 2 | 7.985 |
| 30 | Fly Ash | 2 | 3 | 8.37 |
| 35 | Fly Ash | 2 | 1 | 7.695 |
| 35 | Fly Ash | 2 | 2 | 7.898 |
| 35 | Fly Ash | 2 | 3 | 8.177 |
| 40 | Fly Ash | 2 | 1 | 7.934 |
| 40 | Fly Ash | 2 | 2 | 8.097 |
| 40 | Fly Ash | 2 | 3 | 8.095 |
| 0 | DFGD | 0.5 | 1 | 4.624 |
| 0 | DFGD | 0.5 | 2 | 4.625 |
| 0 | DFGD | 0.5 | 3 | 4.623 |
| 5 | DFGD | 0.5 | 1 | 4.592 |
| 5 | DFGD | 0.5 | 2 | 4.634 |
| 5 | DFGD | 0.5 | 3 | 4.669 |
| 10 | DFGD | 0.5 | 1 | 5.268 |
| 10 | DFGD | 0.5 | 2 | 4.92 |
| 10 | DFGD | 0.5 | 3 | 4.918 |
| 15 | DFGD | 0.5 | 1 | 4.682 |
| 15 | DFGD | 0.5 | 2 | 4.788 |
| 15 | DFGD | 0.5 | 3 | 4.661 |
| 20 | DFGD | 0.5 | 1 | 4.465 |
| 20 | DFGD | 0.5 | 2 | 4.713 |
| 20 | DFGD | 0.5 | 3 | 4.859 |
| 25 | DFGD | 0.5 | 1 | 4.991 |
| 25 | DFGD | 0.5 | 2 | 4.758 |
| 25 | DFGD | 0.5 | 3 | 4.903 |
| 30 | DFGD | 0.5 | 1 | 4.543 |
| 30 | DFGD | 0.5 | 2 | 4.861 |
| 30 | DFGD | 0.5 | 3 | 4.655 |
| 35 | DFGD | 0.5 | 1 | 4.661 |
| 35 | DFGD | 0.5 | 2 | 4.862 |
| 35 | DFGD | 0.5 | 3 | 4.902 |
| 40 | DFGD | 0.5 | 1 | 5.113 |
| 40 | DFGD | 0.5 | 2 | 5.015 |
| 40 | DFGD | 0.5 | 3 | 5.005 |

**Appendix C. (continued).** This appendix contains the spreadsheet of soil pH response data that was inserted into the SAS program contained in Appendix D.

| **Day** | **Product** | **Rate** | **Rep** | **pH** |
|---|---|---|---|---|
| 0 | DFGD | 1 | 1 | 5.086 |
| 0 | DFGD | 1 | 2 | 4.933 |
| 0 | DFGD | 1 | 3 | 4.16 |
| 5 | DFGD | 1 | 1 | 5.723 |
| 5 | DFGD | 1 | 2 | 6.115 |
| 5 | DFGD | 1 | 3 | 5.353 |
| 10 | DFGD | 1 | 1 | 6.549 |
| 10 | DFGD | 1 | 2 | 5.325 |
| 10 | DFGD | 1 | 3 | 6.589 |
| 15 | DFGD | 1 | 1 | 6.404 |
| 15 | DFGD | 1 | 2 | 6.386 |
| 15 | DFGD | 1 | 3 | 6.33 |
| 20 | DFGD | 1 | 1 | 6.518 |
| 20 | DFGD | 1 | 2 | 6.223 |
| 20 | DFGD | 1 | 3 | 6.484 |
| 25 | DFGD | 1 | 1 | 6.527 |
| 25 | DFGD | 1 | 2 | 6.476 |
| 25 | DFGD | 1 | 3 | 6.595 |
| 30 | DFGD | 1 | 1 | 6.928 |
| 30 | DFGD | 1 | 2 | 6.829 |
| 30 | DFGD | 1 | 3 | 6.889 |
| 35 | DFGD | 1 | 1 | 6.31 |
| 35 | DFGD | 1 | 2 | 6.621 |
| 35 | DFGD | 1 | 3 | 6.607 |
| 40 | DFGD | 1 | 1 | 6.981 |
| 40 | DFGD | 1 | 2 | 7.078 |
| 40 | DFGD | 1 | 3 | 6.818 |
| 0 | DFGD | 2 | 1 | 5.835 |
| 0 | DFGD | 2 | 2 | 5.734 |
| 0 | DFGD | 2 | 3 | 5.663 |
| 5 | DFGD | 2 | 1 | 6.982 |
| 5 | DFGD | 2 | 2 | 6.397 |
| 5 | DFGD | 2 | 3 | 7.145 |
| 10 | DFGD | 2 | 1 | 7.345 |
| 10 | DFGD | 2 | 2 | 7.364 |
| 10 | DFGD | 2 | 3 | 7.369 |

**Appendix C. (continued).** This appendix contains the spreadsheet of soil pH response data that was inserted into the SAS program contained in Appendix D.

| **Day** | **Product** | **Rate** | **Rep** | **pH** |
|---|---|---|---|---|
| 15 | DFGD | 2 | 1 | 7.312 |
| 15 | DFGD | 2 | 2 | 7.562 |
| 15 | DFGD | 2 | 3 | 7.87 |
| 20 | DFGD | 2 | 1 | 7.608 |
| 20 | DFGD | 2 | 2 | 7.932 |
| 20 | DFGD | 2 | 3 | 7.512 |
| 25 | DFGD | 2 | 1 | 7.745 |
| 25 | DFGD | 2 | 2 | 8.09 |
| 25 | DFGD | 2 | 3 | 7.854 |
| 30 | DFGD | 2 | 1 | 7.503 |
| 30 | DFGD | 2 | 2 | 7.756 |
| 30 | DFGD | 2 | 3 | 7.59 |
| 35 | DFGD | 2 | 1 | 7.583 |
| 35 | DFGD | 2 | 2 | 7.619 |
| 35 | DFGD | 2 | 3 | 7.789 |
| 40 | DFGD | 2 | 1 | 8.036 |
| 40 | DFGD | 2 | 2 | 7.52 |
| 40 | DFGD | 2 | 3 | 8.354 |

**Appendix D.** This appendix contains the SAS program used to analyze soil pH response data presented in Appendix C.

```
data soil;
  infile 'IncubationSAS.csv' firstobs = 2 delimiter = "," ;
  input Day Product $ Rate rep pH;
run;

proc print data = soil;
run;

proc mixed data = soil method = type3;
  class Product Rate rep Day;
  model pH = Product Rate Product*Rate Day Product*Day
            Rate*Day Product*Rate*Day / ddfm = kr;
  lsmeans Product*Rate*Day / diff;
run;
quit;
```

**Appendix E.** This appendix contains the annual runoff, mean runoff electrical conductivity, and runoff pH data that was inserted into the SAS program presented in Appendix G.

| **Plot** | **Treatment** | **mm** | **EC** | **pH** |
|---|---|---|---|---|
| 1 | Treated | 197.778 | 274.499 | 6.633 |
| 2 | Treated | 218.478 | 236.912 | 6.490 |
| 3 | Control | 338.422 | 231.573 | 6.511 |
| 4 | Control | 163.511 | 258.852 | 6.453 |
| 5 | Treated | 141.367 | 227.020 | 6.432 |
| 6 | Control | 156.222 | 248.312 | 6.502 |

**Appendix F.** This appendix includes the annual FWM concentration data that was inserted into the SAS program presented in Appendix G.

| | | | | | | **(µg L)** | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Plot** | **TRT** | **Be** | **V** | **Cr** | **Co** | **Ni** | **Cu** | **Zn** | **As** |
| 1 | Treated | 0.104 | 8.043 | 2.328 | 2.805 | 8.323 | 30.599 | 668.109 | 3.069 |
| 2 | Treated | 0.043 | 8.063 | 1.138 | 2.596 | 5.499 | 33.628 | 632.789 | 2.456 |
| 3 | Control | 0.078 | 9.738 | 1.911 | 3.648 | 10.798 | 54.842 | 1287.913 | 4.048 |
| 4 | Control | 0.085 | 4.201 | 1.122 | 1.339 | 4.625 | 31.723 | 549.043 | 1.916 |
| 5 | Treated | 0.067 | 9.128 | 0.701 | 1.061 | 2.772 | 25.087 | 365.447 | 1.947 |
| 6 | Control | 0.075 | 4.729 | 1.115 | 1.450 | 4.495 | 24.913 | 537.496 | 2.330 |

**Appendix F. (continued)** This appendix includes the annual FWM concentration data that was inserted into the SAS program in Appendix G.

|  |  |  |  |  | (µg L) |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| **Plot** | **TRT** | **Se** | **Rb** | **Cd** | **Cs** | **Pb** | **Hg** | **Th** | **U** |
| 1 | Treated | 2.200 | 34.748 | 0.764 | 0.228 | 5.232 | 2.222 | 0.393 | 0.243 |
| 2 | Treated | 2.443 | 37.723 | 0.643 | 0.232 | 5.099 | 2.567 | 0.232 | 0.337 |
| 3 | Control | 4.945 | 70.065 | 1.917 | 0.307 | 10.337 | 0.820 | 0.532 | 0.369 |
| 4 | Control | 1.879 | 53.843 | 0.549 | 0.095 | 2.863 | 0.615 | 0.108 | 0.159 |
| 5 | Treated | 2.075 | 17.275 | 0.523 | 0.360 | 2.566 | 0.965 | 0.435 | 0.209 |
| 6 | Control | 2.624 | 27.742 | 0.589 | 0.088 | 2.458 | 1.350 | 0.150 | 0.167 |

**Appendix G.** This appendix contains an example of the SAS program used to analyze the data presented in Appendix E and F.

```
Title3 'Annual FWM, Runoff, EC, pH';

data Runoff;
  infile 'Annual_FWM(µg.L).csv' firstobs = 2 delimiter = "," ;
  input Plot Treatment $ mm EC pH Be V Cr Co Ni Cu Zn As Se Rb Cd Cs Pb Hg Th U;
run;

proc print data = runoff;
run;

title3 'mm';
proc MIXED data=runoff;
 class Treatment;
 model mm=Treatment
 lsmeans Treatment / diff;
 run;


title3 'EC';
proc MIXED data=runoff;
 class Treatment;
 model EC=Treatment
 lsmeans Treatment / diff;
 run;
```

**Appendix H.** This appendix includes the cumulative load data that was inserted into the SAS program in Appendix I.

**(mg/ha)**

| **Plot** | **TRT** | **Be** | **V** | **Cr** | **Co** | **Ni** | **Cu** | **Zn** | **As** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Treated | 2.063 | 125.653 | 36.369 | 43.827 | 130.018 | 478.031 | 10437.341 | 47.942 |
| 2 | Treated | 0.938 | 125.956 | 17.774 | 40.558 | 85.902 | 525.337 | 9885.574 | 38.362 |
| 3 | Control | 2.643 | 152.136 | 29.853 | 56.988 | 168.696 | 856.757 | 20120.064 | 63.235 |
| 4 | Control | 1.397 | 65.632 | 17.526 | 20.923 | 72.258 | 495.586 | 8577.278 | 29.929 |
| 5 | Treated | 1.047 | 147.136 | 10.955 | 16.570 | 43.306 | 391.911 | 5709.100 | 30.421 |
| 6 | Control | 1.167 | 73.882 | 17.421 | 22.655 | 70.222 | 389.201 | 8396.876 | 36.404 |

**Appendix H. (continued).** This appendix includes the cumulative load data that was inserted into the SAS program in Appendix I.

| | | | | | (mg/ha) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Plot** | **TRT** | **Se** | **Rb** | **Cd** | **Cs** | **Pb** | **Hg** | **Th** | **U** |
| 1 | Treated | 34.369 | 542.841 | 11.942 | 3.562 | 81.733 | 12.344 | 6.137 | 6.835 |
| 2 | Treated | 38.168 | 589.320 | 10.047 | 3.624 | 79.660 | 8.556 | 3.623 | 5.259 |
| 3 | Control | 77.247 | 1094.57 | 29.953 | 4.799 | 161.486 | 2.733 | 8.313 | 5.771 |
| 4 | Control | 29.351 | 841.149 | 8.576 | 1.479 | 44.722 | 1.367 | 1.695 | 2.490 |
| 5 | Treated | 32.413 | 269.881 | 8.175 | 5.622 | 40.084 | 2.144 | 6.795 | 3.261 |
| 6 | Control | 40.990 | 433.387 | 9.208 | 1.379 | 38.397 | 3.000 | 2.348 | 2.615 |

**Appendix I.** This appendix contains an example of the SAS program used to analyze the data presented in Appendix H.

```
Title3 'Cumulative Load';

data Runoff;
  infile 'Cumul_Runoff_Load(mg.ha).csv' firstobs = 2 delimiter = "," ;
  input Plot Treatment $ Be V Cr Co Ni Cu Zn As Se Rb Cd Cs Pb Hg Th U;
run;

proc print data = runoff;
run;

title3 'Be';
proc MIXED data=runoff;
 class Treatment;
 model Be=Treatment
 lsmeans Treatment / diff;
 run;

title3 'V';
proc MIXED data=runoff;
 class Treatment;
 model V=Treatment
 lsmeans Treatment / diff;
 run;
```

**Appendix J.** This appendix contains the seasonal runoff flow-weighted mean concentration data that was inserted into the SAS program in Appendix L.

**(FWM µg/L)**

| **Plot** | **TRT** | **Season** | **Be** | **V** | **Cr** | **Co** | **Ni** | **Cu** | **Zn** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | T | 1 | 0.118 | 14.001 | 1.092 | 1.452 | 3.456 | 17.906 | 195.326 |
| 1 | T | 2 | 0.053 | 3.188 | 5.094 | 4.018 | 13.398 | 32.303 | 559.932 |
| 1 | T | 3 | 0.114 | 2.901 | 0.671 | 1.249 | 4.680 | 16.023 | 721.884 |
| 1 | T | 4 | 0.154 | 3.311 | 0.965 | 4.478 | 7.800 | 62.027 | 746.599 |
| 2 | T | 1 | 0.053 | 15.788 | 0.890 | 0.802 | 2.748 | 22.875 | 227.127 |
| 2 | T | 2 | 0.029 | 4.022 | 1.625 | 4.959 | 8.972 | 39.766 | 393.028 |
| 2 | T | 3 | 0.021 | 1.848 | 0.525 | 0.755 | 2.407 | 14.871 | 481.924 |
| 2 | T | 4 | 0.103 | 2.726 | 0.826 | 4.055 | 5.880 | 39.047 | 779.441 |
| 3 | C | 1 | 0.142 | 14.209 | 0.922 | 1.161 | 3.668 | 24.423 | 274.528 |
| 3 | C | 2 | 0.042 | 1.882 | 1.020 | 2.161 | 6.508 | 44.501 | 355.465 |
| 3 | C | 3 | 0.066 | 2.681 | 0.829 | 1.096 | 5.461 | 14.952 | 705.780 |
| 3 | C | 4 | 0.078 | 2.301 | 0.858 | 2.957 | 3.972 | 33.336 | 795.947 |
| 4 | C | 1 | 0.080 | 8.861 | 0.979 | 2.061 | 3.540 | 31.192 | 397.187 |
| 4 | C | 2 | 0.025 | 0.935 | 1.301 | 0.835 | 5.820 | 36.131 | 320.069 |
| 4 | C | 3 | 0.129 | 3.159 | 1.032 | 0.793 | 4.834 | 16.916 | 643.608 |
| 4 | C | 4 | 0.021 | 0.913 | 1.141 | 1.790 | 3.392 | 63.838 | 584.681 |
| 5 | T | 1 | 0.079 | 13.104 | 0.740 | 0.826 | 2.186 | 20.929 | 260.581 |
| 5 | T | 2 | 0.051 | 2.894 | 0.928 | 2.583 | 7.052 | 49.579 | 663.310 |
| 5 | T | 3 | 0.031 | 4.909 | 0.573 | 0.268 | 1.733 | 12.145 | 674.027 |
| 5 | T | 4 | 0.100 | 6.067 | 1.015 | 2.729 | 5.976 | 60.383 | 742.902 |
| 6 | C | 1 | 0.084 | 13.040 | 1.124 | 1.366 | 3.514 | 24.519 | 252.813 |
| 6 | C | 2 | 0.033 | 3.277 | 2.699 | 2.910 | 8.050 | 65.810 | 383.845 |
| 6 | C | 3 | 0.075 | 2.839 | 0.894 | 0.958 | 3.998 | 15.454 | 638.775 |
| 6 | C | 4 | 0.119 | 4.340 | 0.704 | 4.603 | 6.518 | 58.513 | 508.395 |

**Appendix J. (continued)** This appendix contains the seasonal runoff flow-weighted mean concentration data that was inserted into the SAS program in Appendix L.

**(FWM µg/L)**

| **Plot** | **TRT** | **Season** | **As** | **Se** | **Rb** | **Cd** | **Cs** | **Pb** | **Th** | **U** |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | T | 1 | 2.195 | 1.311 | 12.608 | 0.571 | 0.473 | 1.651 | 0.759 | 0.169 |
| 1 | T | 2 | 2.089 | 1.865 | 59.251 | 0.657 | 0.058 | 6.880 | 0.191 | 0.249 |
| 1 | T | 3 | 2.566 | 1.595 | 18.387 | 0.351 | 0.029 | 2.757 | 0.071 | 0.168 |
| 1 | T | 4 | 3.519 | 3.588 | 35.354 | 1.741 | 0.154 | 11.894 | 0.117 | 0.228 |
| 2 | T | 1 | 2.085 | 1.070 | 9.214 | 0.422 | 0.533 | 1.476 | 0.450 | 0.346 |
| 2 | T | 2 | 2.626 | 2.713 | 66.801 | 0.965 | 0.049 | 8.954 | 0.062 | 0.290 |
| 2 | T | 3 | 1.237 | 1.364 | 23.562 | 0.178 | 0.028 | 1.399 | 0.054 | 0.151 |
| 2 | T | 4 | 1.988 | 3.110 | 30.501 | 0.904 | 0.085 | 9.060 | 0.132 | 0.291 |
| 3 | C | 1 | 2.122 | 1.183 | 14.759 | 0.443 | 0.608 | 1.527 | 0.975 | 0.221 |
| 3 | C | 2 | 1.350 | 2.184 | 92.361 | 0.738 | 0.046 | 4.951 | 0.091 | 0.214 |
| 3 | C | 3 | 1.871 | 1.892 | 25.619 | 0.603 | 0.045 | 1.766 | 0.079 | 0.154 |
| 3 | C | 4 | 2.034 | 4.028 | 16.922 | 1.918 | 0.034 | 13.360 | 0.113 | 0.132 |
| 4 | C | 1 | 1.810 | 1.478 | 38.909 | 0.931 | 0.197 | 1.861 | 0.278 | 0.134 |
| 4 | C | 2 | 0.773 | 1.779 | 130.730 | 0.318 | 0.072 | 2.843 | 0.034 | 0.059 |
| 4 | C | 3 | 2.259 | 1.813 | 36.234 | 0.209 | 0.052 | 2.368 | 0.038 | 0.208 |
| 4 | C | 4 | 1.571 | 2.320 | 44.443 | 0.955 | 0.035 | 5.301 | 0.058 | 0.105 |
| 5 | T | 1 | 1.913 | 1.299 | 9.642 | 0.396 | 0.554 | 1.619 | 0.683 | 0.247 |
| 5 | T | 2 | 3.424 | 4.028 | 72.360 | 0.897 | 0.056 | 4.553 | 0.031 | 0.187 |
| 5 | T | 3 | 1.037 | 1.566 | 18.618 | 0.302 | 0.026 | 1.165 | 0.055 | 0.067 |
| 5 | T | 4 | 3.430 | 6.772 | 32.661 | 1.513 | 0.127 | 9.209 | 0.094 | 0.309 |
| 6 | C | 1 | 2.639 | 1.702 | 17.923 | 0.576 | 0.166 | 1.765 | 0.241 | 0.112 |
| 6 | C | 2 | 2.278 | 3.012 | 64.833 | 0.485 | 0.060 | 4.620 | 0.111 | 0.224 |
| 6 | C | 3 | 2.073 | 2.326 | 20.694 | 0.550 | 0.071 | 2.103 | 0.138 | 0.150 |
| 6 | C | 4 | 4.427 | 7.988 | 68.675 | 1.268 | 0.112 | 4.560 | 0.091 | 0.418 |

**Appendix K.** This appendix contains the seasonal runoff, electrical conductivity (EC), and runoff pH, and seasonal load data that was inserted into the SAS program in Appendix L.

| | | | | | | **Load (mg/ha)** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Plot** | **TRT** | **SSN** | **mm** | **EC** | **pH** | **Be** | **V** | Cr | Co | Ni |
| 1 | T | 1 | 59.722 | 226.24 | 6.56 | 0.706 | 83.619 | 6.524 | 8.674 | 18.576 |
| 1 | T | 2 | 45.444 | 429.08 | 6.74 | 0.240 | 14.489 | 23.148 | 18.261 | 54.799 |
| 1 | T | 3 | 76.111 | 225.83 | 6.66 | 0.864 | 22.082 | 5.105 | 9.503 | 32.058 |
| 1 | T | 4 | 16.500 | 216.84 | 6.58 | 0.254 | 5.464 | 1.591 | 7.389 | 11.583 |
| 2 | T | 1 | 54.589 | 143.44 | 6.21 | 0.289 | 86.186 | 4.857 | 4.380 | 13.500 |
| 2 | T | 2 | 29.889 | 363.15 | 6.72 | 0.086 | 12.022 | 4.858 | 14.823 | 24.133 |
| 2 | T | 3 | 99.944 | 202.14 | 6.67 | 0.212 | 18.465 | 5.246 | 7.545 | 21.655 |
| 2 | T | 4 | 34.056 | 238.92 | 6.37 | 0.352 | 9.282 | 2.813 | 13.810 | 18.023 |
| 3 | C | 1 | 59.422 | 138.59 | 6.22 | 0.843 | 84.434 | 5.479 | 6.897 | 19.616 |
| 3 | C | 2 | 53.444 | 370.78 | 6.75 | 0.226 | 10.057 | 5.453 | 11.550 | 31.304 |
| 3 | C | 3 | 151.278 | 126.12 | 6.61 | 0.993 | 40.555 | 12.545 | 16.579 | 74.352 |
| 3 | C | 4 | 74.278 | 290.80 | 6.46 | 0.580 | 17.091 | 6.376 | 21.961 | 26.554 |
| 4 | C | 1 | 43.011 | 256.52 | 6.37 | 0.344 | 38.111 | 4.212 | 8.863 | 13.704 |
| 4 | C | 2 | 23.000 | 363.23 | 6.50 | 0.058 | 2.150 | 2.993 | 1.920 | 12.047 |
| 4 | C | 3 | 73.333 | 149.70 | 6.49 | 0.944 | 23.165 | 7.565 | 5.813 | 31.903 |
| 4 | C | 4 | 24.167 | 265.96 | 6.46 | 0.051 | 2.206 | 2.757 | 4.326 | 7.378 |
| 5 | T | 1 | 95.200 | 178.28 | 5.99 | 0.750 | 124.754 | 7.043 | 7.868 | 18.731 |
| 5 | T | 2 | 12.222 | 340.10 | 6.38 | 0.062 | 3.537 | 1.135 | 3.157 | 7.757 |
| 5 | T | 3 | 15.111 | 105.90 | 6.83 | 0.048 | 2.885 | 0.865 | 0.405 | 2.358 |
| 5 | T | 4 | 18.833 | 283.80 | 6.52 | 0.188 | 11.426 | 1.912 | 5.140 | 10.129 |
| 6 | C | 1 | 26.889 | 264.77 | 6.31 | 0.226 | 35.063 | 3.021 | 3.672 | 8.504 |
| 6 | C | 2 | 16.667 | 425.25 | 6.40 | 0.056 | 5.462 | 4.498 | 4.850 | 12.075 |
| 6 | C | 3 | 103.500 | 149.27 | 6.60 | 0.776 | 29.379 | 9.257 | 9.913 | 37.243 |
| 6 | C | 4 | 9.167 | 153.96 | 6.71 | 0.109 | 3.979 | 0.645 | 4.220 | 5.377 |

**Appendix K. (continued)** This appendix contains the seasonal runoff, electrical conductivity (EC), and runoff pH, and seasonal load data that was inserted into the SAS program in Appendix L.

**Load (mg/ha)**

| **Plot** | **TRT** | **SSN** | **Cu** | **Zn** | **As** | **Se** | **Rb** | **Cd** | **Cs** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | T | 1 | 106.937 | 1166.530 | 13.111 | 7.831 | 75.299 | 3.410 | 2.823 |
| 1 | T | 2 | 146.798 | 2544.581 | 9.494 | 8.476 | 269.261 | 2.986 | 0.263 |
| 1 | T | 3 | 121.953 | 5494.343 | 19.531 | 12.141 | 139.947 | 2.673 | 0.222 |
| 1 | T | 4 | 102.344 | 1231.888 | 5.806 | 5.921 | 58.334 | 2.873 | 0.254 |
| 2 | T | 1 | 124.871 | 1239.863 | 11.381 | 5.840 | 50.300 | 2.305 | 2.909 |
| 2 | T | 2 | 118.857 | 1174.717 | 7.848 | 8.108 | 199.660 | 2.884 | 0.146 |
| 2 | T | 3 | 148.632 | 4816.564 | 12.363 | 13.628 | 235.486 | 1.781 | 0.279 |
| 2 | T | 4 | 132.977 | 2654.430 | 6.770 | 10.592 | 103.874 | 3.077 | 0.290 |
| 3 | C | 1 | 145.129 | 1631.307 | 12.608 | 7.027 | 87.703 | 2.635 | 3.615 |
| 3 | C | 2 | 237.831 | 1899.763 | 7.216 | 11.672 | 493.619 | 3.945 | 0.246 |
| 3 | C | 3 | 226.188 | 10676.880 | 28.306 | 28.626 | 387.558 | 9.129 | 0.681 |
| 3 | C | 4 | 247.610 | 5912.114 | 15.105 | 29.922 | 125.689 | 14.243 | 0.256 |
| 4 | C | 1 | 134.161 | 1708.347 | 7.786 | 6.358 | 167.352 | 4.003 | 0.845 |
| 4 | C | 2 | 83.101 | 736.159 | 1.778 | 4.091 | 300.679 | 0.732 | 0.166 |
| 4 | C | 3 | 124.050 | 4719.792 | 16.569 | 13.295 | 265.714 | 1.535 | 0.383 |
| 4 | C | 4 | 154.275 | 1412.980 | 3.797 | 5.607 | 107.404 | 2.307 | 0.085 |
| 5 | T | 1 | 199.240 | 2480.727 | 18.210 | 12.371 | 91.796 | 3.773 | 5.275 |
| 5 | T | 2 | 60.597 | 810.713 | 4.185 | 4.923 | 88.440 | 1.097 | 0.068 |
| 5 | T | 3 | 18.353 | 1018.529 | 1.567 | 2.366 | 28.134 | 0.456 | 0.039 |
| 5 | T | 4 | 113.720 | 1399.131 | 6.460 | 12.754 | 61.512 | 2.850 | 0.240 |
| 6 | C | 1 | 65.930 | 679.787 | 7.097 | 4.577 | 48.193 | 1.549 | 0.446 |
| 6 | C | 2 | 109.684 | 639.742 | 3.796 | 5.020 | 108.055 | 0.808 | 0.100 |
| 6 | C | 3 | 159.950 | 6611.319 | 21.452 | 24.072 | 214.186 | 5.690 | 0.730 |
| 6 | C | 4 | 53.637 | 466.029 | 4.058 | 7.322 | 62.952 | 1.162 | 0.102 |

**Appendix K. (continued)** This appendix contains the seasonal runoff, electrical conductivity (EC), and runoff pH, and seasonal load data that was inserted into the SAS program in Appendix L.

**Load (mg/ha)**

| Plot | TRT | SSN | Pb | Th | U |
|---|---|---|---|---|---|
| 1 | T | 1 | 9.861 | 4.535 | 1.008 |
| 1 | T | 2 | 31.265 | 0.867 | 1.132 |
| 1 | T | 3 | 20.982 | 0.542 | 1.277 |
| 1 | T | 4 | 19.625 | 0.193 | 3.417 |
| 2 | T | 1 | 8.057 | 2.454 | 1.891 |
| 2 | T | 2 | 26.762 | 0.184 | 0.868 |
| 2 | T | 3 | 13.986 | 0.536 | 1.511 |
| 2 | T | 4 | 30.854 | 0.449 | 0.990 |
| 3 | C | 1 | 9.076 | 5.793 | 1.314 |
| 3 | C | 2 | 26.458 | 0.487 | 1.145 |
| 3 | C | 3 | 26.714 | 1.192 | 2.329 |
| 3 | C | 4 | 99.238 | 0.841 | 0.982 |
| 4 | C | 1 | 8.004 | 1.197 | 0.575 |
| 4 | C | 2 | 6.539 | 0.078 | 0.136 |
| 4 | C | 3 | 17.369 | 0.280 | 1.525 |
| 4 | C | 4 | 12.810 | 0.140 | 0.255 |
| 5 | T | 1 | 15.415 | 6.497 | 2.349 |
| 5 | T | 2 | 5.564 | 0.037 | 0.228 |
| 5 | T | 3 | 1.761 | 0.083 | 0.101 |
| 5 | T | 4 | 17.344 | 0.177 | 0.583 |
| 6 | C | 1 | 4.747 | 0.648 | 0.300 |
| 6 | C | 2 | 7.700 | 0.186 | 0.374 |
| 6 | C | 3 | 21.770 | 1.431 | 1.557 |
| 6 | C | 4 | 4.180 | 0.083 | 0.383 |

**Appendix L.** This appendix contains an example of the SAS program used to analyze the data presented in Appendix J and K.

```
Title3 'Seasonal Runoff Effects';

data runoff;
  infile 'SASSeasonalRunoff2.csv' firstobs = 2 delimiter = "," ;
  input Plot Treatment $ Season $ mm EC pH Be_FWM Be_load V_FWM V_load Cr_FWM
Cr_load Co_FWM Co_load Ni_FWM Ni_load Cu_FWM Cu_load Zn_FWM Zn_load As_FWM
As_load Se_FWM Se_load Rb_FWM Rb_load Cd_FWM Cd_load Cs_FWM Cs_load Pb_FWM
Pb_load Th_FWM Th_load U_FWM U_load;
run;

proc print data = runoff;
run;


title3 'Seasonal Runoff';
proc Mixed data = runoff;
 class Treatment Season;
 model mm = Treatment Season Treatment*Season ;
 lsmeans Treatment Season Treatment*Season / diff ;
 run;

title3 'Seasonal EC';
proc Mixed data = runoff;
 class Treatment Season;
 model EC = Treatment Season Treatment*Season ;
 lsmeans Treatment Season Treatment*Season / diff ;
 run;


title3 'Seasonal pH';
proc Mixed data = runoff;
 class Treatment Season;
 model pH = Treatment Season Treatment*Season ;
 lsmeans Treatment Season Treatment*Season / diff ;
 run;

title3 'Seasonal Be FWM';
proc Mixed data = runoff;
 class Treatment Season;
 model Be_FWM = Treatment Season Treatment*Season ;
 lsmeans Treatment Season Treatment*Season / diff ;
 run;
```

**Appendix M.** This appendix contains dry matter (DM), tissue concentration, and plant uptake data that was inserted into the SAS program in appendix N.

|  |  |  | (Mg/ha) | (µg/kg) |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **DM** | **Be** | **V** | **Cr** | **Co** | **Ni** | **Cu** |
| 0 | 1 | Treated | 4.35 | 0.00 | 245.20 | 326.12 | 165.32 | 832.30 | 6144.70 |
| 0 | 2 | Treated | 4.10 | 0.00 | 113.64 | 167.59 | 162.83 | 820.38 | 7215.32 |
| 0 | 3 | Control | 4.23 | 27.13 | 71.76 | 112.52 | 79.06 | 532.78 | 3560.98 |
| 0 | 4 | Control | 3.99 | 0.00 | 107.33 | 149.17 | 103.82 | 622.50 | 4410.42 |
| 0 | 5 | Treated | 4.11 | 0.00 | 73.88 | 83.98 | 110.81 | 369.36 | 6092.84 |
| 0 | 6 | Control | 3.34 | 0.00 | 46.15 | 74.18 | 123.98 | 586.63 | 4662.22 |
| 1 | 1 | Treated | 3.88 | 0.00 | 564.81 | 343.06 | 235.28 | 696.31 | 8831.49 |
| 1 | 2 | Treated | 3.13 | 26.72 | 356.36 | 507.20 | 194.63 | 495.29 | 7865.22 |
| 1 | 3 | Control | 2.63 | 0.00 | 41.74 | 192.78 | 91.06 | 834.89 | 7670.96 |
| 1 | 4 | Control | 1.11 | 0.00 | 112.58 | 139.31 | 99.85 | 434.98 | 6289.04 |
| 1 | 5 | Treated | 2.90 | 54.15 | 1358.41 | 504.39 | 386.48 | 961.16 | 8378.98 |
| 1 | 6 | Control | 2.21 | 53.91 | 244.87 | 286.79 | 157.52 | 688.74 | 10242.89 |
| 2 | 1 | Treated | 3.44 | 0.00 | 317.01 | 254.93 | 221.04 | 425.04 | 7128.83 |
| 2 | 2 | Treated | 3.01 | 0.00 | 358.62 | 280.79 | 207.14 | 326.57 | 7728.48 |
| 2 | 3 | Control | 1.87 | 27.05 | 60.74 | 86.78 | 130.98 | 684.18 | 8131.68 |
| 2 | 4 | Control | 2.36 | 0.00 | 44.35 | 69.93 | 104.39 | 811.48 | 6131.32 |
| 2 | 5 | Treated | 3.35 | 13.38 | 225.51 | 269.38 | 154.37 | 604.18 | 7927.93 |
| 2 | 6 | Control | 1.78 | 0.00 | 64.39 | 88.48 | 235.39 | 290.21 | 7651.84 |
| 3 | 1 | Treated | 3.46 | 25.70 | 85.65 | 205.55 | 101.20 | 611.36 | 7754.05 |
| 3 | 2 | Treated | 2.99 | 0.00 | 62.98 | 190.20 | 103.15 | 589.57 | 8767.91 |
| 3 | 3 | Control | 1.80 | 0.00 | 50.69 | 87.17 | 115.42 | 535.18 | 4253.34 |
| 3 | 4 | Control | 2.36 | 24.17 | 53.49 | 185.17 | 197.17 | 401.78 | 5809.06 |
| 3 | 5 | Treated | 3.43 | 0.00 | 65.17 | 113.16 | 104.15 | 335.36 | 5624.65 |
| 3 | 6 | Control | 1.72 | 33.32 | 49.20 | 82.50 | 98.50 | 386.63 | 5589.99 |

**Appendix M. (continued).** This appendix contains dry matter (DM), tissue concentration, and plant uptake data that was inserted into the SAS program in appendix N.

| | | | **(Mg/ha)** | **(µg/kg)** | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **DM** | **Be** | **V** | **Cr** | **Co** | **Ni** | **Cu** |
| 6 | 1 | Treated | 2.77 | 0.00 | 63.83 | 161.30 | 196.14 | 604.71 | 5596.08 |
| 6 | 2 | Treated | 2.22 | 12.65 | 56.02 | 76.98 | 204.79 | 252.48 | 6657.10 |
| 6 | 3 | Control | 2.54 | 54.65 | 41.69 | 147.74 | 98.12 | 762.79 | 5763.45 |
| 6 | 4 | Control | 2.05 | 0.00 | 107.65 | 142.53 | 111.36 | 391.04 | 6558.52 |
| 6 | 5 | Treated | 2.29 | 0.00 | 56.98 | 78.31 | 108.32 | 256.83 | 6771.88 |
| 6 | 6 | Control | 2.37 | 31.32 | 55.88 | 153.44 | 120.50 | 629.45 | 7481.15 |
| 12 | 1 | Treated | 3.57 | 11.43 | 55.50 | 140.26 | 170.56 | 525.83 | 4866.16 |
| 12 | 2 | Treated | 3.09 | 22.72 | 60.75 | 71.66 | 137.03 | 435.16 | 3914.95 |
| 12 | 3 | Control | 2.42 | 0.00 | 109.75 | 101.39 | 101.03 | 571.93 | 3020.44 |
| 12 | 4 | Control | 2.10 | 19.53 | 100.26 | 102.84 | 123.89 | 399.22 | 2745.27 |
| 12 | 5 | Treated | 2.90 | 0.00 | 47.16 | 145.15 | 141.83 | 572.80 | 3614.15 |
| 12 | 6 | Control | 2.62 | 22.33 | 56.53 | 70.73 | 97.44 | 308.20 | 4233.73 |

**Appendix M. (continued).** This appendix contains dry matter (DM), tissue concentration, and plant uptake data that was inserted into the SAS program in appendix N.

| | | | **(µg/kg)** | | | | |
|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Zn** | **As** | **Se** | **Rb** | **Cd** |
| 0 | 1 | Treated | 32236.24 | 101.36 | 458.36 | 7139.37 | 48.97 |
| 0 | 2 | Treated | 41904.36 | 80.59 | 573.35 | 4719.21 | 38.60 |
| 0 | 3 | Control | 20298.56 | 55.82 | 326.40 | 4417.87 | 20.99 |
| 0 | 4 | Control | 32267.93 | 64.62 | 614.27 | 6067.36 | 38.08 |
| 0 | 5 | Treated | 36114.47 | 71.81 | 768.45 | 5062.48 | 22.08 |
| 0 | 6 | Control | 34434.52 | 77.57 | 437.99 | 9319.60 | 44.58 |
| 1 | 1 | Treated | 44149.55 | 159.23 | 2237.63 | 8747.94 | 27.92 |
| 1 | 2 | Treated | 34976.57 | 154.67 | 2434.76 | 6368.39 | 40.01 |
| 1 | 3 | Control | 34537.97 | 32.89 | 680.52 | 6998.38 | 31.90 |
| 1 | 4 | Control | 28960.19 | 61.13 | 1063.42 | 10420.33 | 48.92 |
| 1 | 5 | Treated | 31979.55 | 151.03 | 3284.33 | 9649.40 | 36.48 |
| 1 | 6 | Control | 33552.22 | 75.01 | 618.55 | 5998.07 | 21.75 |
| 2 | 1 | Treated | 35407.89 | 70.97 | 956.19 | 9747.77 | 21.43 |
| 2 | 2 | Treated | 37032.52 | 75.41 | 1513.09 | 6384.82 | 46.37 |
| 2 | 3 | Control | 40175.25 | 40.67 | 718.27 | 8899.62 | 24.53 |
| 2 | 4 | Control | 25338.88 | 23.36 | 614.34 | 9733.28 | 49.32 |
| 2 | 5 | Treated | 33476.00 | 79.68 | 2093.40 | 14740.33 | 32.99 |
| 2 | 6 | Control | 30568.26 | 73.00 | 601.10 | 5618.26 | 19.27 |
| 3 | 1 | Treated | 38763.30 | 95.91 | 1964.64 | 7680.69 | 44.51 |
| 3 | 2 | Treated | 37280.70 | 61.09 | 529.48 | 5134.35 | 38.62 |
| 3 | 3 | Control | 31414.62 | 25.15 | 399.58 | 6502.27 | 30.67 |
| 3 | 4 | Control | 26749.95 | 56.46 | 982.26 | 7625.05 | 35.19 |
| 3 | 5 | Treated | 27936.83 | 40.21 | 754.43 | 7690.99 | 26.91 |
| 3 | 6 | Control | 25741.15 | 54.33 | 945.21 | 5262.07 | 33.48 |

**Appendix M. (continued).** This appendix contains dry matter (DM), tissue concentration, and plant uptake data that was inserted into the SAS program in appendix N.

| | | | **(µg/kg)** | | | | |
|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Zn** | **As** | **Se** | **Rb** | **Cd** |
| 6 | 1 | Treated | 36392.66 | 88.98 | 903.31 | 6167.51 | 39.60 |
| 6 | 2 | Treated | 43124.39 | 63.51 | 522.96 | 4887.88 | 16.77 |
| 6 | 3 | Control | 23818.55 | 21.95 | 577.48 | 6149.29 | 46.36 |
| 6 | 4 | Control | 32575.26 | 46.89 | 879.69 | 6967.95 | 19.72 |
| 6 | 5 | Treated | 43867.91 | 64.60 | 531.97 | 4972.16 | 17.06 |
| 6 | 6 | Control | 36961.23 | 37.42 | 660.81 | 6187.65 | 22.56 |
| 12 | 1 | Treated | 31645.79 | 77.37 | 785.49 | 5363.05 | 34.43 |
| 12 | 2 | Treated | 40624.48 | 51.22 | 798.55 | 4420.88 | 20.51 |
| 12 | 3 | Control | 20773.31 | 49.08 | 787.98 | 4159.72 | 29.33 |
| 12 | 4 | Control | 40735.19 | 40.83 | 190.43 | 3640.10 | 36.34 |
| 12 | 5 | Treated | 40139.41 | 110.74 | 632.94 | 6775.22 | 43.35 |
| 12 | 6 | Control | 30021.12 | 50.49 | 427.12 | 5366.82 | 37.68 |

**Appendix M. (continued).** This appendix contains dry matter (DM), tissue concentration, and plant uptake data that was inserted into the SAS program in appendix N.

|  |  |  | (µg/kg) |  |  |  |  |
|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Cs** | **Hg** | **Pb** | **Th** | **U** |
| 0 | 1 | Treated | 220.10 | 15.00 | 145.46 | 51.46 | 9.55 |
| 0 | 2 | Treated | 296.67 | 17.00 | 155.68 | 29.33 | 4.38 |
| 0 | 3 | Control | 141.56 | 13.00 | 106.21 | 22.01 | 2.88 |
| 0 | 4 | Control | 190.39 | 13.00 | 167.71 | 22.19 | 4.46 |
| 0 | 5 | Treated | 193.57 | 12.00 | 107.03 | 15.64 | 2.59 |
| 0 | 6 | Control | 180.83 | 10.00 | 70.88 | 15.91 | 1.10 |
| 1 | 1 | Treated | 686.72 | 19.00 | 136.29 | 27.66 | 19.15 |
| 1 | 2 | Treated | 308.48 | 19.00 | 112.05 | 26.95 | 14.80 |
| 1 | 3 | Control | 65.91 | 13.00 | 62.27 | 7.09 | 5.50 |
| 1 | 4 | Control | 254.70 | 11.00 | 131.83 | 21.32 | 4.50 |
| 1 | 5 | Treated | 1009.12 | 23.00 | 264.76 | 44.50 | 23.93 |
| 1 | 6 | Control | 871.72 | 16.00 | 136.29 | 54.79 | 6.36 |
| 2 | 1 | Treated | 268.22 | 8.00 | 45.73 | 17.86 | 3.86 |
| 2 | 2 | Treated | 71.56 | 7.00 | 35.96 | 14.08 | 0.89 |
| 2 | 3 | Control | 91.38 | 6.00 | 43.17 | 12.48 | 0.80 |
| 2 | 4 | Control | 43.07 | 6.00 | 31.79 | 8.16 | 0.32 |
| 2 | 5 | Treated | 258.60 | 9.00 | 42.15 | 13.08 | 3.33 |
| 2 | 6 | Control | 184.32 | 7.00 | 40.66 | 9.33 | 1.31 |
| 3 | 1 | Treated | 602.94 | 7.00 | 119.67 | 24.29 | 16.81 |
| 3 | 2 | Treated | 516.59 | 5.00 | 459.07 | 46.90 | 14.12 |
| 3 | 3 | Control | 164.97 | 7.00 | 64.66 | 14.51 | 4.01 |
| 3 | 4 | Control | 235.26 | 6.00 | 121.77 | 19.69 | 5.16 |
| 3 | 5 | Treated | 211.63 | 8.00 | 36.08 | 14.09 | 3.04 |
| 3 | 6 | Control | 226.39 | 11.00 | 117.17 | 18.95 | 5.00 |

**Appendix M. (continued).** This appendix contains dry matter (DM), tissue concentration, and plant uptake data that was inserted into the SAS program in appendix N.

| | | | | | **(µg/kg)** | | |
|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Cs** | **Hg** | **Pb** | **Th** | **U** |
| 6 | 1 | Treated | 349.71 | 15.00 | 59.96 | 10.23 | 4.27 |
| 6 | 2 | Treated | 160.36 | 8.00 | 55.37 | 8.12 | 3.14 |
| 6 | 3 | Control | 40.49 | 6.00 | 29.89 | 7.67 | 0.30 |
| 6 | 4 | Control | 246.76 | 8.00 | 42.07 | 16.43 | 3.55 |
| 6 | 5 | Treated | 163.12 | 10.00 | 65.98 | 8.26 | 5.16 |
| 6 | 6 | Control | 84.07 | 7.00 | 39.71 | 11.48 | 0.74 |
| 12 | 1 | Treated | 304.09 | - | 34.75 | 8.90 | 1.10 |
| 12 | 2 | Treated | 161.36 | - | 72.99 | 9.50 | 1.66 |
| 12 | 3 | Control | 191.50 | - | 86.93 | 5.47 | 2.05 |
| 12 | 4 | Control | 179.11 | - | 27.67 | 15.19 | 1.30 |
| 12 | 5 | Treated | 304.99 | - | 37.65 | 4.20 | 2.20 |
| 12 | 6 | Control | 190.47 | - | 90.28 | 7.11 | 0.86 |

**Appendix M. (continued).** This appendix contains dry matter (DM), tissue concentration, and plant uptake data that was inserted into the SAS program in appendix N.

| | | (g/ha) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Plot** | **Treatment** | **Be** | **V** | **Cr** | **Co** | **Ni** | **Cu** | **Zn** |
| 1 | Treated | 0.13 | 5.02 | 5.28 | 3.89 | 13.45 | 145.17 | 780.96 |
| 2 | Treated | 0.18 | 3.16 | 4.08 | 3.09 | 9.56 | 130.50 | 725.17 |
| 3 | Control | 0.30 | 0.99 | 1.92 | 1.52 | 10.02 | 80.10 | 419.43 |
| 4 | Control | 0.10 | 1.22 | 1.86 | 1.73 | 7.47 | 71.99 | 436.15 |
| 5 | Treated | 0.20 | 5.48 | 3.70 | 3.11 | 9.73 | 121.18 | 666.17 |
| 6 | Control | 0.31 | 1.17 | 1.73 | 1.89 | 6.96 | 90.28 | 454.17 |

**Appendix M. (continued).** This appendix contains dry matter (DM),tissue concentration, and plant uptake data that was inserted into the SAS program in appendix N.

| | | | | | | (g/ha) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Plot** | **Treatment** | **As** | **Se** | **Rb** | **Cd** | **Cs** | **Hg** | **Pb** | **Th** | **U** |
| 1 | Treated | 2.16 | 26.06 | 161.28 | 0.78 | 8.68 | 0.23 | 2.02 | 0.54 | 0.20 |
| 2 | Treated | 1.52 | 19.73 | 98.32 | 0.64 | 4.79 | 0.18 | 2.82 | 0.43 | 0.12 |
| 3 | Control | 0.62 | 8.61 | 91.19 | 0.46 | 1.81 | 0.13 | 1.10 | 0.19 | 0.04 |
| 4 | Control | 0.70 | 9.61 | 98.70 | 0.52 | 2.58 | 0.11 | 1.32 | 0.24 | 0.05 |
| 5 | Treated | 1.61 | 25.33 | 155.60 | 0.56 | 6.57 | 0.20 | 1.73 | 0.32 | 0.12 |
| 6 | Control | 0.87 | 8.21 | 92.18 | 0.44 | 3.95 | 0.12 | 1.14 | 0.27 | 0.03 |

**Appendix N.** This appendix contains an example of the SAS program that was used to run the DM and plant tissue concentration data contained in Appendix M.

```
Title3 'Plant Tissue Concentrations';

data biomass;
  infile 'SASPlant.csv' firstobs = 2 delimiter = "," ;
  input Time Plot Treatment $ Biomass Be V Cr Co Ni Cu Zn As Se Rb Cd Cs Pb Hg Th U;
run;

proc print data = biomass;
run;


title3 'Biomass';
proc MIXED data = Biomass;
 class Time Treatment;
 model Biomass = Time Treatment Treatment*Time ;
 lsmeans Time Treatment Treatment*Time / diff ;
 run;


title3 'Be';
proc MIXED data = Biomass;
 class Time Treatment;
 model Be = Time Treatment Treatment*Time ;
 lsmeans Time Treatment Treatment*Time / diff ;
 run;
```

**Appendix N.** This appendix contains an example of the SAS program used to run the cumulative plant uptake data presented in Appendix M.

```
Title3 'Cumulative Plant uptake';

data biomass;
  infile 'SASCumulativePlant.csv' firstobs = 2 delimiter = "," ;
  input Plot Treatment $ Be V Cr Co Ni Cu Zn As Se Rb Cd Cs Hg Pb Th U;
run;

proc print data = biomass;
run;

title3 'Biomass';
proc MIXED data=Biomass;
 class Treatment;
 model Biomass=Treatment
 lsmeans Treatment / diff;
 run;

title3 'Be';
proc MIXED data=Biomass;
 class Treatment;
 model Be=Treatment
 lsmeans Treatment / diff;
 run;
```

**Appendix O.** This appendix contains the bulk density, soil pH, EC, and soil elemental concentrations data that were inserted into the SAS program in Appendix P.

| | | | | **(g/cm3)** | | **(µS/cm)** | **(mg/kg)** | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **BD** | **pH** | **EC** | **P** | **K** | **Ca** | **Mg** |
| 0 | 1 | Treated | 0 | 0.99 | 6.36 | 169.31 | 308.00 | 180.00 | 1809.00 | 180.0 |
| 0 | 2 | Treated | 0 | 1.09 | 6.24 | 157.87 | 151.00 | 163.00 | 2018.00 | 119.0 |
| 0 | 3 | Control | 0 | 1.10 | 6.37 | 123.88 | 250.00 | 194.00 | 1619.00 | 172.0 |
| 0 | 4 | Control | 0 | 0.98 | 6.33 | 167.95 | 152.00 | 95.00 | 1282.00 | 105.0 |
| 0 | 5 | Treated | 0 | 1.16 | 6.14 | 193.35 | 439.00 | 222.00 | 1481.00 | 211.0 |
| 0 | 6 | Control | 0 | 1.05 | 6.08 | 100.11 | 394.00 | 232.00 | 1806.00 | 181.0 |
| 6 | 1 | Treated | 0 | 0.99 | 6.59 | 155.03 | 168.00 | 146.00 | 1760.00 | 110.0 |
| 6 | 2 | Treated | 0 | 1.09 | 6.69 | 195.07 | 160.00 | 150.00 | 2101.00 | 100.0 |
| 6 | 3 | Control | 0 | 1.10 | 6.23 | 88.77 | 225.00 | 163.00 | 1485.00 | 148.0 |
| 6 | 4 | Control | 0 | 0.98 | 6.25 | 144.32 | 193.00 | 137.00 | 1347.00 | 127.0 |
| 6 | 5 | Treated | 0 | 1.16 | 6.47 | 95.70 | 56.00 | 76.00 | 1964.00 | 97.0 |
| 6 | 6 | Control | 0 | 1.05 | 6.21 | 187.86 | 363.00 | 214.00 | 1694.00 | 167.0 |
| 12 | 1 | Treated | 0 | 0.99 | 6.29 | 161.50 | 210.00 | 179.00 | 1910.00 | 181.0 |
| 12 | 2 | Treated | 0 | 1.09 | 6.21 | 197.03 | 384.00 | 248.00 | 2222.00 | 230.0 |
| 12 | 3 | Control | 0 | 1.10 | 6.32 | 144.45 | 277.00 | 187.00 | 1351.00 | 118.0 |
| 12 | 4 | Control | 0 | 0.98 | 6.19 | 189.25 | 146.00 | 104.00 | 1148.00 | 87.0 |
| 12 | 5 | Treated | 0 | 1.16 | 6.28 | 129.52 | 146.00 | 144.00 | 1540.00 | 125.0 |
| 12 | 6 | Control | 0 | 1.05 | 6.35 | 153.22 | 345.00 | 206.00 | 1539.00 | 141.0 |
| 0 | 1 | Treated | 10 | 1.26 | 6.21 | 181.50 | 274.00 | 100.00 | 1274.00 | 118.0 |
| 0 | 2 | Treated | 10 | 1.22 | 6.16 | 123.20 | 350.00 | 160.00 | 1328.00 | 151.0 |
| 0 | 3 | Control | 10 | 1.17 | 6.19 | 137.69 | 266.00 | 141.00 | 1268.00 | 112.0 |
| 0 | 4 | Control | 10 | 1.33 | 6.24 | 195.76 | 156.00 | 56.00 | 996.00 | 47.0 |
| 0 | 5 | Treated | 10 | 1.38 | 6.28 | 133.92 | 159.00 | 81.00 | 1121.00 | 54.0 |
| 0 | 6 | Control | 10 | 1.44 | 6.06 | 173.82 | 363.00 | 158.00 | 1383.00 | 121.0 |
| 6 | 1 | Treated | 10 | 1.26 | 6.66 | 118.05 | 149.00 | 172.00 | 1095.00 | 166.0 |
| 6 | 2 | Treated | 10 | 1.22 | 6.55 | 189.20 | 49.00 | 78.00 | 1114.00 | 67.0 |
| 6 | 3 | Control | 10 | 1.17 | 6.17 | 186.27 | 39.00 | 40.00 | 1190.00 | 67.0 |
| 6 | 4 | Control | 10 | 1.33 | 6.19 | 147.48 | 175.00 | 78.00 | 1009.00 | 61.0 |
| 6 | 5 | Treated | 10 | 1.38 | 6.48 | 144.82 | 278.00 | 142.00 | 1242.00 | 107.0 |
| 6 | 6 | Control | 10 | 1.44 | 6.09 | 120.22 | 272.00 | 120.00 | 1208.00 | 89.0 |

**Appendix O. (continued)** This appendix contains the bulk density, soil pH, EC, and soil elemental concentrations data that were inserted into the SAS program in Appendix P.

| | | | | (g/cm3) | | (µS/cm) | (mg/kg) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **BD** | **pH** | **EC** | **P** | **K** | **Ca** | **Mg** |
| 12 | 1 | Treated | 10 | 1.26 | 6.23 | 137.47 | 224.00 | 98.00 | 1002.00 | 95.0 |
| 12 | 2 | Treated | 10 | 1.22 | 6.11 | 148.85 | 361.00 | 160.00 | 1111.00 | 135.0 |
| 12 | 3 | Control | 10 | 1.17 | 6.28 | 191.04 | 274.00 | 112.00 | 1078.00 | 85.0 |
| 12 | 4 | Control | 10 | 1.33 | 6.02 | 173.11 | 174.00 | 48.00 | 953.00 | 46.0 |
| 12 | 5 | Treated | 10 | 1.38 | 6.18 | 116.37 | 154.00 | 58.00 | 1016.00 | 47.0 |
| 12 | 6 | Control | 10 | 1.44 | 6.14 | 173.22 | 281.00 | 103.00 | 1107.00 | 99.0 |
| 0 | 1 | Treated | 20 | 1.43 | 6.19 | 180.48 | 257.00 | 75.00 | 1140.00 | 86.0 |
| 0 | 2 | Treated | 20 | 1.43 | 6.11 | 182.05 | 320.00 | 127.00 | 1126.00 | 112.0 |
| 0 | 3 | Control | 20 | 1.34 | 6.05 | 122.78 | 266.00 | 97.00 | 1247.00 | 72.0 |
| 0 | 4 | Control | 20 | 1.36 | 6.09 | 140.34 | 196.00 | 62.00 | 1091.00 | 39.0 |
| 0 | 5 | Treated | 20 | 1.39 | 6.01 | 134.08 | 201.00 | 74.00 | 1069.00 | 39.0 |
| 0 | 6 | Control | 20 | 1.43 | 6.06 | 127.03 | 321.00 | 140.00 | 1107.00 | 103.0 |
| 6 | 1 | Treated | 20 | 1.43 | 6.21 | 96.33 | 120.00 | 57.00 | 1464.00 | 96.0 |
| 6 | 2 | Treated | 20 | 1.43 | 6.19 | 114.50 | 33.00 | 57.00 | 896.00 | 36.0 |
| 6 | 3 | Control | 20 | 1.34 | 6.15 | 177.78 | 182.00 | 58.00 | 1017.00 | 34.0 |
| 6 | 4 | Control | 20 | 1.36 | 6.09 | 142.70 | 184.00 | 60.00 | 950.00 | 40.0 |
| 6 | 5 | Treated | 20 | 1.39 | 6.14 | 178.77 | 138.00 | 45.00 | 1004.00 | 55.0 |
| 6 | 6 | Control | 20 | 1.43 | 6.02 | 151.11 | 225.00 | 98.00 | 1035.00 | 52.0 |
| 12 | 1 | Treated | 20 | 1.43 | 6.05 | 162.55 | 227.00 | 83.00 | 909.00 | 68.0 |
| 12 | 2 | Treated | 20 | 1.43 | 6.07 | 161.42 | 328.00 | 286.00 | 986.00 | 117.0 |
| 12 | 3 | Control | 20 | 1.34 | 6.12 | 98.10 | 273.00 | 147.00 | 1058.00 | 65.0 |
| 12 | 4 | Control | 20 | 1.36 | 6.02 | 172.16 | 206.00 | 49.00 | 1004.00 | 34.0 |
| 12 | 5 | Treated | 20 | 1.39 | 6.01 | 129.26 | 176.00 | 60.00 | 1004.00 | 36.0 |
| 12 | 6 | Control | 20 | 1.43 | 6.05 | 104.86 | 238.00 | 105.00 | 990.00 | 86.0 |

**Appendix O. (continued)** This appendix contains the bulk density, soil pH, EC, and soil elemental concentrations data that were inserted into the SAS program in Appendix P.

| | | | | (mg/kg) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **S** | **Na** | **Fe** | **Mn** | **Zn** | **Cu** | **B** |
| 0 | 1 | Treated | 0 | 21.96 | 7.31 | 219.00 | 298.00 | 32.30 | 15.78 | 0.16 |
| 0 | 2 | Treated | 0 | 18.64 | 8.30 | 216.00 | 255.00 | 10.29 | 2.64 | 0.32 |
| 0 | 3 | Control | 0 | 20.83 | 8.47 | 221.00 | 306.00 | 26.46 | 12.02 | 0.50 |
| 0 | 4 | Control | 0 | 20.00 | 6.34 | 210.00 | 321.00 | 12.40 | 3.03 | 0.08 |
| 0 | 5 | Treated | 0 | 25.89 | 9.56 | 225.00 | 275.00 | 40.81 | 22.60 | 0.53 |
| 0 | 6 | Control | 0 | 23.15 | 9.78 | 267.00 | 275.00 | 31.00 | 18.76 | 0.44 |
| 6 | 1 | Treated | 0 | 79.17 | 21.27 | 203.00 | 179.00 | 4.69 | 10.17 | 0.43 |
| 6 | 2 | Treated | 0 | 35.52 | 22.04 | 197.00 | 79.00 | 4.29 | 1.09 | 0.26 |
| 6 | 3 | Control | 0 | 20.02 | 9.61 | 214.00 | 302.00 | 22.49 | 9.28 | 0.35 |
| 6 | 4 | Control | 0 | 18.54 | 10.85 | 198.00 | 288.00 | 19.03 | 7.28 | 0.25 |
| 6 | 5 | Treated | 0 | 61.63 | 18.66 | 173.00 | 71.00 | 4.11 | 0.99 | 0.25 |
| 6 | 6 | Control | 0 | 21.58 | 10.36 | 247.00 | 253.00 | 29.15 | 17.27 | 0.38 |
| 12 | 1 | Treated | 0 | 31.52 | 22.71 | 201.00 | 221.00 | 19.37 | 8.54 | 0.38 |
| 12 | 2 | Treated | 0 | 45.43 | 23.56 | 217.00 | 234.00 | 33.63 | 17.95 | 0.44 |
| 12 | 3 | Control | 0 | 26.42 | 14.32 | 229.00 | 275.00 | 20.89 | 10.40 | 0.02 |
| 12 | 4 | Control | 0 | 25.81 | 10.76 | 190.00 | 285.00 | 12.47 | 3.50 | 0.35 |
| 12 | 5 | Treated | 0 | 32.08 | 15.12 | 204.00 | 203.00 | 7.18 | 2.66 | 0.23 |
| 12 | 6 | Control | 0 | 29.99 | 11.83 | 244.00 | 250.00 | 22.56 | 13.91 | 0.06 |
| 0 | 1 | Treated | 10 | 13.53 | 6.66 | 234.00 | 271.00 | 14.02 | 6.72 | 0.03 |
| 0 | 2 | Treated | 10 | 13.87 | 6.19 | 240.00 | 246.00 | 15.45 | 8.42 | 0.07 |
| 0 | 3 | Control | 10 | 13.59 | 7.09 | 257.00 | 285.00 | 14.44 | 6.72 | 0.15 |
| 0 | 4 | Control | 10 | 12.04 | 6.28 | 237.00 | 305.00 | 9.47 | 2.98 | 0.02 |
| 0 | 5 | Treated | 10 | 13.21 | 7.42 | 252.00 | 245.00 | 6.06 | 2.26 | 0.12 |
| 0 | 6 | Control | 10 | 16.71 | 8.03 | 295.00 | 274.00 | 16.43 | 11.52 | 0.15 |
| 6 | 1 | Treated | 10 | 6.49 | 11.85 | 159.00 | 178.00 | 4.61 | 10.75 | 0.13 |
| 6 | 2 | Treated | 10 | 61.15 | 18.99 | 159.00 | 78.00 | 4.72 | 0.79 | 0.13 |
| 6 | 3 | Control | 10 | 6.28 | 15.47 | 186.00 | 86.00 | 4.04 | 0.90 | 0.11 |
| 6 | 4 | Control | 10 | 11.66 | 8.31 | 213.00 | 262.00 | 10.51 | 3.72 | 0.02 |
| 6 | 5 | Treated | 10 | 13.42 | 9.64 | 254.00 | 266.00 | 14.60 | 8.05 | 0.10 |
| 6 | 6 | Control | 10 | 15.13 | 11.26 | 258.00 | 266.00 | 13.45 | 8.00 | 0.08 |

**Appendix O. (continued)** This appendix contains the bulk density, soil pH, EC, and soil elemental concentrations data that were inserted into the SAS program in Appendix P.

| | | | | | | | **(mg/kg)** | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **S** | **Na** | **Fe** | **Mn** | **Zn** | **Cu** | **B** |
| 12 | 1 | Treated | 10 | 19.73 | 16.78 | 240.00 | 260.00 | 7.55 | 3.17 | 0.02 |
| 12 | 2 | Treated | 10 | 25.35 | 16.24 | 261.00 | 256.00 | 11.77 | 7.04 | 0.03 |
| 12 | 3 | Control | 10 | 20.62 | 11.64 | 258.00 | 283.00 | 9.40 | 4.11 | 0.05 |
| 12 | 4 | Control | 10 | 20.07 | 9.68 | 223.00 | 297.00 | 8.34 | 2.93 | 0.05 |
| 12 | 5 | Treated | 10 | 23.36 | 11.62 | 215.00 | 233.00 | 5.48 | 2.32 | 0.05 |
| 12 | 6 | Control | 10 | 17.61 | 9.62 | 260.00 | 244.00 | 7.13 | 4.37 | 0.05 |
| 0 | 1 | Treated | 20 | 9.66 | 9.12 | 244.00 | 292.00 | 7.47 | 3.03 | 0.01 |
| 0 | 2 | Treated | 20 | 9.51 | 6.65 | 271.00 | 287.00 | 7.58 | 2.96 | 0.01 |
| 0 | 3 | Control | 20 | 9.90 | 7.57 | 271.00 | 329.00 | 10.87 | 2.83 | 0.02 |
| 0 | 4 | Control | 20 | 10.96 | 7.07 | 260.00 | 351.00 | 7.85 | 2.43 | 0.05 |
| 0 | 5 | Treated | 20 | 9.70 | 6.08 | 290.00 | 241.00 | 4.54 | 1.83 | 0.05 |
| 0 | 6 | Control | 20 | 11.06 | 8.52 | 336.00 | 243.00 | 6.50 | 3.82 | 0.03 |
| 6 | 1 | Treated | 20 | 58.82 | 17.62 | 208.00 | 138.00 | 4.88 | 1.36 | 0.06 |
| 6 | 2 | Treated | 20 | 6.33 | 11.31 | 167.00 | 279.00 | 5.32 | 0.69 | 0.05 |
| 6 | 3 | Control | 20 | 10.26 | 11.69 | 239.00 | 312.00 | 7.32 | 2.17 | 0.05 |
| 6 | 4 | Control | 20 | 9.25 | 5.98 | 232.00 | 282.00 | 6.86 | 2.22 | 0.05 |
| 6 | 5 | Treated | 20 | 9.48 | 12.13 | 135.00 | 73.00 | 4.08 | 0.80 | 0.03 |
| 6 | 6 | Control | 20 | 10.46 | 10.86 | 269.00 | 300.00 | 7.28 | 2.78 | 0.05 |
| 12 | 1 | Treated | 20 | 16.13 | 15.78 | 224.00 | 263.00 | 4.99 | 1.73 | 0.05 |
| 12 | 2 | Treated | 20 | 24.21 | 17.98 | 277.00 | 281.00 | 7.48 | 3.01 | 0.01 |
| 12 | 3 | Control | 20 | 16.41 | 9.45 | 268.00 | 314.00 | 6.97 | 2.33 | 0.05 |
| 12 | 4 | Control | 20 | 19.47 | 12.57 | 240.00 | 345.00 | 7.63 | 2.40 | 0.05 |
| 12 | 5 | Treated | 20 | 17.27 | 9.82 | 244.00 | 256.00 | 4.77 | 1.87 | 0.05 |
| 12 | 6 | Control | 20 | 11.64 | 9.62 | 214.00 | 281.00 | 4.17 | 2.26 | 0.05 |

**Appendix O. (continued)** This appendix contains the bulk density, soil pH, EC, and soil elemental concentrations data that were inserted into the SAS program in Appendix P.

|  |  |  |  |  |  |  | **(µg/kg)** |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **Be** | **V** | **Cr** | **Co** | **Ni** | **Zn** | **As** |
| 0 | 1 | Treated | 0 | 0.71 | 15.84 | 17.17 | 6.42 | 3.92 | 46.91 | 4.56 |
| 0 | 2 | Treated | 0 | 0.37 | 11.19 | 15.09 | 4.32 | 3.32 | 43.38 | 3.85 |
| 0 | 3 | Control | 0 | 0.57 | 21.10 | 36.40 | 7.29 | 4.51 | 43.42 | 5.70 |
| 0 | 4 | Control | 0 | 0.65 | 15.74 | 17.81 | 6.44 | 3.79 | 24.40 | 3.95 |
| 0 | 5 | Treated | 0 | 0.60 | 14.37 | 15.08 | 5.74 | 3.16 | 22.93 | 3.58 |
| 0 | 6 | Control | 0 | 0.42 | 15.45 | 16.05 | 6.20 | 3.63 | 42.99 | 5.15 |
| 6 | 1 | Treated | 0 | 0.40 | 7.58 | 8.21 | 4.73 | 2.89 | 36.93 | 1.97 |
| 6 | 2 | Treated | 0 | 0.27 | 15.48 | 13.96 | 5.40 | 3.37 | 29.87 | 4.39 |
| 6 | 3 | Control | 0 | 0.32 | 11.70 | 11.19 | 5.65 | 3.88 | 34.49 | 3.31 |
| 6 | 4 | Control | 0 | 0.52 | 14.24 | 13.13 | 5.76 | 3.57 | 22.38 | 3.60 |
| 6 | 5 | Treated | 0 | 0.50 | 15.75 | 18.40 | 5.67 | 3.71 | 22.17 | 3.53 |
| 6 | 6 | Control | 0 | 0.64 | 14.31 | 12.74 | 6.33 | 5.06 | 66.17 | 5.33 |
| 12 | 1 | Treated | 0 | 0.68 | 4.72 | 5.91 | 7.39 | 3.17 | 27.88 | 1.81 |
| 12 | 2 | Treated | 0 | 0.76 | 6.55 | 5.90 | 10.43 | 6.04 | 61.61 | 3.20 |
| 12 | 3 | Control | 0 | 0.76 | 9.35 | 10.82 | 14.04 | 5.98 | 36.16 | 3.68 |
| 12 | 4 | Control | 0 | 0.33 | 5.76 | 9.87 | 9.08 | 4.22 | 15.83 | 1.98 |
| 12 | 5 | Treated | 0 | 0.65 | 13.34 | 16.62 | 10.53 | 5.05 | 14.94 | 3.20 |
| 12 | 6 | Control | 0 | 0.37 | 2.61 | 14.24 | 0.01 | 6.36 | 10.32 | 3.89 |
| 0 | 1 | Treated | 10 | 0.59 | 18.63 | 23.87 | 6.52 | 4.26 | 27.08 | 5.33 |
| 0 | 2 | Treated | 10 | 0.45 | 18.38 | 19.69 | 6.79 | 4.36 | 28.04 | 5.44 |
| 0 | 3 | Control | 10 | 0.37 | 18.96 | 26.96 | 7.84 | 5.09 | 28.18 | 5.07 |
| 0 | 4 | Control | 10 | 0.62 | 29.29 | 26.16 | 8.98 | 7.60 | 25.87 | 6.77 |
| 0 | 5 | Treated | 10 | 0.74 | 26.54 | 35.44 | 7.65 | 4.39 | 21.34 | 7.31 |
| 0 | 6 | Control | 10 | 0.79 | 22.86 | 30.21 | 14.32 | 6.42 | 29.41 | 6.45 |
| 6 | 1 | Treated | 10 | 0.44 | 15.79 | 19.63 | 5.73 | 3.40 | 25.59 | 4.01 |
| 6 | 2 | Treated | 10 | 0.44 | 11.22 | 11.54 | 5.39 | 3.58 | 48.07 | 3.47 |
| 6 | 3 | Control | 10 | 0.50 | 17.51 | 19.39 | 6.17 | 4.27 | 23.12 | 4.36 |
| 6 | 4 | Control | 10 | 0.47 | 12.71 | 10.45 | 8.91 | 4.13 | 20.90 | 3.35 |
| 6 | 5 | Treated | 10 | 0.74 | 26.34 | 27.79 | 8.43 | 6.07 | 23.01 | 5.81 |
| 6 | 6 | Control | 10 | 0.57 | 14.14 | 11.25 | 5.59 | 3.72 | 23.97 | 4.22 |

**Appendix O. (continued)** This appendix contains the bulk density, soil pH, Ec, and soil elemental concentrations data that were inserted into the SAS program in Appendix P.

| | | | | | | | (µg/kg) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **Be** | **V** | **Cr** | **Co** | **Ni** | **Zn** | **As** |
| 12 | 1 | Treated | 10 | 0.79 | 4.24 | 5.84 | 9.54 | 4.69 | 8.34 | 1.84 |
| 12 | 2 | Treated | 10 | 0.76 | 6.94 | 9.52 | 11.95 | 5.19 | 18.00 | 2.97 |
| 12 | 3 | Control | 10 | 1.08 | 11.38 | 14.41 | 12.01 | 6.61 | 15.85 | 3.31 |
| 12 | 4 | Control | 10 | 0.40 | 6.72 | 9.98 | 9.97 | 4.73 | 10.80 | 2.14 |
| 12 | 5 | Treated | 10 | 0.58 | 5.00 | 7.06 | 8.50 | 3.36 | 7.21 | 1.77 |
| 12 | 6 | Control | 10 | 1.09 | 8.19 | 10.76 | 13.54 | 5.79 | 12.97 | 3.30 |
| 0 | 1 | Treated | 20 | 0.81 | 26.78 | 27.81 | 13.15 | 5.59 | 20.90 | 6.53 |
| 0 | 2 | Treated | 20 | 0.71 | 19.21 | 25.16 | 7.43 | 4.93 | 20.65 | 5.79 |
| 0 | 3 | Control | 20 | 0.77 | 21.69 | 24.79 | 9.42 | 5.91 | 27.50 | 5.45 |
| 0 | 4 | Control | 20 | 0.94 | 26.45 | 32.19 | 7.96 | 5.78 | 23.92 | 7.23 |
| 0 | 5 | Treated | 20 | 0.39 | 14.05 | 14.26 | 7.25 | 3.34 | 13.11 | 3.76 |
| 0 | 6 | Control | 20 | 0.94 | 27.07 | 37.75 | 7.94 | 7.24 | 38.58 | 7.16 |
| 6 | 1 | Treated | 20 | 0.65 | 17.35 | 16.51 | 7.29 | 4.36 | 16.60 | 4.06 |
| 6 | 2 | Treated | 20 | 0.82 | 36.23 | 29.03 | 8.87 | 7.76 | 33.73 | 11.57 |
| 6 | 3 | Control | 20 | 0.67 | 16.30 | 21.46 | 7.22 | 6.22 | 16.80 | 4.17 |
| 6 | 4 | Control | 20 | 0.64 | 18.50 | 17.53 | 8.04 | 5.05 | 24.01 | 4.22 |
| 6 | 5 | Treated | 20 | 0.35 | 11.09 | 11.04 | 5.00 | 3.47 | 12.44 | 2.52 |
| 6 | 6 | Control | 20 | 0.60 | 19.30 | 15.75 | 6.91 | 6.54 | 67.71 | 5.41 |
| 12 | 1 | Treated | 20 | 0.45 | 4.61 | 6.25 | 11.61 | 4.01 | 9.18 | 1.73 |
| 12 | 2 | Treated | 20 | 0.80 | 12.13 | 17.34 | 13.54 | 6.67 | 11.55 | 3.61 |
| 12 | 3 | Control | 20 | 1.04 | 10.65 | 13.60 | 12.49 | 6.34 | 12.72 | 3.22 |
| 12 | 4 | Control | 20 | 0.62 | 7.58 | 10.17 | 10.94 | 5.89 | 13.20 | 2.22 |
| 12 | 5 | Treated | 20 | 0.72 | 5.04 | 9.13 | 8.59 | 3.52 | 6.32 | 1.74 |
| 12 | 6 | Control | 20 | 0.83 | 16.99 | 20.99 | 14.49 | 7.60 | 7.99 | 3.77 |

**Appendix O. (continued)** This appendix contains the bulk density, soil pH, Ec, and soil elemental concentrations data that were inserted into the SAS program in Appendix P.

| | | | | | | | | **(µg/kg)** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **Se** | **Rb** | **Cd** | **Cs** | **Pb** | **Hg** | **Th** | **U** |
| 0 | 1 | Treated | 0 | 1.32 | 7.99 | 0.10 | 0.63 | 24.11 | 1955 | 2.03 | 1.36 |
| 0 | 2 | Treated | 0 | 0.78 | 5.88 | 0.08 | 0.45 | 15.74 | 792 | 0.88 | 1.09 |
| 0 | 3 | Control | 0 | 1.57 | 7.89 | 0.11 | 0.63 | 29.44 | 624 | 1.98 | 1.66 |
| 0 | 4 | Control | 0 | 0.90 | 7.43 | 0.10 | 0.61 | 23.40 | 203 | 1.59 | 1.16 |
| 0 | 5 | Treated | 0 | 1.42 | 7.73 | 0.09 | 0.65 | 23.78 | 117 | 1.82 | 1.30 |
| 0 | 6 | Control | 0 | 1.45 | 6.99 | 0.09 | 0.54 | 23.30 | 195 | 2.13 | 1.42 |
| 6 | 1 | Treated | 0 | 0.73 | 4.88 | 0.09 | 0.32 | 16.11 | 2540 | 2.50 | 0.94 |
| 6 | 2 | Treated | 0 | 0.78 | 5.12 | 0.08 | 0.36 | 17.06 | 805 | 1.80 | 0.93 |
| 6 | 3 | Control | 0 | 0.96 | 6.97 | 0.09 | 0.56 | 20.06 | 747 | 2.47 | 1.15 |
| 6 | 4 | Control | 0 | 0.86 | 6.38 | 0.09 | 0.52 | 19.86 | 209 | 1.91 | 0.98 |
| 6 | 5 | Treated | 0 | 0.94 | 6.37 | 0.10 | 0.50 | 20.18 | 128 | 1.87 | 1.16 |
| 6 | 6 | Control | 0 | 1.99 | 9.79 | 0.13 | 0.70 | 24.52 | 162 | 0.68 | 1.56 |
| 12 | 1 | Treated | 0 | 0.67 | 4.87 | 0.14 | 0.23 | 16.27 | - | 2.66 | 0.10 |
| 12 | 2 | Treated | 0 | 1.11 | 7.10 | 0.20 | 0.32 | 23.38 | - | 4.37 | 0.99 |
| 12 | 3 | Control | 0 | 1.26 | 9.97 | 0.22 | 0.52 | 27.93 | - | 6.73 | 0.83 |
| 12 | 4 | Control | 0 | 0.89 | 6.55 | 0.16 | 0.35 | 21.06 | - | 4.55 | 0.38 |
| 12 | 5 | Treated | 0 | 1.04 | 8.22 | 0.17 | 0.46 | 22.99 | - | 5.81 | 0.96 |
| 12 | 6 | Control | 0 | 1.12 | 1.79 | 0.05 | 0.37 | 7.32 | - | 2.28 | 2.19 |
| 0 | 1 | Treated | 10 | 0.90 | 6.79 | 0.10 | 0.56 | 22.65 | 1599 | 2.24 | 1.15 |
| 0 | 2 | Treated | 10 | 1.51 | 7.49 | 0.11 | 0.60 | 24.13 | 831 | 1.61 | 1.27 |
| 0 | 3 | Control | 10 | 1.19 | 7.34 | 0.10 | 0.58 | 28.40 | 519 | 2.20 | 1.28 |
| 0 | 4 | Control | 10 | 1.24 | 7.18 | 0.12 | 0.60 | 37.82 | 156 | 2.59 | 1.21 |
| 0 | 5 | Treated | 10 | 1.03 | 7.35 | 0.12 | 0.59 | 32.24 | 76 | 3.60 | 1.60 |
| 0 | 6 | Control | 10 | 1.53 | 6.45 | 0.12 | 0.49 | 36.10 | 162 | 2.28 | 1.43 |
| 6 | 1 | Treated | 10 | 0.70 | 6.40 | 0.11 | 0.50 | 21.79 | 2658 | 2.63 | 1.08 |
| 6 | 2 | Treated | 10 | 0.69 | 5.90 | 0.07 | 0.42 | 17.99 | 658 | 2.15 | 1.20 |
| 6 | 3 | Control | 10 | 0.88 | 6.90 | 0.09 | 0.56 | 21.87 | 354 | 2.58 | 1.11 |
| 6 | 4 | Control | 10 | 0.74 | 6.95 | 0.10 | 0.56 | 28.00 | 255 | 2.12 | 1.05 |
| 6 | 5 | Treated | 10 | 1.30 | 5.91 | 0.11 | 0.47 | 23.92 | 94 | 2.89 | 1.19 |
| 6 | 6 | Control | 10 | 1.05 | 6.42 | 0.09 | 0.44 | 19.80 | 164 | 1.96 | 1.08 |

**Appendix O. (continued)** This appendix contains the bulk density, soil pH, Ec, and soil elemental concentrations data that were inserted into the SAS program in Appendix P.

| | | | | | | | | **(μg/kg)** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **Se** | **Rb** | **Cd** | **Cs** | **Pb** | **Hg** | **Th** | **U** |
| 12 | 1 | Treated | 10 | 1.06 | 5.70 | 0.16 | 0.27 | 22.99 | - | 4.05 | 0.26 |
| 12 | 2 | Treated | 10 | 1.43 | 8.29 | 0.19 | 0.40 | 26.63 | - | 5.90 | 0.60 |
| 12 | 3 | Control | 10 | 1.15 | 10.51 | 0.19 | 0.56 | 25.58 | - | 6.18 | 0.37 |
| 12 | 4 | Control | 10 | 0.71 | 7.95 | 0.15 | 0.44 | 21.81 | - | 5.11 | 0.41 |
| 12 | 5 | Treated | 10 | 1.10 | 6.03 | 0.15 | 0.32 | 18.93 | - | 3.72 | 0.40 |
| 12 | 6 | Control | 10 | 1.60 | 10.55 | 0.21 | 0.53 | 31.59 | - | 6.71 | 0.60 |
| 0 | 1 | Treated | 20 | 1.30 | 7.62 | 0.12 | 0.62 | 43.30 | 627 | 3.61 | 1.23 |
| 0 | 2 | Treated | 20 | 1.45 | 8.43 | 0.11 | 0.66 | 27.10 | 166 | 2.86 | 1.21 |
| 0 | 3 | Control | 20 | 1.30 | 8.68 | 0.12 | 0.72 | 31.98 | 158 | 3.16 | 1.32 |
| 0 | 4 | Control | 20 | 0.97 | 8.44 | 0.11 | 0.68 | 29.12 | 72 | 2.98 | 1.48 |
| 0 | 5 | Treated | 20 | 0.44 | 5.97 | 0.08 | 0.45 | 28.15 | 61 | 2.31 | 1.07 |
| 0 | 6 | Control | 20 | 2.24 | 9.47 | 0.14 | 0.69 | 29.02 | 61 | 1.91 | 1.60 |
| 6 | 1 | Treated | 20 | 1.38 | 7.42 | 0.08 | 0.56 | 24.79 | 1049 | 3.41 | 1.17 |
| 6 | 2 | Treated | 20 | 2.03 | 9.88 | 0.14 | 0.70 | 29.25 | 332 | 1.82 | 1.37 |
| 6 | 3 | Control | 20 | 1.41 | 8.48 | 0.07 | 0.67 | 22.24 | 605 | 3.24 | 1.12 |
| 6 | 4 | Control | 20 | 1.53 | 8.29 | 0.12 | 0.68 | 28.68 | 165 | 3.05 | 1.28 |
| 6 | 5 | Treated | 20 | 0.42 | 5.84 | 0.08 | 0.45 | 17.59 | 103 | 2.51 | 0.90 |
| 6 | 6 | Control | 20 | 1.11 | 9.74 | 0.12 | 0.67 | 26.22 | 149 | 1.41 | 1.44 |
| 12 | 1 | Treated | 20 | 0.98 | 7.16 | 0.14 | 0.35 | 23.17 | - | 4.62 | 0.43 |
| 12 | 2 | Treated | 20 | 1.54 | 10.91 | 0.22 | 0.55 | 30.19 | - | 7.18 | 0.59 |
| 12 | 3 | Control | 20 | 1.65 | 10.54 | 0.18 | 0.53 | 26.81 | - | 6.89 | 0.56 |
| 12 | 4 | Control | 20 | 1.02 | 9.33 | 0.17 | 0.48 | 23.35 | - | 4.99 | 0.49 |
| 12 | 5 | Treated | 20 | 0.99 | 6.76 | 0.14 | 0.34 | 20.29 | - | 4.38 | 0.38 |
| 12 | 6 | Control | 20 | 1.43 | 13.12 | 0.15 | 0.72 | 26.93 | - | 7.69 | 0.39 |

**Appendix P.** This appendix contains an example of the SAS program used to analyze the soil concentrations in Appendix O.

```
Title3 'Effect of Application on Soil Concentrations';

data Soil;
  infile 'SASSoil.csv' firstobs = 2 delimiter = "," ;
  input Time Plot Treatment $ Depth pH EC P K Ca Mg S Na Fe Mn Zn Cu B Be V Cr Co Ni As
Se Rb Cd Cs Pb Hg Th U;
run;

proc print data = Soil;
run;


 title3 'pH';
proc MIXED data = Soil;
 class Time Treatment Depth;
 model pH = Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth ;
 lsmeans Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth / diff;
run;

 title3 'EC';
proc MIXED data = Soil;
 class Time Treatment Depth;
 model EC = Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth ;
 lsmeans Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth / diff;
run;


title3 'P';
proc MIXED data = Soil;
 class Time Treatment Depth;
 model P = Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth ;
 lsmeans  Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth / diff;
run;
```

**Appendix Q.** This appendix contains the soil content data that were inserted into the SAS program in Appendix R.

| | | | | (kg/ha) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **P** | **K** | **Ca** | **Mg** | **S** | **Na** |
| 0 | 1 | Treated | 0 | 304.52 | 177.97 | 1788.55 | 177.97 | 21.71 | 7.23 |
| 0 | 2 | Treated | 0 | 164.92 | 178.03 | 2204.04 | 129.97 | 20.36 | 9.07 |
| 0 | 3 | Control | 0 | 273.93 | 212.57 | 1773.95 | 188.46 | 22.82 | 9.28 |
| 0 | 4 | Control | 0 | 149.67 | 93.54 | 1262.36 | 103.39 | 19.69 | 6.24 |
| 0 | 5 | Treated | 0 | 508.36 | 257.08 | 1715.00 | 244.34 | 29.98 | 11.07 |
| 0 | 6 | Control | 0 | 413.70 | 243.60 | 1896.28 | 190.05 | 24.31 | 10.27 |
| 6 | 1 | Treated | 0 | 166.10 | 144.35 | 1740.11 | 108.76 | 78.28 | 21.03 |
| 6 | 2 | Treated | 0 | 174.75 | 163.83 | 2294.69 | 109.22 | 38.79 | 24.07 |
| 6 | 3 | Control | 0 | 246.53 | 178.60 | 1627.12 | 162.16 | 21.94 | 10.53 |
| 6 | 4 | Control | 0 | 190.04 | 134.90 | 1326.36 | 125.05 | 18.26 | 10.68 |
| 6 | 5 | Treated | 0 | 64.85 | 88.01 | 2274.31 | 112.33 | 71.37 | 21.61 |
| 6 | 6 | Control | 0 | 381.15 | 224.70 | 1778.68 | 175.35 | 22.66 | 10.88 |
| 12 | 1 | Treated | 0 | 207.63 | 176.98 | 1888.41 | 178.95 | 31.16 | 22.45 |
| 12 | 2 | Treated | 0 | 419.40 | 270.86 | 2426.84 | 251.20 | 49.62 | 25.73 |
| 12 | 3 | Control | 0 | 303.51 | 204.90 | 1480.30 | 129.29 | 28.95 | 15.69 |
| 12 | 4 | Control | 0 | 143.76 | 102.41 | 1130.41 | 85.67 | 25.41 | 10.60 |
| 12 | 5 | Treated | 0 | 169.07 | 166.75 | 1783.32 | 144.75 | 37.15 | 17.51 |
| 12 | 6 | Control | 0 | 362.25 | 216.30 | 1615.93 | 148.05 | 31.49 | 12.42 |
| 0 | 1 | Treated | 10 | 345.51 | 126.10 | 1606.50 | 148.80 | 17.06 | 8.40 |
| 0 | 2 | Treated | 10 | 425.35 | 194.44 | 1613.88 | 183.51 | 16.86 | 7.52 |
| 0 | 3 | Control | 10 | 312.17 | 165.47 | 1488.09 | 131.44 | 15.95 | 8.32 |
| 0 | 4 | Control | 10 | 207.37 | 74.44 | 1324.00 | 62.48 | 16.00 | 8.35 |
| 0 | 5 | Treated | 10 | 218.63 | 111.38 | 1541.41 | 74.25 | 18.16 | 10.20 |
| 0 | 6 | Control | 10 | 521.57 | 227.02 | 1987.13 | 173.86 | 24.01 | 11.54 |
| 6 | 1 | Treated | 10 | 187.89 | 216.89 | 1380.78 | 209.32 | 8.18 | 14.94 |
| 6 | 2 | Treated | 10 | 59.55 | 94.79 | 1353.81 | 81.42 | 74.31 | 23.08 |
| 6 | 3 | Control | 10 | 45.77 | 46.94 | 1396.55 | 78.63 | 7.37 | 18.16 |
| 6 | 4 | Control | 10 | 232.63 | 103.69 | 1341.28 | 81.09 | 15.50 | 11.05 |
| 6 | 5 | Treated | 10 | 382.26 | 195.25 | 1707.79 | 147.13 | 18.45 | 13.26 |
| 6 | 6 | Control | 10 | 390.82 | 172.42 | 1735.68 | 127.88 | 21.74 | 16.18 |

**Appendix Q. (continued).** This appendix contains the soil content data that were inserted into the SAS program in Appendix R.

| | | | | **(kg/ha)** | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **P** | **K** | **Ca** | **Mg** | **S** | **Na** |
| 12 | 1 | Treated | 10 | 282.46 | 123.58 | 1263.51 | 119.79 | 24.88 | 21.16 |
| 12 | 2 | Treated | 10 | 438.71 | 194.44 | 1350.17 | 164.06 | 30.81 | 19.74 |
| 12 | 3 | Control | 10 | 321.56 | 131.44 | 1265.11 | 99.75 | 24.20 | 13.66 |
| 12 | 4 | Control | 10 | 231.30 | 63.81 | 1266.84 | 61.15 | 26.68 | 12.87 |
| 12 | 5 | Treated | 10 | 211.75 | 79.75 | 1397.03 | 64.63 | 32.12 | 15.98 |
| 12 | 6 | Control | 10 | 403.75 | 147.99 | 1590.57 | 142.25 | 25.30 | 13.82 |
| 0 | 1 | Treated | 20 | 368.75 | 107.61 | 1635.69 | 123.39 | 13.86 | 13.09 |
| 0 | 2 | Treated | 20 | 456.41 | 181.14 | 1605.99 | 159.74 | 13.56 | 9.48 |
| 0 | 3 | Control | 20 | 356.14 | 129.87 | 1669.56 | 96.40 | 13.25 | 10.14 |
| 0 | 4 | Control | 20 | 265.96 | 84.13 | 1480.43 | 52.92 | 14.87 | 9.59 |
| 0 | 5 | Treated | 20 | 278.80 | 102.64 | 1482.80 | 54.10 | 13.45 | 8.43 |
| 0 | 6 | Control | 20 | 458.64 | 200.03 | 1581.67 | 147.17 | 15.80 | 12.17 |
| 6 | 1 | Treated | 20 | 172.18 | 81.78 | 2100.57 | 137.74 | 84.40 | 25.28 |
| 6 | 2 | Treated | 20 | 47.07 | 81.30 | 1277.94 | 51.35 | 9.03 | 16.13 |
| 6 | 3 | Control | 20 | 243.67 | 77.65 | 1361.62 | 45.52 | 13.74 | 15.65 |
| 6 | 4 | Control | 20 | 249.68 | 81.42 | 1289.10 | 54.28 | 12.55 | 8.11 |
| 6 | 5 | Treated | 20 | 191.42 | 62.42 | 1392.64 | 76.29 | 13.15 | 16.83 |
| 6 | 6 | Control | 20 | 321.48 | 140.02 | 1478.79 | 74.30 | 14.95 | 15.52 |
| 12 | 1 | Treated | 20 | 325.70 | 119.09 | 1304.25 | 97.57 | 23.14 | 22.64 |
| 12 | 2 | Treated | 20 | 467.82 | 407.91 | 1406.31 | 166.87 | 34.53 | 25.64 |
| 12 | 3 | Control | 20 | 365.51 | 196.81 | 1416.51 | 87.03 | 21.97 | 12.65 |
| 12 | 4 | Control | 20 | 279.53 | 66.49 | 1362.37 | 46.14 | 26.42 | 17.06 |
| 12 | 5 | Treated | 20 | 244.13 | 83.23 | 1392.64 | 49.94 | 23.96 | 13.62 |
| 12 | 6 | Control | 20 | 340.05 | 150.02 | 1414.50 | 122.88 | 16.63 | 13.74 |

**Appendix Q. (continued).** This appendix contains the soil content data that were inserted into the SAS program in Appendix R.

|  |  |  |  |  |  | (kg/ha) |  |  | (g/ha) |
|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **Fe** | **Mn** | **Zn** | **Cu** | **B** | **Be** |
| 0 | 1 | Treated | 0 | 216.52 | 294.63 | 31.93 | 15.60 | 0.16 | 0.70 |
| 0 | 2 | Treated | 0 | 235.91 | 278.51 | 11.24 | 2.88 | 0.35 | 0.40 |
| 0 | 3 | Control | 0 | 242.15 | 335.29 | 28.99 | 13.17 | 0.55 | 0.63 |
| 0 | 4 | Control | 0 | 206.78 | 316.08 | 12.21 | 2.98 | 0.08 | 0.64 |
| 0 | 5 | Treated | 0 | 260.55 | 318.45 | 47.26 | 26.17 | 0.61 | 0.70 |
| 0 | 6 | Control | 0 | 280.35 | 288.75 | 32.55 | 19.70 | 0.46 | 0.44 |
| 6 | 1 | Treated | 0 | 200.71 | 176.98 | 4.64 | 10.06 | 0.43 | 0.40 |
| 6 | 2 | Treated | 0 | 215.16 | 86.28 | 4.69 | 1.19 | 0.28 | 0.29 |
| 6 | 3 | Control | 0 | 234.48 | 330.90 | 24.64 | 10.17 | 0.38 | 0.35 |
| 6 | 4 | Control | 0 | 194.97 | 283.59 | 18.74 | 7.17 | 0.25 | 0.51 |
| 6 | 5 | Treated | 0 | 200.33 | 82.22 | 4.76 | 1.15 | 0.29 | 0.58 |
| 6 | 6 | Control | 0 | 259.35 | 265.65 | 30.61 | 18.13 | 0.40 | 0.67 |
| 12 | 1 | Treated | 0 | 198.73 | 218.50 | 19.15 | 8.44 | 0.38 | 0.67 |
| 12 | 2 | Treated | 0 | 237.00 | 255.57 | 36.73 | 19.60 | 0.48 | 0.83 |
| 12 | 3 | Control | 0 | 250.92 | 301.32 | 22.89 | 11.40 | 0.02 | 0.83 |
| 12 | 4 | Control | 0 | 187.09 | 280.63 | 12.28 | 3.45 | 0.34 | 0.32 |
| 12 | 5 | Treated | 0 | 236.23 | 235.07 | 8.31 | 3.08 | 0.27 | 0.75 |
| 12 | 6 | Control | 0 | 256.20 | 262.50 | 23.69 | 14.61 | 0.06 | 0.38 |
| 0 | 1 | Treated | 10 | 295.07 | 341.73 | 17.68 | 8.47 | 0.04 | 0.74 |
| 0 | 2 | Treated | 10 | 291.67 | 298.96 | 18.78 | 10.23 | 0.09 | 0.55 |
| 0 | 3 | Control | 10 | 301.61 | 334.47 | 16.95 | 7.89 | 0.18 | 0.43 |
| 0 | 4 | Control | 10 | 315.05 | 405.44 | 12.59 | 3.96 | 0.03 | 0.83 |
| 0 | 5 | Treated | 10 | 346.51 | 336.88 | 8.33 | 3.11 | 0.17 | 1.02 |
| 0 | 6 | Control | 10 | 423.86 | 393.69 | 23.61 | 16.55 | 0.22 | 1.13 |
| 6 | 1 | Treated | 10 | 200.50 | 224.46 | 5.81 | 13.56 | 0.16 | 0.55 |
| 6 | 2 | Treated | 10 | 193.23 | 94.79 | 5.74 | 0.96 | 0.16 | 0.53 |
| 6 | 3 | Control | 10 | 218.28 | 100.93 | 4.74 | 1.06 | 0.13 | 0.59 |
| 6 | 4 | Control | 10 | 283.14 | 348.28 | 13.97 | 4.95 | 0.03 | 0.62 |
| 6 | 5 | Treated | 10 | 349.26 | 365.76 | 20.08 | 11.07 | 0.14 | 1.02 |
| 6 | 6 | Control | 10 | 370.70 | 382.20 | 19.33 | 11.49 | 0.11 | 0.82 |

**Appendix Q. (continued).** This appendix contains the soil content data that were inserted into the SAS program in Appendix R.

| | | | | | | (kg/ha) | | | (g/ha) |
|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **Fe** | **Mn** | **Zn** | **Cu** | **B** | **Be** |
| 12 | 1 | Treated | 10 | 302.64 | 327.86 | 9.52 | 4.00 | 0.03 | 0.99 |
| 12 | 2 | Treated | 10 | 317.19 | 311.11 | 14.30 | 8.56 | 0.04 | 0.93 |
| 12 | 3 | Control | 10 | 302.78 | 332.12 | 11.03 | 4.82 | 0.06 | 1.26 |
| 12 | 4 | Control | 10 | 296.44 | 394.81 | 11.09 | 3.89 | 0.07 | 0.54 |
| 12 | 5 | Treated | 10 | 295.63 | 320.38 | 7.54 | 3.19 | 0.07 | 0.79 |
| 12 | 6 | Control | 10 | 373.57 | 350.59 | 10.24 | 6.28 | 0.07 | 1.57 |
| 0 | 1 | Treated | 20 | 350.09 | 418.97 | 10.72 | 4.35 | 0.01 | 1.16 |
| 0 | 2 | Treated | 20 | 386.52 | 409.34 | 10.81 | 4.22 | 0.01 | 1.01 |
| 0 | 3 | Control | 20 | 362.83 | 440.48 | 14.55 | 3.79 | 0.03 | 1.03 |
| 0 | 4 | Control | 20 | 352.81 | 476.29 | 10.65 | 3.30 | 0.07 | 1.28 |
| 0 | 5 | Treated | 20 | 402.26 | 334.29 | 6.30 | 2.54 | 0.07 | 0.54 |
| 0 | 6 | Control | 20 | 480.07 | 347.20 | 9.29 | 5.46 | 0.04 | 1.34 |
| 6 | 1 | Treated | 20 | 298.44 | 198.00 | 7.00 | 1.95 | 0.09 | 0.94 |
| 6 | 2 | Treated | 20 | 238.19 | 397.93 | 7.59 | 0.98 | 0.07 | 1.17 |
| 6 | 3 | Control | 20 | 319.99 | 417.72 | 9.80 | 2.91 | 0.07 | 0.90 |
| 6 | 4 | Control | 20 | 314.81 | 382.66 | 9.31 | 3.01 | 0.07 | 0.87 |
| 6 | 5 | Treated | 20 | 187.26 | 101.26 | 5.66 | 1.11 | 0.04 | 0.49 |
| 6 | 6 | Control | 20 | 384.34 | 428.64 | 10.40 | 3.97 | 0.07 | 0.86 |
| 12 | 1 | Treated | 20 | 321.40 | 377.36 | 7.16 | 2.48 | 0.07 | 0.65 |
| 12 | 2 | Treated | 20 | 395.08 | 400.78 | 10.67 | 4.29 | 0.01 | 1.13 |
| 12 | 3 | Control | 20 | 358.81 | 420.40 | 9.33 | 3.12 | 0.07 | 1.40 |
| 12 | 4 | Control | 20 | 325.67 | 468.15 | 10.35 | 3.26 | 0.07 | 0.84 |
| 12 | 5 | Treated | 20 | 338.45 | 355.09 | 6.62 | 2.59 | 0.07 | 1.00 |
| 12 | 6 | Control | 20 | 305.76 | 401.49 | 5.96 | 3.23 | 0.07 | 1.19 |

**Appendix Q. (continued).** This appendix contains the soil content data that were inserted into the SAS program in Appendix R.

| | | | | (g/ha) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **V** | **Cr** | **Co** | **Ni** | **Zn** | **As** |
| 0 | 1 | Treated | 0 | 15.66 | 16.97 | 6.35 | 3.88 | 46.38 | 4.50 |
| 0 | 2 | Treated | 0 | 12.22 | 16.48 | 4.72 | 3.63 | 47.38 | 4.21 |
| 0 | 3 | Control | 0 | 23.12 | 39.89 | 7.99 | 4.94 | 47.58 | 6.24 |
| 0 | 4 | Control | 0 | 15.50 | 17.54 | 6.34 | 3.73 | 24.02 | 3.89 |
| 0 | 5 | Treated | 0 | 16.63 | 17.46 | 6.64 | 3.65 | 26.56 | 4.14 |
| 0 | 6 | Control | 0 | 16.22 | 16.86 | 6.51 | 3.82 | 45.14 | 5.41 |
| 6 | 1 | Treated | 0 | 7.49 | 8.12 | 4.67 | 2.86 | 36.51 | 1.95 |
| 6 | 2 | Treated | 0 | 16.90 | 15.25 | 5.90 | 3.68 | 32.63 | 4.80 |
| 6 | 3 | Control | 0 | 12.82 | 12.27 | 6.19 | 4.25 | 37.79 | 3.63 |
| 6 | 4 | Control | 0 | 14.02 | 12.93 | 5.67 | 3.52 | 22.04 | 3.55 |
| 6 | 5 | Treated | 0 | 18.24 | 21.30 | 6.57 | 4.30 | 25.68 | 4.09 |
| 6 | 6 | Control | 0 | 15.02 | 13.37 | 6.65 | 5.31 | 69.48 | 5.59 |
| 12 | 1 | Treated | 0 | 4.66 | 5.84 | 7.30 | 3.13 | 27.56 | 1.79 |
| 12 | 2 | Treated | 0 | 7.15 | 6.44 | 11.39 | 6.60 | 67.29 | 3.50 |
| 12 | 3 | Control | 0 | 10.24 | 11.86 | 15.38 | 6.55 | 39.62 | 4.03 |
| 12 | 4 | Control | 0 | 5.68 | 9.72 | 8.94 | 4.15 | 15.59 | 1.95 |
| 12 | 5 | Treated | 0 | 15.45 | 19.25 | 12.20 | 5.85 | 17.30 | 3.71 |
| 12 | 6 | Control | 0 | 2.74 | 14.95 | 0.01 | 6.68 | 10.83 | 4.09 |
| 0 | 1 | Treated | 10 | 23.50 | 30.09 | 8.23 | 5.37 | 34.14 | 6.72 |
| 0 | 2 | Treated | 10 | 22.34 | 23.93 | 8.26 | 5.30 | 34.07 | 6.61 |
| 0 | 3 | Control | 10 | 22.25 | 31.64 | 9.20 | 5.98 | 33.07 | 5.95 |
| 0 | 4 | Control | 10 | 38.94 | 34.78 | 11.94 | 10.11 | 34.39 | 9.00 |
| 0 | 5 | Treated | 10 | 36.49 | 48.73 | 10.51 | 6.04 | 29.34 | 10.05 |
| 0 | 6 | Control | 10 | 32.84 | 43.40 | 20.57 | 9.22 | 42.26 | 9.27 |
| 6 | 1 | Treated | 10 | 19.91 | 24.76 | 7.23 | 4.29 | 32.27 | 5.06 |
| 6 | 2 | Treated | 10 | 13.64 | 14.02 | 6.55 | 4.36 | 58.42 | 4.22 |
| 6 | 3 | Control | 10 | 20.55 | 22.75 | 7.24 | 5.01 | 27.14 | 5.11 |
| 6 | 4 | Control | 10 | 16.89 | 13.89 | 11.84 | 5.49 | 27.78 | 4.46 |
| 6 | 5 | Treated | 10 | 36.23 | 38.21 | 11.59 | 8.34 | 31.64 | 7.99 |
| 6 | 6 | Control | 10 | 20.31 | 16.17 | 8.04 | 5.35 | 34.43 | 6.06 |

**Appendix Q. (continued).** This appendix contains the soil content data that were inserted into the SAS program in Appendix R.

| | | | | (g/ha) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **V** | **Cr** | **Co** | **Ni** | **Zn** | **As** |
| 12 | 1 | Treated | 10 | 5.34 | 7.37 | 12.03 | 5.91 | 10.51 | 2.32 |
| 12 | 2 | Treated | 10 | 8.44 | 11.58 | 14.52 | 6.31 | 21.88 | 3.61 |
| 12 | 3 | Control | 10 | 13.36 | 16.91 | 14.09 | 7.76 | 18.61 | 3.89 |
| 12 | 4 | Control | 10 | 8.93 | 13.26 | 13.25 | 6.28 | 14.35 | 2.84 |
| 12 | 5 | Treated | 10 | 6.87 | 9.71 | 11.69 | 4.62 | 9.91 | 2.43 |
| 12 | 6 | Control | 10 | 11.76 | 15.47 | 19.46 | 8.31 | 18.64 | 4.74 |
| 0 | 1 | Treated | 20 | 38.42 | 39.90 | 18.86 | 8.02 | 29.99 | 9.36 |
| 0 | 2 | Treated | 20 | 27.40 | 35.89 | 10.59 | 7.03 | 29.46 | 8.26 |
| 0 | 3 | Control | 20 | 29.04 | 33.19 | 12.61 | 7.91 | 36.82 | 7.29 |
| 0 | 4 | Control | 20 | 35.89 | 43.69 | 10.80 | 7.85 | 32.46 | 9.81 |
| 0 | 5 | Treated | 20 | 19.49 | 19.78 | 10.06 | 4.64 | 18.18 | 5.21 |
| 0 | 6 | Control | 20 | 38.68 | 53.93 | 11.35 | 10.35 | 55.12 | 10.23 |
| 6 | 1 | Treated | 20 | 24.90 | 23.69 | 10.46 | 6.26 | 23.82 | 5.83 |
| 6 | 2 | Treated | 20 | 51.67 | 41.41 | 12.65 | 11.07 | 48.11 | 16.51 |
| 6 | 3 | Control | 20 | 21.83 | 28.73 | 9.66 | 8.33 | 22.49 | 5.58 |
| 6 | 4 | Control | 20 | 25.11 | 23.78 | 10.91 | 6.86 | 32.59 | 5.72 |
| 6 | 5 | Treated | 20 | 15.38 | 15.31 | 6.93 | 4.81 | 17.26 | 3.50 |
| 6 | 6 | Control | 20 | 27.58 | 22.50 | 9.87 | 9.34 | 96.74 | 7.72 |
| 12 | 1 | Treated | 20 | 6.62 | 8.97 | 16.66 | 5.75 | 13.17 | 2.48 |
| 12 | 2 | Treated | 20 | 17.30 | 24.73 | 19.31 | 9.51 | 16.48 | 5.15 |
| 12 | 3 | Control | 20 | 14.26 | 18.21 | 16.72 | 8.49 | 17.03 | 4.31 |
| 12 | 4 | Control | 20 | 10.29 | 13.80 | 14.85 | 7.99 | 17.91 | 3.01 |
| 12 | 5 | Treated | 20 | 7.00 | 12.66 | 11.92 | 4.88 | 8.77 | 2.41 |
| 12 | 6 | Control | 20 | 24.27 | 29.99 | 20.70 | 10.86 | 11.42 | 5.39 |

**Appendix Q. (continued).** This appendix contains the soil content data that were inserted into the SAS program in Appendix R.

| | | | | **(g/ha)** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **Se** | **Rb** | **Cd** | **Cs** | **Pb** | **Hg** | **Th** | **U** |
| 0 | 1 | Treated | 0 | 1.31 | 7.90 | 0.10 | 0.62 | 23.84 | 1932.9 | 2.01 | 1.34 |
| 0 | 2 | Treated | 0 | 0.86 | 6.43 | 0.08 | 0.49 | 17.19 | 865.0 | 0.96 | 1.20 |
| 0 | 3 | Control | 0 | 1.72 | 8.64 | 0.12 | 0.69 | 32.26 | 683.7 | 2.17 | 1.82 |
| 0 | 4 | Control | 0 | 0.88 | 7.32 | 0.10 | 0.60 | 23.05 | 199.9 | 1.57 | 1.14 |
| 0 | 5 | Treated | 0 | 1.64 | 8.95 | 0.11 | 0.75 | 27.53 | 135.5 | 2.11 | 1.51 |
| 0 | 6 | Control | 0 | 1.53 | 7.33 | 0.10 | 0.56 | 24.46 | 204.8 | 2.24 | 1.49 |
| 6 | 1 | Treated | 0 | 0.72 | 4.83 | 0.09 | 0.32 | 15.93 | 2511.3 | 2.47 | 0.93 |
| 6 | 2 | Treated | 0 | 0.86 | 5.59 | 0.09 | 0.39 | 18.64 | 879.2 | 1.97 | 1.01 |
| 6 | 3 | Control | 0 | 1.05 | 7.64 | 0.10 | 0.61 | 21.97 | 818.5 | 2.71 | 1.26 |
| 6 | 4 | Control | 0 | 0.85 | 6.28 | 0.09 | 0.51 | 19.56 | 205.8 | 1.88 | 0.96 |
| 6 | 5 | Treated | 0 | 1.08 | 7.38 | 0.11 | 0.58 | 23.37 | 148.2 | 2.16 | 1.35 |
| 6 | 6 | Control | 0 | 2.09 | 10.27 | 0.14 | 0.73 | 25.74 | 169.1 | 0.71 | 1.64 |
| 12 | 1 | Treated | 0 | 0.66 | 4.82 | 0.13 | 0.23 | 16.09 | - | 2.63 | 0.10 |
| 12 | 2 | Treated | 0 | 1.21 | 7.76 | 0.21 | 0.35 | 25.53 | - | 4.77 | 1.08 |
| 12 | 3 | Control | 0 | 1.38 | 10.92 | 0.24 | 0.57 | 30.60 | - | 7.37 | 0.91 |
| 12 | 4 | Control | 0 | 0.87 | 6.45 | 0.16 | 0.35 | 20.74 | - | 4.48 | 0.38 |
| 12 | 5 | Treated | 0 | 1.20 | 9.52 | 0.20 | 0.53 | 26.62 | - | 6.72 | 1.11 |
| 12 | 6 | Control | 0 | 1.17 | 1.87 | 0.05 | 0.39 | 7.69 | - | 2.40 | 2.30 |
| 0 | 1 | Treated | 10 | 1.13 | 8.56 | 0.12 | 0.70 | 28.56 | 2016.3 | 2.83 | 1.45 |
| 0 | 2 | Treated | 10 | 1.84 | 9.10 | 0.13 | 0.73 | 29.33 | 1009.9 | 1.95 | 1.55 |
| 0 | 3 | Control | 10 | 1.39 | 8.61 | 0.12 | 0.68 | 33.33 | 609.1 | 2.58 | 1.50 |
| 0 | 4 | Control | 10 | 1.65 | 9.55 | 0.16 | 0.79 | 50.27 | 207.4 | 3.44 | 1.60 |
| 0 | 5 | Treated | 10 | 1.41 | 10.11 | 0.16 | 0.81 | 44.34 | 104.5 | 4.95 | 2.21 |
| 0 | 6 | Control | 10 | 2.20 | 9.27 | 0.17 | 0.70 | 51.86 | 232.8 | 3.27 | 2.06 |
| 6 | 1 | Treated | 10 | 0.89 | 8.07 | 0.14 | 0.63 | 27.48 | 3351.7 | 3.32 | 1.36 |
| 6 | 2 | Treated | 10 | 0.83 | 7.17 | 0.09 | 0.51 | 21.86 | 199.7 | 2.61 | 1.46 |
| 6 | 3 | Control | 10 | 1.03 | 8.10 | 0.11 | 0.66 | 25.67 | 415.5 | 3.03 | 1.30 |
| 6 | 4 | Control | 10 | 0.99 | 9.24 | 0.13 | 0.74 | 37.22 | 339.0 | 2.81 | 1.39 |
| 6 | 5 | Treated | 10 | 1.79 | 8.13 | 0.15 | 0.65 | 32.89 | 129.3 | 3.97 | 1.64 |
| 6 | 6 | Control | 10 | 1.51 | 9.22 | 0.13 | 0.63 | 28.45 | 235.6 | 2.81 | 1.55 |

**Appendix Q. (continued).** This appendix contains the soil content data that were inserted into the SAS program in Appendix R.

| | | | | | | | | (g/ha) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Time** | **Plot** | **Treatment** | **Depth** | **Se** | **Rb** | **Cd** | **Cs** | **Pb** | **Hg** | **Th** | **U** |
| 12 | 1 | Treated | 10 | 1.33 | 7.19 | 0.20 | 0.34 | 28.99 | - | 5.11 | 0.32 |
| 12 | 2 | Treated | 10 | 1.74 | 10.08 | 0.23 | 0.48 | 32.36 | - | 7.17 | 0.73 |
| 12 | 3 | Control | 10 | 1.35 | 12.33 | 0.22 | 0.65 | 30.02 | - | 7.25 | 0.43 |
| 12 | 4 | Control | 10 | 0.94 | 10.57 | 0.20 | 0.58 | 28.99 | - | 6.79 | 0.54 |
| 12 | 5 | Treated | 10 | 1.51 | 8.30 | 0.20 | 0.44 | 26.03 | - | 5.11 | 0.55 |
| 12 | 6 | Control | 10 | 2.30 | 15.16 | 0.30 | 0.76 | 45.39 | - | 9.64 | 0.87 |
| 0 | 1 | Treated | 20 | 1.87 | 10.93 | 0.17 | 0.89 | 62.13 | 899.6 | 5.18 | 1.77 |
| 0 | 2 | Treated | 20 | 2.07 | 12.02 | 0.15 | 0.94 | 38.65 | 236.8 | 4.08 | 1.72 |
| 0 | 3 | Control | 20 | 1.74 | 11.62 | 0.16 | 0.96 | 42.82 | 211.5 | 4.23 | 1.77 |
| 0 | 4 | Control | 20 | 1.31 | 11.45 | 0.15 | 0.92 | 39.52 | 97.7 | 4.05 | 2.01 |
| 0 | 5 | Treated | 20 | 0.60 | 8.28 | 0.12 | 0.63 | 39.04 | 84.6 | 3.20 | 1.49 |
| 0 | 6 | Control | 20 | 3.20 | 13.53 | 0.21 | 0.99 | 41.46 | 87.2 | 2.72 | 2.28 |
| 6 | 1 | Treated | 20 | 1.98 | 10.65 | 0.11 | 0.81 | 35.57 | 1505.1 | 4.90 | 1.68 |
| 6 | 2 | Treated | 20 | 2.89 | 14.08 | 0.20 | 1.00 | 41.72 | 473.5 | 2.59 | 1.96 |
| 6 | 3 | Control | 20 | 1.89 | 11.35 | 0.10 | 0.90 | 29.77 | 810.0 | 4.34 | 1.50 |
| 6 | 4 | Control | 20 | 2.07 | 11.25 | 0.16 | 0.92 | 38.91 | 223.9 | 4.14 | 1.73 |
| 6 | 5 | Treated | 20 | 0.58 | 8.11 | 0.12 | 0.62 | 24.40 | 142.9 | 3.48 | 1.25 |
| 6 | 6 | Control | 20 | 1.58 | 13.92 | 0.17 | 0.96 | 37.47 | 212.9 | 2.02 | 2.06 |
| 12 | 1 | Treated | 20 | 1.41 | 10.27 | 0.19 | 0.50 | 33.25 | - | 6.64 | 0.62 |
| 12 | 2 | Treated | 20 | 2.19 | 15.55 | 0.32 | 0.79 | 43.06 | - | 10.24 | 0.84 |
| 12 | 3 | Control | 20 | 2.21 | 14.12 | 0.25 | 0.71 | 35.89 | - | 9.23 | 0.76 |
| 12 | 4 | Control | 20 | 1.38 | 12.66 | 0.23 | 0.65 | 31.68 | - | 6.77 | 0.67 |
| 12 | 5 | Treated | 20 | 1.38 | 9.37 | 0.20 | 0.47 | 28.14 | - | 6.08 | 0.53 |
| 12 | 6 | Control | 20 | 2.05 | 18.75 | 0.22 | 1.02 | 38.48 | - | 10.98 | 0.56 |

**Appendix R.** This appendix contains an example of the SAS program used to analyze the soil contents presented in Appendix Q.

```
Title3 'Effect of Application on Soil Contents';

data Soil;
  infile 'SASSoilContent.csv' firstobs = 3 delimiter = "," ;
  input Time Plot Treatment $ Depth P K Ca Mg S Na Fe Mn Zn Cu B Be V Cr Co Ni As Se Rb
Cd Cs Pb Hg Th U;
run;

proc print data = Soil;
run;

title3 'P';
proc GLIMMIX data = Soil;
 class Time Treatment Depth;
 model P = Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth ;
 lsmeans  Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth / diff lines;
run;

 title3 'K';
proc GLIMMIX data = Soil;
 class Time Treatment Depth;
 model K = Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth ;
 lsmeans Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth / diff lines;
run;

title3 'Ca';
proc GLIMMIX data = Soil;
 class Time Treatment Depth;
 model Ca = Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth ;
 lsmeans Time Treatment Depth Treatment*Time Treatment*Depth Time*Depth
Time*Treatment*Depth / diff lines;
run;
```

**Appendix S.** Diagram and pictures of the research plots used in Chapter 3 (Photos by author).